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SYNTHESES, CHARACTERIZATION AND PROPERTIES OF Cu(II)-, Mo(VI)- AND U(VI) COMPLEXES WITH DIAMINOTETRAPHENOLATE LIGANDS

BY

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Doctor of Philosophy

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ABSTRACT

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11 new *N,N,N'N'*-tetra(2-hydroxy-3-alkyl-5-alkylbenzyl)-diaminoalkanes and *N,N,N'N'*-tetra(2-hydroxy-3-alkyl-5-alkylbenzyl)-diaminoethers (diaminotetraphenols) were prepared in a one-step three component process. Intra- and intermolecular hydrogen bonding plays a major role in physical properties (for example, solubility and melting point) of these compounds.

Six new ditopic Cu(II) compounds that exist in the solid state as phenoxido-bridged circular tetramers have been prepared and characterized. Copper(II) complexes are best known for their magnetic properties. The Cu(II)-O-Cu(II) angles have been modified by changing the coordination sphere with water molecules or different solvent adducts in order to change the magnetic exchange coupling constant of the system. A linear correlation between the Cu-O-Cu angle and the magnetic exchange coupling constant of the complexes was observed.

Seven dioxido Mo(VI) complexes were prepared from diaminotetraphenols and characterized. Their catalytic properties to oxidize aromatic alcohols into corresponding aldehydes and ketones were investigated. Benzyl alcohol and 1-phenylethanol were used as model compounds using hydrogen peroxide as oxidant. It was found that the Mo(VI) complexes prepared show moderate catalytic activity for such transformations. The literature procedure can be improved by adding a simple base. The prepared Mo(VI)compounds are also subject to epoxidation reactions; the epoxidation of cyclo-octene was studied as a model reaction.

The coordination chemistry of the uranyl ion with diaminotetraphenols was investigated and six U(VI) 1:1 and 2:1 complexes (uranyl to ligand ratio) were prepared. It was found that diaminotetraphenols are able to extract UO_2^{2+} ions selectively and efficiently from water to dichloromethane in a two-phase system that can be utilized in uranium separation.

Keywords: copper, molybdenum, uranium, diaminotetraphenols, crystal structures, catalytic studies, magnetic properties, metal ion extraction.

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PREFACE

Understanding the chemical properties of transition metal coordination compounds is the basis of the chemical industry in many applications. Most important among them are catalysis and metal separation from liquids and soils.

This thesis is the result of my research carried out at the Department of Chemistry, University of Jyväskylä during 2008-2013. I want to express my greatest gratitude to my supervisor Prof. Reijo Sillanpää for his guidance and encouragement during this work. Great gratitude is due to the Inorganic Materials Chemistry Graduate Program, Department of Chemistry and Mikkelin Päällystöyhdistys for financial support. I am very grateful to the Head of the Department for the opportunity to carry out this work. I also want to thank all personnel who helped me in studies and created an inspiring and pleasant working atmosphere. Special thanks go to Dr. Ari Lehtonen who boosted up the working methods and gave new ideas.

Dear Senja, my wife, thank you for the love and encouragement that you have supported me during these years. I also want to thank my brother Heikki, father Veikko and all my friends for the good things they have brought into my life.

Jyväskylä 1.5.2013
Antti Riisiö

LIST OF ORIGINAL PUBLICATIONS

This thesis is based on the following original publications, which are referred in the text by their roman numerals.

I Antti Riisiö, Oula Wichmann and Reijo Sillanpää, One-Pot Three-Component Solvent-Free Syntheses of *n*-Alkyl-Bridged *N,N,N',N'*-tetra(2-hydroxybenzyl)diamines and *N,N*-bis(2-hydroxybenzyl) amines, *Lett. Org. Chem*. **2010**, *7,* 298-305.

II Antti Riisiö, Mikko M. Hänninen and Reijo Sillanpää, Alkyl and di-ether bridged *N,N,N',N'*-tetra(2-hydroxybenzyl)diamines: effects of hydrogen bonding on structure and solubility, *CrystEngComm*. **2012,** *14*, 7258–7263.

III Antti Riisiö, Mikko M. Hänninen and Reijo Sillanpää, Syntheses and Structural Study of Novel Tetranuclear Bis(phenoxido)-Bridged Cu^{II} Metal–Organic Macrocycles, *Eur. J. Inorg. Chem.* **2012**, 1048–1053.

IV Antti Riisiö, Ari Lehtonen, Mikko M. Hänninen and Reijo Sillanpää, Synthesis, Structure and Catalytic Properties of Dinuclear Mo^{VI} Complexes with Ditopic Diaminotetraphenols, *Eur. J. Inorg. Chem.* **2013**, 1499–1508.

V Antti Riisiö, Ari Väisänen and Reijo Sillanpää, Uranyl Complexes of Alkyl-Bridged Ditopic Diaminotetraphenol Ligands and their use as Uranyl ion Extractors, *manuscript*.

Author's contribution

The author of the present dissertation has done all the synthetic work in papers I-V with following exceptions: studies with aminobisphenols in paper I, compounds 3-5 in paper II and complex 5 in paper IV and all catalytic work except epoxidation. X-ray diffraction studies were done by co-authors. The author has written the first manuscript drafts of papers I and III-V.

ABBREVIATIONS

Acac	Acetylacetonate, pentane-2,4-dionate
Aminobisphenol	*N,N*-bis(2-hydroxybenzyl)amines
Diaminotetraphenol	*n*-alkyl-bridged *N,N,N′,N′*-tetra(2-hydroxy-3-alkyl-5-alkylbenzyl)diaminoalkanes or ether-bridged *N,N,N′,N′*-tetra(2-hydroxy-3-alkyl-5-alkylbenzyl)di-aminoethers
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
EtOH	Ethanol
NEt_3	Triethylamine
MeCN	Acetonitrile
MeOH	Methanol
MOF	Metal-organic framework
*t*Bu	*t*-butyl
*t*BuOOH	*t*-butyl hydroperoxide
THF	Tetrahydrofuran
TOF	Turnover frequency. TOF = TON/time.
TON	Turnover number. This number indicates the number of catalytic cycles for a given process, i.e. how many moles of product one mole of catalyst can produce.

CONTENTS

1 REVIEW OF THE LITERATURE

1.1 Introduction

1.1.1 The background of coordination chemistry and importance of amine and phenoxido ligands in metal complexes

The term coordination chemistry was originally formulated by Alfred Werner about a century ago in 1893.[1, 2] During the following decade he collected enough information to write two books, from which he later in 1913 developed the coordination theory from a general point of view.[3] The key idea of this thinking is to consider the metal atom as a starting point to which the positions of the ligands are compared from a geometrical aspect.

In modern coordination chemistry, the selection of the metal center and the ligand design around the metal cation are both influenced by each other and equally important. For example, the function of many catalysts is based on the substrate coordination to the metal ion in the active state, thus causing changes to its coordination sphere. Sometimes, as seen frequently in biological processes, a redox reaction of the metal center is also involved. In this context, the transition metals with partially occupied d-orbitals with a low energy transition between different orbital states are supreme. This can lower the energy that is required to change the coordination geometry of the metal ion. It is difficult to provide generalizations about the trends in the coordination number of metal ions within the *d*-block elements; however a few points can be highlighted[4]:

- Sterically demanding ligands favor low coordination numbers of the metal centers.
- High coordination numbers are most likely attained with small ligands and large metal ions.
- The size of a metal ion decreases as its formal charge increases.

- Low coordination numbers will be favored by metals in high oxidation states with π bonding ligands.

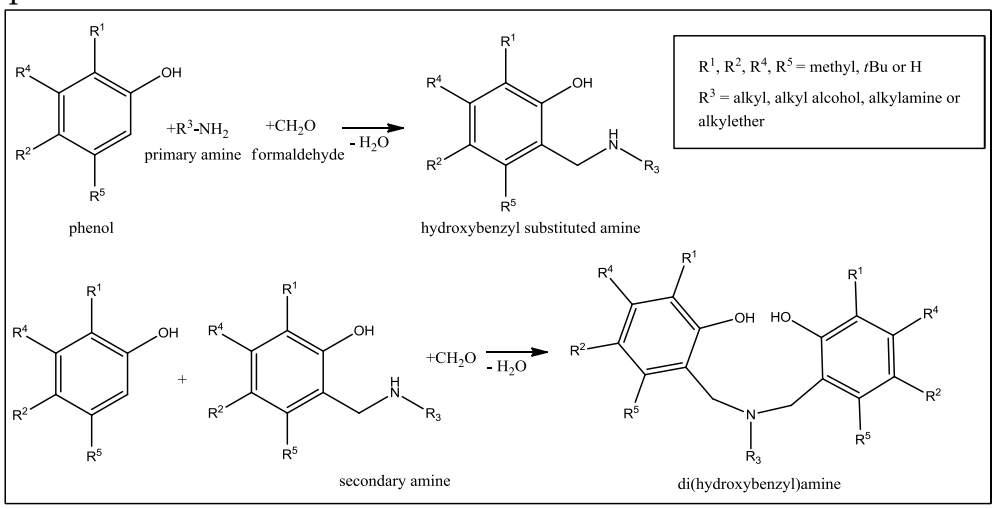
The stability of a complex depends mainly on the favorable Lewis acid-Lewis base interactions and chelate effects. Typically hard Lewis acids, such as metal cations with high oxidation states, can easily form complexes with hard Lewis bases like hydroxyl-containing ligands and *vice versa*.

From this point of view the phenol substituted Schiff base-derived ligands have been workhorses for coordination chemists,[5-7] as one can prepare several different metal complexes from similar ligands and the modification of the ligand is generally an easy task. These ligands can contain both hard and soft electron donors and we can find rigid and flexible parts in their structures.

There are many similarities between the Schiff bases and aminophenols as ligands, although the N-donor in the Schiff bases is much softer than in the aminophenols. Also the metal complexes of aminobisphenols have been used, for example, in the field of molecular magnetism, catalysis and as model compounds used to understand biological processes.[8] Some of them have also been found to be effective extractors of metal cations from water to organic solvents.[9, 10]

1.1.2 Preparation of hydroxybenzyl substituted derivates of primary and secondary amines

Hydroxybenzylamine (aminophenol is the trivial name used) and di(hydroxybenzyl)amine (aminobisphenol, trivial name) are hydroxybenzyl substituted amino compounds. These aminophenols and aminobisphenols can be prepared by a condensation reaction of amine, phenol and formaldehyde as an application of a Mannich condensation reaction.[11, 12]



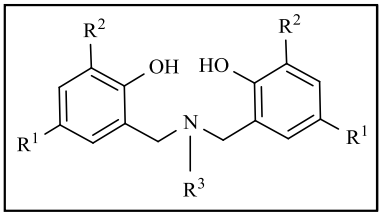
Scheme 1. General equations for preparing hydroxybenzylamines.

This condensation reaction has been known for over a century and is associated with Carl Mannich, who published his work in the 1910s.[13, 14] A general formula for preparing hydroxylbenzyl substituted amino compounds is presented in Scheme 1.

The syntheses are relatively easy to carry out if the nature and location of the substituents in the aromatic ring are well controlled. The substituents in *ortho* and *para* positions of the phenol play an important role as the hydroxyl group is a very strong *ortho* and *para* director. 2-naphthol also reacts using this method like phenols.[15] In most cases the aminobisphenols can be prepared in a single step by refluxing[16-18] or using microwave irradiation.[19] The other method of preparing this type of compounds is to use reductive amination of the carbonyl compound with $NaCNBH_3$,[20] or $NaBH_4$ [21]. The third method is to alkylate a secondary amine with benzylic halides in the presence of a strong base.[22-24]

Both Schiff bases and aminophenols can be used as ligands. In the Schiff bases there is a C=N double bond, and thus the N donor is much softer than in aminophenols. Moreover, aminophenols are in general more flexible than similar Schiff base derivatives.

1.2 Aminobisphenols and their metal complexes as reference compounds



Scheme 2. A general representation of typical aminobisphenols. R^1=R^2= alkyl, R^3=alkyl, alkyl alcohol, alkylamine or alkylether.

The chemistry of aminobisphenols (Scheme 2) is a good starting point for that of diaminotetraphenols. Hence a short introduction to the earlier work in this area is appropriate. The chemistry of metal complexes with aminobisphenolate ligands started after Hinshaw *et al*. published their work in 1989 on Mo(V) and Mo(VI) complexes.[20, 25]

The benzyl substituted phenols like aminobisphenols easily form complexes with hard Lewis acids such as metal cations in a high oxidation state. The CH_2 bridge between the amine and the phenol allows for some flexibility in the structure and the ligand can coordinate to cations with a wide range of ionic

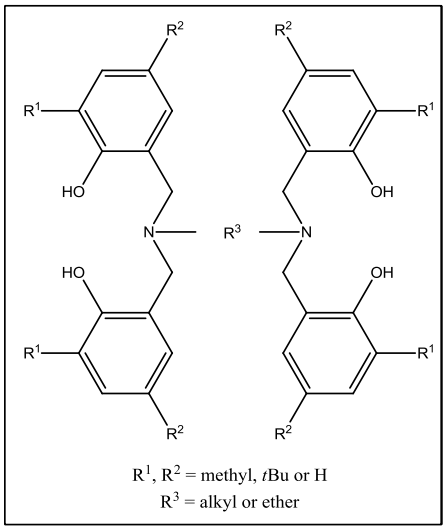
radii. If more than one of the three coordination sites of the ligand is occupied, a chelate is formed. This is why these ligands in a multidentate coordination mode attach strongly to the metal ion. In many cases multiple chelate rings may be observed in the same compound, especially when two aminobisphenolato complexes join to form dinuclear units[9, 26] or a single complex contains two aminobisphenolato ligands.[26, 27] The [O,N,O] coordination mode can be extended by adding suitable coordinating groups or donor atoms in the ligand sidearm. Common donors in this substituent are N and O in different places of an alkyl chain. A comprehensive review of metal complexes with aminobisphenol ligands is reported by Wichmann *et al.*[8]

Among published metal complexes with aminobisphenols relevant to this work are μ-phenoxido-bridged Cu(II) compounds[26, 28], Mo(VI) complexes[29] and U(VI) complexes with different alkyl chains in the R^3 position[9].

1.3 Diaminotetraphenols and their metal complexes

1.3.1 The diaminotetraphenols

The diaminotetraphenol ligands (Scheme 3) are modifications of aminobisphenols[8] discussed in section 1.2. A typical diaminotetraphenol contains four phenol oxygen (hard) and two amine nitrogen (hard) donors connected together by a flexible bridge between the N atoms. The phenolic moieties are connected to the nitrogen atom by a flexible CH_2 group.

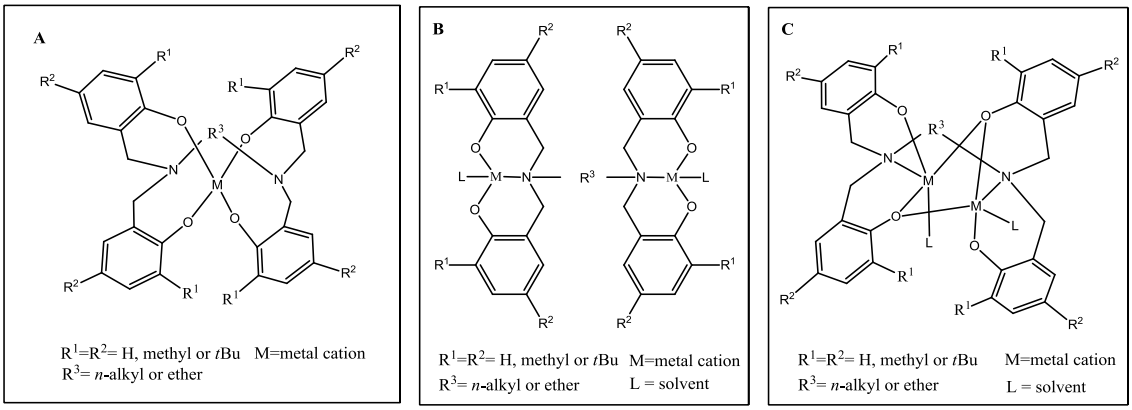


Scheme 3. A general formula of diaminotetraphenols used in this work.

Diaminotetraphenols can be synthesized using methods similar to those that have been presented earlier for hydroxylbenzyl amines (section 1.1.2). Previously, the syntheses have been concentrated to ligands where R^3 is a short alkyl chain such as $(CH_2)_2$ or $(CH_2)_3$ [30, 31], but longer chain diaminotetraphenols have also been prepared.[32] A condensation reaction of phenol, formaldehyde and amine works to prepare diaminotetraphenols, but the number of the side products can be generally large.

The balanced properties of rigidity and flexibility in addition to hard Lewis base donors and two separate 'heads', make these molecules unique building blocks for metal organic frameworks, for instance. Even more variety of metal complexes can be expected than with aminobisphenols. However, metal complexes of diaminotetraphenols are only rarely discussed in the literature, probably due to the fact that the synthesis of the ligands is not straightforward.

1.3.2 Complexes with diaminotetraphenols



Scheme 4. Typical structural types of metal complexes with diaminotetraphenols.

Three main types of coordination compounds with diaminotetraphenols (**A**-**C**) have been reported so far and they are presented in Scheme 4. The first isolated complexes had a metal to ligand ratio of 1:1 (type **A**). Many of these complexes have been made with ligands containing an ethylenediamine bridge (R^3= $(CH_2)_2$).[22, 30, 33] In a report from 1992 Neves *et al*. isolated a V(IV) compound using VCl_3 as a vanadium source in auto-oxidative conditions (air).[22] The ligand was an *N,N,N',N'*-tetra(2-hydroxybenzyl)ethylenediamine with the substituents R^1 = R^2 = H and R^3 = $(CH_2)_2$. In the same year, an Mn(III) complex was isolated using the same ligand[34] and three years later Hefele *et al*.[33] prepared complexes of Ti(IV), V(IV), Mn(IV) and Sn(IV) with this ligand and also characterized the structure of a Ti(IV) complex by single crystal X-ray diffraction. They observed similar auto-oxidation of V(III) to V(IV) as reported earlier[22] despite that $V(acac)_3$ was used as the starting material. A Fe(III) compound was prepared in

1994.[35] Higham *et al*. characterized the Zn(II) complex of the $R^1 = R^2$ = methyl and $R^3 = (CH_2)_2$ substituted ligand.[30] A characteristic for all above mentioned compounds is that the ligand is wrapped around a single metal center forming a cage-like structure as shown in type **A**.

The first structural study of dinuclear metal complexes (type **B)** with linear ethylene-bridged diaminotetraphenol ligands was published in 2009.[36] In this study, type **A** complexes from Co(II), Ti(IV), Zr(IV) and Hf(IV) ions with a 3,5-di-*t*-butyl derivative ligand were also prepared. Homometallic complexes (the same metal ion at both ends) were prepared using Zn(II) and Sn(II) ions, whereas the only known heterometallic complexes of the type **B** with diaminotetraphenol ligands were prepared using Ti(IV)-Zn(II) and Li(I)-Co(II) combinations.[36]

In addition, Boyle's group recently prepared and determined the structures of Ti(IV), Zr(IV) and Hf(IV) compounds[31] with long ether-bridged diaminotetraphenols and studied their thermal properties. The compounds had type **B** structures.

Only one compound with a dinuclear type **C** structure has been reported, namely a Ca(II) compound with the 3,5-di-*t*-butyl derivative ligand mentioned above.[36]

The chemistry of diaminotetraphenols is still close to its starting point and thus structural determinations are in a main role in the literature. In earlier studies, also electron transfer processes of Mn(III) [34] and V(III) [22] complexes have been studied by following their redox reactions.

The longer alkyl- (more than 4 CH_2 groups) or ether-bridged diaminotetraphenols carry a quite flexible chain, which opens interesting possibilities for their metal complexes. As a demonstration of that, an interesting study was recently published discussing the compression of the crystal structure of long alkyl-bridged phosphorous-zinc metal-organic frameworks.[37] Despite the fact that the ligand is totally different, this intriguing observation only adds to the current speculation as to whether MOFs may find a role as a new class of piezoelectric solid-state materials for application as highly sensitive pressure sensors, shock absorbing materials, pressure switches, or smart body armor.

1.3.3 Cu(II) complexes with phenolic ligands and their magnetic properties

Polynuclear copper complexes are of interest from the structural point of view but specially because of their magnetic properties.[38, 39] Cu(II) aminophenolate compounds are also used as model compounds to study the properties of specific enzymes such as galactose oxidase,[40, 41] which is an enzyme that oxidizes alcohols with molecular oxygen. Some oxido-bridged Cu(II) dimers have also been actively used as DNA cleaving agents.[42, 43] Various electron transfer reactions in biological or laboratory systems are also an important topic.[44]

Cu(II) easily forms phenoxido-bridged dimers,[45] and the dinuclear bis(phenoxido)-bridged copper(II) complexes represent a class of important and well-studied compounds in the field of molecular magnetism.[46] For Cu(II) complexes with aminobisphenols a relationship with the Cu-O-Cu angle and the magnetic exchange coupling constant has been established.[26]

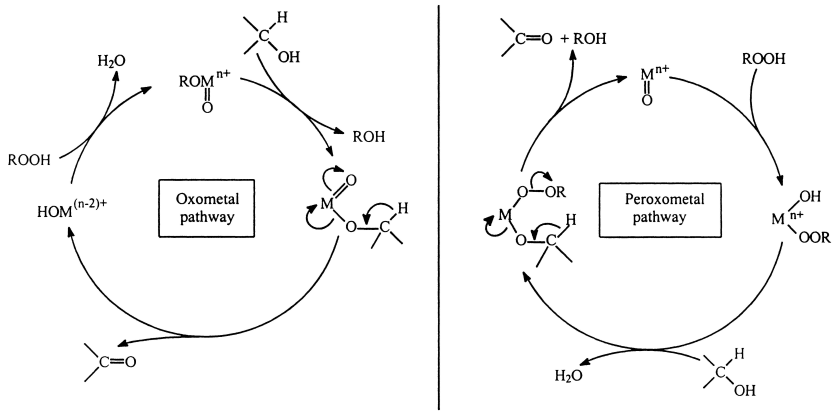
In this work, six diaminotetraphenolate Cu(II) complexes have been prepared and characterized. Different coordinated solvent molecules or solvent adducts are shown to alter the Cu-O-Cu angle and thus the magnetic exchange coupling constant of these compounds.

1.3.4 Phenolic oxidomolybdenum complexes in catalysis

Molybdenum was discovered in the late 18th century when C. W. Scheele heated the molybdenite (MoS_2) mineral to produce molybdenum oxide and P. J. Hjelm reduced molybdenum oxide into metallic molybdenum with charcoal upon heating.[47] Molybdenite is nowadays the main source of molybdenum and molybdenum oxides, which play a key role in many catalytic reactions.

Molybdenum acts as an active center in many biological processes[48-51] and the applications of oxidomolybdenum(VI) complexes are of great importance when preparing fine chemicals via oxygen transfer processes.[52] Some examples are the oxidation of alcohols,[53-55] epoxidation[56-58], oxo-transfer in phosphines,[59-61] oxo-transfer in sulfoxides[62] and the Meyer-Schuster rearrangement[63]. In some cases the catalytic activity of Mo(VI) is enhanced with other metal cations such as Cu(II) or Fe(II).[64] Olefin metathesis reactions[65] and even hydrogen generation from water have been catalyzed by oxido molybdenum complexes.[66]

A number of dioxido Mo(VI) compounds with aminobisphenol ligands have been prepared since 1990s[20, 29] including some with an oxido and chlorido ligand combination.[67-69] Complexes where all oxido ligands have been substituted are also known.[70]



Scheme 5. Alcohol oxidation; oxidometal vs. peroxidometal pathways.[71]

In alcohol oxidation reactions with transition metal ions with a d^0 configuration, e.g., Mo(VI), W(VI), two reaction paths are suggested: oxidometal and peroxidometal pathways (Scheme 5) from which the peroxidometal pathway is most common in the case of an oxido Mo(VI) catalyst.[71] In the epoxidation reactions the first step is the formation of molybdenum peroxido intermediate[72] followed by transfer of the oxido atom from the Mo(VI) peroxido system to the substrate.[73] The intermediate formed depends on the oxidant and the oxidation mechanism. This topic for epoxidation reaction is discussed in detail by Chandra *et al.*[73] For the mechanisms of other catalytic reactions the reader is referred to for example, the work of Arzoumanian.[52]

Several alcohol oxidation reactions with molecular oxygen have been reported using $[MoO_2Cl_2]\cdot 2S$ (S =DMSO, DMF, THF) as catalyst.[55] The reactions were carried out in acetonitrile at the reflux temperature with relatively good conversions with various substrates (69-91 % in 2 h). However, high loads (10 mol-%) of catalyst had to be used and benzyl alcohol could not be oxidized. $[MoO_2(acac)_2]$ is in general a poor catalyst for alcohol oxidation with molecular oxygen but together with $Cu(NO_3)_2$ it works relatively well with a 5 mol-% catalyst load (Mo(VI) and Cu(II)) producing a conversion of 98 % in 2-5 h).[64]

The activity of a bidentate Schiff base dioxido Mo(VI) complex has also been studied (1.6 mol-% catalyst load, TON = 100 and 63 % conversion at 10 h).[53] This compound has a similar coordination environment around the Mo(VI) ion as the complexes discussed in this thesis, but the ligand is totally different.

With hydrogen peroxide as the oxide source, better results have been obtained. A Schiff base complex of Mo(VI) with 8-hydroxyquinoline is reported[54] to produce a 52 % yield at 0.05 mol-% catalyst load (TON = 1070) in 16 h.

In this work seven new dioxido Mo(VI) complexes were prepared and characterized. Ability of the complexes to catalyze alcohol oxidation and alkene epoxidation were also studied.

1.3.5 Uranyl ion complexes in extraction studies

In 2011, the worldwide uranium production was ~55 000 tonnes.[74] Uranium is mainly used as an energy source in fission power plants.[47, 75] Some smaller scale applications exist for uranium in weapons, radiation shields[76-78], as a dye in ceramics[47, 79] and in various hybrid materials[80]. The photochemistry of uranium is also rich.[81] Catalytic studies have also been performed in which uranium complexes are used in the hydrogenation of alkenes and oligomerization, dimerization, hydrosilation, and hydroamination of terminal alkynes.[82] Furthermore, studies concerning the decomposition of chlorine-containing hydrocarbons using uranium have been reported.[83]

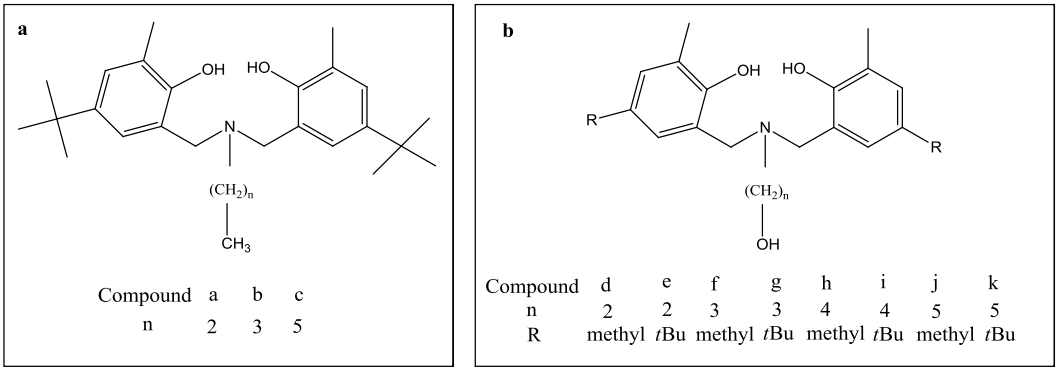
Most of the research interest is of course addressed to the separation of uranium from soils and waters for nuclear plants. In these materials, uranium can be found as various metal complexes.[84] A lot of work has also been done to

find possibilities for recycling uranium from used fuel rods in nuclear plants[85], as only 5 % of the uranium nuclides in the fuel rods is actually used in the process.[86, 87] The other metals in fuel rods, such as zirconium,[4] may cause problems in separation. However, silica- and carbon-coated fuel types have been developed,[88] so that it is hard to judge if this is a long time problem. In addition, one cannot neglect the radioactive elements produced in the fission process, most importantly the plutonium. A detailed presentation of the topic can be found for example, in the article of Hudson *et al.*[89] Uranium is mainly found as a uranyl ion in solutions; this ion is toxic for humans and animals and possibilities to remove uranium from living species as metal-organic complexes have been under investigation.[90]

Through varying organic ligands, several uranyl-organic extended structures with rich structural features have been prepared via various synthetic routes.[91] Uranium-containing inorganic-organic coordination compounds with an extended structure formed from the involvement of the linear uranyl ion, UO_2^{2+}.[91] Sopo *et al*. prepared many U(VI) complexes with aminobisphenols and studied the uranyl ion extraction properties of aminobisphenol ligands.[9] Formally these complexes can be seen as a 'half' of the complexes obtained with diaminotetraphenols.

The liquid-liquid extraction of uranium is quite a extensively studied technique where the uranyl ion is extracted from water into an organic phase using a specific ligand, such as alkylated phosphate ligands. Most important techniques are inclusively discussed by Gorden *et al*. in a recent forum article.[87] Commercially the most interesting technique relies on the use of alkylated phosphate ligands, such as tri-*n*-butyl phosphate (TBP).[85, 92, 93] High loads of TBP are needed as it is used as up to 30 vol-% of the organic phase rather than in a stoichiometric scale to the uranium ions! [15] In addition to uranyl extraction methods reviewed in ref. 87, for example, crown ethers,[94, 95] and bis(2-ethylhexyl) sulfoxides[96] have been used as uranyl extractors.

Quite extensive studies of U(VI) extraction have been made with aminobisphenols[9, 10, 97-99] (Scheme 6).



Scheme 6. Aminobisphenols used in U(VI) extraction studies.[9, 10, 97-99]

Distribution (D) values of uranyl species between organic (CH_2Cl_2) and water phase are collected in Table 1. From these results one can say that in general the extraction efficiency is better when the length of the alkyl chain in both types of aminobisphenols increases. Ligands with short alkyl chains (a-c) work generally quite well. The influence of methyl or t-butyl group in the 4 position of the aromatic ring is not quite clear in d-k, but in the extraction efficiency is better with the ethanol, propanol and butanol derivatives, if the methyl group is in 4 position. However, the results are reversed with the pentanol derivates. This observation raised an interesting question: is the situation similar with diaminotetraphenols?

Table 1. The distribution (D) of U(VI) ions between and organic (CH_2Cl_2) and water phase at equilibrium in extraction with selected aminobisphenols (Scheme 6).

Ligand	a	b	c	d	e	f	g	h	i	j	k
D*	12	18	17	2.8	1.7	12	5.0	13	10	13	16

*$D = m(U)_o / m(U)_w$, where $m(U)_o$ and $m(U)_w$ are the mass of U in organic and water phases.

In this work six novel uranyl complexes with diaminotetraphenols was prepared and characterized. The extraction of uranyl ions with diaminotetraphenols was also studied in a two-phase system.

2 AIMS OF THE STUDY

As presented in the previous chapters, the Schiff base complexes in general[7] provide a multipurpose framework for building various types of transition metal complexes.[8] Due to previous work, there is substantial knowledge available in our laboratory on ligand synthesis and preparation of metal complexes with aminobisphenol ligands.[25, 99] This background of the properties of aminobisphenol-based ligands was a good basis for the current work. The aim of this study was to expand the family of known aminobisphenol ligands and their complexes with ditopic diaminotetraphenols and study the chemical properties of the prepared complexes.

This work is divided into three sub-sections: a) preparation and characterization of the new ligands, b) preparation and characterization of the metal complexes with these ligands and c) the use of these complexes in catalytic applications and the ligands in extraction studies.

The ligand design (a) was oriented towards compounds that are able to produce coordination compounds with many different metal cations, especially those with high oxidation states. Oxygen donors are good in this sense and therefore we selected phenol-derived compounds.

Once the ligands were synthetized and their properties were studied, the preparation of the complexes (b) was investigated. The chemistry of various oxido metal complexes, especially those with *cis*-dioxido Mo(VI) and *trans*-dioxido U(VI) fragments, had been of special interest for a long time. Different orientations of the oxido ligands lead to significant differences in the structures of the complexes formed and therefore these ions were selected for the complex preparation. Also the magnetic properties of the first row elements are interesting; hence novel Cu(II) complexes with diaminotetraphenols were prepared. Some Cu(II) complexes with aminobisphenols had already been studied, and that provided useful guidance in the preparation of the complexes.

The third part of the work consists of the application of the prepared complexes in catalysis or as cation extractors (c). For example the dioxido Mo(VI) complexes are known to be active in catalysis and thus have also industrial interest. Furthermore, it was also known from the previous studies that aminobisphenols are good extractors for the uranyl ion[99] and this capability warranted further study. Only a fraction of this chemistry has been explored in the literature, so that there was an obvious need to reinforce the knowledge in this area.

In order to achieve understanding of the chemical behavior of the prepared complexes, the knowledge about their molecular structure is necessary. Hence, special effort was directed into the preparation of good quality single crystals for X-ray diffraction to solve the solid state structures of the complexes.

3 EXPERIMENTAL

3.1 Physical measurements and reagents

^{1}H and ^{13}C NMR spectra were recorded with a Bruker Avance DRX 500 FT-NMR or Bruker Avance DRX 250 FT-NMR spectrometer. Elemental analyses were performed with a Vario El III elemental analyser, and the IR spectra were measured with a Bruker Tensor 27 IR device with an ATR. For the UV/VIS measurements we used a Perkin Elmer LAMBDA 650 spectrophotometer. The oxidation reactions of alcohols were monitored with an Agilent 7820A GC instrument with an Agilent HP-5 column (model 19091J-413, 320 µm X 30 m X 0.25 µm) and a FID detector. Thermogravimetric measurements were carried out with a Perkin Elmer TGA 7 instrument. The melting points were determined using a Stuart Scientific SMP3 melting point apparatus. The pH meter used was a WTW INOLAB PH 720 with a WTW PH-Electrode SENTIX81. The uranyl concentrations in extraction studies were determined using a Perkin Elmer ICP-OES Optima 8300 instrument.

The X-ray data were collected with either a Nonius-Kappa diffractometer equipped with a CCD area-detector using Mo-K_α radiation (λ = 0.71073 Å) or Cu-K_α radiation (λ = 1.54184 Å), or with an Agilent Supernova diffractometer equipped with Atlas area-detector using Cu-K_α radiation (λ = 1.54184 Å).

$MoO_2(acac)_2$ was prepared following a known procedure[60], but other starting materials and solvents in the syntheses were commercially purchased.

3.2 Computing methods

3.2.1 X-ray data

The data were processed with a DENZO-SMN v0.93.0 [100] and a SADABS[101] or CrysAlisPro[102, 103] program package. The structures were solved by direct methods using the SHELXS-97 [104] or the SIR-97 [105] program, and the full-matrix least squares refinements on F^2 were performed using the SHELXL-97 [104] program. The figures were drawn with ORTEP-3 for Windows[106] and Mercury[107]. For all the compounds the heavy atoms were refined anisotropically. The CH hydrogen atoms were included at the calculated distances with fixed displacement parameters from their host atoms (1.2 or 1.5 times those of the host atom). The OH hydrogen atoms were located from the electron density map and refined isotropically.

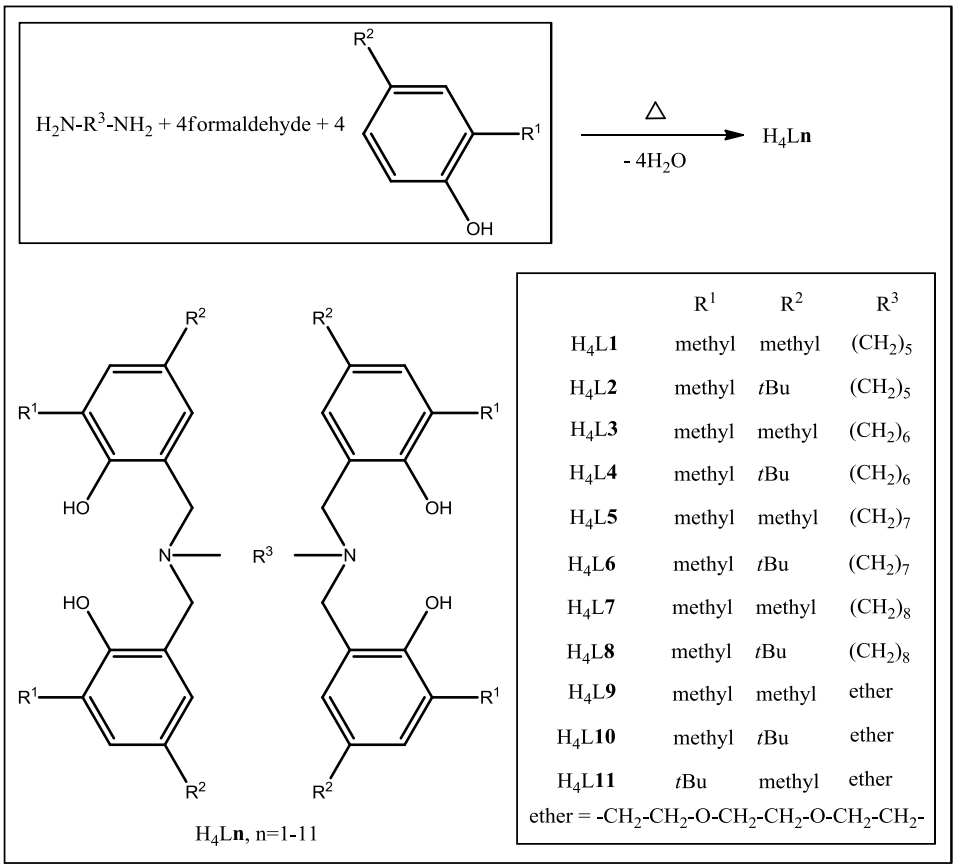
3.2.2 Magnetic calculations and structural analysis for Cu(II) complexes

The magnetic exchange coupling constant J was calculated at the B3LYP level with Ahlrichs TZV basis sets[108-111] using the Turbomole 6.3 program package.[112] The structural parameters for the calculations were taken from the X-ray diffraction data.

3.3 Syntheses and physical properties of the diaminotetraphenols

The diaminotetraphenol ligands H_4L**1**-H_4**11** presented in this work were prepared by a condensation reaction of a phenol, formaldehyde and *n*-alkyl-or ether-bridged diamine (Paper I, Paper II). The net equation and the prepared compounds are presented in Scheme 7.

In a typical reaction, all starting materials were weighed into the same reaction vessel without any solvents and heated in a thermal oven at 120 °C for 1-8 h. The reactions were monitored using high performance liquid chromatography. In order to avoid pressure we used paraformaldehyde (Paper I, Paper II) instead of aqueous formaldehyde,[31] because all syntheses require activation by heating to a high temperature or microwave irradiation.[19] The use of paraformaldehyde makes the reactions safer to carry out and easier to monitor while no extra solvent is needed. The raw product obtained was purified by recrystallization.



	R1	R2	R3
H4L**1**	methyl	methyl	$(CH_2)_5$
H4L**2**	methyl	*t*Bu	$(CH_2)_5$
H4L**3**	methyl	methyl	$(CH_2)_6$
H4L**4**	methyl	*t*Bu	$(CH_2)_6$
H4L**5**	methyl	methyl	$(CH_2)_7$
H4L**6**	methyl	*t*Bu	$(CH_2)_7$
H4L**7**	methyl	methyl	$(CH_2)_8$
H4L**8**	methyl	*t*Bu	$(CH_2)_8$
H4L**9**	methyl	methyl	ether
H4L**10**	methyl	*t*Bu	ether
H4L**11**	*t*Bu	methyl	ether

Scheme 7. The preparation and numbering of diaminotetraphenols H4L**1-11**.

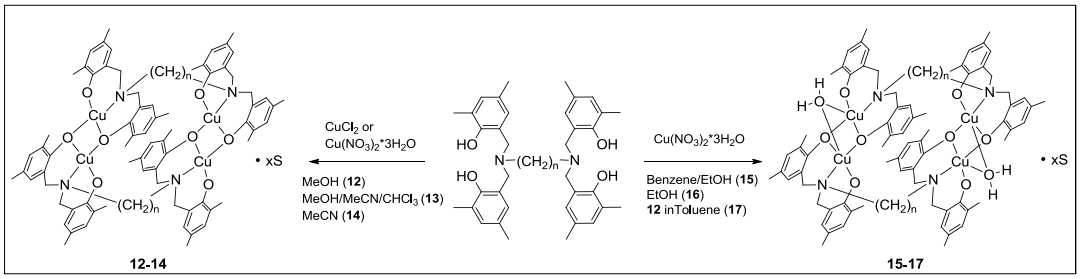
So far there is no general way to purify the raw products, and therefore the diaminotetraphenols were isolated from the mixture using individual purification processes to obtain a reasonable yield. Re-crystallization of the raw material from acetonitrile or its mixtures with less polar solvents was mostly used. In some cases, i.e. compounds H4L**2** and H4L**6**, the raw products had to be transformed into their dihydrochloride salts in order to obtain crystalline products. The yields of the ligands were 30-80 %. The crystal structures for several ligands were determined (see Table 2).

Table 2. The crystal structures of the diaminotetraphenols determined in this study.

No	Ligand	Crystal system	Space group	Paper
3	H4L**3**	Monoclinic	*C*2/*c*	II
4	H4L**4** ·2HCl ·2MeOH	Triclinic	$P\bar{1}$	I
5	H4L**5**	Orthorhombic	$P2_12_12_1$	I
7	H4L**7**	Tetragonal	$P4_12_12$	II
9	H4L**9** ·Et_2O	Monoclinic	*C*2/c	II
10	H4L**10**	Monoclinic	*C*2/c	II
11	H4L**11**	Monoclinic	*C*2/c	II

The solubility of ligands H_4L**3**, H_4L**7**, H_4L**9**-H_4L**11** was studied by making saturated solutions of them in methanol and dichloromethane at 25 °C. These solvents represent polar and nonpolar classes of solvents (Paper II). They are also solvents common in the preparation of metal complexes. The concentrations of the compounds were determined by an UV/VIS spectrophotometer. The absorption maximum for all compounds was found to be situated around 285 nm. The melting points of the same ligands were also determined.

3.4 Syntheses of the Cu(II) complexes



Scheme 8. Preparation of the Cu(II) complexes.

Table 3. The determined crystal structures and numbering of the Cu(II) complexes in this study (Paper III).

No	Formula of the complex	Crystal system	Space group
12	$[Cu_4(L\mathbf{5})_2]\cdot 2MeOH$*)	Orthorhombic	*Pcab*
13	$[Cu_4(L\mathbf{5})_2]\cdot 2CHCl_3$	Orthorhombic	*Pcab*
14	$[Cu_4(L\mathbf{5})_2]\cdot H_2O$	Monoclinic	*C*2/*c*
15	$[Cu_4(L\mathbf{5})_2(H_2O)_2]\cdot 2EtOH\cdot 4benzene$	Triclinic	$P\bar{1}$
16	$[Cu_4(L\mathbf{7})_2(H_2O)_2]\cdot 2EtOH$**)	Triclinic	$P\bar{1}$
17	$[Cu_4(L\mathbf{5})_2(H_2O)_2]\cdot 3toluene$	Triclinic	$P\bar{1}$

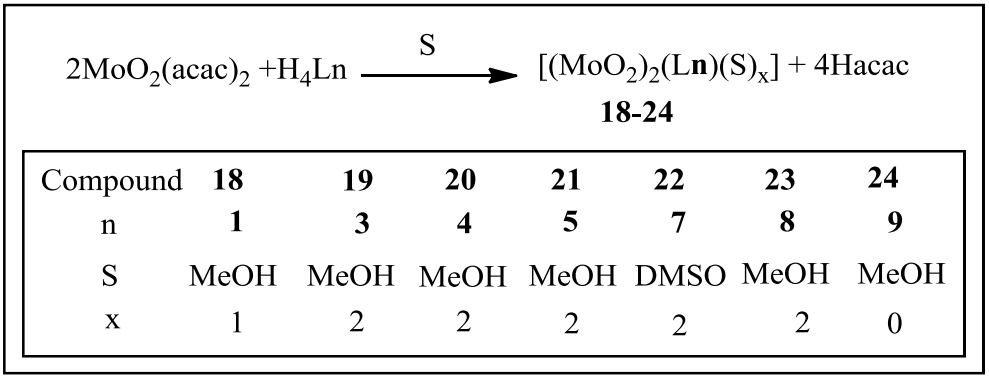
The complex units without solvent of crystallation are marked with bold numbers (Scheme 8). With this system the names can be generated as *) **12**·2MeOH for 12 and **) **16**·2EtOH for 16.

The Cu(II) complexes 12-16 were prepared in a direct reaction of $Cu(NO_3)_2{\cdot}3H_2O$ or dry $CuCl_2$ with the ligand H_4L**5** or H_4L**7** in the presence of NEt_3 (Paper III). The net reaction is described in Scheme 8. Complex 12 was made in methanol, 13 in a MeOH-$CHCl_3$-MeCN (1:1:3) mixture, 14 in MeCN, 15 in a benzene-methanol (5:3) mixture and 16 in ethanol. Complex 17 was made from compound 12 in toluene under exposure to atmospheric moisture. The crystal structures for the complexes 12-17 are in Table 3.

There are several reports on complexes of the first row transition metal ions such as Ni(II) [113], Co(II), Zn(II) [114] and Fe(III) [35, 115] with aminobisphenols, in which there are metal-$O_{phenoxido}$ bonds. Therefore one can expect that these metal cations also form complexes with diaminotetraphenols. A few preliminary complexation experiments between above the metal cations and diaminotetraphenol were performed in alcoholic solutions with NEt_3 as a base, but the exact composition and structures of the solids obtained could not be determined as no separate crystalline phases were formed. It is probable that the length of the alkyl chain between the N atoms, the substituents of the aryl rings and the solvents in the crystal lattice play a key role also in the preparation of these compounds as was the case for Cu(II) compounds (Paper III). Therefore, as this investigation would required time consuming research work, it had to be left outside of this thesis.

The dependence of the magnetic exchange coupling constant J on the Cu-O-Cu bridge angles in complexes **12-17** were obtained by computational methods as described earlier.

3.5 Syntheses of the Mo(VI) complexes



Compound	**18**	**19**	**20**	**21**	**22**	**23**	**24**
n	**1**	**3**	**4**	**5**	**7**	**8**	**9**
S	MeOH	MeOH	MeOH	MeOH	DMSO	MeOH	MeOH
x	1	2	2	2	2	2	0

Scheme 9. A general reaction scheme for preparing Mo(VI) coordination entities of complexes 18-24.

Dioxido Mo(VI) complexes 18-24 (Table 4) of the diaminotetraphenols were prepared in a direct reaction of a dioxidomolybdenum salt and the corresponding diaminotetraphenol in alcohol or DMSO-acetonitrile solution (Scheme 9). The studied MoO_2^{2+} sources were $[MoO_2(acac)_2]$, $[MoO_2Cl_2]\cdot 2DMSO$ and $[MoO_2Cl_2]\cdot 2DMF$, of which $[MoO_2(acac)_2]$ produced the best result. There are many procedures for preparing $[MoO_2(acac)_2]$. For example, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$,[60, 116] $[MoO_2Cl_2]$ [117] or $Na_2MoO_4\cdot 2H_2O$ [118] can be used as starting materials.

Table 4. The numbering system of the Mo(VI) complexes prepared in this study and their unit cell data (Paper IV).

No	Formula of the complex	Crystal system	Space group
18	$[(MoO_2)_2(L\mathbf{1})(MeOH)]\cdot MeOH$	Orthorhombic	*Pcab*
19	$[(MoO_2)_2(L\mathbf{3})(MeOH)_2]\cdot 2THF$*)	Monoclinic	$P2_1/c$
19′	$[(MoO_2)_2(L\mathbf{3})(MeOH)_2]$	Monoclinic	$P2_1/c$
20	$[(MoO_2)_2(L\mathbf{4})(MeOH)_2]\cdot 3MeOH\cdot H_2O$	Monoclinic	$C2/c$
21	$[(MoO_2)_2(L\mathbf{5})(MeOH)_2]\cdot 3MeOH$	Monoclinic	$P2_1$
22	$[(MoO_2)_2(L\mathbf{7})(DMSO)_2]\cdot 0.6MeCN$	Monoclinic	$P2_1/c$
24	$[(MoO_2)_2(L\mathbf{9})]\cdot THF\cdot MeOH$	Orthorhombic	$Pca2_1$

The complexes without solvent of crystallation are marked with bold numbers (Scheme 9). With this system the names can be generated as *) **19**·2THF for 19.

In general, $[MoO_2(acac)_2]$ reacts slowly with the ligands at RT, but the rate can be increased by heating to 70 °C (Paper IV). Due to the low solubility of the starting materials the purification of the compounds needed special attention while the yields remained quite good, 54-80 %. A reference complex 25 was prepared according to the literature.[119]

Thermogravimetric measurements were made for two complexes in order to find their decomposition temperatures: for 18 the temperature range for the evaporation of uncoordinated and coordinated methanol was 70–200 °C. From complex 19 the uncoordinated THF evaporates at room temperature in 5 min and the coordinated methanol in the range of 71–94 °C.

3.5.1 Catalytic studies of the prepared Mo(VI) complexes

The catalytic activity of the Mo(VI) complexes **18-25** was investigated in oxo-transfer reactions. The oxidation of benzyl alcohol into benzaldehyde and 1-phenylethanol into acetophenone was carried out in organic solvents (MeCN, toluene and THF) and in neat alcohol with aqueous H_2O_2 and tBuOOH as oxidant. H_2O_2 worked better in the initial tests and was thus selected as oxidant. The results in toluene and THF were so poor that they were not used in further studies.

General Procedure for Experiment I: A catalyst system that contained Mo(VI) (0.1 mmol; 0.05 mmol of catalyst 22 or 24), substrate (1 mmol; benzyl alcohol or 1-phenylethanol), H_2O_2 (2 mmol; in four portions at 0, 1, 2 and 3 h), NEt_3 (0.1 mmol) and MeCN (4 mL) were placed in a screw-cap test tube with a magnetic stirring bar. In one experiment no NEt_3 was present. The mixture was heated in an oil bath at 60 °C with stirring for 24 h. More H_2O_2 was inserted in four equal parts at 1 h intervals, except in one experiment in which all the H_2O_2 was inserted at once. Samples of 100 µL were removed at 2 h intervals for 6 h, and then one was taken at 24 h. The samples were diluted to 5 mL in a volumet-

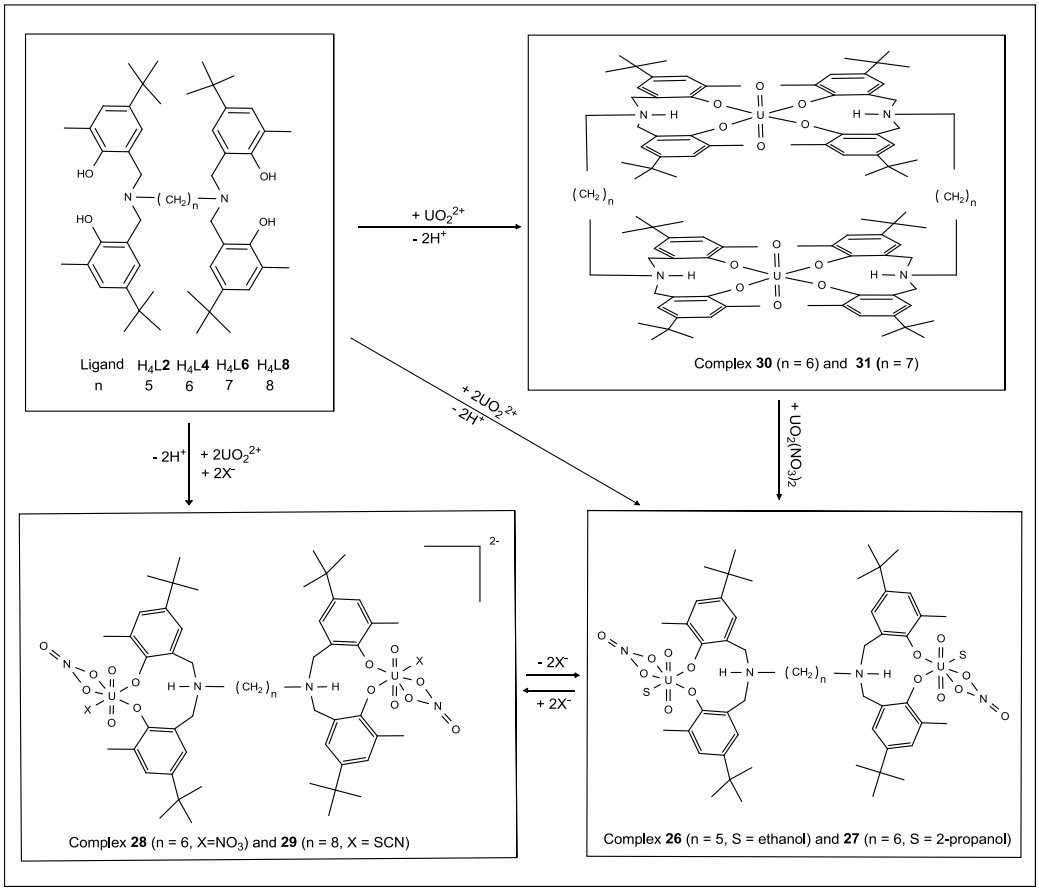
ric flask with CH_2Cl_2, and were monitored with an Agilent 7820A GC instrument with an Agilent HP-5 column. The TON and TOF numbers were calculated at t = 6 h, because the reaction seemed to cease after that.

Because this method in additional solvents proceeded poorly, we oxidized benzyl alcohol using a modified method from Biradar *et al.*[120] in neat alcohol. In this method no other solvent is added and the reaction takes place in the alcohol-carbonyl compound -mixture.

General Procedure for Experiment II (reactions a–m): A catalyst load that contained catalyst 18–25 or $[MoO_2(acac)_2]$ (0.02 mmol), benzyl alcohol (10 mmol), H_2O_2 (20 mmol; in four portions at 0, 2, 4 and 6 h) and NEt_3 (0.05 mmol) was placed in a screw-cap test tube with a magnetic bar. In experiments **a** and **c** the catalyst load was 0.01 and 0.04 mmol, respectively, and in a control reaction no catalyst was present. The sample was heated with stirring at 80 °C in an oil bath. The insertion of H_2O_2 and the sample (8 µL) uptake were performed at 2 h intervals. The samples were diluted to 5 mL in a volumetric flask with CH_2Cl_2, and the reactions **a–m** were monitored for 8 h using GC.

Epoxidation reaction: The oxidation of *cis*-cyclooctene into epoxide was studied using catalyst **24** or **25** with tBuOOH in $CDCl_3$ at 25 °C. The reactions were followed by ^{1}H-NMR. Spectra were run at 30 min intervals. The catalyst:alkene:oxidant ratio was 2.5:100:500 or 5:100:500.

3.6 Syntheses of the U(VI) complexes



Scheme 10. Simplified diagram of the preparation of U(VI) coordination entities of complexes 26-31.

Table 5. The numbering system of the U(VI) complexes prepared in this study and their unit cell data (Paper V).

No	Formula of the complex	Crystal system	Space group
26	$[(UO_2)_2(H_2L\mathbf{2})(NO_3)_2(EtOH)_2]$	Monoclinic	$C2/c$
27	$[(UO_2)_2(H_2L\mathbf{4})(NO_3)_2(2\text{-propanol})_2]$	Triclinic	$P\bar{1}$
28	$[HNEt_3][(UO_2)_2(H_2L\mathbf{4})(NO_3)_2(NO_3)_2]\cdot 2CH_2Cl_2$ *)	Monoclinic	$P2_1/c$
29	$[HNEt_3][(UO_2)_2(H_2L\mathbf{8})(NO_3)_2(SCN)_2]\cdot MeCN$	Triclinic	$P\bar{1}$
30	$[(UO_2)_2(H_2L\mathbf{4})_2]\cdot 4CH_2Cl_2$	Triclinic	$P\bar{1}$
31	$[(UO_2)_2(H_2L\mathbf{6})_2]\cdot 6MeCN$	Triclinic	$P\bar{1}/c$

The complexes without solvent of crystallization and, in case of complexes 28 and 29, the anionic part of the complex, are marked with bold numbers (Scheme 10). With this system the names can be generated as *) $[HNEt_3]_2[\mathbf{28}]\cdot 2CH_2Cl_2$ for 28.

The diaminotetraphenols formed 1:1 and 1:2 complexes with the uranyl ion (Scheme 10). The formulas of the crystal form complexes are in Table 5. Complexes 26, 28 and 29 were prepared from corresponding ligands H_4L**2**·2HCl, H_4L**4**, H_4L**6**·2HCl or H_4L**8**, $UO_2(NO_3)_2 \cdot 6H_2O$ and NEt_3. 26 formed in ethanol and 27 was made by mixing compound 30 and $UO_2(NO_3)_2 \cdot 6H_2O$ (excess) in 2-propanol under reflux. 28 crystallized in a CH_2Cl_2-MeCN-heptane (6:1:4) solution that was dried over molecular sieves. 29 was formed in a CH_2Cl_2-EtOH-heptane (4:7:8) solution. 30 was made in a CH_2Cl_2-MeCN (2:1) solution and 31 in a MeCN-THF (1:1) solution.

3.6.1 Uranyl extraction studies

Diaminotetraphenol ligands, H_4L**2**·2HCl, H_4L**4**, H_4L**6**·2HCl and H_4L**8**, easily form complexes with the uranyl ion, of which many are neutral. For that reason we studied how effectively they transfer uranyl ions from water into an organic phase (CH_2Cl_2). This was done in two separate experiments **I** and **II**.

Experiment I. $UO_2(NO_3)_2 \cdot 6H_2O$ (0.050 mmol) was dissolved in 3.5 ml of water and NH_4OH (0.10 mmol) in 0.5 ml of water was added with mixing. The starting pH of the water phase was 5.70. The ligands (0.055 mmol) were separately dissolved in 4 ml of CH_2Cl_2 and combined with the uranyl solution in 10 ml test tubes. If dihydrochloride salts were used, an additional amount of NH_4OH (0.10 mmol) was added in order to neutralize the acid. The tubes were agitated in a mechanical shaker for a certain time and after that they were allowed to settle for 5 minutes before the samples were taken, which took place at 0, 0.5, 1, 1.5, 2, 4 and 6 h after the extraction started. The U-content of the water and CH_2Cl_2 phases were separately monitored.

The 50 µl samples taken from the CH_2Cl_2 phase were placed into 10 ml volumetric flasks and allowed to dry. The dry samples were heated for 10 min with 500 µl of dilute HNO_3 (~1.4 M HNO_3) at 90 °C. The obtained solutions were filtered through 45 µm Supor (PES) membrane syringe filters to remove the organic solid before the ICP-OES analysis.

The 50 µl samples were taken from the water phase into 10 ml volumetric flasks and diluted. Their uranyl ion contents were analyzed by an ICP-OES instrument at the wavelength of 385.958 nm using axial measurement.

Experiment **II** was done as experiment **I**, but at the beginning $Cu(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 4H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$ (0.050 mmol) were added into the 3.5 ml water solution containing the uranyl ion. Due to the acidity of the ions, more ammonia had to be used (0.15 mmol) to keep the pH at 5.50 in the beginning. The amount of the ligands was reduced to 0.050 mmol. This reaction was followed for 4 h.

The uranyl ion and the ligand can be separated from the evaporated dichloromethane phase using dilute nitric or hydrochloric acid. Procedure **a**: The residue is mixed with 1.4 M HNO_3 in water. The solution is heated at 90 °C for

10 minutes and the separated ligand is removed by filtration. Uranium is collected by evaporating the solution to dryness. Procedure **b**: The residue is mixed with methanol and an excess of conc. HCl is added. The ligand is precipitated by adding water and removed by filtration. Uranium is collected by evaporating the solution to dryness.

4 RESULTS AND DISCUSSION

4.1 General remarks about the preparation of metal complexes with diaminotetraphenols

The diaminotetraphenols with long alkyl (more than four CH_2 groups) or ether bridges are quite new ligands; thus their coordination chemistry is only marginally studied. These new ligands can offer four oxygen and two nitrogen donor atoms for coordination to metal ions. However, the long alkyl chain makes it difficult for the ligand to wrap around a single metal ion and thus other coordination modes can be expected: for ex. a metal ion at both ends of the ligand.

Most diaminotetraphenols can be prepared in a good yield with the method developed in this work. The ligands generally crystallize without any solvents of crystallization but the metal complexes typically crystallize as solvent adducts due to the large cavities in their solid state structures. In many complexes the nonpolar bridge and the polar metal center had to find a balance in the structure in order to form good crystals or crystalline material. Because of this there can be several small solvent molecules in the crystal lattice. Very often after the separation of the crystals from the solution the crystals lose a part of the solvent molecules even at room temperature producing material that is difficult to analyze. Thus, special emphasis had to be paid to prepare high quality crystals for X-ray diffraction study, which is practically the only way to obtain structural information about the compounds formed.

We chose to use three hard metal ions to study the coordination chemistry of these new ligands with hard donors: Cu(II) was selected from the first row transition metals, Mo(VI) from the second row and U(VI) from actinides. The different orientation of the oxido groups in MoO_2^{2+} (*cis*) and UO_2^{2+} (*trans*) ions can cause the formation of different coordination spheres for the metal ion and interesting structures.

We have used a large palette of solvents to produce stoichiometric and crystalline complexes. Alcohols (methanol, ethanol and *iso*-propanol), acetonitrile, DMSO, DMF, dichloromethane, THF, toluene, hexane, acetone and ethyl acetate were among the solvents most used. Recrystallization was in some cases a problem as the original complexes decomposed during the process.

4.2 Syntheses, structures and solubility of diaminotetraphenols

4.2.1 Syntheses

11 new diaminotetraphenols were prepared and characterized. All compounds H_4L**1**- H_4L**11** were prepared in a one-step three-component condensation reaction in which the diamine, phenol and formaldehyde were heated at 120 °C. This simple method appeared to be the most effective and easiest to monitor. However, several side products made the isolation of the desired product difficult.[30] The most significant side products are partially substituted amines with 1-3 phenolic side arms and mono- and dibenzoxazines. Successful syntheses demand substituents in the *ortho* and *para* positions,[11, 121] as the hydroxyl group is a very strong *o*, *p*-director. In the diaminotetraphenol syntheses the amine can be selected quite freely, but the phenol has more requirements. Phenols with electron deficient substituents such as NO_2 react only marginally.

A few comments on the preparation of diaminophenols with a solvent-free method are presented below. It is important that the water formed can escape from the system but, on the other hand, the evaporation of the formaldehyde should be minimal. Fortunately the formaldehyde quickly reacts with other reactants. In the preparation methods in solutions even the addition of water may be beneficial.[10] As a conclusion, the role of water should be investigated case-specifically.

We tested the preparation of H_4L**9**- H_4L**11** in semi-closed beakers where the water formed could escape from the systems, and also in closed containers. The method in closed containers produced the same or lower yield and the method in semi-closed beakers was reported. However, the difference was not as large as in the case of aminobisphenols (Paper I).

The raw products obtained directly from the thermal oven are oily masses that rapidly solidify into a glue-like material as they cool down. Therefore one should begin purification steps immediately after the removal of the reaction vessels from the oven. A mixture of solvents is required in many cases to completely purify the products. No general procedure was found so far and individual purification steps are required for each compound.

4.2.2 Solid state structures

Several crystal structures for the ligands were determined. Two main types of structures were found: those with a linear and those with a "cup-like" conformation. From the pure *n*-alkyl chain ligands with only methyl substituents at the 3 and 5 positions of the aromatic ring, compound H_4L**1** with a bridge of five CH_2 groups is linear, but it crystallizes as a solvent adduct [unpublished results]. H_4L**3** with six CH_2 groups also crystallizes in a linear conformation as shown in Figure 1 with inter- and intramolecular hydrogen bonds. Also the structure of H_4L**9** with an ether bridge is a linear conformation which contains only intramolecular H-bonds OH···N and OH···$O_{ether.}$ Compound H_4L**5** with seven CH_2 units (Figure 2) crystallizes in a cup-like conformation with only intramolecular hydrogen bonds. Compound H_4L**7** has a similar structure. Both inter- and intramolecular hydrogen bonding, phenolic substituents and the length of the bridging fragment have a substantial effect on the packing of the compounds and their solubility and other physical properties, especially in the solid state (Paper II).

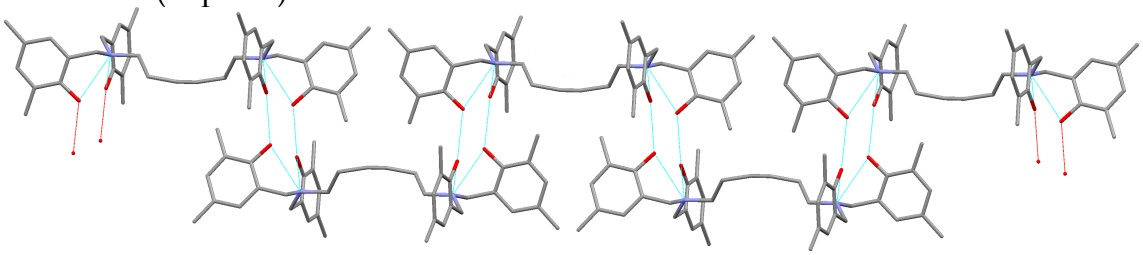


Figure 1. Packing diagram of H_4L**3**.

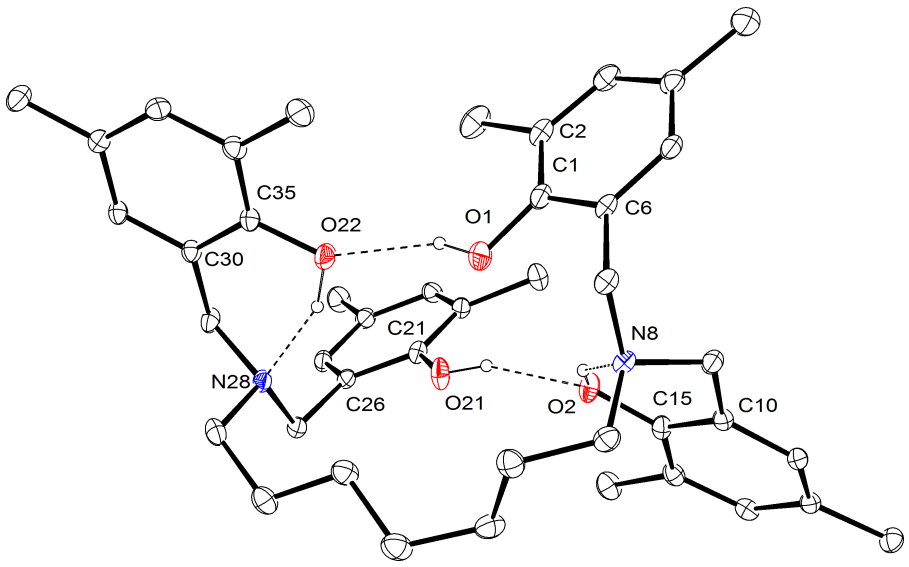


Figure 2. Solid state structure of H_4L**5**.

4.2.3 Solubility studies

The physical properties were studied to point out the dramatic effect of inter- and intramolecular hydrogen bonding on the solubility of the compounds. The solubility and the melting points of the compounds are shown in Table 6. In general, the diaminotetraphenols dissolve much better in slightly polar solvents (THF, CH_2Cl_2) than in more polar ones (MeOH). For example, the solubility in MeOH can be ~0.5-20 mmol/l whereas in CH_2CH_2 it is 100-18000 times higher. Exceptions are for example DMSO and DMF, which have a high ability to break intermolecular hydrogen bonds between the diaminotetraphenol moieties and thus to improve solubility of diaminotetraphenols. Compound H_4L**7** with a cup-like conformation has a high solubility in a slightly polar solvent, dichloromethane, showing that the ether bridge does not have a significant influence on the solubility.

Table 6. The maximum solubility of some diaminotetraphenols in methanol and dichloromethane at 25 °C and the melting points of the compounds (Paper II).

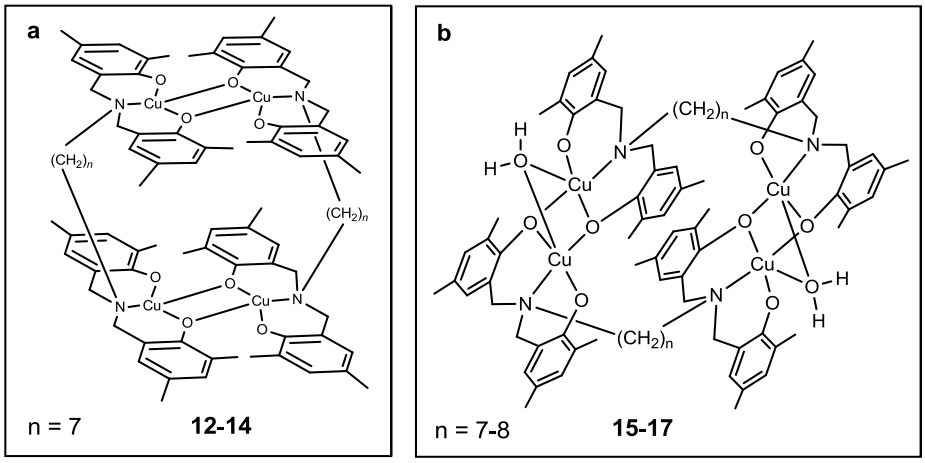
Compound	c [mmol/l] in methanol	c [mmol/l] in CH_2Cl_2	m. p [°C]
H_4L**3**	n. s.[a]	0.6	196–197
H_4L**7**	1.9	170	140–141
H_4L**9**	19	320	69–71
H_4L**10**	0.47	1300	153–154
H_4L**11**	0.04	720	172–173

[a]n.s. = not soluble

As a clear demonstration of the importance of intermolecular hydrogen bonds, we found that in the compound H_4L**3** the H-bonds are so strong that this compound is virtually insoluble in common solvents. The other diaminotetraphenols have a much higher solubility. The ether-bridged compounds, H_4L**9** - H_4L**11**, have similar linear structures without intermolecular H- bonds. Their solubility in methanol follows the order H_4L**9** > H_4L**10** > H_4L**11**. This depends mainly on the polarity of the ligand. In H_4L**10** the *t*-butyl is in 5 the position and the ligand is very soluble in CH_2CH_2.

4.3 Structural and magnetic studies of Cu(II) complexes

4.3.1 Structural studies



Scheme 11. General structural types of the Cu(II) coordination entities of complexes 12-17.

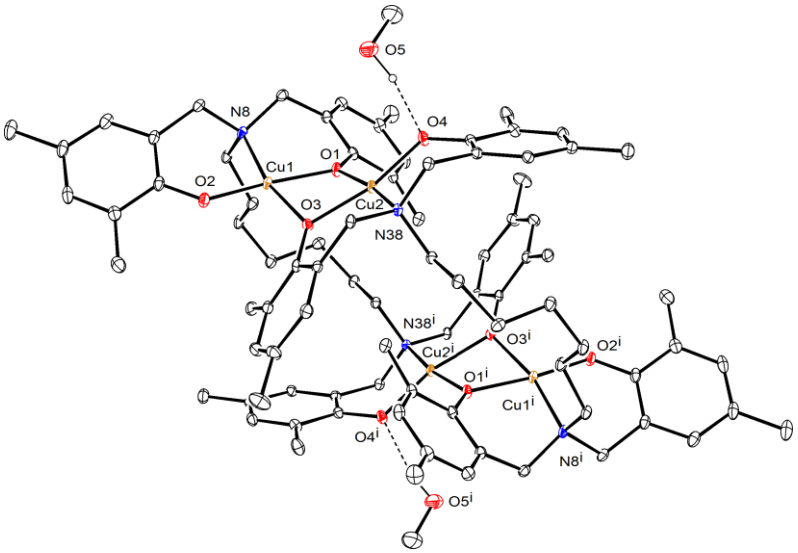


Figure 3. Complex 12 in the solid state. Thermal ellipsoids are drawn at the 20 % probability level. CH hydrogen atoms have been omitted for clarity.

Six new cyclic phenoxido-bridged Cu(II) compounds were prepared and characterized. In addition, their magnetic exchange coupling constants were estimated using computational methods (Paper III). The Cu(II) complexes of ligands H_4L**5** and H_4L**7** exist in a solid state as tetranuclear Cu(II) macrocycles made of two distinct and identical Cu_2-(μ-OPh)$_2$ dinuclear units, which are con-

nected by the alkyl bridges between the amino groups. There are two different structural types, **a** and **b**, in these complexes (Scheme 11).

Three of the complexes have the formula $[Cu_4(L\mathbf{5})_2]\cdot xS$ (compound 12 = **12**·2MeOH, 13 = **13**·2$CHCl_3$ and 14 =**14**·H_2O). These complexes represent type **a** in Scheme 11 and their coordination sphere around the Cu(II) ion is distorted square planar. The structure of 12 is shown in Figure 3. The solvent molecules are found in the empty place in the crystal lattices as shown for 13 in Figure 4.

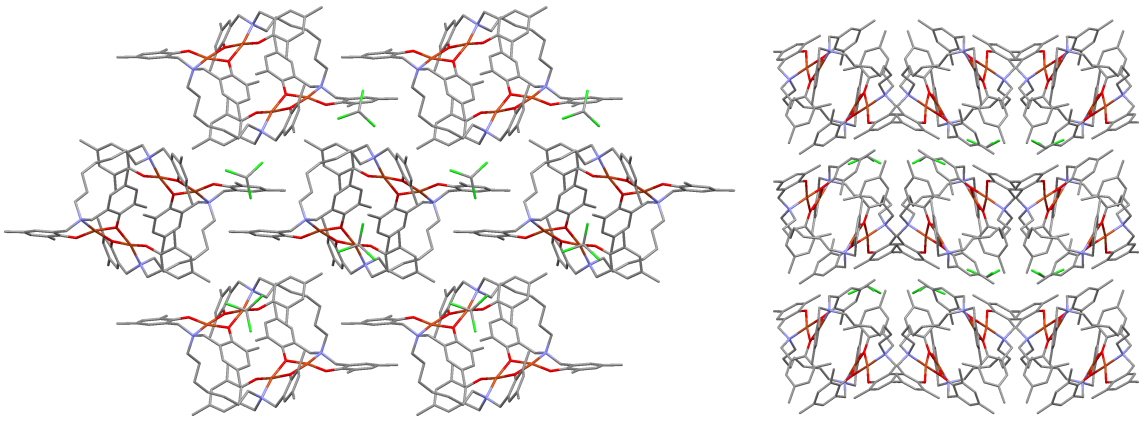


Figure 4. Packing diagram of 13 looking down the crystallographic *c* axis (left) and *a* axis (right). CH hydrogen atoms have been omitted for clarity.

The other three complexes have similar tetranuclear structures in which the dinuclear copper units are also bridged by a weakly bonded water molecule. These complexes represent the type **b** construction in Scheme 11. The formulas of the complexes are: $[Cu_4(L\mathbf{5})_2(H_2O)_2]\cdot xS\cdot yS'$ (15 = **15**·2EtOH·4benzene), (16 = **16**·2EtOH) and 17 = **17**·2EtOH·3toluene). Figure 5 shows the structure of the complex unit in **17**. The coordination geometry around the Cu(II) ions in these complexes is strongly distorted square pyramidal (type **b** in Scheme 11). Different solvent molecules fill the cavities in the lattice as was the case for set **a** compounds, but the main packing effect is controlled by H-bonds between the complex units. This is presented in Figure 6 for 16.

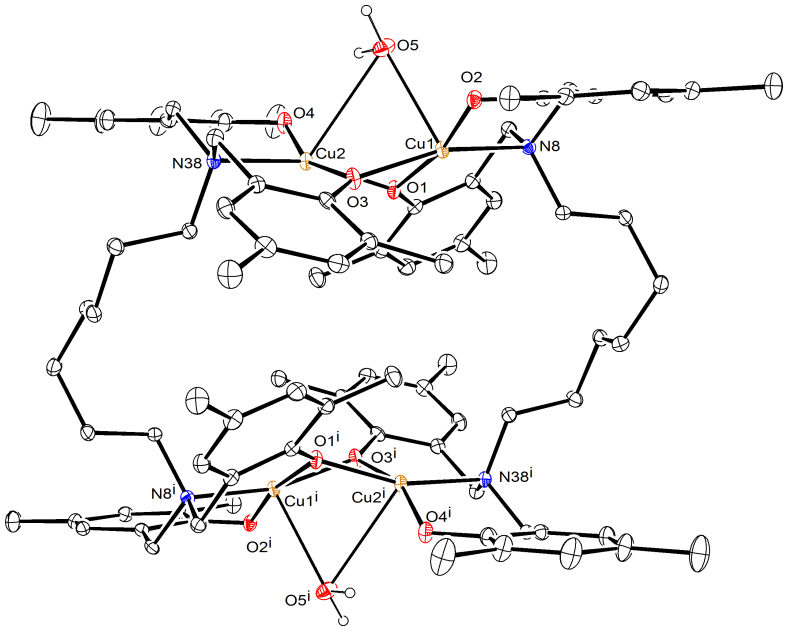


Figure 5. Solid state structure of 17. Thermal ellipsoids are drawn at the 20 % probability level. CH hydrogen atoms and the solvent (EtOH, toluene) molecules have been omitted for clarity.

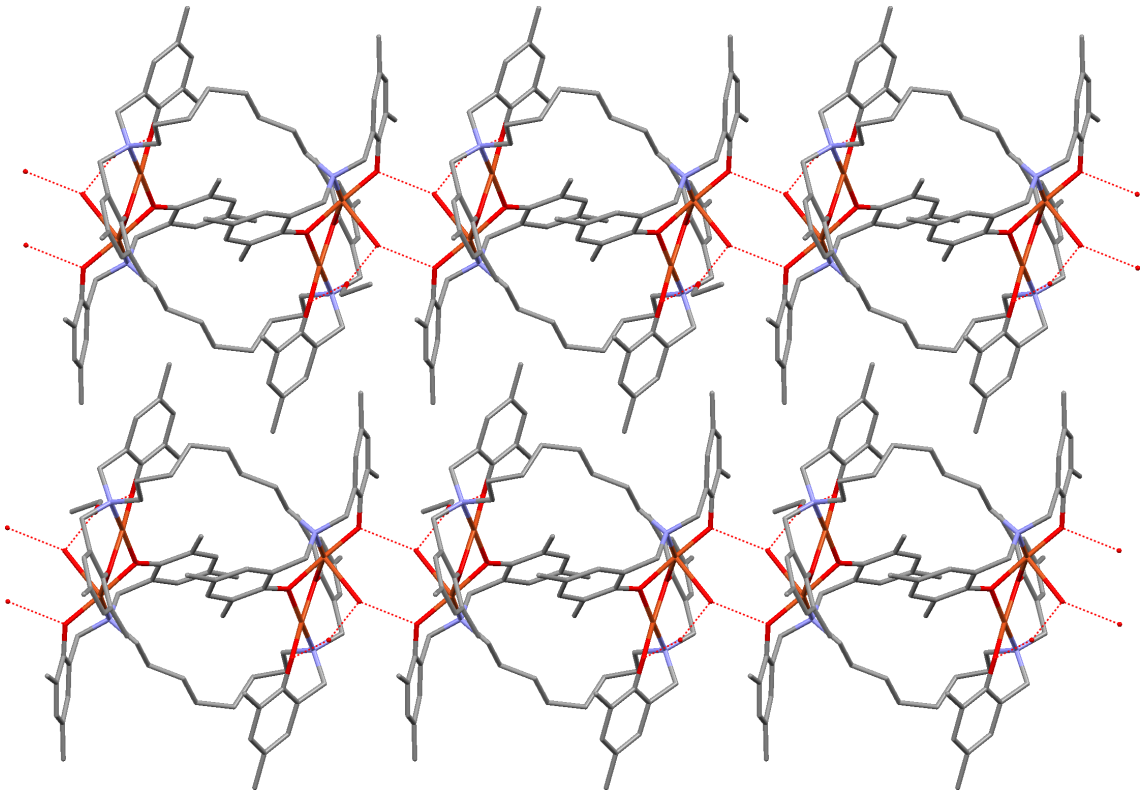


Figure 6. Packing diagram of complex 16 looking down the reciprocal cell *a** axis. CH hydrogen atoms and the solvent (EtOH, toluene) molecules have been omitted for clarity.

4.3.2 Computational magnetic studies

Earlier studies have shown that the Cu-O-Cu bridging angle (Θ) and the exchange parameter (J) have a linear dependence in hydroidxo, alkoxido and phenoxido complexes.[122] In general, in the phenoxido bridged complexes, if the Cu-O-Cu angle is over ~86 °, the complexes exhibit antiferromagnetic coupling between the Cu(II) cations.

A clear correlation in the relationship between Θ and J was established also for complex units **12-17** using DTF calculations by the Turbomole 6.3 program package[112] as described in section 3.2.2. The results presented in Figure 7 are calculated for complex units without solvents of crystallization. In the complexes 15-17 a coordinating water molecule is primarily responsible for the smaller values of Cu-O-Cu angle compared with 12–14. All complexes 12–17 have additional noncoordinating solvent of crystallization, which notably influence the packing of the complexes, hence changing even their geometrical parameters and magnetic behavior. The influence of the solvent of crystallization on the structural parameters is not very large in complexes 12–14. All prepared complexes exhibit antiferromagnetic coupling, but in complex unit **17** the Cu-O-Cu angle ~94 ° is not far from the limit angle ~86 ° (Figure 7), which would presumably change the magnetic coupling to ferromagnetic.

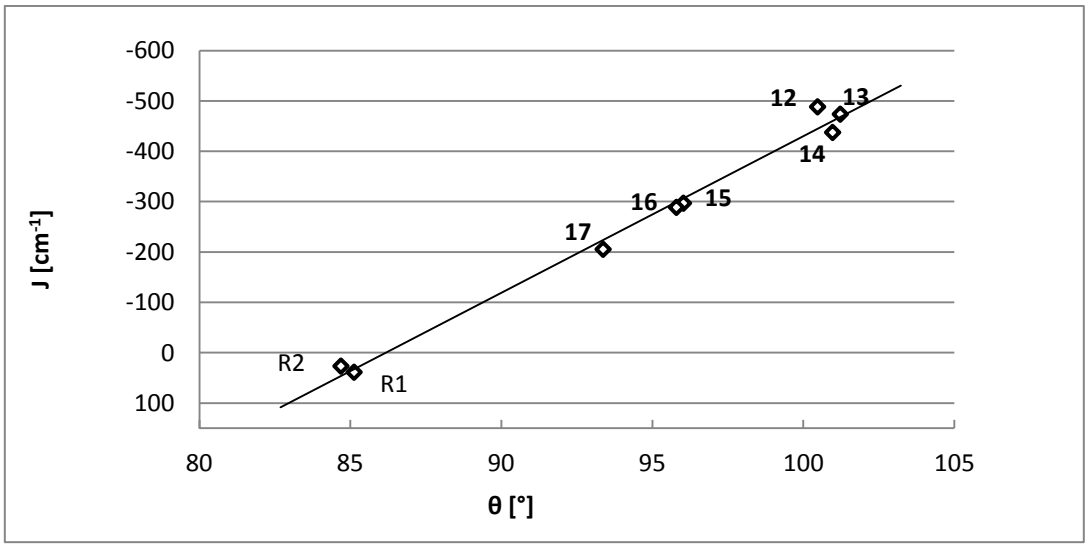
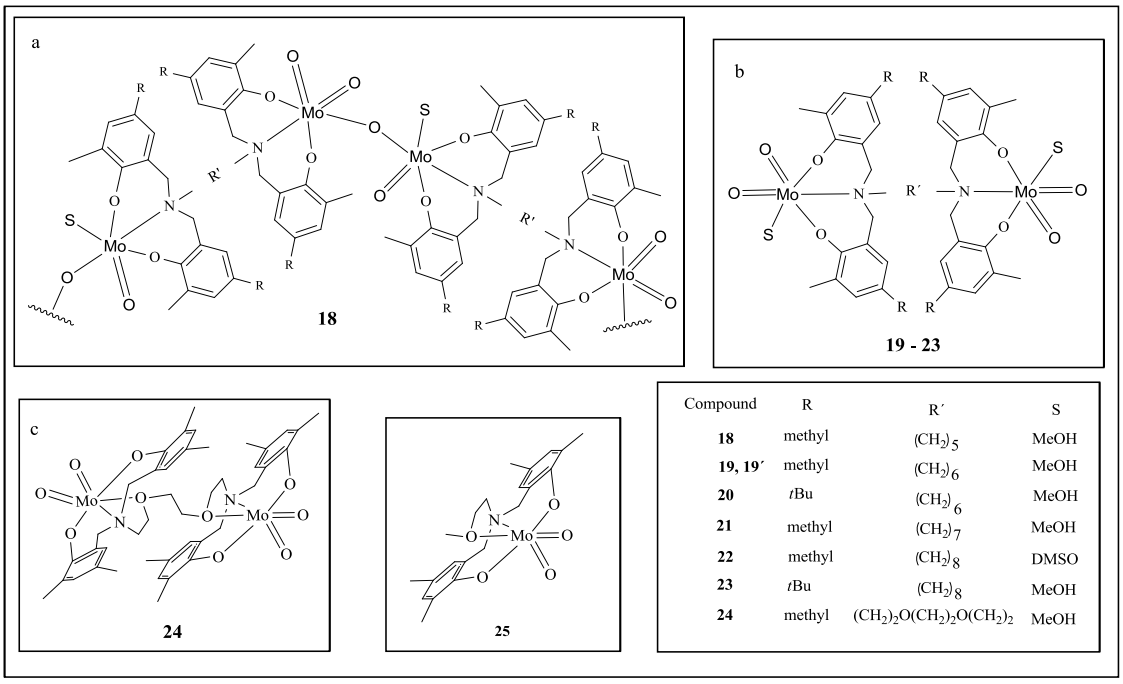


Figure 7. Cu-O-Cu angle Θ and J in complexes **12-17** without their solvent adducts and in reference compounds R1-R2 [28].

4.4 Structural and catalytic studies of Mo(VI) complexes

4.4.1 Structural studies



Compound	R	R´	S
18	methyl	$(CH_2)_5$	MeOH
19, 19´	methyl	$(CH_2)_6$	MeOH
20	*t*Bu	$(CH_2)_6$	MeOH
21	methyl	$(CH_2)_7$	MeOH
22	methyl	$(CH_2)_8$	DMSO
23	*t*Bu	$(CH_2)_8$	MeOH
24	methyl	$(CH_2)_2O(CH_2)_2O(CH_2)_2$	MeOH

Scheme 12. Schematic representation of Mo(VI) coordination entities of complexes 18-24. Compound 25 [119] was used as a reference material in oxidation reactions.

A direct reaction of $MoO_2(acac)_2$ and diaminotetraphenols in polar solvents such as MeOH or a DMSO-MeCN mixture resulted in the formation of ditopic dioxido Mo(VI) complexes 18-24 (Scheme 12, Figures 8-12). The molecular structures of all complexes reveal a similar distorted octahedral coordination sphere around the $[MoO_2]^{2+}$ cations with two *cis*-positioned oxido ligands strongly bound to the Mo(VI) ion, whereas two phenoxide oxygen atoms are placed in *trans* positions to each other. This is in agreement with known energetic and steric reasons.[123]

In complexes 19-23 the remaining two coordination sites are occupied by an amine nitrogen atom and an oxygen atom from the coordinating solvent (methanol or DMSO). In 24 in the place of a solvent oxygen atom there is an oxygen atom from the ether bridge between the N atoms.

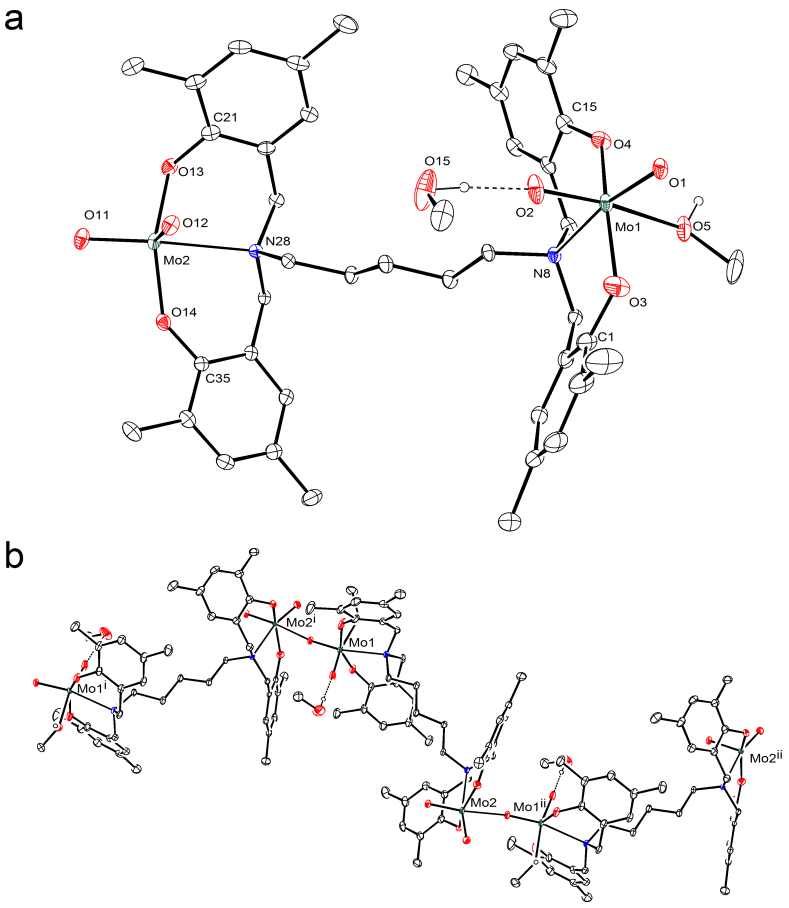


Figure 8. Solid state structure of 18. CH hydrogens are omitted for clarity. (a) Asymmetric unit of 18. (b) Part of the polymeric molecular chain of 18. Symmetry operations: i: 1 – x, –y + ½, –z – ½; ii: 1 – x, –y + ½, –z + ½. Thermal ellipsoids are drawn at the 20 % probability level.

Compound 18 is a polymer and it crystallizes in the orthorhombic *Pcab* (61) space group (Figure 8). The bridging between two dioxide molybdenum(VI) moieties in 18 takes place unsymmetrically along the *c* axis through the O1 atom. Only one methanol molecule is needed to attain the desired coordination number of 6 for both Mo atoms. The structural parameters around the bridging O1 are: Mo1=O1 1.733(3), Mo2^{i}–O1 2.305(3) Å (i: 1 – *x*, –*y* + ½, –*z* – ½); Mo1=O1–Mo2^{i} 170.21 (17) °. The Mo=O1 bond is 0.036 Å longer than the Mo1=O2 bond (1.697(3) Å), which indicates only a slight weakening of the π bonding in the Mo1=O1 bond. In the literature[29] the dimerization of a chemically similar dioxide Mo(VI) complex with aminobisphenol has been reported to take place through both oxido atoms. In this case, the nonlinear bridging parameters in the centrosymmetric structure are: Mo=O1 1.7519(16), Mo^{i}–O1 2.3901(16) Å (i: – *x*, 1 – *y*, 1 – *z*); Mo=O1–Mo^{i} 103.72(7) °; therefore the bridging has only marginal influence on the Mo=O bond in 18.

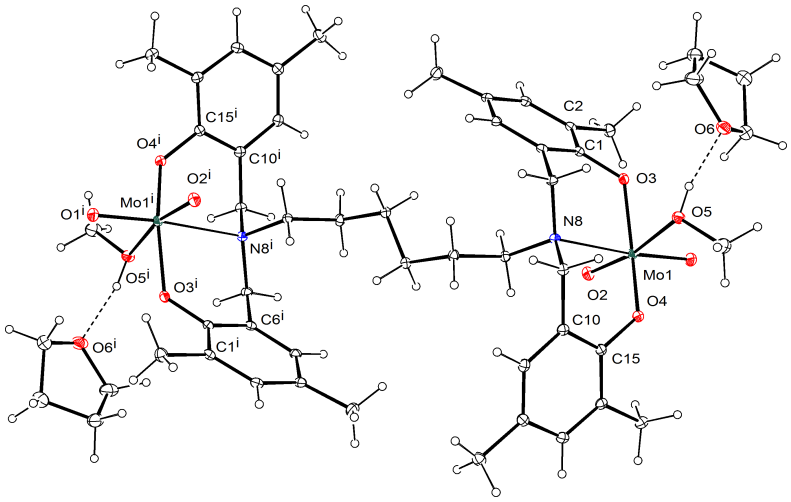


Figure 9. Molecular structure of 19. Thermal ellipsoids are drawn at the 20 % probability level. The structure of 19′ is similar to 19 without the THF molecules.

Other prepared complexes 19-24 are open chain ditopic molecules with rod-like structures. Figure 9 describes the structure of 19. The X-ray diffraction data for 23 were not satisfactory due to unorganized methanol molecules but we were able to get good quality crystals from DMSO, which allowed proper solving of the structure of **23**. In general, the crystallization of all complexes from DMSO-MeCN mixtures is relatively easy, but the DMSO molecules are often disordered. Therefore the methanol-containing structures are presented when possible. Attempts to prepare methanol-containing crystals from 22 and 23 were not successful. Methanol is also more easily replaced than DMSO, which is relevant in catalytic systems.

The temperature range in which the coordinated and uncoordinated solvent molecules are removed from the complexes is wide. Generally uncoordinated solvent molecules escape first by heating. The coordinated solvent stays much longer. The reason is that Mo(VI) keeps a coordination number 6 as long as possible; after the solvent has escaped it fills its coordination sphere by polymerization.

It was interesting to compare the removal of coordinated and uncoordinated solvent molecules, methanol in complex 18 and methanol and THF in complex 19, from the freshly prepared crystals. In 18 the temperature range of uncoordinated and coordinated methanol evaporation was 70–200 °C. In complex 19 the uncoordinated THF evaporates at room temperature in 5 min and the coordinated methanol in the range of 71–94 °C.

The uncoordinated solvent molecules are in the cavities of the structure and their location and stability depend on hydrogen bonding and other weak interactions. In Figure 10 the positions of solvent molecules in 19 and 20 are presented. The figure shows that solvent molecules are similarly organized but the alkyl chains are differently orientated.

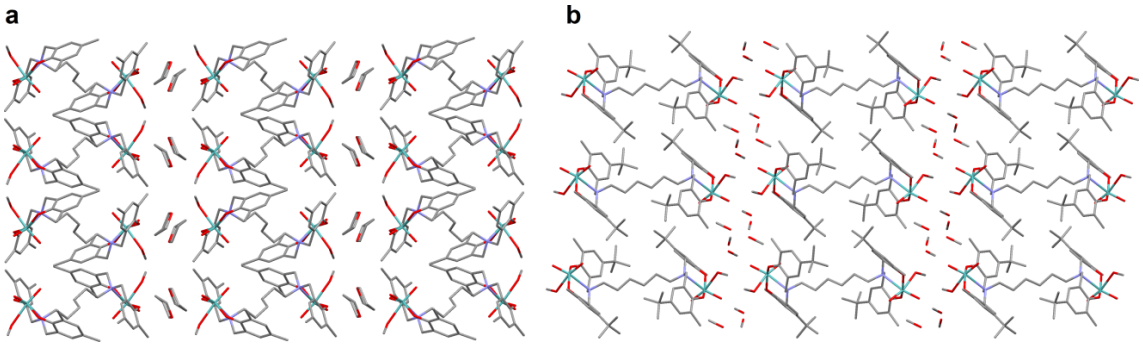


Figure 10. a) Packing diagrams of 19 and b) packing diagram of 20 showing the THF and MeOH layers, respectively. CH hydrogen atoms, disordered methanol molecules and the water molecule have been omitted for clarity reasons.

In Figure 11 is shown the structure of 22, in which disordered DMSO fulfills the 6th coordination site of the Mo(VI) ion and acetonitrile molecules fill the empty places in the lattice.

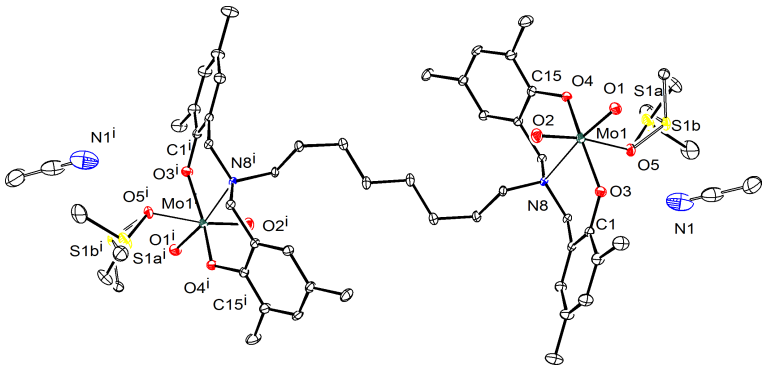


Figure 11. Molecular structure of 22. MeCN and DMSO molecules can be in two positions. Thermal ellipsoids are drawn at the 20 % probability level. Hydrogen atoms have been omitted for clarity reasons.

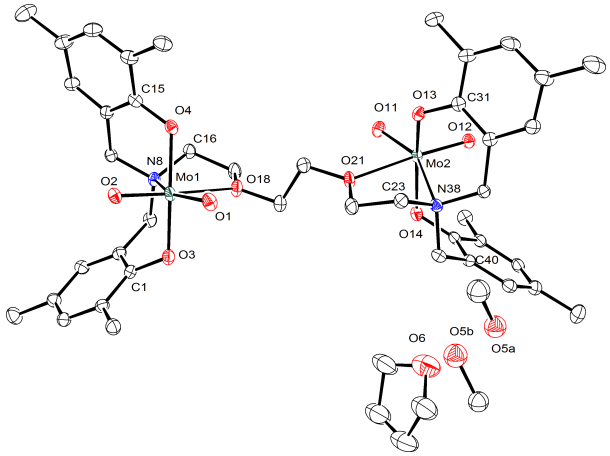


Figure 12. Molecular structure of 24. Thermal ellipsoids are drawn at the 20 % probability level. CH hydrogen atoms have been omitted for clarity.

In Figure 12 one can see how the oxygen atoms of the ether chain-bridged ligands of 24 are coordinated to Mo(VI) ions. The methanol atoms are disordered over two positions.

4.4.2 Catalytic studies

We have studied how dioxido Mo(VI) complexes of the ditopic diaminotetraphenolates catalyse the oxidation of benzyl alcohol into benzaldehyde with H_2O_2 as oxidant. Following the common procedure aromatic alcohol oxidation reactions proceeded poorly in common organic solvents such as acetonitrile, THF and toluene upon heating. In a neat substrate benzyl alcohol is moderately oxidized into benzaldehyde when using H_2O_2 as oxidant (Table 7). In our best catalytic system we used catalyst:benzyl alcohol:H_2O_2 in a 1:500:1000 ratio and also added NEt_3 to the system (2.5 times the Mo(VI) ions). The method used was similar to the same reaction catalyzed by the (oxido)(peroxido)Mo(VI) acetylide complex [CpMoO(O_2)(C≡CPh)] (TON = 396, 92 % selectivity)[120]; however, in this compound the coordination environment around Mo(VI) is totally different and no additional base was used. In our studies the best catalyst was complex **18**, with 50 % conversion and 100 % selectivity in 8 h (TON = 248, TOF = 31) as no benzoic acid was detected in the reaction. It is important to note that all complexes **18**-**24** had their catalytic efficiency in a similar range.

Table 7. Conversion %, TON, TOF and selectivity of Mo(VI) complexes in benzyl alcohol oxidation reactions.

Reaction	Catalyst[a]	Conversion [%]	TON	TOF [h^{-1}]	Selectivity [%]
a	**18** (0.01)	32	315	39	100
b	**18** (0.02)	50	248	31	100
c	**18** (0.04)	54	136	17	87
d	**19**	57	283	35	71
e	**20**	54	268	33	89
f	**21**	48	240	30	94
g	**22**	52	262	33	93
h	**22**[b]	33	160	20	64
i	**23**	53	267	33	93
j	**24**	53	264	33	82
k	**25**	37	183	23	100
l	R1	45	223	28	91
m	none	20	-	-	19

[a] 0.02 mmol catalyst; for **18** the amount of the catalyst is in parentheses. [b] No base. R1=$MoO_2(acac)_2$

Complex **25** is formally a half of complex **24**. An interesting observation was made when the catalytic activity of ether-bridged dioxido-Mo(VI) diamino-tetraphenol compound **24** was compared to the activity of the similar aminobi-sphenol counterpart **25**. The TON was 264 for **24** and 183 for **25**, indicating that both Mo(VI) centers in **24** are not active in the conversion, or **24** just acts poorly because of its rigidity and large size. The effect of coordinated solvent mole-cules (MeOH or DMSO) of the Mo(VI) cations, or the polymeric versus open chain structure of the molecules, had only minimal effects on the results. This is an indication that the substrate coordinates to the catalyst breaking the polymerization.

It was found that oxidations in neat alcohol and elevated temperatures were much faster and productive than the reactions in MeCN solutions. Effi-ciency is gained at the cost of selectivity, as benzoic acid started to form as a side product in many reactions. The role of the added base was not completely clarified, but it is supposed to improve the deprotonation of the hydroxyl groups of alcohol and peroxide, which after deprotonation are more liable to coordinate to the Mo(VI) centre making a catalyst more soluble and making the whole system more homogeneous. The increased yields of oxidation support this assumption. This may also indicate that these reactions proceed by the peroxidometal pathway (Scheme 5 in section 1.3.4).

If benzoic acid forms, it neutralizes the base and slows the reaction. An overdose of the base also slows down the reaction. Therefore the best result was obtained by adding the oxidant and the base in portions.

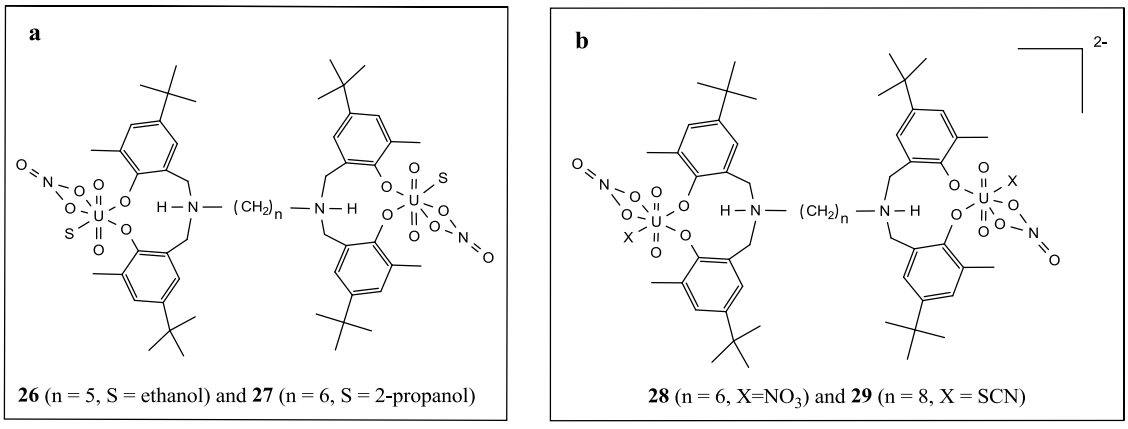
In another study we followed the epoxidation of cyclo-octene with *t*BuOOH in $CDCl_3$. The change of oxidant was in order to have the reaction proceed better, and we wanted to avoid a competing reaction in which cycloal-kenes are converted into cycloalkane-1,2-diols.[73] In general the results (Table 8) are similar to those in alcohol oxidation, 54 % conversion at 6 h using a cata-lyst:alkene:oxidant ratio of 5:100:500 and **24** as catalyst. However it was interest-ing that the monomeric counterpart **25** produced an equally good result (52 %) with only a half quantity of Mo(VI) ions. Furthermore, TONs were similar for both complexes (**24** TON=264 and **25** TON=183). A similar observation was made in the benzyl alcohol oxidation reaction. This demonstrates that if the re-action mechanism is the same for both types of complexes both Mo(VI) ions are not participating in the catalytic reaction in the ditopic molecules.

Table 8. Conversion percentages in cyclo-octene epoxidation using Mo(VI) catalysts at two concentrations.

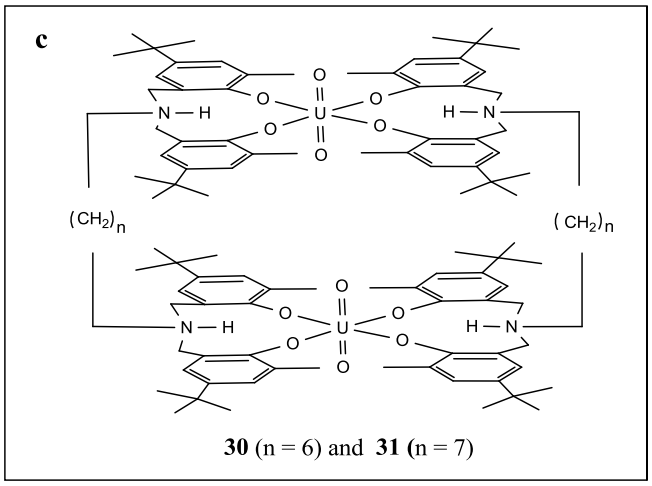
Time [min]	Catalyst **24** [2.5 mol-%]	Catalyst **24** [5 mol-%]	Catalyst **25** [5 mol-%]
0	0	0	0
30	4	7	7
60	9	15	15
105	16	26	25
115	18	31	28
125	19	32	32
135	19	35	36
145	20	38	39
155	20	41	40
165	21	43	42
175	21	45	43
185	22	46	44
195	24	47	46
240	27	49	49
300	29	53	51
360	31	54	52

4.5 Structural studies of uranyl complexes and extraction studies of uranyl ion

4.5.1 Structural studies



Scheme 13. Structure type **a** and **b** of U(VI) coordination entities of complexes 26-29.



Scheme 14. Structure type **c** of U(VI) coordination entities of complexes 30-31**.**

With diaminotetraphenols we were able to prepare and characterize three types of uranyl complexes (**a**-**c** in Schemes 13-14, Paper V). The 2:1 complexes **a**-**b** are of two types. Type a contains neutral complexes of the form $[(UO_2)_2(H_2L\mathbf{n})(NO_3)_2(S)_2]$ (in **26** n=2, S=ethanol and in **27** n=4, S=2-propanol), while type **b** compounds are anionic complexes of the form $[(UO_2)_2(H_2L\mathbf{n})(NO_3)_2(anion)_2]^{2-}$ (n=4, anion=nitrate in **28** and n=6 and ani-on=thiocyanate in **29**). 1:1 complexes (type **c**) were also prepared using ligands H_4L**4**-H_4L**6**; they have the general formula $[(UO_2)_2(H_2L\mathbf{n})_2]$ (n=4 in **30** and n=6 in **31**).

In the types **a** and **b** complexes **26**-**29** the ligand is in a linear or twisted conformation with a uranyl ion at both ends of the ligand. The ligands and nitrates are didentately coordinated to the uranyl ion. In type **a** complexes solvent molecules are filling the fifth coordination site in the equatorial plane, as presented in Figures 13a and 13b for 26 and 27, respectively.

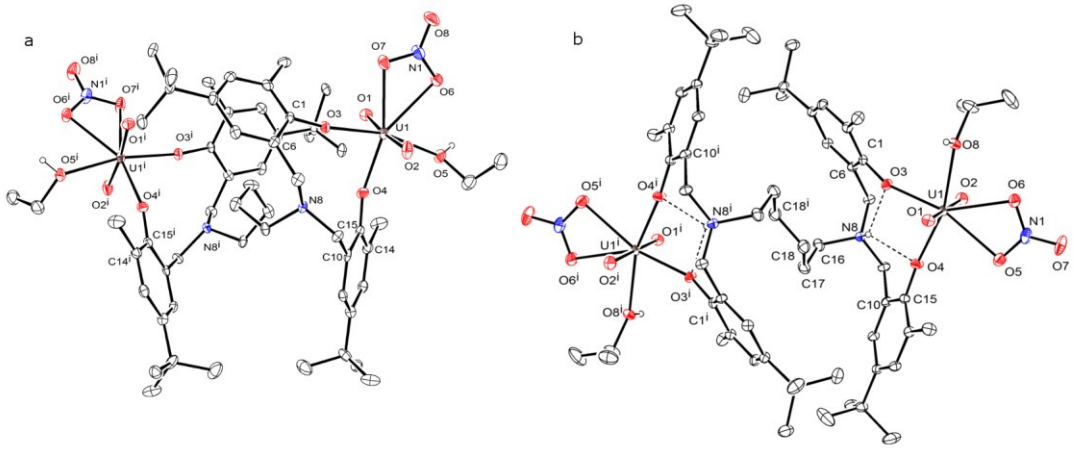


Figure 13. Molecular structures of 26 (a) and 27 (b). Thermal ellipsoids are drawn at the 20 % probability level. CH (and NH in 26) hydrogen atoms have been omitted for clarity.

In solid state molecules 26 and 27 form intermolecular OH···O=U hydrogen bonds (Figure 14). These H-bonds organize the molecules into rows. In both complexes and also in the rest of the uranyl complexes there are weak bifurcated intramolecular H-bonds from H8 to O3 and O4.

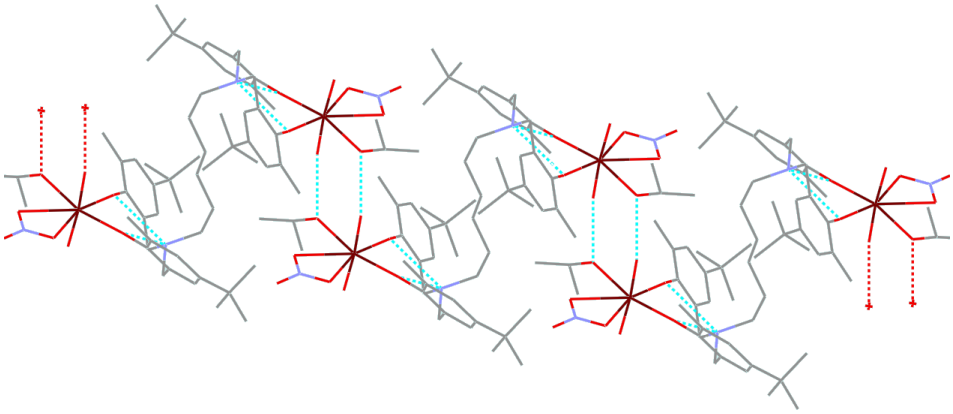


Figure 14. The packing diagram of 27 showing the intra and intermolecular hydrogen bonds.

In type **b** complexes (28 and 29, Figure 15) a donor atom of the anionic ligand (nitrate or thiocyanate) is in the place of the alcohol. The counter cation is a triethyl ammonium ion. In all complexes the uranyl oxido atoms are above and below the plane fulfilling the coordination geometry around the U atom as a distorted pentagonal bipyramid. Complexes where nitrate and thiocyanate anions are simultaneously coordinated into a uranyl ion like in **29** are rare, and only two previous examples are found in the literature.[124, 125]

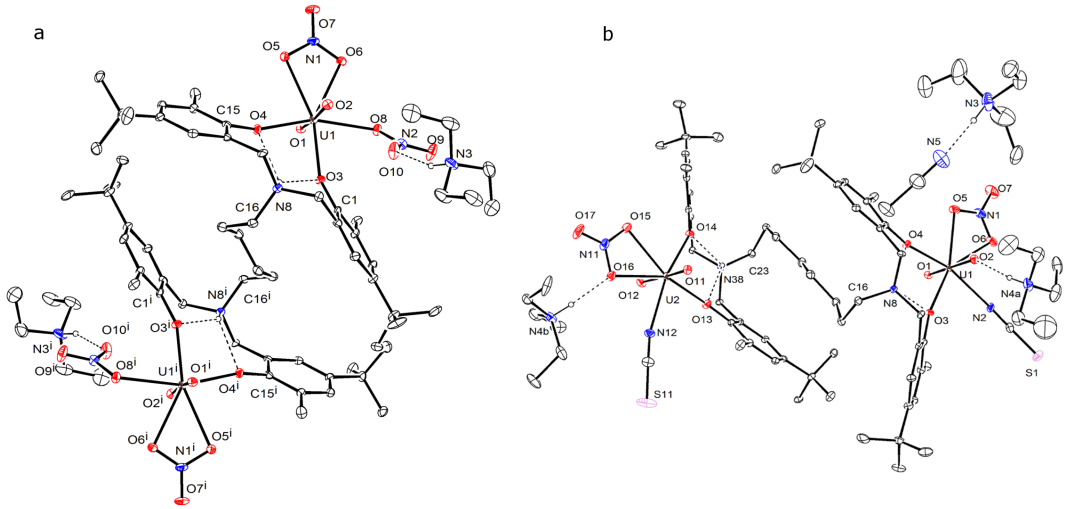


Figure 15. Complexes 28 (a) and 29 (b) in a solid state. Thermal ellipsoids are drawn at the 20 % probability level. CH_2Cl_2 and MeCN molecules and the CH hydrogen atoms have been omitted for clarity.

Type **c** complexes are dinuclear rings in which the U to the ligand ratio is 1:1. Type **c** complexes 30 and 31 could be isolated using ligands H_4L**4** and H_4L**6**. The closest reference compound where the coordination sphere of a $[U^{VI}O_2]^{2+}$ cation is similar is a uranyl complex with *p*-methyl-*N*-benzyltetrahomodiazacalix[4]arene.[126] However, among type **c** complexes there are two diaminotetraphenolate-bridged U planes in the same complex that have not been reported before.

The structures of 30 and 31 are quite similar, including their main structural parameters (Figure 16). In these molecules two uranyl ions and two ligands form a macromolecular ring with two separated planes. Four phenoxido atoms (two from each ligand) are coordinated to the U atoms. The uranyl oxido atoms are above and below the plane and the coordination geometry around the U atoms is octahedral.

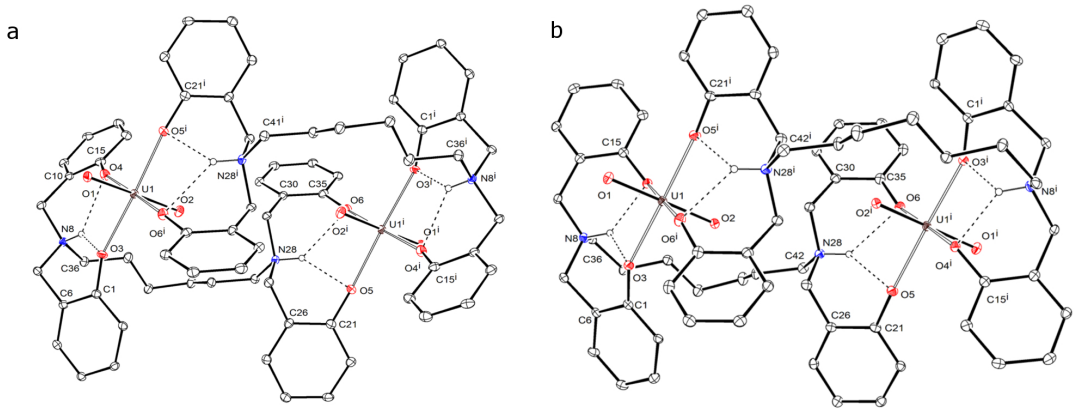


Figure 16. Solid state structure of 30 (a) and 31(b). Thermal ellipsoids have been drawn at the 20 % probability level. CH_2Cl_2 and MeCN molecules, methyl and *t*Bu substituents of the aromatic ring, as well as CH hydrogens are omitted for clarity. Note the different atom labeling compared to those in compounds 26-29.

The crystal packing as demonstrated by the structure of 30 (Figure 17), reveals that there are no strong intermolecular contacts and the rings are well separated. However, the structures are stabilized via weak CH···O=U hydrogen bonds and van der Waals forces while dichloromethane molecules fill the space between the cyclic molecules.

The shape of the neutral dinuclear rings is such that these complexes are soluble in slightly polar solvents. Uranyl ions can be extracted with these ligands from water into dichloromethane.

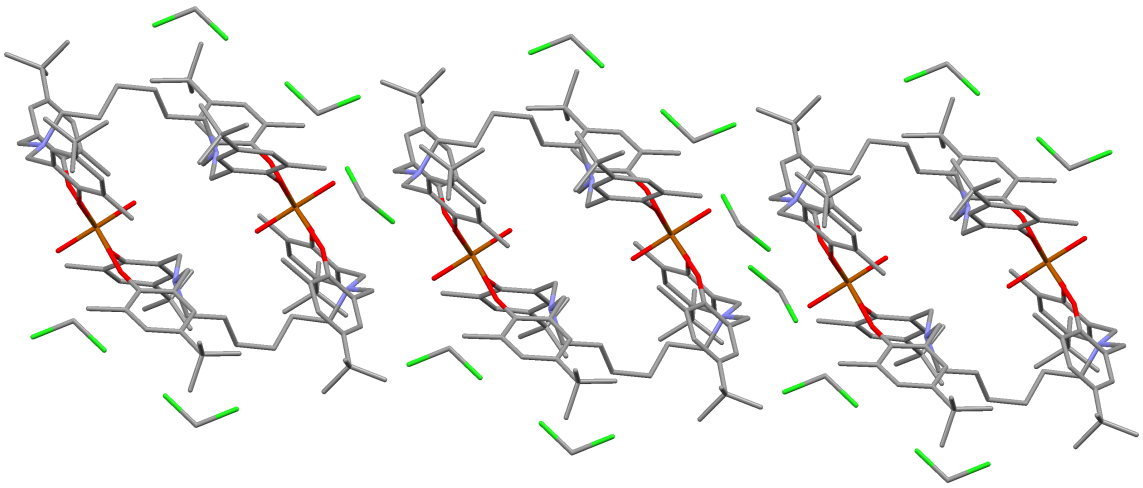


Figure 17. The packing diagram of 30. CH and NH hydrogen atoms are omitted for clarity.

4.5.2 Extraction studies

The diaminotetraphenol ligands, H_4L**2**, H_4L**4**, H_4L**6** and H_4L**8**, were studied as uranyl extractors. Their extraction efficiency was studied in two separate experiments **I** and **II** (see experimental part). In experiments **I** an ammonic uranyl ion solution (concentration 12 mM, 2.8 g/l) at pH 5.7 was extracted with the ligand (same molar concentration) in CH_2Cl_2. Samples from both phases were collected at certain time intervals as shown in Figure 18, which presents the uranyl concentration (%) in the CH_2Cl_2 phase vs. time.

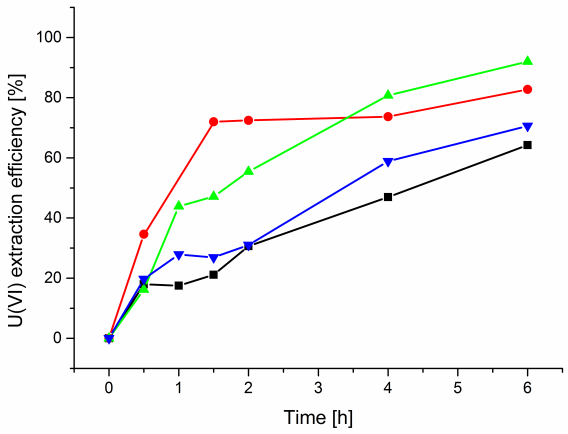


Figure 18. The extraction efficiency of U(VI) ions from water into a dichloromethane phase. Codes for the ligands are: H_4L**2** = black, H_4L**4** = red, H_4L**6** = green and H_4L**8** = blue.

One can conclude that all these ligands extract uranyl ions quite well. Ligands H_4L**4** and H_4L**6** are more effective than H_4L**2** and H_4L**8**. The highest extraction efficiency (~92 %) was obtained for ligand H_4L**6**, whereas the lowest (64 %) was for ligand H_4L**2** in a 6 h period. However, during most of the extraction experiments a yellow foam-like precipitate formed between the phases, which prevented high-yield uranyl extraction. The cleanest extraction process was achieved with H_4L**6**.

The distribution coefficients (D) calculated from the U content in the organic and water phase are in Table 9 tell the same story. However, with these values it is easier to compare present results to earlier ones.

Table 9. The distribution (D) of U(VI) ions between water phase and organic phase at equilibrium in extraction experiment I with selected diaminotetraphenols at pH 5.7.

Ligand	H_4L**2**	H_4L**4**	H_4L**6**	H_4L**8**
D*	9.1	7.5	12	10

*$D = m(U)_o/m(U)_w$, where $m(U)_o$ and $m(U)_w$ are the mass of U in organic and water phases.

From the distribution coefficients (Table 9) we can conclude that the extraction efficiency follows the order H_4L**6** > H_4L**8** > H_4L**2** > H_4L**4**. In the work of Sopo *et al.* the D coefficient was generally better with longer *n*-alkyl-substituted ligands,[9] but because they did their experiments without mixing using a much higher amount of the ligand and followed only the U concentration in the water phase, the results cannot be directly compared. In addition, the extraction kinetics plays an important role in these uranyl extraction systems.

In earlier uranyl extraction studies with aminobisphenols the uranyl ion concentration was 26 mM (6.3 g/l)[9, 10, 98] and the U to ligand ratio was 1:4 in a dichloromethane-water two-phase system. With aminoalcohol bisphenols, in which alkyl alcohol is a third substituent of the N atom, the uranyl extraction efficiency was 63-94 %. With aminoalkylbisphenols, which are formally a half of those used in Paper V, the uranyl extraction efficiency was 40-93 %.[9] In our study with diaminotetraphenols the initial uranyl ion concentration in the water phase was only one half of that used earlier 2.8 g/l. Also, the U to ligand ratio used was 1:1. One can conclude that with diaminotetraphenols a similar decrease in the U content in the water phase, 64-92 %, can be obtained in a more dilute system with a much smaller amount of the ligand.

In experiment **II**, the UO_2^{2+} extraction was done in the presence of Cu^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+} ions in order to find out if the extraction system is selective towards the uranyl ion. The results from the U content in the CH_2Cl_2 phase are in Figure 19.

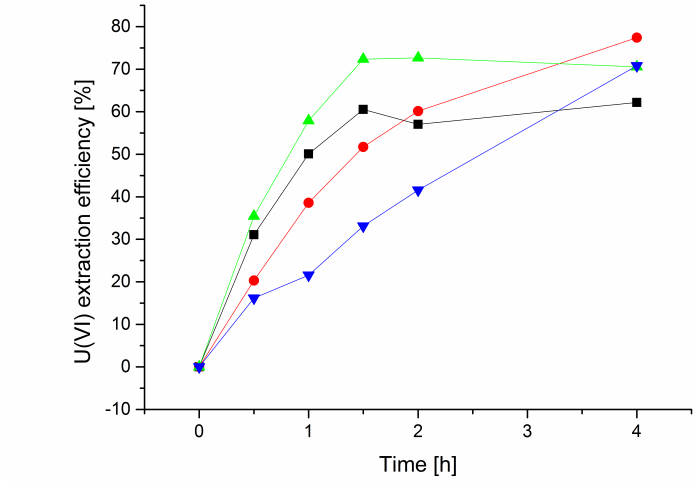


Figure 19. The extraction efficiency of U(VI) into the CH_2Cl_2 phase in multimetal systems. Codes for the ligands are: H_4L**2** = black, H_4L**4** = red, H_4L**6** = green and H_4L**8** = blue.

In this experiment the most effective extractor at the beginning is ligand H_4L**6** (ca. 72 % extraction at 1.5 hours). It works even faster during first 2 h than H_4L**4**; which is best at 4 hours (ca. 77 % extraction) The slowest uranyl extractor is H_4L**2** (60 % at 4 h), but it is very selective towards U(VI) as practically none of other transition metal ions studied were extracted. The distribution coefficients (Table 10) in experiment **II** at 4 h are several orders of magnitude lower than in experiment I. The reasons for that are presented below.

Table 10. The distribution (D) of U(VI) ions between water phase and organic phase at equilibrium in extraction experiment II with selected diaminotetraphenols.

Ligand	H_4L**2**	H_4L**4**	H_4L**6**	H_4L**8**
D*	1.4	3.3	2.8	2.4

*$D = m(U)_o/m(U)_w$, where $m(U)_o$ and $m(U)_w$ are the mass of U in organic and water phases.

With H_4L**4**, H_4L**6** and H_4L**8** small amounts of Cu(II) (5-10 %) were extracted with very little of Co(II), Ni(II) and Zn(II) cations (~2 % or less). The extraction of Cu(II) ions is possibly due to the formation of neutral $[Cu_4(L\mathbf{n})_2(H_2O)_2]$ or $[Cu_4(L\mathbf{n})_2]$ (n= **3**-**8**) complexes, which are soluble in organic solvents. Such complexes were reported in the cases of H_4L**5** and H_4L**7** (Paper III). On the other hand, H_4L**2** does not form isolable neutral tetranuclear Cu(II) complexes and thus cannot extract Cu(II) ions.

Ligand H_4L**2** extracted only 60 % of uranyl ions at 4 h, but it was very selective towards other metal ions (Cu^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+} ions), which practically did not extract at all. Evidently, H_4L**2** can form with those metal cations

several ionic complexes which do not extract. Generally the low availability of the ligands causes uranyl extraction to be lower in experiment **II**, as other metal cations consume a part of the ligands by complexation.

One good property of these extracted diaminotetraphenol complexes with the uranyl ion is that uranyl can be released from the complexes using acid (nitric or hydrochloric). With nitric acid the yield of the recycled ligand is lower than with hydrochloric acid. In this respect the decomposition of the extracted complex in methanol with HCl is recommended. With this procedure at least 79 % of the ligand can be recovered and used again.

5 CONCLUSIONS

The preparation of 11 new diaminotetraphenols using one-step three component condensation is described. The reaction of phenol, formaldehyde and amine carried out without any solvent results in aminobisphenols and diaminotetraphenols in a very high yield in a short time. Hydrogen bonding plays a key role in controlling the crystal packing and conformation of the these ditopic molecules, thus affecting the solubility and physical properties of the compounds.

These diaminotetraphenol ligand precursors present three coordination sites (two phenoxide O and one amine N donor) at both ends of the flexible alkyl or ether chain. This type of ligand can coordinate to metal ions in several ways; they were studied as ligands in the preparation of new Cu(II)-, Mo(VI)-, and U(VI) complexes in order to synthesize new metallo-organic compounds. The ligands and complexes were characterized by elemental analysis, IR and NMR spectroscopy and X-ray diffraction.

Cu(II) cations formed six slightly different tetranuclear diphenoxido-bridged rings in a 2:1 ratio (Cu:L) in which the magnetic coupling of the complexes varies as a function of the Cu−O−Cu-bridging angle. The magnetic interaction in these Cu(II) complexes was shown to be antiferromagnetic.

Seven new dioxido Mo(VI) complexes were prepared from $[MoO_2(acac)_2]$ and diaminotetraphenol ligands. Generally they are linear molecular complexes, where a MoO_2^{2+} unit is bonded with three donor atoms from the ligand and a donor atom of a solvent molecule (methanol or DMSO) at both ends of the ligand. The ether-bridged ligands formed similar complexes without coordinating solvents, as the oxygen atom in the bridge replaces the solvent. One complex with an oxido-bridged polymeric structure was also obtained.

The Mo(VI) complexes generally have catalytic activity in oxo-transfer reactions. Oxidation of benzyl alcohol into benzaldehyde and oxidation of cyclo-octene into epoxide were used as model reactions. The literature

procedure of alcohol oxidation in neat alcohol could be improved by adding a base to the reaction mixture. The results of the oxidation reactions with prepared complexes show that their activity is moderate but their selectivity is very good.

Uranyl ions form both 2:1 and 1:1 (metal to ligand ratio) complexes. In 2:1 complexes uranyl ions are at both ends of the ligand bond to two ligand donor atoms and two oxygen atoms of nitrate. The fifth coordination position in the equatorial pentagonal plane is occupied by a donor atom from the solvent (alcohol) or from an anion. In the latter case an anionic complex is formed. In the 1:1 complexes two uranyl ions and two ligands form a neutral ring, which is a very unusual structure. These ring-like uranyl complexes have a moderate solubility in weak polar water-immiscible solvents.

The diaminotetraphenol ligands extract selectively and efficiently uranyl ions from water into an organic phase as uranium to diaminotetraphenol (1:1) complexes. In the pure uranyl ion experiment with U:L (1:1) ratio a ~92 % extraction efficiency was obtained for ligand H_4L**6** in a 6 h period. In similar uranyl ion concentrations in the presence of Cu^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+} ions, the extraction efficiency with the same ligand was ca. 72 % in 4 hours, while the selectivity for the uranyl ion was still good. Practically, only a small amount of Cu(II) ions was extracted. The uranyl ion can be separated from the complexes, for example, with hydrochloric acid, thus allowing the reuse of the ligand in the uranium separation process.

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ORIGINAL PAPERS

PAPER I

One-Pot Three-Component Solvent-Free Syntheses of *n*-Alkyl-Bridged *N,N,N',N'*-tetra(2-hydroxybenzyl)diamines and *N,N*-bis(2-hydroxybenzyl) amines

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Abstract: A simple solvent-free method to prepare four *N,N,N',N'*-tetra(2-hydroxy-3,5-dimethylbenzyl)diaminoalkanes and four *N,N,N',N'*-tetra(2-hydroxy-5-*t*-butyl-3-methylbenzyl)-diaminoalkanes containing a long *n*-alkyl-bridge (5-8 CH_2 groups between N-atoms) is described. In addition, preparations of four dihydrochlorides of prepared *n*-alkyl-bridged *N,N,N',N'*-tetra(2-hydroxybenzyl)diamines are described. This method was also tested in the preparation of eight previously reported *N,N*-bis(2-hydroxybenzyl)amine derivatives.

Keywords: Aminobisphenols, condensation reactions, diaminotetraphenols, solvent free synthesis, X-ray diffraction.

INTRODUCTION

Aminobisphenols are important ligands in catalytic chemistry [1]. Their preparation is generally performed by the Mannich condensation reaction using phenol, formaldehyde and amine as starting materials [2]. Usually these reactions are carried out in polar solvents such as methanol, ethanol or acetonitrile with or without water. The reactions can be carried out over a wide temperature range from RT to the boiling point of the solvent. These methods usually require a long reaction time from a few days up to many weeks. Recently Collins *et al.* [3a] performed some Mannich condensation reactions in pure water. Later Kerton *et al.* [3b] did the reactions "on water" or in polyethyleneglycol (PEG) assisted with microwaves, which reduced reaction times to as short as 10 minutes. Some Mannich reactions have also been shown to proceed without solvent at 80-85 °C, but slowly [4].

We have used amino 2,4-substituted bisphenols for uranyl ion complexation and extraction studies [5] and for tungsten(VI) and molybdenum(VI) complexation [6]. In our previous investigations the length of alkyl amine tail had an influence on uranyl ion extraction from water to dichloromethane in a two phase system [5b].

Now our further focus is on studies of long *n*-alkyl-bridged *N,N,N',N'*-tetra(2-hydroxybenzyl)diamines, which formally are alkylaminobisphenols, where another amino-bisphenol group is situated at the end of an alkyl chain. The alkyl-bridged diaminotetraphenols are interesting difunctional ligands, which have the potential to form homo- and heteronuclear metal complexes with interesting magnetic and catalytic properties, and they can also be effective metal ion extractors. Such ligands have been prepared from 1,2-ethylenediamine using 2,4-disubstituted phenols [4] and a phenol [7]. Also 2-naphthol readily forms a tetra naphtol derivative from 1,7-diaminoheptane [8].

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As earlier used methods produced *n*-alkyl-bridged *N,N,N',N'*-tetra(2-hydroxybenzyl)diamines slowly and in a low yield, we now report a one-pot, three-component preparation method for these compounds *via* a condensation reaction without solvents or radiation devices in open air reaction vessels. This reduces the amount of organic waste in the synthesis and makes the synthesis safer to carry out and easier to monitor. The usefulness of the method is demonstrated by preparing eight new *n*-alkyl-bridged *N,N,N',N'*-tetra(2-hydroxybenzyl)diamines (diaminotetraphenols) from 1,n-diamines (n = 5-8) (two of them were isolated only as dihydrochlorides). The reaction path is shown in Scheme **1**. Also eight known aminobisphenols are synthesized using this new method and the yields obtained are compared to those obtained earlier.

RESULTS AND DISCUSSION

Preparation of *n*-alkyl-bridged *N,N,N',N'*-tetra(2-hydroxybenzyl)diamines

Generally the yield of the Mannich condensation reaction depends on the phenol and amine. For example in the synthesis of aminobisphenols from 2,4-substituted phenols the smaller the substituent at positions 2 and 4, the lower is the yield [3b]. The role of the phenol is also shown by the fact that 2-naphthol reacts so easily [2,8]. To avoid low yields and long reaction times with slowly reacting starting materials we performed the reactions at elevated temperatures without solvent using paraformaldehyde as the aldehyde. In order to demonstrate the usefulness of this synthetic procedure, we have used 2,4-dimethylphenol and 4-*t*-butyl-2-methylphenol as phenolic starting materials, which generally produce low yields in this type of condensation reactions. Diamines ($H_2N(CH_2)_nNH_2$, n = 5-8) were used as amines in these Mannich condensations. The codes and the yields of the prepared *n*-alkyl-bridged *N,N,N',N'*-tetra(2-hydroxybenzyl)di-amines **1**-**8** are shown in Table **1**.

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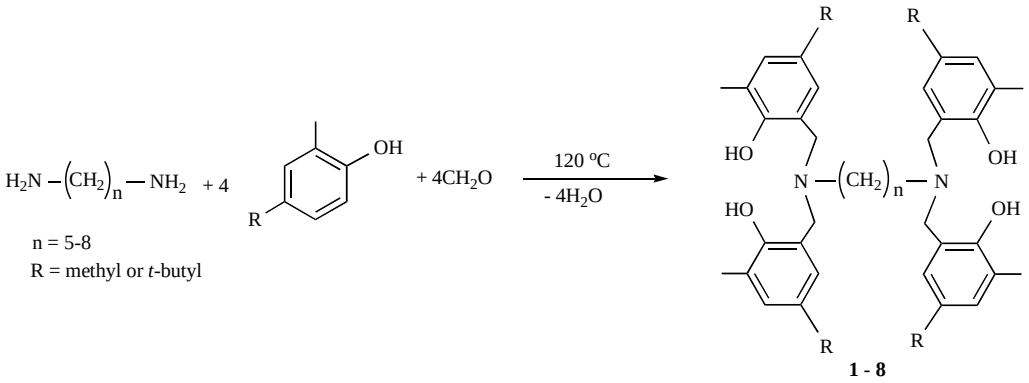


Scheme 1. The reaction path for *n*-alkyl-bridged *N,N,N',N'*-tetra(2-hydroxybenzyl)diamines.

In general the crude product was obtained by placing all starting materials in the same vessel and heating the vessel at 120 °C in the thermal oven for one hour (in the synthesis of **4** the heating time was 8 h). All syntheses proceed in a similar way; the progress of the reactions was monitored by HPLC measurements.

Table 1. The Codes and the Yields of the Prepared *n*-Alkyl-Bridged *N,N,N',N'*-tetra(2-hydroxybenzyl)diamines 1-8

Compound	n	R in Scheme 1	Isolated Yield
1	5	methyl	81 % / 40 %[a]
2·2HCl	5	*t*-butyl	40 %
3	6	methyl	35 % / 20 %[a]
4	6	*t*-butyl	47 % / 38 %[b]
5	7	methyl	33 %
6·2HCl	7	*t*-butyl	35 %
7	8	methyl	56 %
8	8	*t*-butyl	34 % / 30 %[b]

[a]yield using the solution method, [b]yield isolated as a dihydrochloride.

It is essential that the reactions are performed at higher temperatures than 100°C (optimum is around 120°C). This ensures that water produced in the reaction is evaporated from the system. Lower temperatures lead to very low yields and a poor predictability of the system.

Reactions should be performed in the open reaction vessel covered by a glass plate. Covering the reaction vessel may slow down the evaporation of formaldehyde and amine (if volatile) at the beginning of the reaction processes. Totally open reaction vessel gives slightly lower yields than the covered one, but the tightly closed one produces several side products and considerably lower yields.

In the syntheses of **2**, **6**, **7**, **8** a longer reaction time (up to 8 hours) increased the yield only marginally, but the amount of side products increased, which made isolation of the desired product more difficult. According to these studies only the synthesis of **4** seems to benefit from a longer (8 h) reaction time.

In the case of compounds **4** and **7** experiments were done to find out the influence of a higher temperature (140 °C and 160 °C) on the yields. The lower yields obtained at these temperatures for **4** and **7** supported that temperature of 120 °C was near the optimal one. An excess of paraformaldehyde and phenol (25 %) seems to increase the yields of *n*-alkyl-bridged *N,N,N',N'*-tetra(2-hydroxybenzyl)diamines, but it can cause purification problems later. A large excess of paraformaldehyde can increase the formation of dibenzoxazines [4]. In the syntheses of **2** and **6** the isolation of the product was much easier when the crude product was transformed to a dihydrochloride. This is generally not a desirable step, as one has later to remove the HCl in order to get an actual diaminotetraphenol, but for **2** and **6** it was necessary. In the syntheses of **2**•2HCl, **4**•2HCl and **5** overcritical solutions were easily formed, and mixing of these solutions before cooling significantly reduced the precipitation time.

Generally the yields of diaminotetraphenols were moderate to good (30-56 %), but compound **1** gave a very good 81 % yield. Similar yields (30-92 %) were obtained for diaminoalkylbisphenols using microwave heating [3b]. The yield for *N,N,N',N'*-tetra(2-hydroxy-3,5-dimethylbenzyl)-1,2-diaminoethane was 27 % [4]. Preparation of **1** and **3** was also done in solution, which gave 40 % yield for **1** and 20 % yield for **3** (reaction time **6 days**). Reactions at 120 °C in one hour by solventless method gave 81 % and 35 % yields for **1** and **3** respectively. These two tests show that solventless reactions at 120 °C give much better yields in a short time.

The reported new *n*-alkyl-bridged diaminotetraphenols can be useful compounds for metal ion complexation. Their conformations and crystal packing system in solid state are interesting as such. Thus single crystals were grown for **4**•2HCl and **5** and their structures were solved from X-ray data. The Ortep view of **4**•2HCl•2MeOH is presented in Fig. (**1**), which shows a centrosymmetric structure with an intensive H-bond system.

A crystal structure determination of **5** (Fig. **2**) revealed the cyclic H-bonded arrangement in the molecule.

This intramolecular H-bond system causes a cup like conformation for the molecule. This arrangement is similar to the structure formed by two alkylaminobisphenols [9].

Preparation of *N,N*-bis(2-hydroxybenzyl)amine Derivatives

We also tested the suitability of this one-pot three-component method for the preparation of known

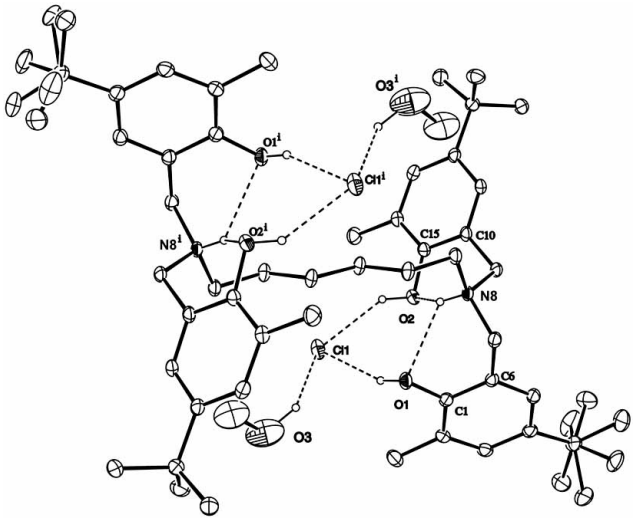


Fig. (1). The ORTEP plot of the solid state structure of **4**•2HCl•2MeOH. (CH hydrogens are omitted for clarity). The *t*-butyl groups at C4 are disordered over two positions.

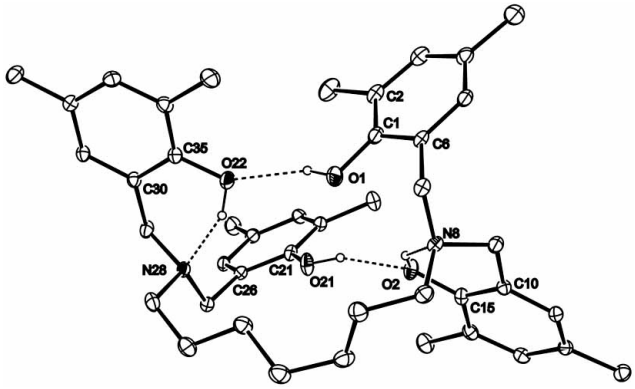
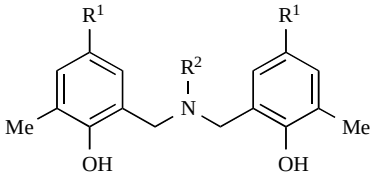


Fig. (2). The ORTEP plot of the solid state structure of **5**. (CH hydrogens are omitted for clarity).

aminobisphenols [5b-5d] and thus several reactions with phenols, paraformaldehyde and amines (aminoalcohols and alkylamines) were carried out at 120 °C. The synthetic procedure for **9**-**16** is similar to that for **1**-**8** in Scheme **1**: the *n*-alkyldiamine is replaced with a primary amine. The compounds prepared are shown in Scheme **2**.

Most of **9**-**16** were isolated as hydrochlorides because for these compounds the isolation as a free base is difficult. The compounds were identified by ^{1}H NMR measurements by comparing their spectra with those reported earlier [5b-5d]. These syntheses were carried out either by refluxing the starting materials in methanol or keeping the reaction mixture in a water bath (50 °C) using 37 % formaldehyde (in water) as aldehyde. The results of the syntheses of compounds **9**-**16** are presented in Table **2**.

The results shows that the isolated yields increased in all cases and the reaction times are much shorter in the solvent-free method. This method provides an easy route for synthesizing these types of compounds.



Compound	R^1	R^2
9	methyl	ethyl-2-ol
10	methyl	propyl-3-ol
11	methyl	butyl-4-ol
12	methyl	pentyl-5-ol
13	*t*-butyl	ethyl-2-ol
14	*t*-butyl	propyl-3-ol
15	*t*-butyl	hexyl
16	*t*-butyl	cyclohexyl

Scheme 2. The synthesized *N*,*N*-bis(2-hydroxybenzyl)amines (isolated as hydrochlorides).

HPLC provided great assistance in monitoring the reaction process. Reaction times longer than five hours did not improve the yield. On the contrary, longer reaction times increased the amount of side products. In particular a methylenebisphenol product was formed. This isolated compound was always observed in chromatograms at longer reaction times.

The actual yields of *N*,*N*-bis(2-hydroxybenzyl)amino alcohols were improved in all cases, some even from very low to moderately good. For compound **10** two experiments *E1* and *E2* were performed. In both experiments the starting materials were heated in the thermal oven in the same way for 4.7 h. Compound **10** was isolated in experiment *E1* by crystallization from cold toluene, as was also done earlier [5c]. The yield was now 38 %, which is much higher than earlier (5.2 %) [5c]. When **10** was isolated from experiment *E2* as hydrochloride, the yield of the hydrochloride was 60 %. This gives some evidence, in particular with compound **10**, that improvements in yield depend on both the reaction and the purification method used.

The final conclusion from this work is that the one-pot three-component synthetic method for the preparation of *N*,*N*-bis(2-hydroxybenzyl)amines and *n*-alkyl-bridged *N*,*N*,*N*,*'N'*-tetra(2-hydroxybenzyl)diamines works very well for the purpose. Isolation of the products can be a problem in some cases. The treatment of the crude product with hydrochloric acid provided an easy and universal method for the purification of the product, especially for the aminobisphenols. This can significantly save time during the purification process.

EXPERIMENTAL

General

The starting materials for all syntheses were purchased from commercial sources and were used as purchased. The solvents were of HPLC grade. All syntheses and extraction

Table 2. The Yields and Reaction Times of 9-16

Compound	Old Method [5b-5d]		New Method	
	Yield [%]	(Time [h])	yield [%]	(Time [h])
9	43*	(24)	66	(2.5)
10	5.2*	(24)	38* / 60	(4.7)
11	13	(118)	48	(2.2)
12	18	(25)	63	(2.3)
13	44*	(30)	89	(4)
14	17	(9)	63	(5)
15	44	(74)	79	(2.5)
16	29	(74)	81	(3.3)

*Isolated as a free aminoalcoholbisphenol.

experiments were performed under ambient laboratory atmosphere. The NMR spectra were recorded on a Bruker AVANCE DRX 500 FT-NMR or on a Bruker AVANCE DPX 250 FT-NMR spectrometer. The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, MeOD or d_6-DMSO at 30 °C. The chemical shifts are reported in ppm and referenced internally using the residual polar solvent resonances relative to tetramethylsilane ($CDCl_3$ δ = 7.26, ^{1}H NMR; δ = 77.0, ^{13}C NMR; MeOD δ = 3.30, ^{1}H NMR; δ = 49.15, ^{13}C NMR; DMSO-d_6 δ = 2.50, ^{1}H NMR; δ = 39.50, ^{13}C NMR). Elemental analyses were performed using a VarioEl III elemental analyzer and found figures are averages of two measurements. TOF accurate mass spectra were measured by a Micromass LCT ESI-TOF instrument using leucine encephalin (Sigma, 99 %) as the internal standard. The single crystal X-ray measurement was performed with an Enraf Nonius Kappa CCD area-detector diffractometer. For liquid chromatography measurements a Perkin Elmer series 200 equipment was used (Column: Phenomenex Luna 5u C18 250x4.60 mm, solvent: methanol-tris-buffer (97.5 % methanol, 2 % water and 0.5 % tris(hydroxymethyl) aminomethane) 100-90 % and water 0-10 %, flow rate 2 mL/min for 1-8 and 1 mL/min for 9-16, λ = 254 nm).

Synthesis of *n*-alkyl-bridged N,N,N',N'-tetra(2-hydroxybenzyl)diamines

N,N,N',N'-tetra(2-hydroxy-3,5-dimethylbenzyl)-1,5-diaminopentane (1)

The crude product of **1**: 1,5-diaminopentane (0.613 g, 6 mmol), 2,4-dimethylphenol (3.66 g, 30 mmol (24 mmol equiv.)) and paraformaldehyde (0.900 g, 30 mmol (24 mmol equiv.)) were placed in a 50 mL decanter and covered with a glass plate. The vessel was then kept at 120 °C for one hour in a thermal oven and the product was allowed to cool to RT. Purification: The yellowish product was dissolved in hot dichloromethane (10 mL) and *n*-pentane (20 mL) was added. The solution was kept in a refrigerator (7 °C) overnight. The formed milky mixture was centrifuged. The white precipitate obtained was dried and dissolved in boiling acetonitrile (30 mL). The solution was placed in a refrigerator for three hours and precipitated **1** was separated by filtration as a white powder. The filtrate was kept in a refrigerator overnight and a small amount of extra precipitate was filtered and added to the product. Yield 3.1 g (81 %).

^{1}H NMR ($CDCl_3$, 500 MHz, ppm): δ = 7.79 (s, 4H, aryl-O*H*), 6.85 (d, *J* = 2 Hz, 4H, aryl *H*), 6.71 (s, 4H, aryl *H*), 3.62 (s, 8H, N-CH_2-aryl), 2.47 (t, *J* = 7 Hz, 4H, N-CH_2-alkyl), 2.25 (s, 12H, aryl-CH_3), 2.20 (s, 12H, aryl-CH_3), 1.53 (m, *J* = 7 Hz, 4H, alkyl CH_2) and 1.25 (m, *J* = 7 Hz, 2H, alkyl CH_2).

^{13}C NMR ($CDCl_3$, 126 MHz, ppm): 152, 131, 129, 128, 124, 122 (aryl *C*), 56.0 (N-*C*H_2-aryl), 53.0 (N-*C*H_2-alkyl), 25.8 and 24.8 (alkyl *C*), 20.4 and 15.9 (aryl-*C*H_3).

ESI-TOF MS 639.4146 $[M+H]^+$. The calculated value 639.4162 $[M+H]^+$.

Elemental anal. for **1**. Calc. for $C_{41}H_{54}N_2O_4$: C, 77.0; H, 8.84; N, 4.38. Found: C, 77.6; H, 8.73; N, 4.14.

N,N,N',N'-tetra(2-hydroxy-5-t-butyl-3-methylbenzyl)-1,5-diaminopentane•2HCl (2•2HCl)

Crude product of **2**: 1,5-diaminopentane (0.307 g, 3 mmol), 4-*t*-butyl-2-methylphenol (2.46 g, 15 mmol (12 mmol equiv.)) and paraformaldehyde (0.450 g, 15 mmol (12 mmol equiv.)) were placed in a 50 mL decanter and covered with a glass plate. The vessel was then kept at 120 °C for one hour in a thermal oven. Purification: The warm solid was dissolved in 10 mL boiling acetonitrile and 6 M HCl (2.0 mL, double amount) and water (500 µL) was added. The solution was cooled down to RT (10 minutes) after which it was vigorously stirred for 10 min with a magnetic stirrer and allowed to settle down at RT for three hours. The filtered solid was purified twice by dissolving it into hot methanol (4 mL) and acetonitrile (40 mL) was added. The vessel was kept in the refrigerator (6 °C) for 4 hours after which **2**•2HCl was collected by filtration as white powder. Yield 1.0 g, 40 %.

^{1}H NMR for **2**•2HCl (MeOD, 500 MHz, ppm): 7.24 (d, *J* = 2 Hz, 4H, aryl *H*), 7.15 (d, *J* = 2 Hz, 4H, aryl *H*), 4.37 (s, 8H, N-CH_2-aryl), 3.12 (t, *J* = 8 Hz, 4H, N-CH_2-alkyl), 2.25 (s, 12H, aryl-CH_3), 1.79 (m, *J* = 8 Hz, 4H, alkyl CH_2), 1.27 (m, 38H, aryl-*t*-butyl, alkyl CH_2 (overlapping)).

^{13}C NMR (MeOD, 126 MHz, ppm): 153, 145, 131, 127, 126, 118 (aryl *C*), 57.1 (N-*C*H_2-aryl), 54.2 (N-*C*H_2-alkyl),

35.0 and 32.0 (*t*-butyl *C*), 24.7 and 24.5 (alkyl *C*), 16.9 (aryl-*C*H_3).

ESI-TOF MS 807.6058 $[M+H]^+$. The calculated value 807.6040 $[M+H]^+$.

Elemental anal. for **2**•2HCl. Calc. for $C_{53}H_{80}N_2O_4Cl_2$: C, 72.3; H, 9.16; N, 3.18. Found: C, 72.0; H, 9.16; N, 2.99.

N,N,N',N'-tetra(2-hydroxy-3,5-dimethylbenzyl)-1,6-diaminohexane (3)

The crude product of **3** was prepared as that of **1** using 1,6-diaminohexane (0.698 g, 6 mmol) in place of 1,5-diaminopentane. Purification started by dissolving the yellowish product in hot THF (40 mL). A small amount of undissolved solid was filtered and discarded. To the THF solution were added acetone (20 mL) and H_2O (16 mL). The mixture was kept in a refrigerator (7 °C) overnight and **3** was obtained as white powder after filtration. The product was recrystallized from a THF-acetone-water-mixture (10:5:4) as described for the crude product. Both crystallization solutions produced a small amount of substance when stored in a refrigerator for another day. These products were added to the main product. Yield 1.4 g (35 %) (white powder).

^{1}H NMR (DMSO-d_6, 500 MHz, ppm): 9.47 (s, 4H, aryl-O*H*), 6.75 (s, 4H, aryl *H*), 6.69 (d, *J* = 1 Hz, 4H, aryl *H*), 3.57 (s, 8H, N-CH_2-aryl), 2.33 (t, *J* = 7 Hz, 4H, N-CH_2-alkyl), 2.13 (s, 12H, aryl-CH_3), 2.09 (s, 12H, aryl-CH_3), 1.42, (m, *J* = 7 Hz, 4H, alkyl CH_2) and 1.03 (m, *J* = 3 Hz, 4H alkyl CH_2).

^{13}C NMR (DMSO-d_6, 126 MHz, ppm): 152, 130, 128, 127, 124, 123 (aryl *C*), 54.5 (N-*C*H_2-aryl), 52.3 (N-*C*H_2-alkyl), 26.3 and 25.0 (alkyl *C*), 20.0 and 16.0 (aryl-*C*H_3).

ESI-TOF MS 653.4305 $[M+H]^+$. The calculated value 653.4318 $[M+H]^+$.

Elemental anal. for **3**: Calc. for $C_{42}H_{56}N_2O_4$: C, 77.2; H, 8.65; N, 4.29. Found: C, 77.4; H, 8.45; N, 3.90.

N,N,N',N'-tetra(2-hydroxy-5-t-butyl-3-methylbenzyl)-1,6-diaminohexane (4)

The crude product of **4** was obtained like for **2** using 1,6-diaminohexane (0.349 g, 3 mmol) and heating the mixture for 8 h in a thermal oven (120 °C). Purification: The yellow product was dissolved in boiling CH_2Cl_2 (10 mL) and acetonitrile (20 mL) was added. The vessel was vigorously stirred for 5 minutes and then kept at RT for 2.5 hours. The formed solid was separated by filtration. The product was dissolved in warm THF (4.0 mL) and acetonitrile (8.0 mL) was added. The solution was stored at RT for 3 hours after which the precipitate was separated and the filtrate was discarded. The solid was purified once more in THF-acetonitrile (1:2) mixture as previously described. Finally **4**•2MeCN was collected as pale yellow solid after filtration and dried in open air. Yield 1.2 g, 47 %. Acetonitrile-free product was prepared by heating the adduct overnight at 100 °C in open air in a thermal oven.

^{1}H NMR ($CDCl_3$, 500 MHz, ppm): ca. 7.7 (s, 4H, aryl-O*H*), 7.05 (d, *J* = 2 Hz, 4H, aryl *H*), 6.92 (d, *J* = 2 Hz, 4H, aryl *H*), 3.70 (s, 8H, N-CH_2-aryl), 2.49 (t, *J* = 7 Hz, 4H, N-CH_2-alkyl), 2.22 (s, 12H, aryl-CH_3), 1.58 (m, *J* = 7 Hz, 4H, alkyl CH_2), 1.28 (s, 36H, aryl-*t*-butyl) and 1.20 (m, *J* = 3 Hz, 4H alkyl CH_2).

^{13}C NMR ($CDCl_3$, 126 MHz, ppm): 152, 142, 127, 124, 123, 121 (aryl *C*), 56.1 (N-*C*H_2-aryl), 53.2 (N-*C*H_2-alkyl), 33.9 and 31.6 (*t*-butyl *C*), 27.1 and 25.9 (alkyl *C*), 16.2 (aryl-*C*H_3).

ESI-TOF MS 821.6193 $[M+H]^+$. The calculated value 821.6196 $[M+H]^+$.

Elemental anal. for **4**•Calc. for $C_{54}H_{80}N_2O_4$: C, 79.0; H, 9.82; N, 3.41. Found: C, 79.4; H, 9.91; N, 3.34.

From compound **4**•2MeCN an ethyl acetate adduct was prepared by dissolving it in boiling ethyl acetate. In the freezer (-17 °C) colourless crystals with the formula **4**·ethyl acetate were obtained.

Dihydrochloride of **4** was also prepared. The synthesis of **4**•2HCl•2MeOH started as for **4**. After the thermal oven treatment the yellow solid was dissolved in hot chloroform (10 mL) and 6 M HCl (2.0 mL, double amount) was added. The solution was vigorously stirred for 10 minutes and then kept in a refrigerator (6 °C) for two hours. The formed precipitate was separated by filtration. The isolated solid was dissolved in hot methanol (20 mL). The vessel was kept at RT overnight and the solid was filtered out. The solid was dissolved in MeOH (50 mL) and acetonitrile (40 mL) was added. The solution was concentrated into 30 mL using a rotavapor (300 mbar, 50 °C). The white solid begun to form in a few minutes, and the solid was let to form for 5 hours in a refrigerator. The white powder was filtered out and it had the formula of **4**•2HCl•2MeOH. Yield 1.1 g (38 %). **4**•2HCl•2MeOH was dried in vacuum overnight before elemental analysis.

^{1}H NMR for **4**•2HCl•2MeOH (MeOD, 500 MHz, ppm): 7.24 (d, *J* = 2 Hz, 4H, aryl *H*), 7.16 (s, *J* = 2 Hz, 4H, aryl *H*), 4.36 (s, 8H, N-CH_2-aryl), 3.06 (t, 4H, *J* = 8 Hz, N-CH_2-alkyl), 2.24 (s, 12H, aryl-CH_3), 1.75 (m, *J* = 8 Hz, 4H, alkyl CH_2), 1.28 (s, 36H, aryl *t*-butyl), 1.18 (m, *J* = 3 Hz, 4H, alkyl CH_2).

^{13}C NMR for **4**•2HCl•2MeOH (MeOD, 126 MHz, ppm): 153, 145, 131, 127, 126, 119 (aryl *C*), 57.1 (N-*C*H_2-aryl), 54.0 (N-*C*H_2-alkyl), 49.3 (methanol), 35.0 and 32.0 (*t*-butyl *C*), 26.9 and 24.9 (alkyl *C*), 16.9 (aryl-*C*H_3).

ESI-TOF MS 821.6180 $[M+H]^+$. The calculated value 821.6196 $[M+H]^+$.

Elemental anal. for **4**•2HCl•2MeOH. Calc. for $C_{56}H_{90}N_2O_6Cl_2$: C, 70.2; H, 9.47; N, 2.92. Found: C, 70.4; H, 9.28; N, 2.91.

Colourless single crystals for X-ray studies were obtained by dissolving **4**•2HCl•2MeOH in a methanol-acetonitrile (1:5) solution in a test tube and allowing the solvent to evaporate at RT to near dryness.

N,N,N,'N'-tetra(2-hydroxy-3,5-dimethylbenzyl)-1,7-diaminoheptane (5)

Crude product of **5** was obtained using 1,7-diaminoheptane (0.781 g, 6 mmol). The product from the thermal oven was cooled and dissolved in hot acetonitrile (40 mL). The solution was vigorously stirred at RT for 20 min, which caused precipitation to form. The solution was kept in a refrigerator (7 °C) for two hours after which the solid was filtered off. The filtrate was kept in a freezer (-17

°C) overnight. The formed oil was separated by decantation. The combined products were recrystallized twice from acetonitrile (40 mL). Compound **5** was obtained as white powder. Yield 1.3 g (33 %).

^{1}H NMR ($CDCl_3$, 500 MHz, ppm): 7.1 (s, 4H, aryl-O*H*), 6.85 (s, 4H, aryl *H*), 6.72 (s, 4H, aryl *H*), 3.65 (s, 8H, N-CH_2-aryl), 2.47 (t, *J* = 7 Hz, 4H, N-CH_2-alkyl), 2.22 (s, 12H, aryl-CH_3), 2.17 (s, 12H, aryl-CH_3), 1.57 (m, *J* = 7 Hz, 4H, alkyl CH_2), 1.24 (m, *J* = 7 Hz, 4H, alkyl CH_2) and 1.18 (m, *J* = 7 Hz, 2H, alkyl CH_2).

^{13}C NMR ($CDCl_3$, 126 MHz, ppm): 152, 131, 129, 128, 124, 122 (aryl *C*), 56.1 (N-*C*H_2-aryl), 53.4 (N-*C*H_2-alkyl), 29.1, 27.0 and 26.1 (alkyl *C*), 20.4 and 15.9 (aryl-*C*H_3).

ESI-TOF MS 667.4470 $[M+H]^+$. The calculated value 667.4475 $[M+H]^+$.

Elemental anal. for **5:** Calc. for $C_{43}H_{58}N_2O_4$: C, 77.4; H, 8.77; N, 4.20. Found: C, 77.3; H, 8.85; N, 4.22. Single crystals of **5** were prepared by dissolving 90 mg of white powder product in acetonitrile (10 mL) in a test tube and placing the tube in a freezer (-17 °C) overnight. One colourless single crystal was analyzed by X-ray diffraction.

N,N,N',N'-tetra(2-hydroxy-5-t-butyl-3-methylbenzyl)-1,7-diaminoheptane•2HCl (6•2HCl)

The crude product was obtained similarly to compound **2** using 1,7-diaminoheptane (0.781 g, 6 mmol), 4-*t*-butyl-2-methylphenol (30 mmol, 24 mmol equiv.) and paraformaldehyde (30 mmol, 24 mmol equiv.). After the thermal oven treatment, the product was dissolved in boiling acetonitrile (20 mL) and 6 M HCl (4.0 mL, double amount) and water (1.0 mL) were added. The cooled solution was vigorously stirred for 10 minutes and allowed to settle down at RT for 1.5 hours and the precipitate was filtered off. A small amount of product was separated from the filtrate after 4 hours and was added to main product. Finally the solid was dissolved in hot MeOH (10 mL) and acetonitrile (35 mL) was added. The vessel was kept in a freezer (-17 °C) overnight and **6**•2HCl was collected by filtration. Yield 1.9 g, 35 %.

^{1}H NMR (MeOD, 500 MHz, ppm): 7.24 (d, *J* = 2 Hz, 4H, aryl *H*), 7.17 (d, *J* = 2 Hz, 4H, aryl *H*), 4.38 (s, 8H, N-CH_2-aryl), 3.09 (t, *J* = 8 Hz, 4H, N-CH_2-alkyl), 2.26 (s, 12H, aryl-CH_3), 1.73 (m, *J* = 7 Hz, 4H, alkyl CH_2), 1.28 (m, 36H, aryl *t*-butyl), 1.19 (m, *J* = 7 Hz, 4H, alkyl CH_2), 1.10 (m, *J* = 7 Hz, 2H, alkyl CH_2).

^{13}C NMR (MeOD, 126 MHz, ppm): 153, 145, 131, 128, 126, 119 (aryl *C*), 57.2 (N-*C*H_2-aryl), 54.2 (N-*C*H_2-alkyl), 35.0 and 32.0 (*t*-butyl *C*), 29.3, 27.1 and 25.0 (alkyl *C*), 16.9 (aryl-*C*H_3).

ESI-TOF MS 835.6313 $[M+H]^+$. The calculated value 835.6353 $[M+H]^+$.

Elemental anal. for **6**•2HCl. Calc. for $C_{55}H_{84}N_2O_4Cl_2$: C, 72.7; H, 9.32; N, 3.08. Found: C, 72.0; H, 9.39; N, 3.25.

N,N,N'N'-tetra(2-hydroxy-3,5-dimethylbenzyl)-1,8-diamino-octane (7)

The crude material of **7** was prepared as that of **1** using 1,8-diamino-octane (0.866 g, 6 mmol). After reaction in a thermal oven at 120 °C the yellowish product was dissolved in hot acetonitrile (40 mL) and the solution was stored in a refrigerator (7 °C) overnight. The formed solid was decantated and recrystallized twice from acetonitrile (40 mL) in a refrigerator. Compound **7** was obtained as white powder. Yield 2.3 g (56 %).

^{1}H NMR ($CDCl_3$, 500 MHz, ppm): 8.3 (s, 4H, aryl-O*H*), 6.83 (s, 4H, aryl *H*), 6.73 (d, *J* = 2 Hz, 4H, aryl *H*), 3.64 (s, 8H, N-CH_2-aryl), 2.52 (t, *J* = 7 Hz, 4H, N-CH_2-alkyl), 2.22 (s, 12H, aryl-CH_3), 2.07 (s, 12H, aryl-CH_3), 1.60 (m, *J* = 7 Hz, 4H, alkyl CH_2), 1.46 (m, *J* = 7 Hz, 4H, alkyl CH_2) and 1.26 (m, *J* = 7 Hz, 4H, alkyl CH_2).

^{13}C NMR ($CDCl_3$, 126 MHz, ppm): 152, 131, 129, 128, 124, 122 (aryl *C*), 55.9 (N-*C*H_2-aryl), 54.1 (N-*C*H_2-alkyl), 30.0, 26.9 and 26.8 (alkyl *C*), 20.3 and 16.1 (aryl-*C*H_3).

ESI-TOF MS 681.4644 $[M+H]^+$. The calculated value 653.4631 $[M+H]^+$.

Elemental anal. for **7:** Calc. for $C_{44}H_{60}N_2O_4$: C, 77.5; H, 8.88; N, 4.11. Found: C, 77.3; H, 8.87; N, 4.24.

N,N,N'N'-tetra(2-hydroxy-5-t-butyl-3-methylbenzyl)-1,8-diamino-octane (8)

The crude material of **8** was prepared as that of **2** using 1,8-diamino-octane (0.433 g, 3 mmol). After reaction in a thermal oven at 120 °C the yellowish product was dissolved in hot acetonitrile (15 mL) and water was dropwise added (500 μL). The solution was left to stand in a refrigerator (7 °C) for 3 hours after which the top layer of the cold solution was separated by decantation. The top layer was discarded, and the yellow bottom layer was dissolved in dichloromethane (5 mL) and acetonitrile (15 mL) was added. The solution was placed in a freezer (-20 °C) and filtered after 7 hours. The product was recrystallized in a CH_2Cl_2-MeCN (1:3) mixture as previously described. Compound **8** was allowed to dry in open air and obtained as a white powder. Yield 0.86 g, 34 %.

^{1}H NMR (DMSO-d_6, 500 MHz, ppm): 9.52 (s, 4H, aryl-O*H*), 6.97 (d, *J* = 2 Hz, 4H, aryl *H*), 6.92 (d, *J* = 2 Hz, 4H, aryl *H*), 3.62 (s, 8H, N-CH_2-aryl), 2.36 (t, *J* = 7 Hz, 4H, N-CH_2-alkyl), 2.12 (s, 12H, aryl-CH_3), 1.44 (m, *J* = 7 Hz, 4H, alkyl CH_2), 1.20 (s, 36H, aryl *t*-butyl), 1.03 (m, *J* = 7 Hz, 8H, alkyl CH_2).

^{13}C NMR (DMSO-d_6, 126 MHz, ppm): 152, 141, 126, 124, 123, 122 (aryl *C*), 54.6 (N-*C*H_2-aryl), 52.4 (N-*C*H_2-alkyl), 33.4 and 31.3 (*t*-butyl *C*), 28.5, 26.5 and 25.1 (alkyl *C*), 16.3 (aryl-*C*H_3).

ESI-TOF MS 849.6473 $[M+H]^+$. The calculated value 849.6509 $[M+H]^+$.

Compound **8** was crystallized twice from a CH_2Cl_2-MeCN (1:3) mixture and heated at 90 °C in a thermal oven before elemental analysis. Elemental anal. for **8**: Calc. for $C_{56}H_{84}N_2O_4$: C, 79.2; H, 9.97; N, 3.30. Found: C, 78.9; H, 9.93; N, 3.19.

In the synthesis of compound **8**•2HCl the amounts of starting materials and heating in a thermal oven were the same as those for the HCl free compound. The yellow solid from the thermal oven was dissolved in boiling acetonitrile (10 mL) and 6 M HCl (2 mL, double amount) was added.

The solution was stored at RT for 45 min after which the solid was separated by filtration. The filtrate was kept in a refrigerator (7 °C) overnight during which a small amount of the product separated. The combined solid was dissolved in methanol (10 mL) and acetonitrile (30 mL) was added. The vessel was kept in a freezer (-17 °C) overnight. The separated (by filtration) **8**•2HCl was once more crystallized from a methanol – acetonitrile mixture (36 mL, 1:5) in a freezer (-17 °C). Yield 0.84 g, 30 %.

For NMR and elemental analysis, **8**•2HCl was recrystallized twice from 10 mL MeOH – 40 mL ethyl acetate mixture in a freezer, and dried overnight in a thermal oven (90 °C).

^{1}H NMR (MeOD, 500 MHz, ppm): 7.25 (s, 4H, aryl *H*), 7.17 (s, 4H, aryl *H*), 4.38 (s, 8H, N-C*H*$_2$-aryl), 3.09 (t, 4H, alkyl N-C*H*$_2$), 2.25 (s, 12H, aryl-C*H*$_3$), 1.73 (m, 4H, alkyl C*H*$_2$), 1.29 (s, 36H, aryl *t*-butyl), 1.17 (m, 4H, alkyl C*H*$_2$), 1.09 (m, 4H, alkyl C*H*$_2$).

^{13}C NMR (MeOD, 126 MHz, ppm): 153, 145, 131, 128, 126, 119 (aryl), 57.2 (N-CH$_2$-aryl), 54.1 (alkyl N-CH$_2$), 35.0 and 32.0 (*t*-butyl *C*), 29.7, 27.2 and 25.0 (alkyl C), 16.9 (aryl-CH$_3$).

ESI-TOF MS 849.6505 $[M+H]^+$. The calculated value 849.6509 $[M+H]^+$.

Elemental anal. for **8**•2HCl: Calc. for $C_{56}H_{86}N_2O_4Cl_2$: C, 72.9; H, 9.40; N, 3.04. Found: C, 72.2; H, 9.35; N, 2.87.

The compounds **1** and **3** were also prepared using the solution method [5d] by dissolving corresponding diaminoalkane (3 mmol), 2,4-dimethylphenol (12 mmol), aqueous solution of formaldehyde (36.5 %) (15 mmol, 25 % excess), triethylamine (1.4 mmol) and water (2 mL) in methanol (10 mL). The sealed flasks were kept in a 50 °C water bath for 6 days, after which the oily product was separated and purified as mentioned for **1** and **3**. The HPLC analysis showed that after 3 days the amount of product did not increase, whereas the amount of unknown side products did. The yield of this method was lower in both cases: For **1** the yield was 40 % (81 % in the one-pot method) and for **3** 20 % (35 % in the one-pot method).

General Preparation Process of Aminobisphenols (9-16)

The phenol (22 mmol), formaldehyde (22 mmol) and amine (10 mmol) were measured into the reaction vessel and it was placed in the thermal oven (T = 120 °C). The reaction was followed by HPLC to ensure some optimization of the yield. The reaction time was between one and five hours. The resulting yellow syrup was dissolved in diethyl ether and 6 M HCl (2 mL) was added to the solution. After that, in the case of amino alcohols, the best result was obtained by adding water (10 mL) to the HCl-treated ether solution of the crude product and then extracting the non-hydrochloride impurities a few times with diethyl ether. The precipitation occurred then in the water phase. In the case of alkylamines the precipitation occurred readily in the Et_2O-phase after addition of the acid. Crude precipitates were crystallized from a mixture of acetonitrile and methanol. The purity and identity of the products were analysed by ^{1}H NMR in $CDCl_3$ or MeOD.

X-Ray Studies

Suitable colorless single crystals of **4**•2HCl•2MeOH and **5** were obtained as mentioned earlier. Crystallographic data were collected at 173 K with a Nonius-Kappa CCD area detector diffractometer using graphite-monochromatized Mo-K_α radiation (λ = 0.71073 Å).

The structures were solved by direct methods using the SHELXS-97 program [10] and full-matrix, least-squares refinements on F^2 were performed using the SHELXL-97 program [10]. The CH hydrogen atoms were included at the fixed distances with the fixed displacement parameters from their host atoms (1.2 times that of the host atom). The OH hydrogen atoms were refined isotropically with a thermal displacement of 1.2 times that of the host atom, except that a fixed value of 0.10 for H3 in the refinement of **4**•2HCl•2MeOH was used.

Crystal Data for 4•2HCl•2MeOH

$C_{56}H_{90}Cl_2N_2O_6$, M_r = 958.20, triclinic, space group *P-1* (no. 2), a = 8.7529(3), b = 12.4612(4), c = 13.4645(5) Å, α = 72.397(2), β = 88.404(2), γ = 80.020(2)°, V = 1378.17(8) Å^3, T = 173 K, Z = 1, μ(Mo-K_α) = 0.166 mm^{-1}, 4844 unique reflections (R_{int} = 0.0295), which were used in the calculations. The final *R1* and *wR*(F^2) for all data were 0.1012 (0.0805) and 0.2358 (0.2183), respectively. The values in parentheses are for I > 2σ(I).

Crystal Data for 5

$C_{43}H_{58}N_2O_4$, M_r = 666.91, orthorhombic, space group $P2_12_12_1$ (no. 19), a = 10.1000(2), b = 10.1927(2), c = 37.1338(9) Å, α, β, γ = 90°, V = 3822.79(14) Å^3, T = 173 K, Z = 4, μ(Mo-K_α) = 0.073 mm^{-1}, 4686 unique reflections (R_{int} = 0.0718), which were used in the calculations. The final *R1* and *wR*(F^2) for all data were 0.064 (0.0486) and 0.113 (0.1052), respectively. The values for I > 2σ(I) are in parentheses.

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SUPPLEMENTARY MATERIAL

Supplementary material is available on the publishers Web site along with the published article.

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PAPER II

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PAPER

Alkyl and diether bridged *N*,*N*,*N*′,*N*′-tetra(2-hydroxybenzyl)diamines: effects of hydrogen bonding on structure and solubility†

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A solvent-free one-step method has been used to prepare two *N*,*N*,*N*′,*N*′-tetra(2-hydroxy-3,5-dimethylbenzyl)diaminoalkanes containing a long *n*-alkyl bridge (6 and 8 CH_2 groups between N-atoms). In addition, three novel *N*,*N*,*N*′,*N*′-tetra(2-hydroxy-5-alkyl-3-alkylbenzyl)-diaminoalkane-ethers (alkyl = methyl or *t*-butyl) have been prepared using the same method. The compounds were studied in the solid state using single crystal X-ray diffraction and their solubility was studied using UV/Vis spectroscopy. In the solid state, hydrogen bonding plays a key role in controlling the crystal packing and conformations of the molecules, thus affecting the solubility and properties of the compounds.

Introduction

Hydrogen bonding controls the packing of molecular compounds and is also a key factor in crystal engineering, formation of supramolecular assemblies and in material sciences.[1] The traditional aminobisphenol ligands are relatively straightforward to prepare and are versatile high-end ligands from which several novel coordination compounds have been made.[2] Especially, the dinuclear bis(phenoxido)-bridged copper(II) complexes with preceding ligands represent a class of important and well-studied compounds in the field of molecular magnetism.[3]

Multidentate compartmental Schiff bases are extensively studied ligands in coordination chemistry,[4] while their reduced derivatives have not gained as much attention, most likely due to the synthetic problems confronted with these compounds. However, in some cases the relatively rigid nature of Schiff bases restricts the use of these ligands when designing, for example, metal–organic supramolecules with multiple metal ions. In order to improve the coordination ability and to extend the possible coordination modes of traditional aminobisphenols, we have bound two aminobisphenol moieties together with a bridging unit in which length and atom content can be easily altered. These diaminotetraphenols with an alkyl chain between nitrogen atoms can be prepared with a straightforward, one step solvent-free syntheses, which we have recently reported.[5] This novel and very simple route was used to produce several highly flexible and tunable ditopic alkyl bridged diaminotetraphenolate ligands, which can be utilized in traditional coordination chemistry, but also in syntheses of supramolecules or metal–organic frameworks. One of the first examples of the coordination ability of such ligands was in producing modern macromolecules, which could be further utilized, for example, in metal–organic frameworks with interesting magnetic properties.[6]

In this work, we have studied the structural and chemical influence of changing the bridging unit in diaminotetraphenols from an acyclic alkyl chain to the ethylene glycol bridged one. The effect of a solid state structure on the solubility of the compounds is also studied. Rather surprisingly, detailed studies on the crystal structure–solubility relationship of similar organic compounds are scarce, considering the importance of the solubility, for example, in drug development and in industrial processes.[7] The solid state structures of earlier prepared[5] compounds (**1** and **2**) are compared to the structures of new diaminotetraphenols with a $CH_2CH_2OCH_2CH_2OCH_2CH_2$ bridge between nitrogen atoms (**3–5**). The schematic presentation for the synthesis of all compounds is depicted in Fig. 1. The compounds have been prepared with the method adapted from ref. 5 with small modifications for **3**.

Experimental section

Syntheses

Compounds **1** and **2** were prepared according to ref. 5. Single crystals of **1** were obtained by recrystallizing 100 mg of **1** from 4 ml THF–MeCN (1 : 1) mixture, and the crystals of **2** were obtained directly from the reaction batch.

Compound **3** was prepared by placing 20 mmol (2.96 g) 2,2′-(ethylenedioxy)bis-(ethylenediamine), 88 mmol (2.64 g) paraformaldehyde and 88 mmol (10.76 g) 2,4-dimethylphenol in the same round bottomed flask closed with a cap. The mixture was heated with stirring at 130 °C in an oil bath for 5 h and cooled down. The warm mixture was dissolved in 50 ml diethyl ether

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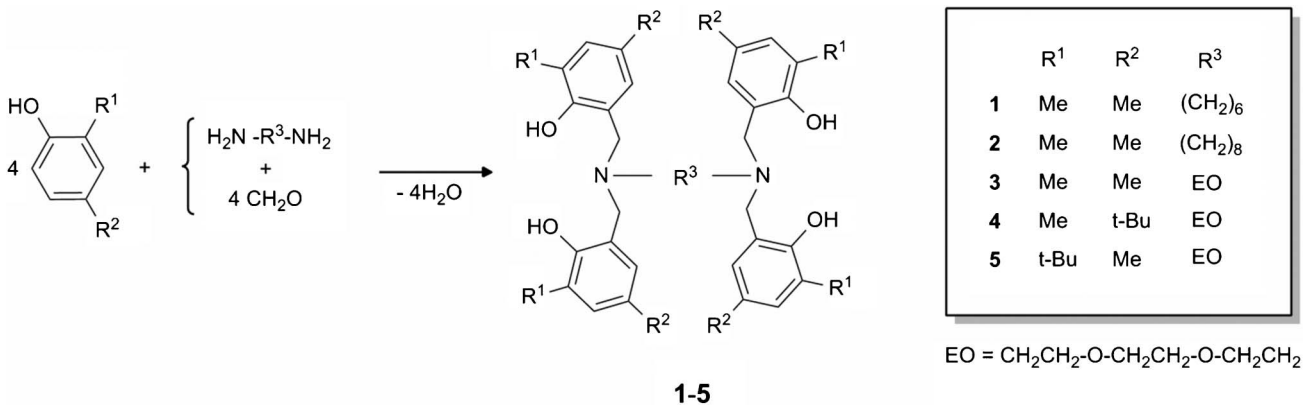
† Electronic Supplementary Information (ESI) available: The NMR spectra of the compounds **3–5** and crystallographic data are provided. CCDC 888651-5 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. See DOI: 10.1039/c2ce26027a



	R^1	R^2	R^3
1	Me	Me	$(CH_2)_6$
2	Me	Me	$(CH_2)_8$
3	Me	Me	EO
4	Me	t-Bu	EO
5	t-Bu	Me	EO

Fig. 1 A schematic presentation of the preparation of compounds **1–5**.

and kept at room temperature for 18 h. The precipitated compound was decanted and the remaining solution was kept at 6 °C in a refrigerator for 24 h and decanted, which increased the yield significantly. The combined solids were washed with 20 ml ether and dried in air. Yield 6.49 g, 47%. Single crystals of **3**·Et_2O were grown from diethyl ether. ^{1}H NMR ($CDCl_3$, 250 MHz, 30 °C): δ = 8.2 (s, 4H, Ar-O*H*), 6.85 (d, $J_{H,H}$ = 2 Hz, 4H, Ar*H*), 6.65 (d, $J_{H,H}$ = 2 Hz, 4H, Ar*H*), 3.80 (s, 4H, OCH_2CH_2O), 3.70 (m, 12H, NCH_2Ar, OCH_2CH_2N), 3.49 (q, ether), 2.70 (t, $J_{H,H}$ = 5 Hz, 4H, OCH_2CH_2N), 2.19 (d, $J_{H,H}$ = 5 Hz, 24H, $ArCH_3$), 1.23 (t, ether). Calc. for $C_{42}H_{56}N_2O_6$ (684.90): C, 73.65; H, 8.24; N, 4.09. Found: C, 73.78; H, 8.17; N, 3.81%.

Compound **4** was prepared by placing 5 mmol (0.74 g) 2,2′-(ethylenedioxy)bis-(ethylenediamine), 22 mmol (0.66 g) paraformaldehyde and 22 mmol (3.61 g) 2-methyl-4-*t*-butylphenol in a small (about 15 ml) reaction vial which was closed partially with a screw cap. The vial was placed in a thermal oven (120 °C) for 5 h and cooled down. The resulting yellow oil was dissolved in 40 ml acetonitrile and kept at room temperature in which a white solid precipitated overnight. The precipitate was filtered, washed with cold methanol and dried in air. Yield 2.79 g, 65%. Single crystals were grown by dissolving 35 mg of **4** in 0.5 ml CH_2Cl_2 and 1.5 ml acetonitrile was added. After 24 h the crystals were collected for X-ray diffraction analysis. ^{1}H NMR ($CDCl_3$, 250 MHz, 30 °C): δ = 7.04 (d, $J_{H,H}$ = 2 Hz, 4H, Ar*H*), 6.85 (d, $J_{H,H}$ = 2 Hz, 4H, Ar*H*), 3.80 (s, 4H, OCH_2CH_2O), 3.74 (m, 12H, NCH_2Ar, OCH_2CH_2N), 2.73 (t, $J_{H,H}$ = 14 Hz, 4H, OCH_2CH_2N), 2.20 (s, 12H, $ArCH_3$), 1.26 (s, 36H, $ArC(CH_3)_3$). Calc. for $C_{54}H_{80}N_2O_6$ (853.22): C, 76.02; H, 9.45; N, 3.28. Found: C, 76.36; H, 9.51; N, 3.24%.

Compound **5** was prepared by placing 5 mmol (0.74 g) 2,2′-(ethylenedioxy)bis-(ethylenediamine), 22 mmol (0.66 g) paraformaldehyde and 22 mmol (3.61 g) 2-*t*-butyl-4-methylphenol in a small (about 15 ml) reaction vial, which was partially closed with a screw cap. The vial was placed in a thermal oven (120 °C) for 5.5 h and cooled down. The resulting brown oil was dissolved in 10 ml dichloromethane and 50 ml of acetonitrile was added to the solution. The solution was evaporated at normal atmosphere until a white solid started to precipitate and the solution was left at room temperature overnight. The resulting precipitate was filtered, washed with cold methanol and dried in air. Yield 1.67 g, 39%. Single crystals were grown by dissolving 50 mg of **5** in 1 ml CH_2Cl_2 and 2 ml acetonitrile was added. After 24 h the crystals were collected for the X-ray diffraction analysis. ^{1}H NMR ($CDCl_3$, 250 MHz, 30 °C): δ = 8.31 (s, 4H, ArO*H*), 6.98 (d, $J_{H,H}$ = 2 Hz, 4H, Ar*H*), 6.66 (d, $J_{H,H}$ = 2 Hz, 4H, Ar*H*), 3.83 (s, 4H, OCH_2CH_2O), 3.65 (m, 12H, NCH_2Ar, OCH_2CH_2N), 2.70 (t, $J_{H,H}$ = 10 Hz, 4H, OCH_2CH_2N), δ 2.21 (s, 12H, $ArCH_3$), 1.37 (s, 36H, $ArC(CH_3)_3$). Calc. for $C_{54}H_{80}N_2O_6$ (853.22): C, 76.02; H, 9.45; N, 3.28. Found: C, 76.20; H, 9.38; N, 2.91%.

Materials and methods

All reagents and solvents were obtained from commercial sources and used without further purification. The NMR spectra were recorded using a Bruker AVANCE DPX 250 FT-NMR spectrometer. The ^{1}H NMR spectra were recorded in $CDCl_3$ at 30 °C. The chemical shifts are reported in ppm and referenced internally using the residual polar solvent resonances relative to tetramethylsilane ($CDCl_3$ δ = 7.26). The NMR spectra of compounds **1–2** is already reported in the literature.[5,6] Elemental analyses were performed using a VarioEl III elemental analyzer. The melting points were determined using a Stuart Scientific SMP3 melting point apparatus. The solubility of the compounds were determined by UV/Vis spectroscopy using a PerkinElmer LAMBDA 650 spectrophotometer. The molar absorptivity of the compounds was defined using several solutions with known concentrations, after which the concentration of the saturated solution of the compound in a selected solvent could be calculated using the Beer–Lambert law.

X-ray crystallography

Suitable single crystals of **1–5** for X-ray measurements were obtained as reported above. Crystallographic data of **2–5** were collected at 153, 173 and 223 K with a Nonius-Kappa CCD area detector diffractometer using graphite-monochromatized Mo-Kα radiation (α = 0.71073 Å) or with a Agilent SuperNova dual wavelength diffractometer equipped with Atlas CCD area detector with Cu-Kα radiation (α = 1.54184 Å) using the CrysAlisPro program package[8] for **1**. The structures were solved by direct methods using SIR97 or SHELXS-97 programs[9,10] and full-matrix, least-squares refinements on F^2 were performed using SHELXL-97. [10]The CH hydrogen atoms were included at fixed distances with fixed displacement parameters from their host atoms (1.2 or 1.5 times that of the host atom). The OH hydrogen atoms were refined isotropically with a thermal

displacement of 1.2 times that of the host atom. The disorder of the bridging chain of **1**, **2** and **5** was modelled, but presented in the figures only for **1** because of the clarity. The figures were drawn with Ortep-III for Windows[11] and Mercury.[12]

Results and discussion

Syntheses

The preparation of the compounds is particularly straightforward and the synthesis can be performed in one step with either the thermal oven method [5] or on a larger scale with improved yields in an oil bath with stirring. The products can be isolated by recrystallization with good to reasonable yields, as reported in the experimental part.

The diamine has little influence on how the reaction proceeds, hence it can be altered quite easily, whereas the selected phenols affect the syntheses more significantly. The main by-products in the reactions are mono- and dibenzoxazines in addition of partially reacted amines, which may lead to 1–3 benzylic side products.[13] High-performance liquid chromatography (equipped with a UV/Vis detector) was used to follow the progress of the reactions since it is an efficient and fast method that also gives qualitative information about the product distribution in the reaction vessel.

Description of the structures

Compounds **1**, **3–5** all crystallize in the same monoclinic space group ($C2/c$), while compound **2** crystallizes in the tetragonal space group ($P4_12_12$). The solid state structure of compound **1** is determined almost solely by intermolecular hydrogen bonds, whereas the structures of compounds **2–5** are mainly controlled by intramolecular ones, with additional sterical factors. The C–O, C–N and C–C bonding parameters in all of the compounds do not present any unusual features, hence the discussion is focused on the crystal packing and rather unusual conformations of the compounds.

Compound **1** forms linear molecules in the asymmetric unit, as is presented in Fig. 2a. The alkyl chain between nitrogen atoms is disordered and only one of two similar chains is depicted. In general, a strong intramolecular H-bond (O1H···N8 in **1–3**, O2H···N8 in **4–5**) controls the conformation of the one phenol fragment of the aminobisphenol moiety in all studied compounds, while the position and alignment of the other phenolic fragment is dependent on the bridging group (between nitrogens) and the intermolecular interactions. In the solid state, the asymmetric units of **1** form a polymeric structure (Fig. 2b) by intermolecular H-bonds (O2H···O1) in such a way that the polar areas of the compounds end up surrounded by the nonpolar areas of the compound. As a consequence of that and the polymeric nature of the compound, **1** is quite insoluble in simple organic solvents like methanol, ethanol or acetonitrile and dichloromethane, while THF and DMSO dissolve **1** adequately for synthetic purposes (see below). The intermolecular hydrogen bonding system resembles that of *N*,*N*-bis(2-hydroxy-5-methylbenzyl)cyclohexylamine (HETGOD), where separate molecules join to make dimers in the solid state.[14] In another similar compound 2,2′,2′′,2′′′-(ethane-1,2-diylbis(nitrilobis(methylene))) tetracis(4,6-di-*t*-butylphenol)

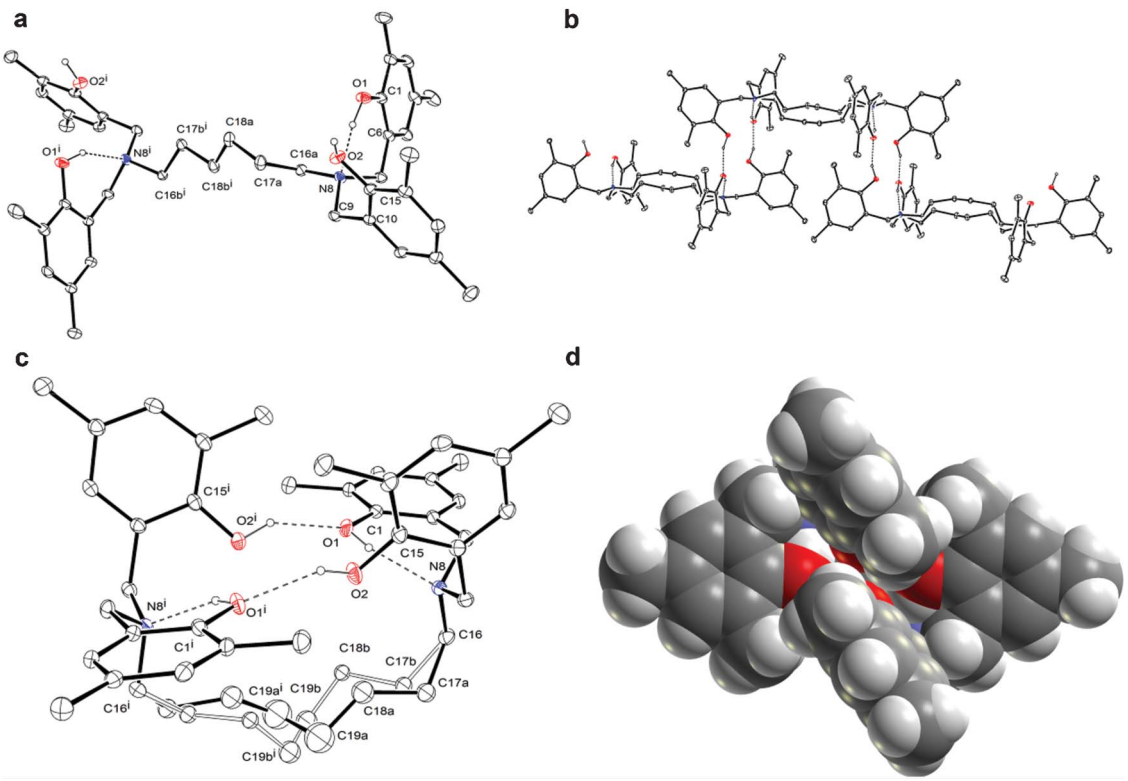


Fig. 2 (a) The asymmetric unit of **1** with CH hydrogens omitted. Symmetry code i = $-x + 1/2$, $y + 1/2$, z. For clarity, only one part of the disordered bridging unit is presented. (b) Part of the polymeric unit of **1**. (c) The asymmetric unit of **2**. CH hydrogen atoms have been omitted. Symmetry code i = y, x, $-z$. (d) A spacefill presentation of **2**.

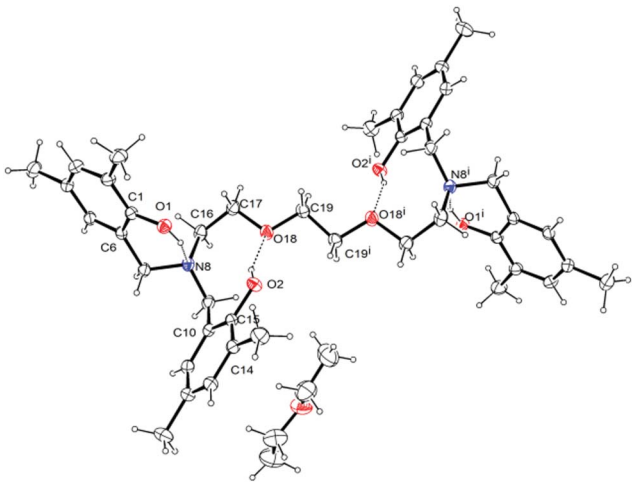


Fig. 3 The asymmetric unit of **3**·Et_2O. Symmetry code i = $-x + 1/2, -y + 1/2, 1 - z$.

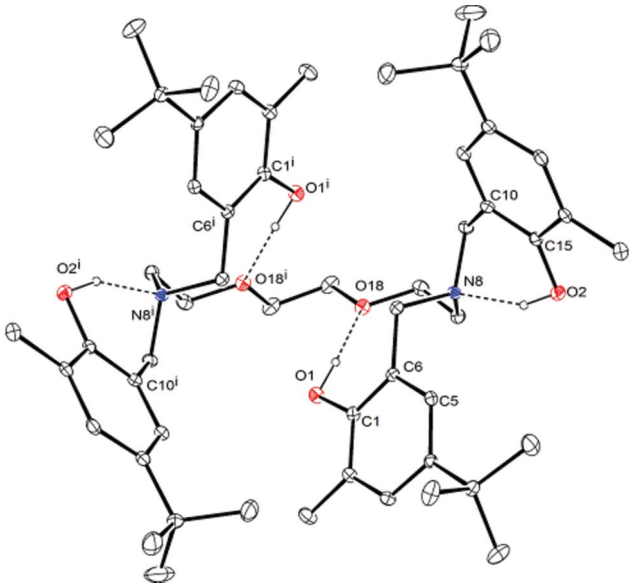


Fig. 4 The asymmetric unit of **4**. CH hydrogen atoms have been omitted. Symmetry code i = $-x, y, -z - 1/2$.

pyridine solvate (HUNDOK), (in this compound the bridging unit is quite short with only two CH_2 groups between N-atoms), the molecule also has a linear conformation, but the pyridine nitrogens form hydrogen bonds to O2 atoms, thus preventing the polymerization.[15]

The solid state ordering of compound **2** reveals in turn four intramolecular hydrogen bonds, as presented in Fig. 2c, forming an interlocked structure similar to the compound with an alkyl chain of 7 carbon atoms.[5] The absence of any intermolecular interactions forces **2** to pack as isolated molecules, which in turn inflicts the good solubility of the compound to organic solvents. Tight H-bonds between hydroxyl and amine groups inside the molecule induce a similar polar–nonpolar arrangement to that in **1**. The nonpolar exterior and the interlocked structure of **2** are nicely shown in the space fill presentation of the molecule (Fig. 2d). In this compound, the alkyl chain of 8 carbon atoms is disordered in two positions, which are both visible in Fig. 2c.

The molecular formula of compound **3** does not diverge much from that of **2** since the only alteration is the exchange of the $(CH_2)_8$ alkyl bridge between nitrogen atoms to a similar length $CH_2CH_2OCH_2CH_2OCH_2CH_2$ ether bridge. The effect of this modification on the solid state structures between **2** and **3** is relatively large. The compound **3** (as ether solvate) forms four intramolecular hydrogen bonds between hydroxyl groups and amine nitrogen or ether oxygen. The interactions are similar to bis(3-*t*-butyl-2-hydroxy-5-methylbenzyl)(tetrahydrofuran-2-ylmethyl)amine[16] and this type of hydrogen bonding is also present in compounds **4** and **5**, due to the equal modifications in the bridge between aminobisphenol moieties.

The asymmetric unit of **3**, presented in Fig. 3, reveals a linear conformation with diethyl ether of crystallization. In spite of the intramolecular hydrogen bonds, the polar parts of the molecule are relatively exposed, hence the solubility in methanol is considerably better than compound **1** (see below). The solid state packing of **3** does not show any surprising features. The diaminotetraphenol molecules are packed relatively tightly with and imbricate arrangement and the diethyl ether molecules are filling the small cavities in the lattice (Fig. S1†). Several attempts did not produce solvent-free crystals.

Compound **4** differs from **3** by the phenolic substituents in the way that the methyl group at position 4 of the phenol ring has been replaced with a *t*-butyl, which induces some changes in the solid state packing. The structure of **4** (Fig. 4) does not contain any solvents of crystallization and the ether bridge between the aminobisphenol fragments is bent to a U-shape, causing the molecule to be far more compact than **3**. Originating from the shape of the bridging group, the structure of an individual molecule resembles a "plastic cup" and in the lattice, the cups are stacked on top of each other forming piles, which are shown in Fig. 5. However, the packing and conformation of single molecules leaves the polar areas of compounds more exposed, as in **3**.

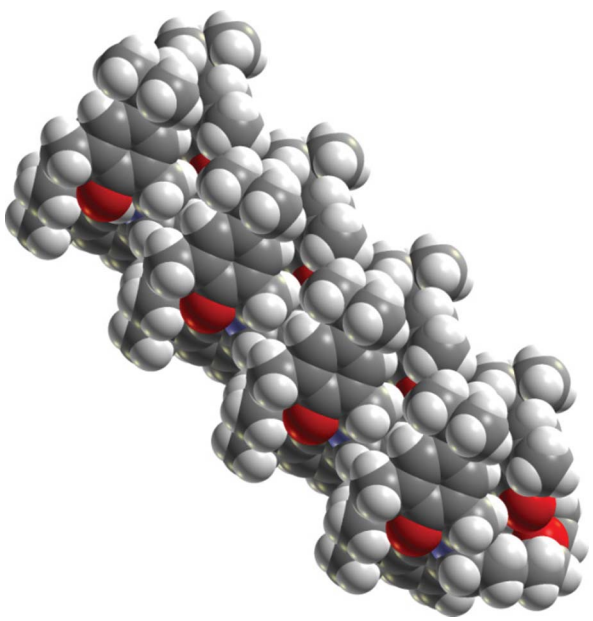


Fig. 5 A spacefill presentation of **4** showing the stacked "plastic cups".

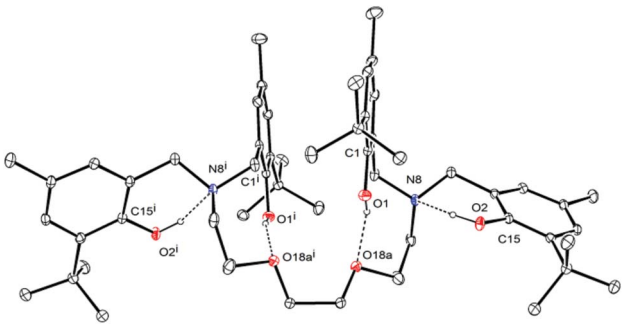


Fig. 6 The asymmetric unit of **5**. Symmetry code i = 1 $-x$, y, $-z$ + 1/2. For clarity, CH hydrogen atoms and only one part of the disordered bridging unit are presented.

In compound **5** (Fig. 6), the phenolic substituents are interchanged compared to **4** so that a methyl group is in position 4, whereas *t*-butyl is in position 2 of the phenol ring. This causes notable changes in the conformation of **5** in contrast to the geometry of **4**. An almost linear bridge of **4** has turned to a more closed conformation in compound **5** with two of the phenyl groups in close proximity. However, no π–π or CH–π interaction is expected since the phenyl groups are not stacked (no face-to-face interaction) and the separation between the rings is over 4 Å. Furthermore, the structure does not have any properly aligned hydrogen atoms for any CH–π interaction (Fig. S2†). The ethylene oxide chain between N atoms is disordered, but only one of the two similar chains is shown in Fig. 6. The disorder in the bridging chains of both **1** and **5** is most likely due to the flexible nature of the compounds, which gives numerous degrees of freedom for the chain.

The hydrogen bond lengths are presented in Table 1. From the intramolecular H-bonds, the O–H···N bonds are the strongest, whereas the O–H···O (ether) bonds are slightly weaker as the bond distances fall in the range 2.65–2.75 Å and 2.83–3.06 Å, respectively. The disordered bridging chain in **5** causes the hydrogen bonds to be relatively long. On the other hand, the disorder of the bridge can also be thought to originate from the weaker hydrogen bonds, which would allow the bridging unit to order in different ways in the lattice. The intermolecular O–H···O (hydroxyl) distances in **1** are only marginally longer than the OH–···N ones with 2.78 Å separations. Similar, but intramolecular, the O–H···O (hydroxyl) bond present in **2** is again weaker than the strongest hydrogen bond within the series, but still only ∼0.1 Å longer.

Table 1 Hydrogen bond distances of **1–5**[a]

	Donor (D)	Acceptor (A)	O···A (Å)	H···A (Å)	<O–H···A (°)
1	O1–H1	N8	2.656(2)	1.81(2)	151(2)
	O2–H2	O1[i]	2.776(2)	1.90(2)	160(2)
2	O1–H1	N8	2.685(3)	1.90(4)	145(4)
	O2–H2	O1[ii]	2.792(3)	1.98(5)	148(4)
3	O1–H1	N8	2.754(3)	1.91(3)	148(2)
	O2–H2	O18	2.881(3)	2.07(3)	158(3)
4	O1–H1	O18	2.828(3)	1.87(4)	167(4)
	O2–H2	N8	2.711(3)	1.82(2)	155(3)
5	O1–H1	O18A	3.015(5)	2.20(3)	160(3)
	O1–H1	O18B	3.06(1)	2.29(3)	150(3)
	O2–H2	N8	2.742(3)	1.90(3)	152(2)

[a] Symmetry operation i: −1 + x, $-y$, − 0.5 + z. ii: y, x, $-z$

Solubility of the compounds

The solubility of the compounds **1–5** was studied in methanol and dichloromethane solutions using a UV/Vis spectrophotometer. The absorption maximum for all compounds was found to reside around 285 nm. The molar absorption coefficient ε and found concentrations in saturated solutions at 25 °C for all compounds, are listed in Table 2. The value of ε is calculated from absorbance values obtained from four known standard solutions using the Beer-Lambert equation.

The observed values for molar absorption coefficient ε are around 10 000 for all compounds and it is approximately the same in both studied solvents. In general, compounds **1–3** dissolve better in dichloromethane than in methanol by the factor of 20 to about 100, whereas the solubility of **4** and **5** in dichloromethane can be from 2700 up to 18 000 times better than in methanol. Compound **1** is practically insoluble in methanol and only slightly soluble in dichloromethane because of its hydrogen bonded polymeric structure, hence **1** dissolves only in strongly coordinating solvents, like THF and DMSO. Compound **2** is soluble in both studied solvents, while dichloromethane solvates **2** almost 100 times better than methanol. Of the studied compounds, **3** has clearly the best solubility in methanol (19 mmol l^{-1}), which is due a to lack of intermolecular interactions and more exposed hydroxyl groups (in the solid state), but also the solvent of crystallization (diethyl ether) might play some role in the observed solubility of the compound.

Both compounds **4** and **5** are again more soluble in dichloromethane, although the relative solubility in methanol is much worse compared to compounds **2** and **3**. The position of the *t*-butyl substituent can induce quite dramatic changes in the solubility of **4** and **5** in methanol; compound **4** is about 10 times more soluble than **5**. This is because of the protection provided by the bulky substituents to the hydroxyl groups of the phenols, thus preventing the interactions with polar solvents, such as methanol. This behaviour is somewhat expected since generally the bulkier aromatic substituents induce better solubility in non-polar organic solvents and *vice versa*.

Melting points of the compounds

The melting points of the compounds were determined (Table 3) and are in unison with the solubility data. The melting points of the molecules are dependent on the intermolecular forces between the solid and liquid phase and also on the molecular

Table 2 Values of ε and the concentration of the saturated solutions of **1–5** in methanol (left) and in dichloromethane (right)

	ε^a	c (mmol l^{-1})[a]	ε^b	c (mmol l^{-1})[b]
1	n. s.[c]	n. s.	10 000	0.6
2	9400	1.9	9600	170
3	9500	19	9400	320
4	9400	0.47	9300	1300
5	11 000	0.04	11 000	720

[a] Values in methanol. [b] Values in dichloromethane [c] n. s. = non-soluble

Table 3 The observed melting points of 1–5

	mp (°C)
1	196–197
2	140–141
3	69–71
4	153–154
5	172–173

masses. In this case, molecular masses are relatively similar so the intermolecular forces dominate the observed values. The melting point of **1** is clearly the highest of the group, which is due to the polymeric nature of the compound, whereas compound **3** has the lowest one, most likely because of the solvent of crystallization, which can interact with the host molecule. The melting points of **2**, **4** and **5** fall in the range of 140–173 °C, which is quite expected considering the molecular packing and the slightly higher molecular masses of the compounds.

Conclusions

In this study, we have prepared and determined the crystal structure of two *N*,*N*,*N*′,*N*′-tetra(2-hydroxy-3,5-dimethylbenzyl)diaminoalkanes containing a long *n*-alkyl bridge (6 and 8 CH_2 groups between N-atoms). In addition, three *N*,*N*,*N*′,*N*′-tetra(2-hydroxy-5-alkyl-3-alkylbenzyl)-diaminoalkane-ethers (alkyl = methyl or *t*-butyl) have been prepared using the same or similar method. In all of the compounds an intramolecular O1H···N8 (or O2H···N8 for **4** and **5**) bond determines the conformation of molecule to some extent. In **1**, the intermolecular hydrogen bonds O2H···O1 control the packing of the molecules. However, in **2–5** there are only intramolecular H-bonds and the steric effect of the substituents at the 2 and 4 positions of the aromatic rings controls the conformation of the molecules in the solid state.

In the case of diaminotetraphenols with a *n*-alkyl chain between N-atoms, the length of the alkyl chain controls the conformation of the compounds. If the alkyl chain has 6 members or less, as in **1**, the molecule is linear with two intramolecular and two intermolecular H-bonds resulting in a polymeric structure, but if *n* is 7 or larger the molecule forms a cup-like structure with four intermolecular hydrogen bonds, as found in **2** and *N*,*N*,*N*′,*N*′-tetra(2-hydroxy-3,5-dimethylbenzyl)-diaminoheptane.[5] In the latter arrangement only weak intermolecular interactions are present, as is the case with **3–5**, in which only intramolecular H-bonds are found due to the oxygen atoms present in the alkyl chain preventing the formation of a hydrogen-bonded polymer in the solid state. In **3–5** the formation of a cup-like conformation is not necessary as intramolecular OH···N and OH···O hydrogen-bonds can form separately at both ends of the molecules.

In conclusion, in both inter- and intramolecular hydrogen bonding, phenolic substituents and the length of the bridging fragment have a substantial effect on the solubility of the compounds and, consequently, on the complexation properties of the compounds as ligands in coordination chemistry.

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PAPER III

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Syntheses and Structural Study of Novel Tetranuclear Bis(phenoxido)-Bridged Cu^{II} Metal–Organic Macrocycles

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Keywords: Copper / Supramolecular chemistry / Magnetic properties / Density functional calculations

Six new tetranuclear copper(II) complexes were prepared exploiting novel ditopic alkylenediamine-*N*,*N*,*N*′,*N*′-tetraphenolate ligands. The geometrical parameters of the compounds can be varied by introducing different solvents of crystallization into the lattice. The structures of all six complexes were determined from single-crystal X-ray diffraction analyses and the magnetic properties of the complexes were estimated by computational DFT calculations. The relationship between the magnetic exchange coupling constant (*J*) and the Cu–O–Cu angle (θ) in these bis(phenoxido)-bridged complexes was investigated and a magnetostructural correlation was established between *J* and the θ angle. All studied complexes showed strong antiferromagnetic behaviour.

Introduction

The amine-bis(phenol) ligands are versatile and important ligands that can be prepared relatively straightforwardly from common benchtop synthetic methods. The coordination chemistry of these ligands is eminently rich and the compounds have been exploited in numerous applications in applied coordination chemistry including mimicking the activity of biological compounds, catalysis and in molecular magnetism.[1,2] Progress has also been achieved in manipulating DNA[2c] using mono- and dinuclear aminophenol copper(II) complexes. Furthermore, the dinuclear bis(phenoxido)-bridged copper(II) complexes represent a class of important and well-studied compounds in the field of molecular magnetism.[3]

Recently, we have used amine-bis(phenol)s to prepare a series of bis(μ-phenoxido)dicopper(II) complexes with ω-[bis(2-hydroxy-3,5-dimethylbenzyl)amino]alkan-1-ol ligands[4] and established a linear relationship between the Cu–O–Cu angle (θ) and the magnetic exchange coupling constants (*J*). Our findings supported the experimental and theoretical magnetostructural studies performed during the past decades,[3] which have revealed several important correlations between the structural parameters and the magnetic properties of the compounds; the θ angle is probably the most important of these.

Earlier we reported on a novel and simple synthetic route for highly flexible and tunable ditopic alkylenediamine-*N*,*N*,*N*′,*N*′-tetraphenolate ligands,[5] which can be used in traditional coordination chemistry but also have potential as building blocks for molecular manufacturing used to produce molecular rings and metal–organic frameworks. This area of chemistry provides limitless possibilities in the design of molecular materials possessing extraordinary sensing, magnetic, catalytic and optical properties.[6] Until now, the ditopic alkylenediamine-*N*,*N*,*N*′,*N*′-tetraphenolate ligands and their complexes have not been extensively studied for these supramolecular applications.

In this contribution we have studied the reactions of these novel ligands (H_4L1, n = 7 and H_4L2, n = 8 in Scheme 1) with copper(II) salts and obtained a series of tetranuclear phenoxido-bridged copper(II) complexes. We were able to crystallize the complexes, with or without water bridges, as several different solvent adducts that alter the structural parameters around the Cu^{II} cations in the compounds. In addition, we have performed computational studies at the DFT level to estimate the magnetic exchange coupling constants of the complexes.

Results and Discussion

The syntheses of six new tetranuclear copper(II) diamine-bis(phenolate)s were performed according to Scheme 1. In the isolated complexes the copper(II) cations form two separate dinuclear units, which are connected by the alkyl chains to form molecular rings. Three of the complexes are tetranuclear $[Cu_4(L1)_2]\cdot x$S {x = 2 and S = methanol (**1**), x = 2 and S = chloroform (**2**), and x = 1 and S = H_2O (**3**)}. The other three are similar tetranuclear complexes with a water bridge on the coordination sphere of

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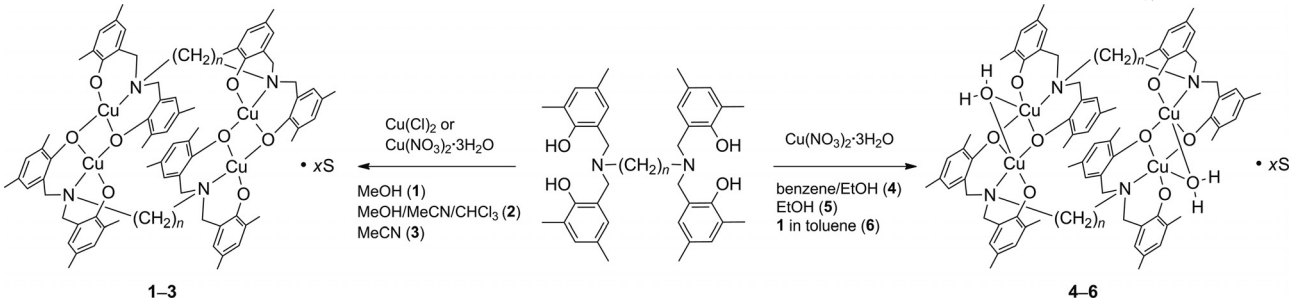

Scheme 1. Schematic synthetic route for the preparation of compounds **1**–**6**.

the Cu^{II} cations and solvates in the lattice: $[Cu_4(L1)_2(H_2O)_2]$·2EtOH·4benzene (**4**), $[Cu_4(L2)_2(H_2O)_2]$·2EtOH (**5**) and $[Cu_4(L1)_2(H_2O)_2]$·2EtOH·3toluene (**6**).

The complexes were characterized by elemental analyses, IR spectra, thermogravimetric measurements and X-ray diffraction. Furthermore, the magnetic properties of the complexes were estimated by DFT calculations. A thermogravimetric analysis revealed that in compounds **1**–**6** the solvent molecules can be removed quite easily. This is most likely because of the weak intermolecular interactions without strong hydrogen bonds. However, the removal of the solvents is a slow process, which begins at room temperature and lasts to about 160 °C. The solvent-free complexes start to decompose after 230 °C.

All solvents can be removed by 2 h of heating in a conventional thermal oven at 160 °C. The recrystallization attempts from the acquired solvent-free material did not improve the quality of the crystals or produce any additional solvates compared with the syntheses carried out from free ligand and copper(II) nitrate or chloride. However, we are confident that other packing structures, originating from the high flexibility of the ligand framework, are possible.

Complexes **1** and **2** crystallize in orthorhombic (*Pcab*) and complex **3** in monoclinic (*C*2/*c*) space groups, whereas complexes **4**–**6** crystallize in a triclinic ($P\bar{1}$) space group. All complexes **1**–**6** are similarly built from two tetra-anionic $L1^{4-}$ or $L2^{4-}$ (all phenol groups are deprotonated) alkylenediamine-*N*,*N*,*N*′,*N*′-tetraphenolate ligands coordinated to four copper(II) cations in a tridentate bridging manner, thus forming a neutral molecular metal–organic macrocycle (Figure 1, Figure 2 and Figures S1–S4). The selected geometrical parameters are presented in Table 1. The macrocycles **1**–**3** consist of two distinct Cu_2-(μ-OPh)$_2$ dinuclear units that are connected by alkyl bridges of the amino groups in amine-bis(phenol) ends of the alkylenediamine-*N*,*N*,*N*′,*N*′-tetraphenolate ligand. In complexes **1**–**3** the copper(II) cations have a slightly distorted square-planar coordination sphere around the copper(II) centres with the same donor atom sets, and the complexes **1** and **2** are isostructural. In complexes **4**–**6** each of the dinuclear copper units is also bridged by a weakly bonded water molecule, thus producing a strongly distorted square-based pyramidal fivefold coordination for the copper(II) cations with two μ_2-phenoxido, phenoxido and water oxygen atoms and an amine nitrogen atom.

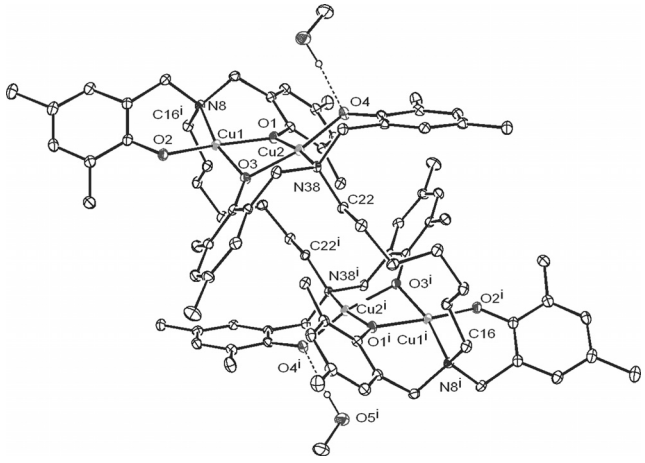

Figure 1. The tetranuclear unit of **1** showing the atomic labelling scheme with thermal ellipsoids drawn at the 20% probability level. CH hydrogen atoms have been omitted for clarity.

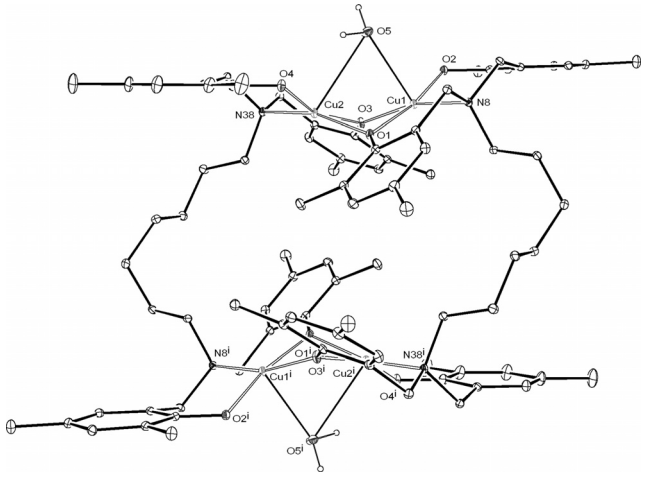

Figure 2. The tetranuclear unit of **6** showing the atomic labelling scheme with thermal ellipsoids drawn at the 20% probability level. CH hydrogen atoms and toluene molecules have been omitted for clarity.

All complexes **1**–**6** have additional noncoordinating solvents of crystallization, which notably alter the packing of the complexes, hence, changing the geometrical parameters and magnetic behaviour of the complexes. The unit cells of **1**–**3** contain noncoordinating methanol, chloroform and water molecules, respectively. The data for complex **3** is of

Table 1. Selected bond lengths [Å] and angles [°] for complexes **1**–**6**.

	1	**2**	**3**	**4**	**5**	**6**
Cu1–O1	1.918(2)	1.921(3)	1.920(9)	1.932(2)	1.942(2)	1.953(2)
Cu1–O2	1.857(2)	1.847(3)	1.847(9)	1.884(2)	1.890(2)	1.895(2)
Cu1–O3	1.995(2)	1.989(3)	1.995(9)	1.963(2)	1.937(2)	1.981(2)
Cu1–O5	–	–	–	2.776(3)	2.807(3)	2.496(3)
Cu1–N8	2.026(3)	2.029(3)	2.021(11)	2.009(2)	2.010(2)	2.025(3)
Cu2–O1	1.940(2)	1.960(3)	1.926(9)	1.981(2)	1.980(2)	1.956(2)
Cu2–O3	1.936(2)	1.926(3)	1.937(9)	1.937(2)	1.972(2)	1.940(2)
Cu2–O4	1.885(2)	1.878(3)	1.876(9)	1.881(2)	1.914(2)	1.881(2)
Cu2–O5	–	–	–	2.660(3)	2.330(3)	2.743(3)
Cu2–N38	1.996(2)	2.009(3)	1.996(10)	2.026(2)	2.010(2)	1.991(3)
Cu1–O1–Cu2 (θ)	101.76(9)	101.85(12)	102.6(5)	95.84(8)	95.59(9)	93.56(9)
Cu1–O3–Cu2	99.15(9)	100.60(12)	99.5(5)	96.24(8)	96.01(8)	93.20(8)
O1···O3–C31 (τ)[a]	12.5(2)	10.1(2)	16.1(9)	15.6(2)	19.5(2)	23.1(2)
O3···O1–C1 (τ)	18.6(2)	25.6(2)	19.6(9)	16.2(2)	16.7(2)	9.9(2)
Cu1–O5–Cu2	–	–	–	64.53(6)	68.17(8)	65.69(7)
Cu1–O1···O3–Cu2 (γ)[b]	–27.6(1)	–25.3(1)	–26.6(5)	–39.1(1)	–39.7(1)	–43.9(1)

[a] τ is the substituent angle from the bridging O···O line. [b] γ is the dihedral angle of the bridging O–Cu–O planes.

poor quality (i.e. large uncertainties in bond lengths and angles). Unfortunately, originating from the complexes tendency to crystallize with additional solvents in the lattice, we were not able to duplicate the synthesis of **3**, hence, the crystal structure is the only experimental data we can report.

Although the shapes of all the complexes are quite similar, the coordination environments around the copper centres can be clearly divided into two groups (**1**–**3** and **4**–**6**). Inside of these two groups the coordination spheres are comparable, but not identical. In the first group (**1**–**3**) the geometrical parameters around the central metal are uniform (see Table 1). Also the complexes **4** and **5** of the second group have similar main structural parameters regardless of the carbon chain being one carbon longer in **5** than in **4** and the quite unsymmetrical water bridge [Cu–O distances are 2.330(3) and 2.807(3) Å] in complex **5**. The structure of **6** shows several differences from that of **4** and **5** since the polar ethanol is missing from the structure of **6** (Table 1).

The solvents of crystallization affect the structural parameters of the coordination spheres in **1**–**6** by changing the packing system of the complexes. This is clearly seen from the packing diagrams of **1**–**2** where the water molecule is absent. The complexes form separate neutral units in the lattice without any major interaction between each other and the solvents of crystallization only fill the lattice with hydrogen bonds to the molecular rings (Figure 3). The bridging water molecule in complexes **4**–**6** causes new demands on the packing system since the OH hydrogen needs H acceptors. Complex **5** (Figure 4) is shown as an example of the packing diagrams of complexes **4**–**6**. It is evident that the bridging water molecule induces a hydrogen-bonding network connecting the complexes to 1D chains (see also Figures S7 and S8). In addition, there are no interactions or transmission pathways for magnetic effects in the other two directions, hence, these complexes could possess single-chain magnet behaviour (Figure S9). In addition, in complex **3**, weakly H-bonded water molecules connect the individual complexes forming a similar chain arrangement of

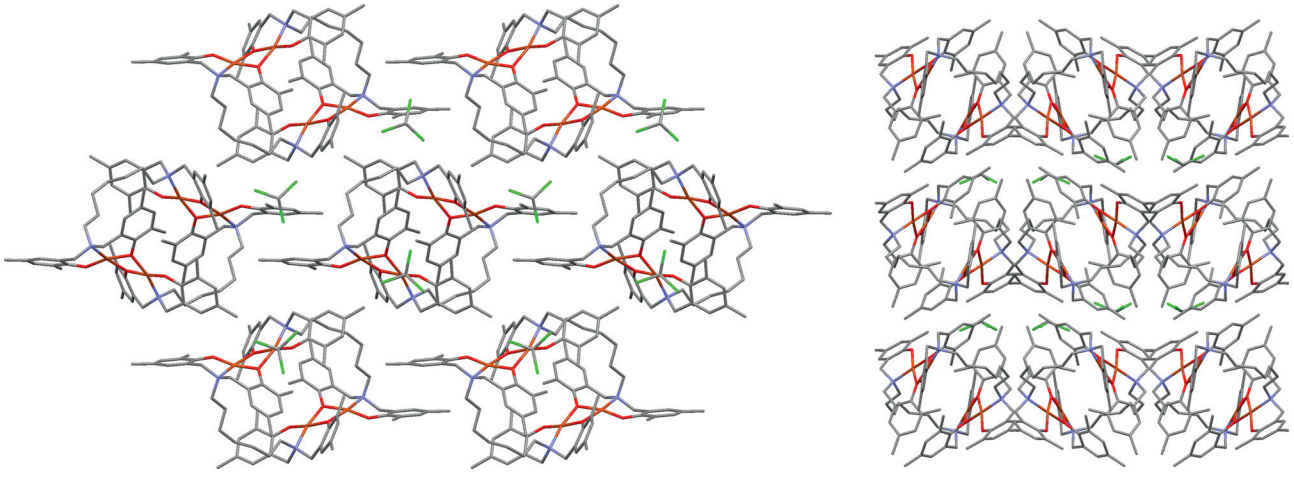

Figure 3. Packing diagram of complex **2** shown down the crystallographic c axis (left) and a axis (right).

the complexes (Figure S6). The solvate dependent structural changes have also been found in dinuclear [Cu_2(*o*-pba)$_2$] complexes [*o*-pba = *o*-phenylenebis(acetylacetonate)].[7]

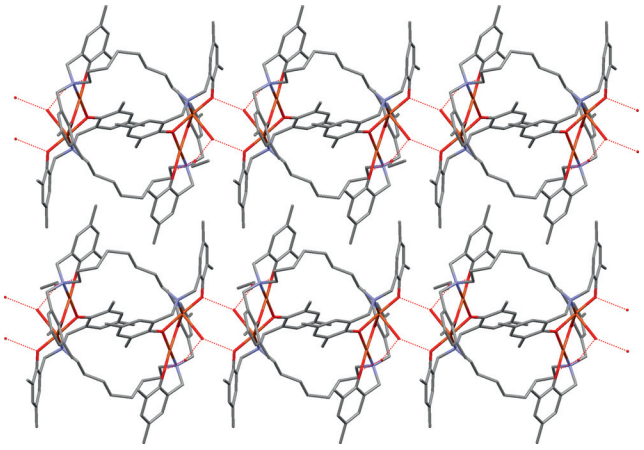

Figure 4. Packing diagram of complex **5** shown down the reciprocal cell a* axis.

In general, complexes **1**–**6** are interesting from the sense of molecular magnetism but also from a structural point of view. All complexes form metal–organic macrocycles, which by themselves could be used to trap small molecules in the cavities of the lattice or more likely as building blocks to large metal–organic frameworks. As shown by the coordinated water molecules, the individual complexes could be linked together with proper donor molecules with bridging abilities (for example some dinitroderivatives or dicarboxylic acids).

Furthermore, we are able to modify the length of the alkyl chain between the amine nitrogens connecting two amine-bis(phenol) ends of the ligand (eight methylene groups in complex **5** compared to seven methylenes in the other complexes), hence, the size of the macrocycle can be varied. We have prepared ligands with up to 12 carbon atoms between amine-bis(phenol) ends but unfortunately we were not able to crystallize any copper(II) complexes of these ligands (we also prepared similar ligands with five or six methylene groups, but no molecular rings were obtained). It is also possible to introduce heteroatoms to the alkyl chain (providing more donor atoms for metal cation bonding) and modify the substituents in the aromatic rings. The potential of these ligands and complexes is immense and the capability of these compounds to produce metal–organic frameworks and related materials is under study by our group.

Theoretical Studies

Because of the unstable nature of the solvent molecules in the lattice of the complexes **1**–**6**, the experimental measurement of the magnetic properties of the complexes would be at least ambiguous. Hence, we performed a thorough DFT computational analysis to evaluate the strength of the magnetic coupling in these novel tetranuclear complexes. The analysis was performed at the B3LYP/TZV[8] level using the Turbomole 6.3 program package.[9] In all calculations, the coupling between separate dinuclear units was neglected since there is no transmission pathway for magnetic effects between the copper centres, and the calculations showed that the coupling is virtually nonexistent compared to the coupling constant values within the dinuclear units. Hence, the final coupling constants (*J*) were obtained as the energy difference between the broken symmetry singlet state and the corresponding quintet state by single-point calculations to the crystallographic geometries without noncoordinating solvent molecules. The energy difference between the preceding states in this system of two separate dinuclear copper units is –2*J*. The calculated magnetic coupling constants (Table 2) are in good agreement with the experimental and computational values obtained earlier.[3,4]

Table 2. Calculated magnetic coupling constant values *J* [cm^{-1}] for complexes **1**–**8**.

	$J_{calcd.}$	J_{exp}	θ[a]	d[b]	Ref.
1	–488.3	–	100.48	2.994	this work
2	–473.8	–	101.23	3.013	this work
3	–437.1	–	100.97	3.001	this work
4	–297.0	–	96.04	2.904	this work
5	–288.4	–	95.80	2.906	this work
6	–205.2	–	93.38	2.849	this work
7	9.6	26.62	84.69	2.671	[10]
8	30.2	38.66	85.13	2.680	[10]

[a] Mean value of both Cu–O–Cu angles in °. [b] Cu···Cu distance in Å.

To estimate the effects of different noncoordinated solvent molecules in the lattice we tried to create a magnetostructural correlation between certain structural parameters and the magnetic behaviour. Previously these correlations have been found for example between the Cu–O–Cu (θ) angle and the coupling constant *J*.[3,4] For the complexes **1**–**6** the magnetostructural correlation of the *J* value to the Cu–O–Cu angle is evident, since there is an almost linear relationship (R = 0.993) between the *J* values and the θ angle (Figure 5). In addition, we were able to find a similar

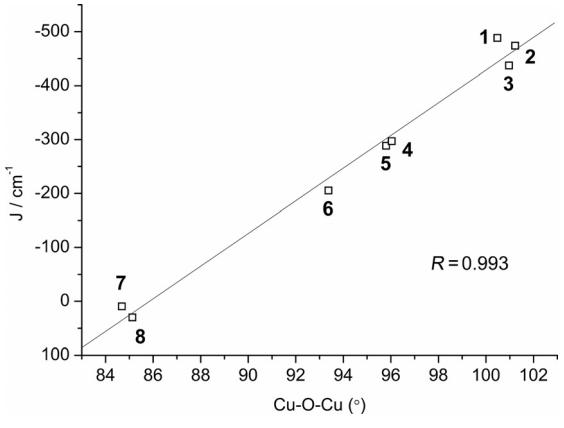

Figure 5. Plot of the calculated *J* value versus the average Cu–O–Cu angle of complexes **1**–**8**.

correlation between the Cu–Cu bond length and the coupling constant *J*. The correlation of the Cu–Cu bond length is clearly due to double bridges in the complexes, which bind the Cu–Cu bond firmly to the Cu–O–Cu angle and vice versa.

The effect of the weakly coordinating water molecule is obvious from the calculated *J* values. The water molecule bends the Cu–O–Cu angle thus weakening the magnetic transmission pathway between the copper centres. Hence, the values of coupling constants for **4**–**6** are more than 100 cm^{-1} smaller than complexes without the water bridge (**1**–**3**).

The reliability of the computed values was also estimated by calculating the coupling constants of recently published similar dinuclear copper(II) complexes **7** and **8**.[10] The calculated *J* values (Table 2, Entries 7 and 8) are in good agreement with experimental ones and they fit nicely in to the data from complexes **1**–**6** (Figure 5), thus confirming the observed magnetostructural correlation.

Conclusions

In this study we have shown that novel ditopic alkylenediamine-*N*,*N*,*N*′,*N*′-tetraphenolate ligands form tetranuclear complexes with copper(II) cations producing flexible metal–organic macrocycles. The geometries and structural parameters around the copper centres can be varied by introducing a weakly coordinated water molecule and different solvents of crystallization into the lattice. According to theoretical studies all these complexes show antiferromagnetic behaviour. Furthermore, we were able to constitute a magnetostructural correlation between the calculated coupling constant values (*J*) and Cu–O–Cu angle (θ). Future studies are aimed at investigating the performance of the prepared ligands and complexes as metal organic frameworks and/or molecular rings.

Experimental Section

Materials: $Cu(NO_3)_2{\cdot}3H_2O$, $CuCl_2$ and solvents were purchased from commercial sources and used as received. H_4L1 and H_4L2 were prepared using a known procedure.[5] X-ray crystallography, elemental and IR analyses were performed in situ after the removal of the liquid reaction medium because of the rapid decomposition of the crystalline complexes.

$[Cu_4(L1)_2]{\cdot}2MeOH$ (1): $Cu(NO_3)_2{\cdot}3H_2O$ (0.2 mmol, 48 mg) was dissolved in MeOH (1.0 mL) and H_4L1 (0.1 mmol, 66 mg) in MeOH (9.0 mL). The solutions were layered and after 18 h a few crystals of $[Cu_4(L1)_2]{\cdot}2MeOH$ were formed (confirmed by X-ray diffraction). NEt_3 (0.4 mmol, 56 μL) was dissolved in MeOH (5 mL) and was added to the mixture. After 24 h six-cornered, dark-green plates of $[Cu_4(L1)_2]{\cdot}2MeOH$ were collected by decantation, washed with methanol (10 mL) and air dried; yield 58 mg (88%). $C_{88}H_{116}Cu_4N_4O_{10}$ (1644.09): calcd. C 64.3, H 7.11, N 3.41; found C 64.3, H 7.03, N 3.10. IR: $\tilde{\nu}$ = 1474 (vs), 1305 (s), 1235 (s), 1159, 979, 803, 641, 506 cm^{-1}.

$[Cu_4(L1)_2]{\cdot}2CHCl_3$ (2): $CuCl_2$ (0.1 mmol, 14 mg) was dissolved in MeOH (1.0 mL) and H_4L1 (0.05 mmol, 33 mg) in $CHCl_3$ (1.0 mL). The solutions were mixed and MeCN (3.0 mL) was added. After the addition of NEt_3 (0.22 mmol, 30 μL) into the solution it was kept at room temp. for 24 h. Six-cornered, light-green plates of **2** were separated by decantation and washed with ether (3 mL); yield 29 mg (64%). $C_{88}H_{110}Cl_6Cu_4N_4O_8$ (1818.76): calcd. C 58.1, H 6.10, N 3.08; found C 58.7, H 6.29, N 3.25. IR: $\tilde{\nu}$ = 1473 (vs), 1307 (s), 1248 (vs), 1161 (m), 804 (s), 753 (s), 614 (m), 504 (m) cm^{-1}.

$[Cu_4(L1)_2]{\cdot}H_2O$ (3): The compound was obtained from a dilute acetonitrile mixture using stoichiometric amounts of $Cu(NO_3)_2{\cdot}3H_2O$ (0.1 mmol, 24 mg), H_4L1 (0.05 mmol, 33 mg) and NEt_3 (0.2 mmol, 30 μL). Starting materials were mixed in acetonitrile and immediately a precipitate formed, which was separated by decantation. The solution was kept at room temperature for several weeks. Only a few crystals were formed and they were characterized by X-ray diffraction. However, despite several attempts, we have not been able to crystallize this compound since then. Difficulties in preparation of **3** as a crystalline product revealed that the solvent-free tetranuclear complex is not thermodynamically stable. The high values of the thermal ellipsoids of **3** also support this.

$[Cu_4(L1)_2(H_2O)_2]{\cdot}2EtOH{\cdot}4benzene$ (4): $Cu(NO_3)_2{\cdot}3H_2O$ (1.0 mmol, 24 mg) and H_4L1 (0.05 mmol, 33 mg) were dissolved in a mixture of benzene (5.0 mL) and EtOH (3.0 mL). NEt_3 (0.22 mmol, 30 μL) was added and the solution was concentrated to 2.0 mL over 24 h. Compound **4** was separated by decantation and air dried; yield 35 mg (69%). $C_{114}H_{148}Cu_4N_4O_{12}$ (2020.63): calcd. C 67.8, H 7.38, N 2.77; found C 67.5, H 7.41, N 2.83. IR: $\tilde{\nu}$ = 1476 (s), 1309 (s), 1253 (s), 806 (s), 672 (vs), 614 (m), 504 (m) cm^{-1}.

$[Cu_4(L2)_2(H_2O)_2]{\cdot}2EtOH$ (5): $Cu(NO_3)_2{\cdot}3H_2O$ (0.2 mmol, 48 mg) was dissolved in EtOH (3.0 mL) and H_4L2 (0.1 mmol, 68 mg) was dissolved in boiling EtOH (3.0 mL) and the solutions were mixed. NEt_3 (0.44 mmol, 60 μL) was dissolved in EtOH (3 mL) and added as a layer on top of the previous mixture. After 4 d **5** was separated by decantation; yield 62 mg (71%). $C_{92}H_{128}Cu_4N_4O_{12}$ (1736.23): calcd. C 63.64, H 7.43, N 3.23; found C 63.16, H 7.47, N 3.13. IR: $\tilde{\nu}$ = 1473 (vs), 1309 (s), 1254 (vs), 1048 (s), 880 (s), 805 (s), 612 (s), 502 (s), 457 (m) cm^{-1}.

$[Cu_4(L1)_2(H_2O)_2]{\cdot}3toluene$ (6): Compound **1** (20 mg, 0.012 mmol) was dissolved in hot toluene (5.0 mL). The solution was concentrated to a final volume of 1.0 mL and allowed to obtain moisture from the air for 24 h. Crystals of **6** were separated by decantation and air dried; yield 23 mg (98%). $C_{107}H_{136}Cu_4N_4O_{10}$ (1892.46): calcd. C 67.9, H 7.24, N 2.96; found C 67.8, H 7.15, N 2.89. IR: $\tilde{\nu}$ = 1472 (s), 1305 (m), 1252 (s), 804 (s), 727 (vs), 693 (s), 463 (s) cm^{-1}.

IR Spectra: The infrared spectra were measured using a Bruker Tensor 27 IR device with an ATR. The spectra were recorded in situ directly from the surface of the sample after removal from the reaction mixture. The IR spectra of complexes **1**, **2**, **4**–**6**, H_4L1 and H_4L2 over the wavenumber region 2000–300 cm^{-1} are provided in the Supplementary Information.

X-ray Measurements: Suitable single crystals of **1**–**6** for X-ray measurements were obtained directly from the batches of isolated complexes. Crystallographic data were collected at 123 or 173 K with a Nonius-Kappa CCD area-detector diffractometer using graphite-monochromatized Mo-K_α radiation (α = 0.71073 Å) (Table 3). The structures were solved by direct methods using the SIR97 or SHELXS-97 programs[11,12] and full-matrix, least-squares refinements on F^2 were performed using the SHELXL-97 program.[12] The CH hydrogen atoms were included at the fixed distances with the fixed displacement parameters from their host atoms (1.2 or 1.5 times that of the host atom). The OH hydrogen atoms were

Table 3. Summary of crystallographic data for complexes **1**–**6**.

	1	**2**	**3**	**4**	**5**	**6**
Empirical formula	$C_{88}H_{108}Cu_4N_4O_{10}$	$C_{88}H_{110}Cl_6Cu_4N_4O_8$	$C_{86}H_{108}Cu_4N_4O_9$	$C_{114}H_{148}Cu_4N_4O_{12}$	$C_{92}H_{128}Cu_4N_4O_{12}$	$C_{107}H_{136}Cu_4N_4O_{10}$
M_r [g mol^{-1}]	1644.01	1818.66	1579.92	2020.52	1736.14	946.18
Crystal system	orthorhombic	orthorhombic	monoclinic	triclinic	triclinic	triclinic
Space group (no.)	*Pcab* (61)	*Pcab* (61)	*C2/c* (15)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a [Å]	17.6471(2)	17.5688(2)	21.6901(19)	13.4103(3)	13.5339(3)	13.5582(3)
b [Å]	20.5513(2)	20.8245(3)	13.3687(11)	14.8022(3)	14.0812(3)	14.1141(3)
c [Å]	22.2862(3)	22.7194(3)	27.680(2)	16.0649(4)	14.2794(4)	14.2786(3)
α [°]	90	90	90	104.3620(10)	92.913(2)	103.478(2)
β [°]	90	90	93.887(4)	102.2830(10)	117.3250(10)	108.7970(10)
γ [°]	90	90	90	115.2330(10)	110.0820(10)	101.3790(10)
V [Å]	8082.56(16)	8312.15(19)	8007.9(11)	2603.39(10)	2198.65(9)	2402.77(9)
Z	4	4	4	1	1	1
$D_{calcd.}$ [g cm^{-1}]	1.351	1.453	1.324	1.289	1.311	1.308
μ (Mo-K_α) [mm^{-1}]	1.099	1.261	1.106	0.868	1.015	0.934
T [K]	123(2)	123(2)	173(2)	123(2)	173(2)	123(2)
Observed reflections	7945	9040	6888	10179	8475	9184
R_{int}	0.0813	0.0615	0.1029	0.0582	0.0505	0.0447
Parameters	490	504	447	652	523	587
R_1[a]	0.0750 (0.0423)[b]	0.0782 (0.0539)	0.2512 (0.1341)	0.0717 (0.453)	0.0780 (0.0486)	0.0707 (0.0464)
wR_2[c]	0.0984 (0.0855)	0.1664 (0.1452)	0.3256 (0.2680)	0.0945 (0.0853)	0.1084 (0.0986)	0.1135 (0.1034)
$\Delta\rho_{max./min.}$ [e Å^{-3}]	0.470/–0.492	0.679/–1.16	0.657/–0.444	0.402/–0.342	0.386/–0.327	0.924/–0.484

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] Values in parentheses are for reflections with $I > 2\sigma(I)$. [c] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ and $w = 1/[\sigma^2(F_o^2) + (aP)^2 + (bP)]$, where $P = (2F_c^2 + F_o^2)/3$.

refined isotropically with a thermal displacement of 1.2 times that of the host atom. The figures were drawn with the programs Ortep-III for Microsoft Windows®[13] and Mercury.[14]

CCDC-848123 (for **1**), -848124 (for **2**), -848125 (for **3**), -848126 (for **4**), -848127 (for **5**) and -848128 (for **6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Details: All the calculations were performed for crystallographic geometries using the Turbomole 6.3[9] program package. B3LYP[8] hybrid functional and Ahlrichs TZV[8] basis sets were used throughout the entire analysis. A Mulliken population analysis[15] was used to confirm that the SCF procedure converged to a proper electronic state.

Supporting Information (see footnote on the first page of this article): Molecular structures of complexes **2**–**6** (Figures S1–S4), packing diagrams of **1**, **3**, **4** and **6** (Figures S5–S9) and IR spectra of all complexes as well as H_4L1 and H_4L2 are reported.

Acknowledgments

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PAPER IV

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FULL PAPER

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Synthesis, Structure and Catalytic Properties of Dinuclear Mo^{VI} Complexes with Ditopic Diaminotetraphenols

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Keywords: Diaminotetraphenols / X-ray diffraction / Molybdenum / Alcohols / Oxidation

Mo^{VI} complexes with novel ditopic diaminotetraphenol ligands have been prepared by using a one-pot procedure in methanol or DMSO with $[MoO_2(acac)_2]$ (acac = acetylacetonate) as the molybdenum source. The complexes were characterised with X-ray diffraction, NMR spectroscopic studies, elemental analysis and IR spectroscopy. In the solid state, the compounds represent either a rodlike molecular or oxido-bridged polymeric structure. The catalytic activity of the complexes was investigated by oxidising benzyl alcohol and 1-phenylethanol with hydrogen peroxide to the corresponding aldehyde and ketone, respectively. Furthermore, the catalytic activity was surveyed also in epoxidation of cyclooctene.

Introduction

The role of high-valent molybdenum complexes containing *cis*-$[MoO_2]^{2+}$ units has attracted considerable interest in catalytic oxidation reactions,[1,2] especially in the oxidation of alcohols,[3] epoxidation,[4] oxo-transfer[5,6] and hydrosilylation reactions.[7] Oxo-transfer reactions are also of special interest, because they are observed in several important biological systems.[8,9] Furthermore, the versatility of oxidomolybdenum compounds has been highlighted by an interesting application of hydrogen generation from water.[10]

Recently, our group has been working with oxidomolybdenum(VI) compounds bearing aminodiphenolate ligands.[11–13] Aminodiphenolates are ligands that allow easy modification of the coordination sphere around the metal centre; they are particularly useful ligands for transition-metal ions with high oxidation states.[14] These ligands can be used for a variety of applications such as producing dinuclear bis(phenoxido)-bridged Cu^{II} ions with interesting magnetic properties.[15] Most of the studies have concentrated on tetrapodal aminodiphenols with N or O side-arm donors, whereas reports on ditopic ligands with an alkyl or ether bridge are scarce. Only a handful of papers that discuss the metal complexes of long-alkyl-bridged ditopic diaminotetraphenols have been published, most recently our report on the structures and magnetic properties of some copper(II) complexes of these ligands.[16] However, other types of flexible ditopic ligands with carboxylate and nitrogen donors have gained much attention in the synthesis of coordination polymers that could be used in several applications.[17]

The oxidation of alcohols by Mo compounds as catalysts have been studied previously with several different approaches. Oxidations by molecular oxygen have been reported, for example, with the $[MoO_2]^{2+}$ Schiff base complex[3b] [in 10 h, the benzaldehyde yield can reach about 63% (turnover number TON = 100)], $[MoO_2(acac)_2]$ (acac = acetylacetonate) on polyaniline[18a] with a high yield and selectivity in 12 h, $[MoO_2Cl_2(L)_2]$ in which L is DMSO, DMF or THF[18b] with a high yield in 2 h, and $[MoO_2(acac)_2]/Cu(NO_3)_2$ as catalysts with a high conversion and selectivity.[19] Hydrogen peroxide has also been used as oxidant with $[Mo(O_2)(QO)_2]$ (QO = 8-quinolinolate anion)[3b] [with yields up to 66% in 16 h; the selectivity depends on the substrate, and oxidation with O_2 gave much lower yields] and with (oxido)(peroxido)Mo^{VI} acetylide complex $[CpMoO(O_2)(C{\equiv}CPh)]$ with a high conversion and moderate selectivity.[20] In addition, Mo polyoxoanions with several oxidants have been used to catalyse alcohol oxidations with high yields and selectivity.[21]

Herein, we report the syntheses, characterisation and solid-state structures of several novel Mo^{VI} complexes, six with *n*-alkyl-bridged *N*,*N*,*N*′,*N*′-tetrakis(2-hydroxybenzyl)-diamines and one ether-bridged complex (Scheme 1). With these novel dinuclear molybdenum(VI) dioxide complexes in our hands, we were prompted to study their catalytic activities in oxygen-transfer reactions. The oxidation of aromatic alcohols with hydrogen peroxide was selected as a test reaction by using all of these structurally comparable $[MoO_2]^{2+}$ aminodiphenol complexes as catalysts. Benzyl

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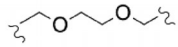
Compound	Ligand	R	R′	S
1	H_4L1	methyl	$(CH_2)_5$	MeOH
2, 2′	H_4L2	methyl	$(CH_2)_6$	MeOH
3	H_4L3	*t*Bu	$(CH_2)_6$	MeOH
4	H_4L4	methyl	$(CH_2)_7$	MeOH
5	H_4L5	methyl	$(CH_2)_8$	DMSO
6	H_4L6	*t*Bu	$(CH_2)_8$	MeOH
7	H_4L7	methyl		MeOH

Scheme 1. Synthetic routes for the preparation of new Mo^{VI} complexes **1**–**7**. The formula of **8**, which is used for comparable purposes and is a known compound,[22] is presented at the bottom on the right. Compound **2′** is same as **2**, but without uncoordinated solvent molecules in the lattice.

alcohol (1° alcohol) and 1-phenylethanol (2° alcohol) were used as substrates in the oxidations. In addition, we briefly surveyed the performance of a few complexes as catalysts in alkene epoxidation with *t*Bu hydroperoxide.

Results and Discussion

Syntheses

Six new dinuclear dioxidomolybdenum(VI) complexes with *n*-alkyl-bridged *N*,*N*,*N*′,*N*′-tetrakis(2-hydroxybenzyl)-diamino ligands and one with the ether-bridged *N*,*N*,*N*′,*N*′-tetrakis(2-hydroxybenzyl)diamino ligand were prepared and characterised. These compounds can be prepared in methanol or in a mixture of DMSO/MeCN by using $[MoO_2(acac)_2]$ and the corresponding aminophenolato ligand (Scheme 1) as starting materials. The formation of ditopic complexes is quite slow at room temperature owing to the poor solubility of the ligand precursors,[23b] although the reactions can be accelerated by heating. Solid products crystallise or precipitate from the reaction mixtures, and they can be further purified by recrystallisation or by washing with CH_2Cl_2 and MeOH. However, these purification steps might change the composition of the products, as coordinated MeOH or solvent of crystallisation may be lost, which leads to the nonstoichiometric (e.g., in **5** the uncoordinated acetonitrile molecules are partly lost) amount of solvent molecules in the final product.

In addition, the removal of the coordinated MeOH molecule from the coordination sphere of the Mo^{VI} ion causes the complexes to polymerise (similar to compound **1** or in the literature[11]) and become practically insoluble in any other solvents except hot DMSO. Uncoordinated lattice molecules, MeOH in **1** and THF in **2**, escape from the freshly prepared crystals differently according to the thermogravimetric (TG) measurement: in **1** in the temperature range of 70–200 °C together with coordinated methanol (Figure S1 in the Supporting Information), and in **2** the uncoordinated THF evaporates at room temperature in 5 min and the coordinated methanol in the range of 71–94 °C (Figure S2 in the Supporting Information).

In the following catalytic studies (see below) the good solubility of the catalyst in neat alcohol or acetonitrile is possibly owing to the formation of an alkoxide complex of the catalyst precursor. As the reactions have been performed in basic solutions, the coordinated methanol can be replaced by an alkoxide ion from the substrate.

Crystal Structures

The solid-state structures of complexes **1**–**5** and **7** were determined by single-crystal X-ray diffraction. Compounds **1** and **7** crystallise in orthorhombic space groups, whereas compounds **2**–**5** crystallise in monoclinic ones. The molecular structures of all complexes reveal a similar distorted octahedral coordination sphere around $[MoO_2]^{2+}$ cations with two *cis*-positioned oxido ligands bound strongly to the Mo^{VI} ion, whereas two phenoxide oxygen atoms are placed in *trans* positions to each other. The remaining two coordination sites are occupied by an amine nitrogen atom and an oxygen donor from the coordinating solvent or ligand (complex **7**) in *trans* positions to the oxido ligands. Owing to the *trans* influence of the oxido ligands and the different formal charge of the coordinating atoms, the latter bonds are considerably longer than Mo–$O_{phenoxido}$ bonds. The selected bonding parameters are presented in Table 1. On the whole, the coordination geometry around the metal centre in these ditopic compounds is very similar to those found for corresponding mononuclear Mo^{VI} aminodiphenolates.[11,22]

This indicates that methanol molecules are bonded with variable strengths to Mo^{VI} in the studied complexes. These complexes are generally poorly soluble, but they dissolve in hot DMSO and in basic mixtures of aromatic alcohols (benzyl alcohol and 1-phenylethanol). Consequently, DMSO replaces coordinated methanol molecules during NMR spectroscopic analysis. According to these NMR spectroscopic results all complexes are molecular ones in DMSO. The crystalline complexes were used in the catalytic studies.

In compounds **2**–**5**, the bonding parameters around Mo^{VI} ions are rather identical owing to the closely related coordination environment, which is $[MoO_2(O_{phenoxido})_2N_{amine}(O_{MeOH})]$ {or $[MoO_2(O_{phenoxido})_2N_{amine}(O_{DMSO})]$ in **5**}. The coordination spheres around Mo^{VI} cations in **7** are of the type $[MoO_2(O_{phenoxido})_2N_{amine}(O_{ether})]$ as an ether oxygen atom of the linkage between the bisphenoxido moieties coordinates to Mo^{VI}. The most striking difference between the studied structures is that the crystals of **2**–**5** and **7** contain separated molecular units, whereas **1** has a clearly polymeric structure. In complex **1** there is only one coordinating MeOH molecule for two Mo^{VI} units, thus one oxido group at the Mo1 end of the ditopic unit acts as a bridging ligand to complete the preferred coordination number of six for both Mo^{VI} ions, which makes the structure of **1** polymeric. The asymmetric unit is depicted in Figure 1a, which shows the linear bridging arrangement between the nitrogen atoms, whereas a part of the polymeric chain is depicted in Figure 1b. The coordination sphere around Mo1 is similar

Table 1. Selected bond lengths [Å] and angles [°] for compounds **1**–**5** and **7**.

	1	**2**	**2′**	**3**	**4**[a]	**5**	**7**[b]
Mo1=O1	1.733(3)	1.703(2)	1.720(2)	1.712(4)	1.717(2)	1.706(2)	1.704(4)
Mo1=O2	1.697(3)	1.695(2)	1.692(2)	1.705(5)	1.687(2)	1.700(3)	1.704(3)
Mo1–O3	1.889(4)	1.947(2)	1.934(2)	1.922(4)	1.933(2)	1.926(2)	1.977(4)
Mo1–O4	1.891(3)	1.933(2)	1.934(2)	1.930(4)	1.934(2)	1.951(2)	1.939(3)
Mo1–O5/O18	2.251(3)	2.341(2)	2.356(2)	2.304(5)	2.345(2)	2.285(3)	2.367(3)
Mo1–N8	2.447(3)	2.519(2)	2.472(2)	2.513(5)	2.518(2)	2.510(3)	2.361(4)
Mo2–O11	1.703(3)				1.683(2)		1.713(4)
Mo2–O12	1.702(3)				1.707(2)		1.689(3)
Mo2–O13	1.946(3)				1.924(2)		1.945(3)
Mo2–O14	1.922(3)				1.935(2)		1.945(3)
Mo2–O1^{i}/O15/O21	2.305(3)				2.299(2)		2.364(3)
Mo2–N28/N38	2.473(3)				2.525(2)		2.373(4)
O1=Mo1=O2	103.40(14)	105.36(8)	105.51(8)	105.0(2)	105.41(10)	103.85(14)	108.7(2)
O1–Mo1–N8	167.32(12)	167.54(7)	164.17(7)	167.6(2)	165.52(8)	167.32(12)	150.20(16)
O2–Mo1–O5/O18	167.80(14)	166.63(6)	169.68(7)	166.62(19)	169.21(9)	167.59(11)	169.58(17)
O3–Mo1–O4	155.36(16)	150.08(6)	152.01(7)	152.2(2)	152.38(9)	153.16(11)	156.68(15)
C1–O3–Mo1	139.8(3)	128.91(12)	132.31(14)	137.3(4)	129.86(18)	139.9(2)	119.1(3)
C15–O4–Mo1	138.8(3)	132.88(12)	135.53(14)	133.2(4)	133.89(19)	129.7(2)	125.4(3)
O11=Mo2=O12	104.95(14)				105.26(11)		107.88(17)
O11–Mo2–N28/N38	166.43(12)				165.89(10)		151.68(15)
O12–Mo2–O1^{i}/O15/O21	168.35(13)				166.93(9)		169.15(16)
O13–Mo2–O14	152.94(12)				152.49(9)		156.06(14)
C21/C31–O13–Mo2	122.2(2)				136.21(18)		124.0(3)
C35/C45–O14–Mo2	144.1(3)				129.3(2)		118.7(3)
Mo1–O1–Mo2^{ii}	170.21(17)						

[a] Atom label for coordinated O15 is used only for **4**. [b] Atom labels O18, O21, N38, C31 and C45 are used only for **7**. O1^{i} has been generated by the symmetry operation $1 - x, -y + ½, -z - ½$ and Mo2^{ii} by $1 - x, -y + ½, -z + ½$.

to those of other studied complexes with the $[MoO_2(O_{phenoxido})_2N_{amine}(O_{MeOH})]$ arrangement. In an Mo2-centred unit, one coordination site is occupied by an oxido ligand of a neighbouring complex, thereby producing an $[MoO_2(O_{phenoxido})_2N_{amine}(O_{oxido})]$ system. The bond lengths around Mo atoms in **1** are quite similar to those in **2**–**5**, but surprisingly, the bond lengths around Mo2 with a bridged oxido ligand in place of coordinated methanol more closely resembles the structural parameters of **2**–**5** than those of Mo1 with a coordinated methanol molecule. As the Mo1=O1 bond [1.733(3) Å] is longer than Mo=O bonds, which are normally 1.71 Å, the rest of the bonds around Mo1 become much shorter than they are around Mo2 in **1** and complexes **2**–**5**.

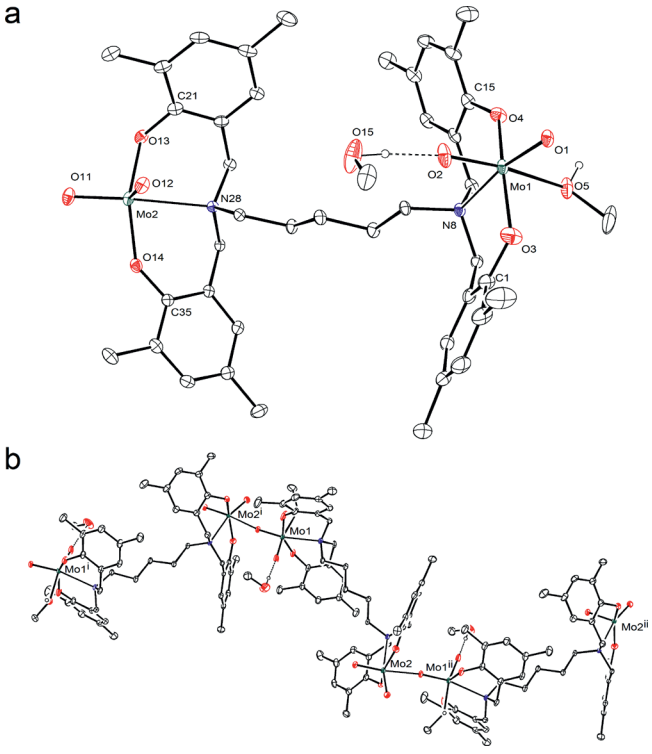


Figure 1. (a) Asymmetric unit of $[(MoO_2)_2(L1)(MeOH)]\cdot MeOH$ (**1**). (b) Part of the polymeric molecular chain of **1**. Symmetry operations: i: 1 – *x*, –*y* + ½, –*z* – ½; ii: 1 – *x*, –*y* + ½, –*z* + ½. Thermal ellipsoids are drawn at the 20% probability level.

Bridging between two dioxidomolybdenum(VI) moieties in **1** takes place along the *c* axis unsymmetrically through the O1 atom. The structural parameters around bridging O1 are: Mo1–O1 1.733(3), $Mo2^i$–O1 2.305(3) Å (i: 1 – *x*, –*y* + ½, –*z* – ½); Mo1–O1–$Mo2^i$ 170.21(17)°. The Mo–O1 bond is 0.036 Å longer than the Mo1–O2 bond, which indicates only a slight weakening of the π bonding in the Mo1=O1 bond. In an *N*-methylated aminodiphenolate complex of Mo^{VI}, a di-μ-oxido-bridged system forms, because no coordinated solvent atoms are present.[11] In this case, the nonlinear bridging parameters in the centrosymmetric structure are: Mo–O1 1.7519(16), Mo^i–O1 2.3901(16) Å (i: – *x*, 1 – *y*, 1 – *z*); Mo–O1–Mo^i 103.72(7)°.

Molecular complexes **2**–**5** have all similar coordination spheres around Mo^{VI} ions with an $[MoO_2(O_{phenoxido})_2N_{amine}(O_{MeOH})]$ coordination arrangement in **2**–**4** (the structures are presented in Figures 2, 3 and 4) and $[MoO_2(O_{phenoxido})_2N_{amine}(O_{DMSO})]$ for **5** (see Figure 6 for the structure). Complex **4** crystallises with two closely similar Mo-centred units attached by an alkane chain, whereas the other complexes have a centrosymmetric ditopic structure. In addition to the coordinated solvent molecules, all structures but **2′** enclose some uncoordinated solvents of crystallisation, which form hydrogen bonds with coordinated methanol or with each other. Clearly, there are no such hydrogen bonds in complex **5** with coordinated DMSO and acetonitrile adduct molecules. The Mo=O bond lengths of **2**–**5** vary from 1.683(2) to 1.720(2) Å, whereas the *cis* angles (O1=Mo1=O2) are in a narrow range from 103.9(2) to 105.4(1)°. Mo^{VI}–phenoxido bonds are in the normal range from 1.922(3) to 1.951(2) Å and the angles O3–Mo1–O4 are between 150.08(6) and 153.2(1)°. All the structural parameters are in agreement with the simple *N*-methylated aminodiphenolate complexes found in the literature.[11] A more complete list of the bond parameters can be found in Table S2 of the Supporting Information. The geometrical parameters show significant distortions from ideal octahedral geometry, which, however, are commonly observed in structures that contain the $[MoO_2]^{2+}$ cation.

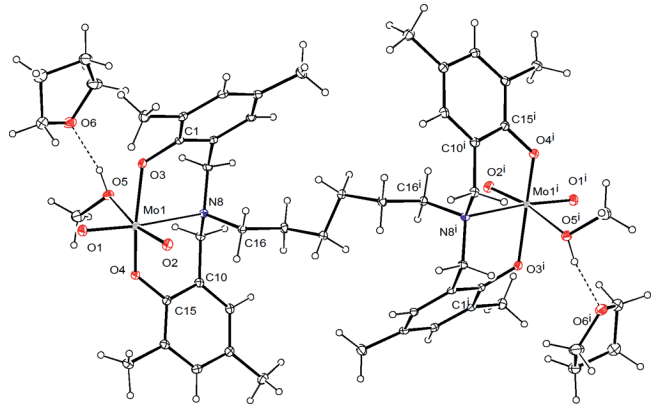


Figure 2. Molecular structure of $[(MoO_2)_2(L2)(MeOH)_2]\cdot 2THF$ (**2**). Thermal ellipsoids are drawn at the 20% probability level. The structure of **2′** is similar to **2** without THF molecules.

Compounds **2**, **2′** (Figure 2) and **3** (Figure 3) carry analogous ligands with a bridging alkyl chain of six carbon atoms, whereas the *para*-methyl substituents in **2** (and **2′**) are replaced by *t*Bu groups in **3**. All complexes have a centrosymmetric structure with linear chain conformations, although different solvent molecules are present in the unit cell. The solid-state packing is relatively similar in **2** and **3** (Figure S3 in the Supporting Information) without any major interactions between distinct complexes.

The alkane chain of seven carbon atoms in complex **4** has a nonlinear solid-state conformation without the centre of symmetry in the structure (Figure 4). Five molecules of methanol are distributed unevenly in the structure with

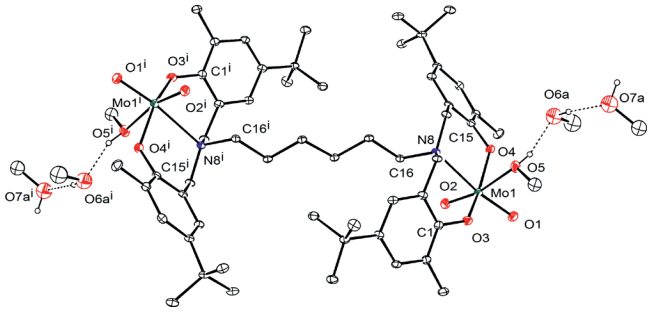


Figure 3. Molecular structure of $[(MoO_2)_2(L3)(MeOH)_2]\cdot 3MeOH\cdot H_2O$ (**3**). Thermal ellipsoids are drawn at the 20% probability level. CH hydrogen atoms, disordered methanol molecules and the water molecule have been omitted for clarity reasons.

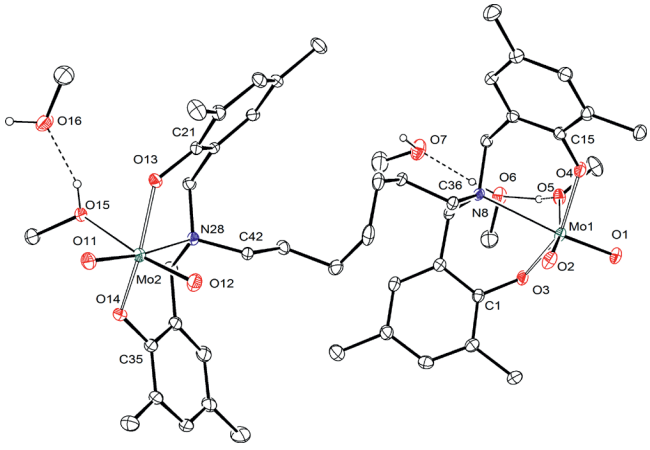


Figure 4. Molecular structure of $[(MoO_2)_2(L4)(MeOH)_2]\cdot 3MeOH$ (**4**). Thermal ellipsoids are drawn at the 20% probability level. CH hydrogen atoms have been omitted for clarity.

three MeOH molecules around Mo1 and two molecules around Mo2. The uncoordinated methanol molecules in the second coordination sphere of the metal atom form bridges between the individual complexes, thus tying the complexes together (Figure S4 in the Supporting Information). However, under ambient atmosphere the methanol molecules leave the lattice easily, consequently breaking the ordered single crystals.

In complex **5** (Figure 5), the DMSO molecule occupies the remaining coordination sites around the Mo^{VI} ion, and noncoordinating acetonitrile molecules fill some cavities in the lattice, thus leading to the noninteger number of 0.6 molecules of MeCN per one molecule of **5**. The MeCN molecules can be easily removed from the lattice, which was realised during the X-ray analyses. Part of the acetonitrile molecules were lost even if the crystals were taken directly from the reaction vessel and immediately put under oil prior to the X-ray measurements. The solid-state data reveal that there are virtually no strong intermolecular interactions between individual complexes and noncoordinating solvents (Figure S5 in the Supporting Information).

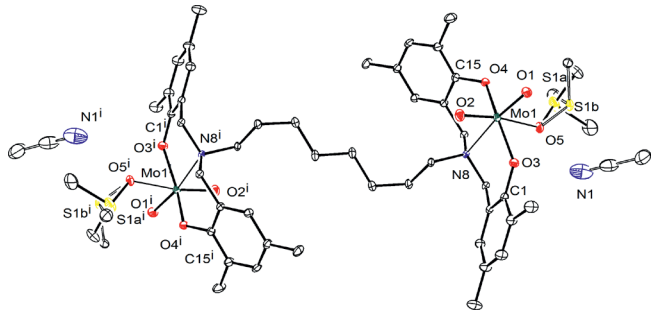


Figure 5. Molecular structure of $[(MoO_2)_2(L5)(DMSO)_2]\cdot 0.6MeCN$ (**5**). MeCN and DMSO can be in two positions. Thermal ellipsoids are drawn at the 20% probability level. Hydrogen atoms have been omitted for clarity reasons.

In complex **7**, two ether oxygen atoms (formally at the 3- and 6-positions) in the eight-atom chain between nitrogen atoms in the ligand H_4L7 coordinate to the molybdenum atoms to complete the octahedral coordination. This forces the Mo atoms quite close to each other as shown in Figure 6. The structure of **7** is not centrosymmetric owing to the uncoordinated THF and methanol molecules, which fill the empty cavities in the lattice without forming any hydrogen bonds. There are substantial differences between structural parameters around Mo atoms in **7** relative to those in **2**–**5** (see Table 1). Mo–N bond lengths are shorter (2.376 Å, average of two) in **7** than those in **2**–**5** (2.517 Å, average of five). Also the O=Mo=O bond angles are larger in **7** (107.8 and 108.3°) than the corresponding angles in **2**–**5** (103.4–105.5°). Generally the bond parameters around Mo atoms in **7** are close to the values found in the mononuclear complex [*N*-methoxyethyl-*N*,*N*-bis(2-oxy-3,5-dimethylbenzyl)-amine]dioxidomolybdenum(VI).[22]

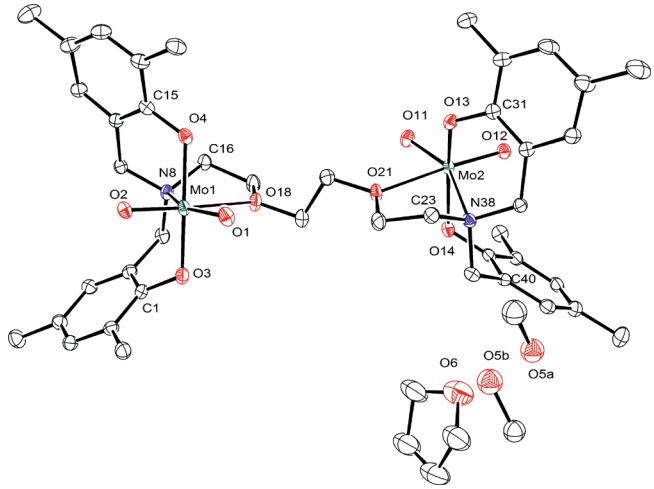


Figure 6. Molecular structure of **7**. $[(MoO_2)_2(L7)]\cdot THF\cdot MeOH$. Thermal ellipsoids are drawn at the 20% probability level. CH hydrogen atoms have been omitted for clarity.

Catalytic Activity

In the initial experiments, compounds **5**, **7** and **8** were used to catalyse the oxidation of aromatic alcohols. In these

complexes the aminodiphenolate ligands offer a chelating (O,N,O) donor set for the $[MoO_2]^{2+}$ unit. The sixth coordination site around the Mo^{VI} ion is differently occupied: in **2**–**5** this site is occupied by a solvent molecule, whereas in **7** and **8** the site is filled with an ether oxygen atom of the ligand. Compound **8** is formally "a half of **7**" and it was selected to distinguish any differences in catalytic activity between mono- and ditopic molecules. Oxidations of benzyl alcohol and 1-phenylethanol were investigated in MeCN solutions or neat alcohol by using hydrogen peroxide (30%) in water as an oxidant. The catalysts are practically insoluble in MeCN without the presence of substrate and a base.

At first, the reaction conditions for the oxidation of benzyl alcohol were optimised in MeCN (reactions **a**–**c**). The results are shown in Table 2, and experimental details are shown in Table S2 in the Supporting Information. The experiments were performed by using catalyst **5**/benzyl alcohol/H_2O_2 in a 1:20:40 ratio in MeCN. In experiments **b** and **c**, NEt_3 (2 equiv.) was also added to solubilise the catalyst. In experiment **b**, the H_2O_2 solution was inserted into the reaction batch at once, whereas in experiments **a** and **c** the oxidant was added as four aliquot parts at 1 h intervals. The experiments were run at 60 °C, and the reaction outcome was analysed by gas chromatography.

Table 2. Turnover number (TON)[a] and turnover frequency (TOF)[b] for reactions **a**–**h** at 60 °C after 6 h.

	Reaction[c]	Catalyst	Conversion [%]	TON	TOF [h^{-1}]
a	(BnOH)[d]	**5**	16	3	1
b	(BnOH)[e]	**5**	35	7	1
c	(BnOH)	**5**	55	11	2
d	(BnOH)	**7**	53	11	2
e	(BnOH)	**8**	49	5	1
f	(1-PhEtOH)	**5**	55	11	2
g	(1-PhEtOH)	**7**	53	11	2
h	(1-PhEtOH)	**8**	56	5	1

[a] TON = conversion coefficient (mol of substrate/mol of catalyst). [b] TOF = TON/time. [c] BnOH = benzyl alcohol, 1-PhEtOH = 1-phenylethanol. [d] No base. [e] H_2O_2 in one portion.

The reaction conditions evidently play an important role in these oxidations. In experiment **a**, in which no NEt_3 is present, the reaction proceeded slowly owing to the low solubility of complex **5** in the reaction medium. In experiments **b** and **c**, the presence of triethylamine improves the solubility of the catalyst, and the red colour formed in the reaction vessel remains during the whole experiment. The best result (ca. 55% conversion) was obtained in reaction **c** when the H_2O_2 solution was added in four equal portions at 0, 1, 2 and 3 h from the beginning of the reaction. The role of the base is still unclear, but it is supposed to improve the deprotonation of the alcohol hydroxy group that after deprotonation is more liable to coordinate to the Mo^{VI} centre, thus forming a soluble alkoxide complex from the catalyst. However, it was found that a higher amount of the base or H_2O_2 in the reaction mixture can deactivate the process. Under similar conditions, 45% of the benzyl alcohol was converted to benzaldehyde at 80 °C in 8 h.[20] By contrast, the selectivity was low as 15% of benzoic acid was formed. In our experiments complex **5** works slightly better under milder conditions (ca. 55% conversion in 6 h also at 60 °C and no benzoic acid formed).

The selectivity of the oxidation reactions was high, as no conversion of benzaldehyde into benzoic acid was detected if the reactions were performed in acetonitrile. Correspondingly, we have earlier shown that comparable dioxidomolybdenum(VI) compounds can act as inhibitors in aldehyde oxidation reactions.[13]

After optimisation of the reaction system, the catalytic activity of complexes **5** and **7**–**8** in oxidations of benzyl alcohol and 1-phenylethanol was studied in more detail in acetonitrile, as described above in experiment **c**. The experimental details are presented in the Supporting Information (Table S2). Experiments **d** and **e** were performed like **c**, but **7** and **8** were used as catalysts. Correspondingly, reactions **f**–**h** were run by using 1-phenylethanol as a substrate with catalysts **5**, **7** and **8**, respectively. Catalyst **8** was used with a similar Mo^{VI} concentration (i.e., twice the amount of **5** and **7**). The results show that the catalytic activity of all three catalysts is similar in oxidation of both primary and secondary alcohols with similar Mo^{VI} concentrations. Approximately 53% of the alcohols were oxidised, and no overoxidation to carboxylic acid was detected. Catalyst **8** converted benzyl alcohol with a yield of 49% (the lowest). In all experiments, the oxidation reactions seem to stop after 6 h upon inactivation of the catalyst. The TON and TOF numbers were calculated for reactions **c**–**h** at 6 h (Table 2). These results show that **5**, **7** and **8** (the TON of **8** is half those of **5** and **7**) can be used as catalysts in the oxidation the primary and secondary alcohols to the aldehydes with H_2O_2 without overoxidation in a 50% yield during 6 h.

To improve the catalytic performance the catalytic activity of all complexes **1**–**8** and $[MoO_2(acac)_2]$ (**9**, for comparison) was studied in neat alcohol in the presence of NEt_3

Table 3. TON and TOF values for BnOH oxidations in reactions **i**–**u** at 80 °C after 8 h.

Reaction	Catalyst[a]		Conversion [%]	TON	TOF [h^{-1}]	Selectivity [%]
i	**1**	(0.01)	32	315	39	100
j	**1**	(0.02)	50	248	31	100
k	**1**	(0.04)	54	136	17	87
l	**2**		57	283	35	71
m	**3**		54	268	33	89
n	**4**		48	240	30	94
o	**5**		52	262	33	93
p	**5**[b]		33	160	20	64
q	**6**		53	267	33	93
r	**7**		53	264	33	82
s	**8**		37	183	23	100
t	**9**[c]		45	223	28	91
u	none		20	–	–	19

[a] 0.02 mmol; for **1** the amount of the catalyst is in parentheses. [b] No base. [c] **9** = $[MoO_2(acac)_2]$.

by applying the method used in the literature.[20] The catalyst systems **i**–**u** were prepared by using catalyst/benzyl alcohol/H_2O_2 in a 1:500:1000 ratio in four portions at 0, 2, 4 and 6 h in the presence of NEt_3 (0.05 mmol). Reaction **p** was performed with catalyst **5** without the base. Also, test reaction **u** was carried out without a catalyst. The reactions were run at 80 °C. Details of the experiments are given in Table S3 of the Supporting Information. The results are shown in Table 3.

The ditopic Mo^{VI} aminophenolate complexes **1**–**7** catalyse the oxidation of benzyl alcohol better than $[MoO_2(acac)_2]$, but the catalytic activity of **8** is slightly lower than that of $[MoO_2(acac)_2]$. The results might indicate (if the mechanism is the same) that only one metal atom in a ditopic complex can act as an active centre in these systems, since complex **8** has almost the same activity as complexes **5** and **7**. It is also demonstrated by comparing reactions **o** and **p** that the presence of NEt_3 (a base) is very important for the catalytic system.

This method allows remarkably low catalyst loads with reasonable conversions (about 50%) in the alcohol oxidation. However, one can find from Table S3 in the Supporting Information that the reactions proceed smoothly during the first 4 h until overoxidation of benzaldehyde to benzoic acid starts. The selectivity varies: no benzoic acid was detected when **1** and **8** were used as the catalysts, whereas with catalysts **2**–**7**, a varying amount of the acid can be observed. The highest amounts of the side product were formed with **2**, **5** and **7** as the catalyst [29, 36 (without a base) and 18%, respectively]. The results also indicate that compounds **3**, **4** and **6** inhibit overoxidation of benzaldehyde quite well (only 11, 6 and 7% benzoic acid forms, respectively). In the literature[20] under similar conditions the conversion was 86%, and the formation of benzoic acid was 8% at 80 °C over 8 h.

In other catalytic model reactions, ether derivatives **7** and **8** were studied for the epoxidation of *cis*-cyclooctene by using *t*BuOOH as an oxidant in $CDCl_3$. The catalyst/alkene/oxidant were used in 1:20:25 and 1:40:50 ratios. The reactions were run at room temperature, and the reaction course was monitored by ^1H NMR spectroscopy. For comparison, the epoxidations were repeated by using monometallic counterpart **8** prepared earlier by our group.[22] The results are given in Table S4 in the Supporting Information. When the oxidations were carried out by using 5 mol-% of the catalyst, the reaction half-life was approximately 250 min with both complexes as they performed identically. With 2.5 mol-% loading of ditopic complex **7**, the activity was remarkably lower as the conversion of the epoxide was 27% after 250 min. All catalytic reactions ceased after 3 h, and some precipitate was formed, presumably owing to the decomposition of the catalysts. These results might indicate that also in this reaction only one metal atom in a ditopic complex can act as an active centre. Previously, the 50% conversion has been reported to take 26 h with 2.5 mol-% of structurally corresponding Mo^{VI} [O,O,N,N]-donor compound as a catalyst and *t*BuOOH as an oxidant in toluene at elevated temperature (65 °C).[4b]

Conclusion

The presented compounds **1**–**7** can be synthesised in a one-pot reaction in 45–72% yield. The reactions of $[MoO_2(acac)_2]$ with hexadentate *n*-alkyl-bridged *N*,*N*,*N*′,*N*′-tetrakis(2-hydroxybenzyl)diamines produced similar ditopic Mo^{VI} complexes (compounds **2**–**5**) with a linear conformation of bridging $(CH_2)_n$ chains (n = 6–8) and thus formed monomeric rodlike compounds. Each distorted-octahedral Mo unit also contained a coordinated solvent molecule. As the complexes are quite large, noncoordinated solvent molecules tend to fill the formed cavities in the solid-state structures. The solvents, which are capable of forming hydrogen bonds, are especially useful in that sense.

Compound **1** with a $(CH_2)_5$ chain has an oxido-bridged polymeric structure with two different $[MoO_2]^{2+}$ centres. Compound **7** has a ditopic structure with a folded $(CH_2)_2$-$O(CH_2)_2O(CH_2)_2$ linkage in which the coordination sphere of Mo^{VI} is filled with an oxygen donor from the ether bridge instead of an O atom from a solvent molecule. All studied compounds showed catalytic activity in oxidation reactions. Benzyl alcohol and 1-phenylethanol were oxidised to the corresponding aldehyde and ketone without overoxidation to carboxylic acids in acetonitrile. Although there are differences in solid-state structures of **5** and **7** [i.e., the sixth coordination site is occupied either by a solvent molecule or ether oxygen from the ligand (in **7**)], they have practically similar catalytic performance with the same Mo^{VI} concentrations in MeCN solutions. A small amount of NEt_3 as a base can improve the method reported earlier.[20] The oxidation capacity is significantly better if the reaction is performed in neat alcohol, but the formation of carboxylic acids can be a problem. Only **1** and **8** catalysed the oxidation without formation of benzoic acid. The best conversion of benzyl alcohol to benzaldehyde was obtained by using **2** as a catalyst (conversion 57%, TON = 283 and TOF = 35 at 8 h), but formation of benzoic acid was 29%. However, catalyst **1** appeared to be the most useful one (50% conversion in 8 h, TON = 248, TOF = 31), and no benzoic acid was detected. In addition, the length of the $(CH_2)_n$ chain (n = 5–8) does not seem to have much influence on the performance of the catalyst in the oxidation, but has a substantial effect on the selectivity (if the chain length n = 5, the system produces 100% aldehyde).

Epoxidation of *cis*-cyclooctene with *t*BuOOH was also studied by using solutions of ether derivatives **7** and **8** in $CDCl_3$. The results from these studies also indicate that only one metal atom in a ditopic complex can act as an active centre. With 5 mol-% catalyst loading, the reaction half-life was approximately 4 h at room temperature.

Experimental Section

Methods and Materials: The ligands H_4L1–H_4L7 were synthesised as described in the literature.[23] $[MoO_2(acac)_2]$ was prepared according to a known method.[24] All other reagents and solvents

were purchased from commercial sources and were used as received. Compounds **1**–**7** were prepared in a one-pot reaction according to Scheme 1 by using stoichiometric amounts of the diaminotetraphenol and $[MoO_2(acac)_2]$ in methanol or in a DMSO/MeCN mixture. Crystals of compounds **1**–**7** are formed more readily in saturated solutions than in dilute ones. Compound **8** was prepared according to a known procedure.[22] Earlier we showed that the organic ligands H_4L1–H_4L7 have a low solubility in methanol, but they dissolve better in nonpolar solvents such as CH_2Cl_2 and THF,[23b] whereas the solubility of $[MoO_2(acac)_2]$ is completely the opposite. Therefore, the products must be either recrystallised from appropriate solvent mixtures such as THF/MeOH, CH_2Cl_2/MeOH or DMSO/MeCN or washed with CH_2Cl_2 and MeOH. Details for the preparations of **1**–**7** are presented below.

Physical Measurements: The NMR spectra were recorded with a Bruker Avance DRX 500 FT-NMR spectrometer. The ^1H and ^{13}C NMR spectra were recorded in $[D_6]$DMSO. The ^1H NMR spectra were recorded at 30 °C for all compounds, and ^{13}C NMR spectra were recorded for compounds **1**, **2** and **4**. For **3**, **6** and **7**, the ^{13}C NMR spectra were recorded at 90 °C to dissolve samples in reasonable concentrations. The chemical shifts are reported in ppm and referenced internally by using the residual solvent resonances relative to tetramethylsilane ($[D_6]$DMSO: ^1H NMR: δ = 2.50 ppm; ^{13}C NMR: δ = 39.50 ppm). Elemental analyses were performed with a VarioEl III elemental analyser, and the IR spectra were measured with a Bruker Tensor 27 IR device with an ATR. Only a few main vibrations are listed, and the reader is encouraged to study the recorded IR spectra in the Supporting Information (Figures S6–S12). Elemental analyses were generally carried out from complexes without any solvent of crystallisation. The oxidation reactions of alcohols were monitored with an Agilent 7820A GC instrument with an Agilent HP-5 column (model 19091J-413, 320 μm × 30 m × 0.25 μm) and FID detector. TG measurements were carried out with a Perkin–Elmer TGA 7 instrument.

Synthesis of $[(MoO_2)_2(L1)(MeOH)]\cdot$MeOH (1): $[MoO_2(acac)_2]$ (2.0 mmol, 655 mg) and of H_4L1 (1 mmol, 640 mg) were weighed into a glass flask, and MeOH (30 mL) was added. The closed flask was heated at 70 °C for 5 h. The pale yellow solution was cooled to room temp., and single crystals for X-ray and IR analysis were selected. The formed yellow crystals were separated by decantation, washed with CH_2Cl_2 (10 mL) and boiling MeOH (10 mL) and dried in air. Yield 0.59 g (61%). $C_{43}H_{58}Mo_2N_2O_{10}$ (954.82): Calcd. C 54.09, H 6.12, N 2.93; found C 54.20, H 6.12, N 2.88. ^1H NMR ($[D_6]$DMSO): δ = 6.88 (s, 4 H, aryl), 6.68 (s, 4 H, aryl), 4.16 (d, 4 H, N–C*H*$_2$–aryl), 4.06 (1 H, MeOH), 3.25 (d, 4 H, N–C*H*$_2$–aryl), 3.18 (s, 4 H, MeOH), 2.26 (m, 4 H, N–C*H*$_2$–alkyl), 2.17, 2.08 (s, 12 H, aryl–C*H*$_3$), 1.17 (m, 4 H, alkyl), 0.25 (m, 2 H, alkyl) ppm. ^{13}C NMR ($[D_6]$DMSO): δ = 159, 131, 128, 127, 124, 123 (aryl *C*), 54.8, 50.0 (N–*C*H$_2$–aryl), 48.5 (MeOH), 23.6 (alkyl), 20.2 (aryl–*C*H$_3$), 17.6 (alkyl), 15.8 (aryl–*C*H$_3$) ppm. IR: $\tilde{\nu}$ = 3392 (m), 2938 (m), 1475 (s), 1307 (s), 1233 (s), 1155 (s), 1011 (s), 858 (s), 811 (s), 594 (s), 561 (s) cm^{-1}.

Synthesis of $[(MoO_2)_2(L2)(MeOH)_2]\cdot$2THF (2): The crude product of **2** was prepared by heating $[MoO_2(acac)_2]$ (2.0 mmol) and H_4L2 (1.0 mmol, 653 mg) in methanol (30 mL) at 70 °C for 5 h. The solid was isolated at room temp. It contained brownish-yellow crystals, of which one (named **2′**) was studied by X-ray diffraction and shown to be $[(MoO_2)_2(L2)(MeOH)_2]$. The isolated solid was dissolved in boiling THF (10 mL), and MeOH (90 mL) was added. After 30 min, the unreacted H_4L2 separated and was removed by filtration. Colourless $[(MoO_2)_2(L2)(MeOH)_2]\cdot$2THF crystals formed over 5 h and were separated by decantation and washed with methanol. Yield 0.44 g (45%). The solvent-free $[(MoO_2)_2(L2)]$ compound for elemental and NMR spectroscopic analysis was obtained as orange powder after the evaporation of solvents under vacuum by heating. $C_{42}H_{52}Mo_2N_2O_8$ $[(MoO_2)_2(L2)]$ (904.76): Calcd. C 55.8, H 5.79, N 3.10; found C 55.8, H 5.86, N 2.94. ^1H NMR ($[D_6]$DMSO) $[(MoO_2)_2(L2)]$: δ = 6.87 (s, 4 H, aryl), 6.72 (s, 4 H, aryl), 4.15 (d, 4 H, N–C*H*$_2$–aryl), 3.29 (d, 4 H, N–C*H*$_2$–aryl, overlapping with water signal), 2.30 (m, 4 H, N–C*H*$_2$–alkyl), 2.12, 2.08 (s, 12 H, aryl–C*H*$_3$), 1.25, 0.52 (m, 4 H, alkyl) ppm. ^{13}C NMR ($[D_6]$DMSO) $[(MoO_2)_2(L2)]$: δ = 159, 131, 128, 127, 124, 123 (aryl–*C*), 54.8 (N–*C*H$_2$–aryl), 50.0 (N–*C*H$_2$–alkyl), 25.8 (alkyl), 20.1 (aryl–*C*H$_3$), 17.6 (alkyl), 15.8 (aryl–*C*H$_3$) ppm. IR {$[(MoO_2)_2$(L2)$(MeOH)_2]\cdot$2THF}: $\tilde{\nu}$ = 3377 (m), 2943 (m), 1477 (s), 1311 (s), 1230 (s), 1155 (s), 1002 (s), 888 (s), 825 (s), 589 (s), 557 (s) cm^{-1}.

Synthesis of $[(MoO_2)_2(L3)(MeOH)]\cdot$3MeOH$\cdot H_2O$ (3): The raw product of **3** was prepared similarly to **1** by using $[MoO_2(acac)_2]$ (2.0 mmol) and H_4L3 (1.0 mmol, 821 mg) in methanol (30 mL) and water (100 μL). Single crystals for X-ray and IR analyses were selected and were identified as $[(MoO_2)_2(L3)(MeOH)_2]\cdot$3MeOH$\cdot H_2O$ The rest of the product was washed with CH_2Cl_2 (10 mL) and boiling MeOH (10 mL) to remove unreacted starting materials. In this process, the lattice methanol molecules and the water molecule were lost, and the remaining solid took the form $[(MoO_2)_2$(L3)(MeOH)] similarly to **1**. Yield 0.61 g (54%). $C_{55}H_{80}Mo_2N_2O_9$ $[(MoO_2)_2(L3)(MeOH)]$ (1105.13): Calcd. C 59.78, H 7.30, N 2.53; found C 60.12, H 7.55, N 2.24. ^1H NMR ($[D_6]$DMSO) $[(MoO_2)_2$(L3)(MeOH)]: δ = 7.06 (s, 4 H, aryl), 6.97 (s, 4 H, aryl), 4.22 (d, 4 H, N–C*H*$_2$–aryl), 4.01 (s, 1 H, MeOH), 3.32 (d, 4 H, N–C*H*$_2$–aryl, overlapping with moisture), 3.17 (d, 4 H, MeOH) 2.18 (m, 4 H, N–C*H*$_2$–alkyl), 2.12 (s, 12 H, aryl–C*H*$_3$), 1.31 (m, 4 H, alkyl), 1.19 (s, 36 H, aryl–*t*Bu), 0.47 (m, 4 H, alkyl) ppm. ^{13}C NMR ($[D_6]$DMSO): δ = 159, 142, 127, 125, 124 (two peaks) (aryl *C*), 55.3 (N–*C*H$_2$–aryl), 50.6 (N–*C*H$_2$–alkyl), 48.9 (MeOH), 34.0 and 31.8 (aryl–*t*Bu), 27.0, 18.6 (alkyl), 16.5 (aryl–*C*H$_3$) ppm. IR {$[(MoO_2)_2$(L3)$(MeOH)_2]\cdot$3MeOH$\cdot H_2O$}: $\tilde{\nu}$ = 3345 (m), 2962 (m), 1480 (s), 1252 (s), 1213 (s), 1027 (m), 942 (m), 846 (s), 779 (s), 596 (s) cm^{-1}.

Synthesis of $[(MoO_2)_2(L4)(MeOH)_2]\cdot$3MeOH (4): $[MoO_2(acac)_2]$ (2.0 mmol) and H_4L4 (1.0 mmol, 666 mg) were placed into a test tube with MeOH (10 mL), and the closed tube was heated until all solids were dissolved. The red solution was kept at room temp. for 4 d before collecting yellow crystals of $[(MoO_2)_2(L4)(MeOH)_2]\cdot$3MeOH by filtration and washing two times with MeOH (10 mL). Yield 0.65 g (65%). $C_{45}H_{62}Mo_2N_2O_{10}$ $[(MoO_2)_2(L4)(MeOH)_2]$ (982.87): Calcd. C 54.99, H 6.36, N 2.85; found C 54.95, H 6.52, N 2.78. ^1H NMR ($[D_6]$DMSO) $[(MoO_2)_2(L4)(MeOH)_2]$: δ = 6.87 (s, 4 H, aryl), 6.73 (s, 4 H, aryl), 4.17 (d, 4 H, N–C*H*$_2$–aryl), 4.07 (s, 2 H, MeO*H*), 3.32 (d, 4 H, N–C*H*$_2$–aryl), 3.17 (s, 5 H, MeOH), 2.33 (m, 4 H, N–C*H*$_2$–alkyl), 2.13, 2.08 (s, 12 H, aryl–C*H*$_3$), 1.28 (m, 4 H, alkyl), 0.73 (m, 2 H, alkyl), 0.59 (m, 4 H, alkyl) ppm. ^{13}C NMR ($[D_6]$DMSO) $[(MoO_2)_2(L4)(MeOH)_2]$: δ = 159, 131, 128, 127, 124, 123 (aryl *C*), 54.9 (N–*C*H$_2$–aryl), 50.1 (N–*C*H$_2$–alkyl), 48.5 (MeOH), 27.2, 25.7, (alkyl), 20.1, (aryl–*C*H$_3$), 17.2 (alkyl), 15.7 (aryl–*C*H$_3$) ppm. IR spectra of the organic ligand can be found in the literature.[16] IR $[(MoO_2)_2(L4)(MeOH)_2]\cdot$3MeOH: $\tilde{\nu}$ = 3377 (m), 2919 (m), 1475 (s), 1304 (s), 1230 (s), 1156 (s), 1016 (s), 859(s), 825 (s), 590 (s), 560 (s) cm^{-1}.

Synthesis of $[(MoO_2)_2(L5)(DMSO)_2]\cdot x$MeCN (5): $[MoO_2(acac)_2]$ (0.8 mmol, 261 mg) and H_4L5 (0.4 mmol, 272 mg) were dissolved in hot DMSO (4.0 mL), and a bright yellow solution formed. The solution was kept at room temp. for 2 h, and MeCN (4 mL) was

added to speed up precipitation. After 18 h, crystals of $[(MoO_2)_2(L5)(DMSO)_2]\cdot x$MeCN were filtered and recrystallised from a mixture of DMSO/MeCN (1:1, 8 mL). The product was washed with a small amount of MeCN to remove DMSO and then air-dried. Yield 0.35 g (80%). X-ray-quality single crystals with the formula $[(MoO_2)_2(L5)(DMSO)_2]\cdot 0.6$MeCN formed from a DMSO/MeCN (9:1) mixture within 4 d. $C_{48}H_{68}Mo_2N_2O_{10}S_2$ $[(MoO_2)_2(L5)(DMSO)_2]$ (1089.07): Calcd. C 52.94, H 6.29, N 2.57; found C 52.72, H 6.37, N 2.38. ^{1}H NMR ([D$_6$]DMSO) $[(MoO_2)_2(L5)(DMSO)_2]$: δ = 6.88 (s, 4 H, aryl), 6.75 (s, 4 H, aryl *C*), 4.18 (d, 4 H, N–C*H*$_2$–aryl), 3.33 (d, 4 H, N–C*H*$_2$–aryl, overlapping with moisture), 2.54 (s, 15 H, DMSO, not deuterated), 2.38 (m, 4 H, N–C*H*$_2$–alkyl), 2.13, 2.09 (s, 12 H, aryl–C*H*$_3$), 1.31, 0.85, 0.64 (m, 4 H, alkyl) ppm. ^{13}C NMR ([D$_6$]DMSO) $[(MoO_2)_2(L5)(DMSO)_2]$: δ = 159, 131, 128, 127, 124, 123 (aryl–*C*), 54.8 (N–*C*H$_2$–aryl), 50.2 (N–*C*H$_2$–alkyl), 40.4 (DMSO, not deuterated), 27.7, 25.9, (alkyl), 20.1, (aryl–*C*H$_3$), 17.5 (alkyl), 15.8 (aryl–*C*H$_3$) ppm. IR spectra of the organic ligand can be found in the literature.[16] IR $[(MoO_2)_2(L5)(DMSO)_2]$: $\tilde{\nu}$ = 2913 (m), 2849 (m), 1609 (v), 1476 (s), 1307 (s), 1236 (s), 1158 (s), 1003 (s), 896 (s), 820 (s), 592 (s), 559 (s) cm^{-1}.

Synthesis of $[(MoO_2)_2(L6)(MeOH)_2]$ (6): The raw product of **6** was prepared by using $[MoO_2(acac)_2]$ (2.0 mmol) and H_4L6 (1.0 mmol, 849 mg) in methanol (30 mL). MeOH (30 mL) was added. The closed flask was heated at 70 °C for 5 h. The raw product formed on cooling to room temp. was decanted and dissolved in hot CH_2Cl_2 (20 mL) (a small amount of methanol improves the solubility). MeOH (60 mL) was added, and the solution was kept in a freezer (–20 °C) for 24 h. Yield 0.83 g (72%). The compound was heated at 120 °C in [D$_6$]DMSO to make it soluble for NMR spectroscopic analysis that replaced MeOH with DMSO. $C_{58}H_{86}Mo_2N_2O_{10}$ $[(MoO_2)_2(L6)(MeOH)_2]$ (1163.20): Calcd. C 59.89, H 7.45, N 2.41; found C 59.82, H 7.73, N 2.32. ^{1}H NMR ([D$_6$]DMSO): δ = 7.08 (s, 4 H, aryl), 6.96 (s, 4 H, aryl *C*), 4.22 (d, 4 H, N–C*H*$_2$–aryl), 3.36 (d, 4 H, N–C*H*$_2$–aryl) 2.26 (m, 4 H, N–C*H*$_2$–alkyl), 2.11 (s, 12 H, aryl–C*H*$_3$), 1.32 (m, 4 H, alkyl), 1.19 (s, 36 H, aryl–*t*Bu), 0.89, 0.56 (m, 4 H, alkyl) ppm. ^{13}C NMR ([D$_6$]-DMSO at 90 °C): δ = 158, 142, 126, 124, 123 (two peaks) (aryl–*C*), 54.9 (N–*C*H$_2$–aryl), 49.8 (N–*C*H$_2$–alkyl), 33.0 and 30.8 (aryl–*t*Bu), 28.1, 26.0, 24.6 (alkyl), 15.4 (aryl–*C*H$_3$) ppm. IR $[(MoO_2)_2(L6)(MeOH)_2]$: $\tilde{\nu}$ = 3366 (m), 2951 (m), 1541 (s), 1249 (s), 1022 (s), 914 (s), 835 (s), 775 (s), 591 (s) cm^{-1}.

Synthesis of $[(MoO_2)_2(L7)]\cdot$THF·MeOH (7): The crude product of **7** was prepared similarly to **1** by using $[MoO_2(acac)_2]$ (2.0 mmol) and H_4L7 (1.0 mmol, 685 mg) in methanol. $[(MoO_2)_2(L7)]\cdot$THF·MeOH was recrystallised from a THF/MeOH (1:1, 100 mL) mixture. The samples for X-ray diffraction and IR analysis were taken from the recrystallised product. The solventless sample for elemental and NMR spectroscopic analysis was obtained by heating. Yield 0.55 g (55%). $C_{42}H_{52}Mo_2N_2O_{10}$ $[(MoO_2)_2(L7)]$ (936.76): Calcd. C 53.85, H 5.59, N 2.99; found C 53.99, H 5.75, N 2.79. ^{1}H NMR ([D$_6$]DMSO) $[(MoO_2)_2(L7)]$: δ = 6.88 (s, 4 H, aryl), 6.82 (s, 4 H, aryl *C*), 4.19 (s, 4 H, N–CH$_2$–C*H*$_2$–O), 3.60 (s, 4 H, O–C*H*$_2$–C*H*$_2$–O, overlapping with moisture), 3.32 (8 H, N–C*H*$_2$–aryl), 2.69 (m, 4 H, N–C*H*$_2$–ether), 2.16, 2.07 (s, 12 H, aryl–C*H*$_3$) ppm. ^{13}C NMR ([D$_6$]DMSO at 90 °C): δ = 158, 130, 128, 127, 124, 123 (aryl *C*), 70.4 (N–CH$_2$–*C*H$_2$–O), 65.1 (O–*C*H$_2$–*C*H$_2$–O), 57.9 (N–*C*H$_2$–aryl), 50.5 (N–*C*H$_2$–ether), 19.6, (aryl–*C*H$_3$), 15.1 (aryl–*C*H$_3$) ppm. IR $[(MoO_2)_2(L7)]$: $\tilde{\nu}$ = 2914 (m), 1475 (s), 1249 (s), 1233 (s), 1214 (s), 1062 (s), 909 (s), 802 (s), 599 (s), 556 (s) cm^{-1}.

Catalytic Studies: Crystalline compounds **1**–**8** were used as the catalysts. Some of them lose the uncoordinated solvent molecules at room temperature. However, this has a minimal effect on the concentration of the catalyst and the performance.

General Procedure for Experiments a–h: A catalyst load that contained Mo^{VI} (0.1 mmol; 0.05 mmol catalyst **5** and **7**), substrate (1 mmol; benzyl alcohol in **a**–**e** and 1-phenylethanol in **f**–**h**), H_2O_2 (2 mmol; in four portions at 0, 1, 2 and 3 h), NEt_3 (0.1 mmol) and MeCN (4 mL) was placed in a screw-cap test tube with a magnetic bar. In experiment **a**, no NEt_3 was present. The mixture was heated in an oil bath at 60 °C with stirring for 24 h. More H_2O_2 was inserted in four equal parts at 1 h intervals, except in experiment **b** in which all H_2O_2 was inserted at once. Samples of 100 µL were removed at 2 h intervals for 6 h, and then one was taken at 24 h. The samples were diluted to 5 mL in a volumetric flask with CH_2Cl_2. The samples were monitored with an Agilent 7820A GC instrument with an Agilent HP-5 column. TON and TOF numbers were calculated at t = 6 h, because the reaction seemed to cease after that.

General Procedure for Experiments i–u: A catalyst load that contained catalyst **1**–**8** and $[MoO_2(acac)_2]$ (**9**) (0.02 mmol), benzyl alcohol (10 mmol), H_2O_2 (20 mmol; in four portions at 0, 2, 4 and 6 h) and NEt_3 (0.05 mmol) was placed in a screw-cap test tube with a magnetic bar. In experiments **i** and **k** the catalyst load was 0.01 and 0.04 mmol, respectively. The sample was heated with stirring at 80 °C in an oil bath. The insertion of H_2O_2 and the sample (8 µL) uptake were performed at 2 h intervals. The samples were diluted to 5 mL in a volumetric flask with CH_2Cl_2. The reactions **i**–**u** were monitored for 8 h.

Crystallography: Crystallographic data for complexes **2**, **2′**, **4** and **5** were collected with a Nonius Kappa diffractometer equipped with CCD area detector by using Mo-K_α radiation (λ = 0.71073 Å), for complex **1** with a Nonius Kappa diffractometer equipped with a CCD area-detector by using Cu-K_α radiation (λ = 1.54184 Å) and for complexes **3** and **7** with an Agilent Supernova diffractometer equipped with an Atlas area-detector by using Cu-K_α radiation (λ = 1.54184 Å). SADABS absorption correction was applied to the data for complexes **1**, **2**, **2′**, **4** and **5**.[25] For complex **3**, analytical numeric absorption correction by using a multifaceted crystal model was applied, whereas for **7**, only empirical absorption correction (using spherical harmonics as implemented in SCALE3 ABSPACK scaling algorithm) was performed by using the CrysAlisPro program package.[26] The structures were solved by direct methods using SIR97,[27] and SHELXS-97[28] programs and full-matrix least-squares refinements on F^2 were performed by using the SHELXL-97[28] program. Molecular structure figures were drawn with ORTEP3 for Windows[29] and the packing diagrams with Mercury.[30] Selected crystallographic data is collected in Table 4 and some bonding parameters in Table 1. A more detailed list of bonding parameters is in Table S1 in the Supporting Information or in the deposited CIF files. CCDC-903506 (for **1**), -903507 (for **2**), -903508 (for **2′**), -903509 (for **3**), -903510 (for **4**), -903511 (for **5**), and -903512 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Selected bonding parameters for **1**–**5** and **7** (Table S1), detailed information on the benzyl alcohol and 1-phenylethanol oxidation reactions (Tables S2 and S3), epoxidation reaction (Table S4), IR spectra of compounds **1**–**7** (Figures S1–S7), H_4L1–H_4L3, H_4L6 and H_4L7 (Figures S8–S12) in the region of 2000–400 cm^{-1}, packing diagrams of **2**, **4** and **5** (Figures S13–S15), TG curve of **1** and **2** (Figures S16 and S17).

Table 4. Crystallographic data for compounds **1**–**5** and **7**.

	1	**2**	**2′**	**3**	**4**	**5**	**7**
Empirical formula	$C_{43}H_{54}Mo_2N_2O_{10}$	$C_{52}H_{76}Mo_2N_2O_{12}$	$C_{44}H_{60}Mo_2N_2O_{10}$	$C_{59}H_{98}Mo_2N_2O_{14}$	$C_{48}H_{74}Mo_2N_2O_{13}$	$C_{49.2}H_{69.8}Mo_2N_2O_{10}S_2$	$C_{47}H_{56}Mo_2N_2O_{12}$
M_r	954.79	1113.03	968.82	1251.27	1078.79	1113.68	1040.88
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group (no.)	*Pcab* (61)	$P2_1/c$ (14)	$P2_1/c$ (14)	$C2/c$ (15)	$P2_1$ (4)	$P2_1/c$ (14)	$Pca2_1$ (29)
a [Å]	15.7385(2)	16.3232(2)	13.6455(3)	17.9614(7)	7.9670(1)	8.1732(2)	22.3914(8)
b [Å]	23.1938(3)	13.0723(2)	13.9469(2)	9.9938(6)	20.6358(3)	18.8709(4)	13.6953(5)
c [Å]	24.7419(3)	12.0758(2)	11.4456(2)	36.446(2)	15.5231(2)	16.9902(3)	15.4849(9)
α [°]	90	90	90	90	90	90	90
β [°]	90	91.218(1)	98.723(1)	94.438(5)	90.978(1)	94.620(1)	90
γ [°]	90	90	90	90	90	90	90
V [Å]	9031.7(2)	2576.17(7)	2153.04(7)	6522.5(6)	2551.71(6)	2611.98(10)	4748.6(4)
Z	8	2	2	4	2	2	4
$D_{calcd.}$ [g cm^{-3}]	1.404	1.435	1.494	1.274	1.404	1.416	1.456
T [K]	173	123	123	123	173	173	123
μ(Cu-K_α)/μ(Mo-K_α) [cm^{-1}]	5.004[a]	0.549	0.642	3.629[a]	0.553	0.616	4.84[a]
Observed reflections	7272	5579	4685	5805	11955	5062	6313
R_{int}	0.0845	0.0282	0.0373	0.0336	0.0374	0.0456	0.0213
Parameters	530	315	280	360	614	347	576
R_1[b]	0.057 (0.053)[c]	0.040 (0.030)	0.039 (0.030)	0.076 (0.074)	0.043 (0.036)	0.058 (0.045)	0.035 (0.033)
wR_2[d]	0.137 (0.134)	0.074 (0.069)	0.077 (0.073)	0.171 (0.169)	0.077 (0.074)	0.103 (0.098)	0.096 (0.094)

[a] Cu-K_α radiation. [b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] Values in parentheses for reflections with $I > 2\sigma(I)$. [d] $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ and $w = 1/[\sigma^2(F_o^2) + (aP)^2 + (bP)]$, in which $P = (2F_c^2 + F_o^2)/3$.

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