UNIVERSITY OF JYVÄSKYLÄ
DEPARTMENT OF CHEMISTRY
RESEARCH REPORT No. 125

URANYL(VI) ION COMPLEXES OF SOME ORGANIC AMINOBISPHENOLATE LIGANDS: SYNTHESES, STRUCTURES AND EXTRACTION STUDIES

BY

HARRI SOPO

Academic Dissertation
for the Degree of
Doctor of Philosophy

Jyväskylä, Finland
2008

DEPARTMENT OF CHEMISTRY, UNIVERSITY OF JYVÄSKYLÄ
RESEARCH REPORT No. 125

URANYL(VI) ION COMPLEXES OF SOME ORGANIC AMINOBISPHENOLATE LIGANDS: SYNTHESES, STRUCTURES AND EXTRACTION STUDIES

BY

HARRI SOPO

Academic dissertation for the degree of
Doctor of Philosophy

To be presented, by permission of the Faculty of Mathematics and Natural Sciences of the University of Jyväskylä, for public examination in Auditorium KEM 4, on February 23rd, 2008, at 12 noon.

University of Jyväskylä
Jyväskylä, Finland
ISBN 978-951-39-3086-8
ISSN 0357-346X

URN:ISBN:978-952-86-0256-9
ISBN 978-952-86-0256-9 (PDF)
ISSN 0357-346X

University of Jyväskylä, 2024

ABSTRACT

This thesis reports the syntheses and characterization of 18 organic aminobisphenolate ligands and 20 new uranyl complexes of the prepared ligands, as well as extraction studies of the uranyl ion from an aqueous phase to a water-immiscible organic solvent phase (dichloromethane) in various chemical environments with these ligands.

The 18 aminobisphenolate ligands prepared can be subdivided into three sections that have chemically different functional groups in their “tail” part of the molecule. These groups are aminoalcoholbisphenols, aminoalkylbisphenols and diaminobisphenols. 12 of these ligands are new compounds and one of them, bis(5-*tert*-butyl-2-hydroxy-3-methylbenzyl)(6-hydroxyhexyl)ammonium chloride monohydrate, proved to be an anion receptor.

All the 20 new uranyl complexes prepared formed crystals suitable for single-crystal X-ray analysis and of these crystals 19 structures were solved. The solved structures formed three different kinds of compounds, viz. $[UO_2(H_nLm)_2]\cdot kS$ (n=1 or 2, m=1-17, k=0, 1, 2 or 4, S=solvent molecule), $[UO_2(HLm)(NO_3)]\cdot kS$ (m=15 or 16, k=1 or 2, S=solvent molecule) and $[(UO_2)_2(H_2L1)_2(NO_3)_2]$. 16 complexes are of the form $[UO_2(H_nLm)_2]\cdot kS$, two are of the form $[UO_2(HLm)(NO_3)]\cdot kS$ and one of the compounds has a dinuclear structure $[(UO_2)_2(H_2L1)_2(NO_3)_2]$.

The ability of all the prepared ligands to extract uranyl ions from an aqueous uranyl nitrate solution to dichloromethane was studied. The aminoalcoholbisphenol and aminoalkylbisphenol ligands proved to be excellent uranyl ion extractors under the conditions studied. In addition, the extraction of uranyl ions was studied in various chemical circumstances with selected ligands.

Finally, the behaviour of some of the prepared uranyl complexes in $CHCl_3$ and DMSO solutions was studied by NMR.

The results of the above studies are presented in five scientific articles.

Author´s address
Harri Sopo
Department of Chemistry
University of Jyväskylä
P.O. Box 35
40014 University of Jyväskylä
Finland
hasopo@jyu.fi

Supervisor
Professor Reijo Sillanpää
Department of Chemistry
University of Jyväskylä
Finland

Reviewers
Professor Matti Haukka
Department of Chemistry
University of Joensuu
Finland

Docent Jorma Arpalahti
Department of Chemistry
University of Turku
Finland

Opponent
Professor Jouni Pursiainen
Department of Chemistry
University of Oulu
Finland

PREFACE

The present research was carried out at the Department of Chemistry, University of Jyväskylä from January 2003 to May 2007.

I wish to thank my supervisor Prof. Reijo Sillanpää for providing me with the possibility to work in his group during these years in the fascinating field of coordination chemistry and crystallography. His guidance and sharing of knowledge of the secrets of chemistry has been invaluable for me. I am grateful to Prof. Jussi Valkonen for the opportunity to carry out this work at the Laboratory of Inorganic Chemistry. I would like to thank Docent Ari Lehtonen and Docent Reijo Suontamo for helpful discussions and Dr. Ari Väisänen for performing the ICP measurements. I am indebted to Prof. Erkki Kolehmainen and Lab. Technician Reijo Kauppinen for their advice and assistance with the NMR measurements. I thank Elina Hautakangas for her help with the elemental analysis and Mirja Lahtiperä for her help with the MS measurements.

Docent Jorma Arpalahti and Prof. Matti Haukka, the referees of this work, are gratefully acknowledged for their suggestions and valuable comments. I am also indebted to Prof. Matti Nurmia for correction of the language of this thesis.

My deepest gratitude goes to my colleagues in the field of medicine for encouraging me into this venture.

Finally, I gratefully acknowledge the financial support of the Finnish Ministry of Education (Graduate School of Inorganic Material Chemistry).

Jyväskylä, November 2007

Harri Sopo

LIST OF ORIGINAL PUBLICATIONS

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

I H. Sopo, J. Sviili, A. Valkonen, R. Sillanpää, Uranyl ion complexes with aminoalcoholbis(phenolate) [O,N,O,O´] donor ligands, *Polyhedron* **2006,** 25, 1223-1232.

https://doi.org/10.1016/j.poly.2005.08.044

II H. Sopo, A. Väisänen, R. Sillanpää, Uranyl ion complexes with long chain aminoalcoholbis(phenolate) [O,N,O,O´] donor ligands, *Polyhedron* **2007,** 26, 184-196.

https://doi.org/10.1016/j.poly.2006.08.006

III H. Sopo, K. Goljahanpoor, R. Sillanpää, Aminoalkylbis(phenolate) [O,N,O] donor ligands for uranyl(VI) ion coordination: Syntheses, structures and extraction studies, *Polyhedron* **2007,** 26, 3397-3408.

https://doi.org/10.1016/j.poly.2007.03.032

IV H. Sopo, R. Sillanpää, Bis(5-*tert*-butyl-2-hydroxy-3-methylbenzyl)(6-hydroxyhexyl)ammonium chloride monohydrate, an anion receptor complex, *Acta Cryst.* **2007**, C63, o386-o388.

https://doi.org/10.1107/S0108270107023797

V H. Sopo, A. Lehtonen, R. Sillanpää, Uranyl(VI) complexes of [O,N,O,N´]-type diaminobis(phenolate) ligands: Syntheses, structures and extraction studies, *Polyhedron* **2008**, 27, 95-104.

https://doi.org/10.1016/j.poly.2007.08.047

ABBREVIATIONS

Average	$\bar{x} = \frac{\sum x}{n}$
DMSO	Dimethylsulfoxide
^{1}H-^{1}H COSY	^{1}H-^{1}H correlation spectroscopy
^{1}H-^{13}C HMBC	^{1}H-^{13}C heteronuclear multiple bond correlation
^{1}H-^{13}C HMQC	^{1}H-^{13}C heteronuclear multiple quantum coherence
ICP-OES	Inductively coupled plasma-optical emission spectrometry
NMR	Nuclear magnetic resonance
NOESY	Nuclear Overhauser enhancement spectroscopy
PUREX	Plutonium and Uranium Recovery by Extraction
SD	Standard deviation, $SD = \sqrt{\frac{\sum x^2 - \frac{(\sum x)^2}{n}}{n}}$

TABLE OF CONTENTS

1 INTRODUCTION

According to the World Nuclear Association (WNA) the annual uranium consumption in 2005 was approximately 70 000 tonnes and, even in the most optimistic growth projections, the future uranium consumption would peak at 125 000 tonnes by the year 2025. This is used mainly as fuel for nuclear reactors and in different kinds of military uses. About 16 % of the world's supply of electrical power is generated using nuclear sources.[1] In addition, small amounts have been used as a pigment to color ceramics and glass.[2] The production and consumption of uranium on this scale causes a variety of needs for its removal from e.g. wastes, soil, ground water or the human body because it poses a threat to human health and the environment due to its toxicity and radioactivity.[3-5] Uranium toxicity derives from the interaction of the UO_2^{2+} cation with biological compounds, e.g. proteins, and radioactive damage derives from the radioactive decay of the uranium nucleus.

The industrial procedure used to reprocess spent nuclear fuel is called PUREX in which the irradiated fuel is dissolved into nitric acid and an organic solvent composed of 30 % tributyl phosphate in kerosene is used to recover the uranium and plutonium.[6,7] This liquid-liquid extraction method was developed in the 1950s and it is still the industry standard, although the process remains far from perfect.[8] Other applications of interest for uranyl extraction are the separation of uranium from sea water[9] and phosphate rocks[10]. It has been estimated that the total amount of uranium dissolved in the world´s oceans is $4.5 \cdot 10^{12}$ kg.[11 13] This is about 1000-fold that available from terrestrial sources.

In medicine the focus on uranium concerns the treatment of the person exposed internally to uranium. This treatment consists of chelation therapy, which is aimed at binding the metal and subsequently favoring its excretion as a metal-chelate complex.[14]

Numerous kinds of compounds, e.g. expanded and modified calixarenes[15-18], catechols, β-diketones, hydroxyl ketones[19], aminoketones[20], crown ethers[21,22], expanded porphyrins[23], polyphenols[24,25] and organic phosphorous oxides[26] etc. have been used for the above-mentioned purposes. A common feature is that they are organic multidentate ligands with hard oxygen donor atoms and, in some cases, nitrogen donor atoms.

1.1 Chemistry of uranium

The chemistry of uranium has been extensively studied and thus the basic concepts of its behaviour are generally accepted. Uranium is found in four different oxidation states, viz. III-VI. Examples of uranium in each of these four oxidation states can be seen in the uranium complexes presented in references 27-32. In the known compounds of uranium the oxidation state VI is the most common one, while the environmentally important oxidation states are IV and VI.[33] The outermost and highest energy atomic orbitals of the uranium atom are the $5f^36d^17s^2$ orbitals, which accommodate a total of six electrons.[34] Generally, it is considered that the chemistry of uranium is dominated by the 5f orbital chemistry, although the 5f, 6d and 7s orbitals are nearly degenerate. This feature gives rise to a multitude of possible configuration interactions that complicate theoretical calculations and the assignment of e.g. experimental spectra.[35-37] Due to the chemical diversity of uranium it has compounds with exciting structures, interesting physicochemical properties and a high activity in catalytic reactions.[38-43]

In the majority of naturally occurring uranium minerals and in nuclear waste reprocessing systems uranium is present as the linear uranyl cation, UO_2^{2+},[42] which is a chemically robust species[35]. The uranyl cation is the typical appearance of uranium also in biological systems. For this reason the focus of this thesis is on the chemistry of the UO_2^{2+} ion.

The coordination chemistry of the UO_2^{2+} ion is dominated by between four to six donor atoms, all occupying equatorial positions perpendicular to the two axial uranyl oxido moieties resulting in an octahedral, pentagonal bipyramidal or hexagonal bipyramidal coordination, respectively, for U(VI). This is very well established by the vast number of crystal structures of uranyl complexes, with a great variety of neutral and anionic ligands, that have been solved.[24,44-48] Examples from the literature of each of these structures are presented in Figure 1:[24,44-46]

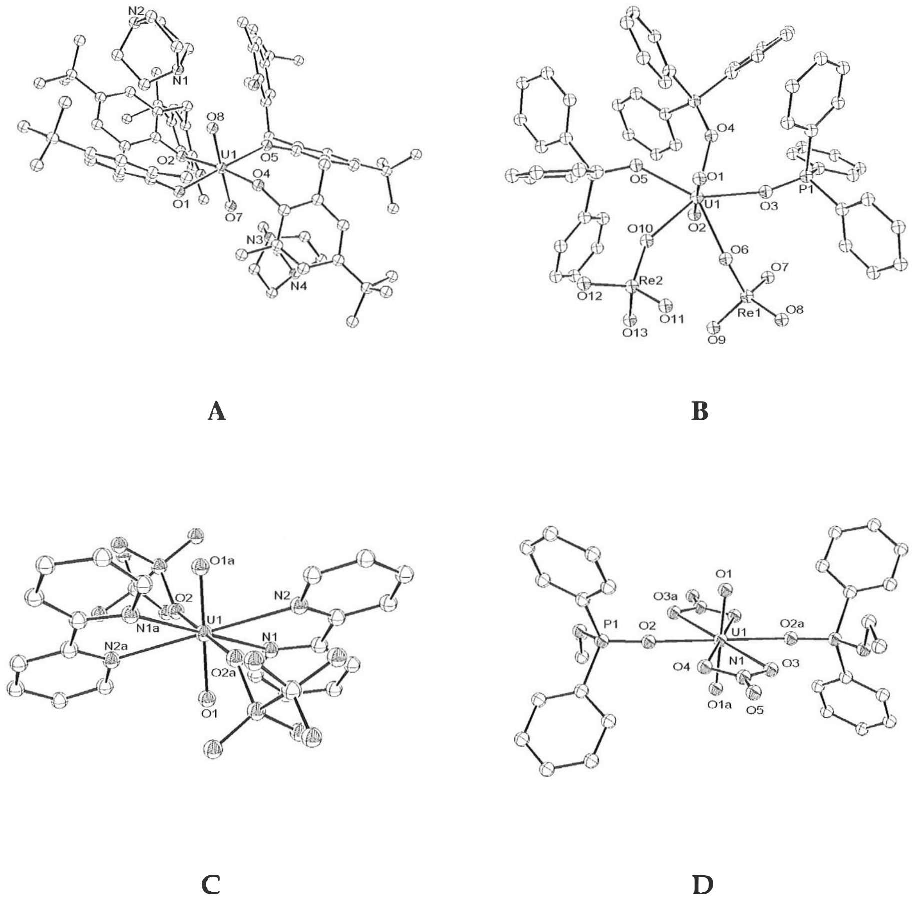


Figure 1. Examples of octahedral (**A**),[24] pentagonal bipyramidal (**B**)[44] and hexagonal bipyramidal (**C, D**)[45,46] coordination for uranyl ion presented in the literature. In compound **C** the equatorial coordinating atoms deviate from planarity. The hydrogen atoms have been omitted for clarity.

In some uranyl compounds one of the coordinated atoms is clearly displaced from the equatorial plane, likely because of steric requirements due to the ligand geometry.[49,50] Complexes in which several of the coordinating atoms deviate significantly from planarity (by more than ± 0.2 Å) are very rare, being limited quite exclusively to hexacoordinated uranyl derivates with di- or polydentate ligands.[23,51-55] One of these latter cases is presented in Figure 1 as compound **C**[45], where the six coordinating atoms reside in two parallel equilateral triangles forming a trigonal antiprism, whereas **D**[46] is an example of the typical hexacoordination of the uranyl ion with coordinating atoms residing in the equatorial plane. The tendency of the coordinating atoms to reside in the equatorial plane originates from the fact that UO_2^{2+} falls between U^{4+} and U^{3+} in acidity ($U^{4+} > UO_2^{2+} > U^{3+}$), which suggests that the effective charge at the metal center (U^{6+}) is greater than +3 leading to an increased binding strength of the ligands in the equatorial plane.[56-59] This phenomenon is visualized in Figure 2.

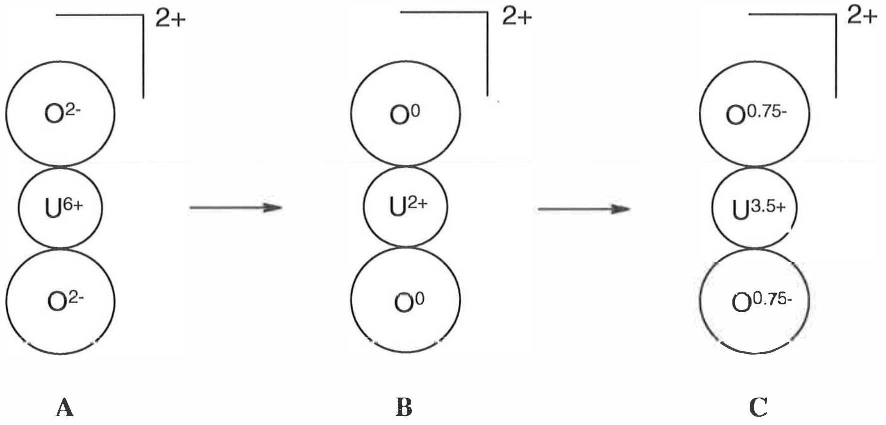


Figure 2. A schematic presentation of the effective charge of the metal center (U^{6+}) in the uranyl cation (UO_2^{2+}). According to current concepts version **C**, with a high positive charge density on the uranium, describes the reality and explains why the atoms coordinating to uranyl reside in the equatorial plane.[56-59]

Typical hard Lewis bases such as F^-- or O-donors, like organic phenolate O, are good ligands for the hard UO_2^{2+}- cation.[3,4,60] An inorganic example of enduring O-containing complexing agent for uranyl ion is carbonate, CO_3^{2-}, which forms in nature several minerals such as rutherfordine, $UO_2(CO_3)$,[61] liebigite, $Ca_2[UO_2(CO_3)_3]\cdot 10\text{-}11H_2O$,[62] and andersonite, $Na_2Ca[UO_2(CO_3)_3]\cdot 6H_2O$[63] with the uranyl ion. Also, in natural waters uranium is present mostly as dissolved $[UO_2(CO_3)_2]^{2-}$ ions.[64,65] These observations suggest that the carbonate ion is ideally suited in a geometric, structural and electronic sense to coordinate uranyl ions.[66] In addition to these hard donor atoms, uranyl ions also exhibit some covalency in their interactions with softer donors such as Cl^-, N and S.[8]

The Lewis basicity of uranyl oxo ligands is generally considered quite weak and they rarely produce, for example, dinuclear complex units by forming an oxido bridge between the U(VI) ions[67] or a direct $U\cdot\cdot\cdot O{=}U{=}O\cdot\cdot\cdot U$ bridge.[68] Instead, an H-bond formation of uranyl oxo ligands is a common feature.[66]

1.2 Aim of the study

The aim of this study was to synthesize new low molecular weight, multidentate nitrogen-containing phenolic ligands and their uranyl complexes with useful extraction properties.

This work concentrated on the preparation of the ligands and uranyl complexes, the characterization of the uranyl complexes, and the extraction studies of uranyl ions from water to dichloromethane with the ligands prepared. The other objective was to study how effectively and selectively the selected ligands extract uranyl ions from a water solution to organic water-insoluble liquids in different chemical environments. These different chemical environments include e.g. varying the pH of the water solution, the presence of other metal ions in the water solution and the effect of different anions in the aqueous phase.

It has been shown that ligand architecture is a key factor in its extraction behaviour[69-71], because a slight change in the ligand structure may have a significant effect on its coordinating properties. In practice, an ideal ligand for uranyl extraction under environmental and biological conditions should exhibit a stronger coordination to uranyl ions than the naturally occurring ones, such as carbonate or nitrate ions, and it should show selectivity for uranyl ions over other commonly encountered metal ions. It has been shown that a ligand with good extraction properties for UO_2^{2+} from water to an organic water-immiscible solvent needs to have a good balance between its hydrophilic and hydrophobic properties.[6,72] Especially, if the formed complex is neutral, the extraction efficiency is significantly enchanced.

For the above-mentioned reasons three groups of ligands, i.e. ligands having three chemically different functional groups in their "tail" part with varying length of the "tail", were prepared. These three groups of ligands are presented below:

1. Aminoalcoholbisphenols (compounds **1-9**, Scheme 2) have four possible donor atoms (three oxygen and one nitrogen) with the hydroxyl group at the end of the extended "tail" that affects the polarity of the molecule and thus the solubility of the compound.

2. Aminoalkylbisphenols (compounds **10-14**, Scheme 2) have three possible donor atoms (two oxygen and one nitrogen) with the extended "tail" being an alkyl group, which makes the exterior of the coordinated molecule lipophilic after complexation and so promotes the solubility of the formed complex into organic solvents. This is an important feature in the extraction.[6]

3. Diaminobisphenols (compounds **15-18**, Scheme 2) have four possible donor atoms (two oxygen and two nitrogen) with the extended "tail"

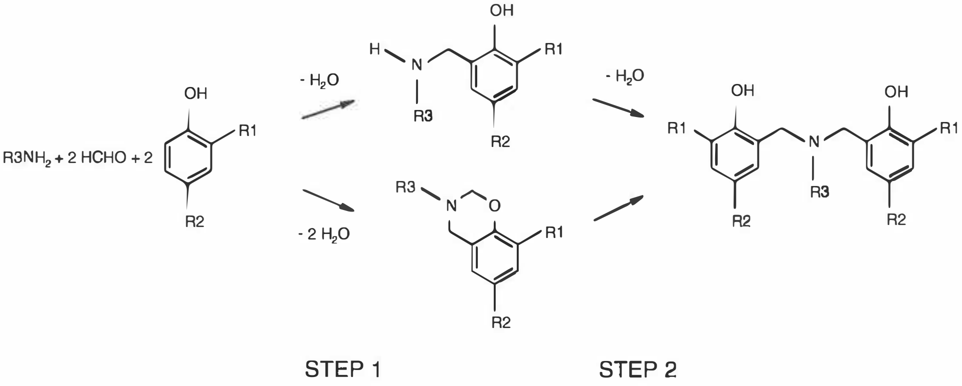
being an amine group. This other nitrogen in the "tail" of the same molecule offers another site to accommodate the phenolic proton released in the complexation process, and thus opens up a possibility for the bridging nitrogen, where the proton usually resides, to coordinate with the uranyl ion.

At the beginning of this work no aminobisphenol complexes of uranyl ion of this type had been reported in the literature.[I]

2 EXPERIMENTAL

2.1 Syntheses of the organic ligands

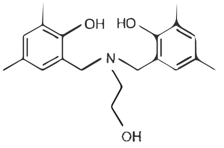
The organic ligands presented in this study were prepared by multicomponent Mannich condensation reaction.[73] This reaction consists of aminoalkylation of an acidic proton placed next to a carbonyl or hydroxyl group with formaldehyde and a primary or secondary amine. The main path of the reaction is shown in Scheme 1.



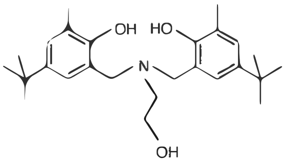
Scheme 1. The stepwise formation of aminobisphenol ligands with reaction intermediates.

In this reaction the proper choice of reaction conditions as well as reaction partners is a key point for a successful aminoalkylation in a selective manner.[74-76] In the literature the Mannich reaction is usually conducted with stoichiometric amounts of starting materials refluxed in a proper solvent with or without a catalyst.[77-81] In this study, the syntheses were made mainly using methanol or ethanol with 20-25 % water (v/v) as a solvent and triethylamine as a base catalyst. The reaction solutions were kept in a water bath (50°C) for 74-168 hours. After that the solutions were placed in a freezer for 24-168 hours. During that time an oil phase usually separated from the main liquid. The liquid was decanted off and the oil was recrystallized from the proper solvent or (if the recrystallization did not work) dissolved in cold methanol into which an excess of 6 M HCl was added leading to a formation of a white solid, which also was recrystallized from the proper solvent. The yields were generally 30-45 %. The reason for the modest yields was the co-formation of aminomonophenols and aminomonophenol-oxazines (the reaction intermediates) as shown in Scheme 1. In some cases these intermediates could be separated and identified by NMR and they are also well established in the literature. [82-85] An exception concerning the yields were the diaminobisphenol ligands, which were formed almost quantitatively with the method presented in this thesis. For example, [(N,N-bis(2-hydroxy-3,5-dimethylbenzyl)-N´,N´-dimethylethylenediamine)] formed in an 87% yield.[V]

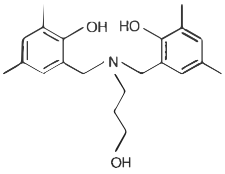
In this study 18 ligands were synthesized, 12 of which are new compounds.[I-V] All the ligands prepared are presented in Scheme 2. The ligands **2** and **4-14** are new ones, while **1**, **3** and **15-18** have been prepared before. During the purification process the compounds **4-14** were transformed to hydrochlorides in order to make their separation easier.[I-III]



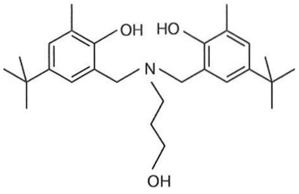
1 (H_3L1)



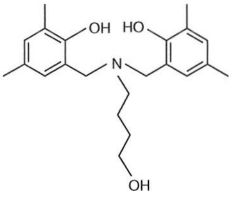
2 (H_3L2)



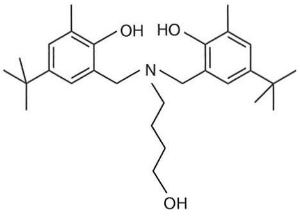
3 (H_3L3)



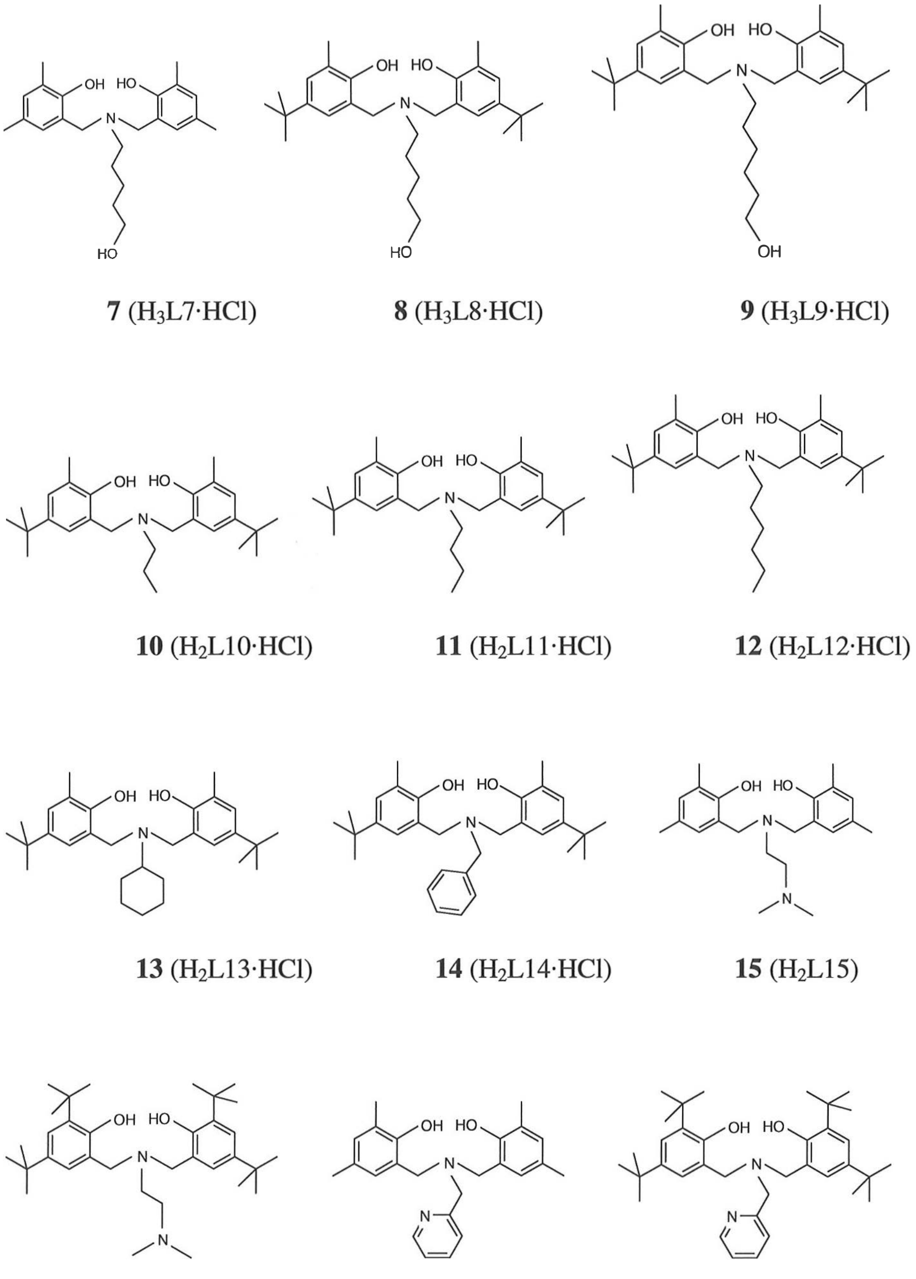
4 ($H_3L4{\cdot}HCl$)



5 ($H_3L5{\cdot}HCl$)



6 ($H_3L6{\cdot}HCl$)



7 ($H_3L7·HCl$) **8** ($H_3L8·HCl$) **9** ($H_3L9·HCl$)

10 ($H_2L10·HCl$) **11** ($H_2L11·HCl$) **12** ($H_2L12·HCl$)

13 ($H_2L13·HCl$) **14** ($H_2L14·HCl$) **15** (H_2L15)

16 (H_2L16) **17** (H_2L17) **18** (H_2L18)

Scheme 2. The 18 ligands prepared in this study, 12 of which are new compounds (ligands **2** and **4-14**). If the ligand was isolated as a hydrochloride salt, it has been shown by adding a HCl after the ligand, for example $H_3L4·HCl$.

2.2 Syntheses of the uranyl complexes

Generally, the uranyl complexes were synthesized by dissolving the stoichiometric amounts (1:2, metal to ligand) of uranyl nitrate hexahydrate and the ligand (H_nLm) (n =2 or 3 and m = **1** – **18**) in acetonitrile, methanol or ethanol. Usually, a base (triethylamine) was also added in the amount needed to deprotonate the phenolic ligand to an anion ($H_{n-1}L^-$). If the ligand was a hydrochloride, one equivalent of the base was added to neutralize the HCl.

In some cases, although triethylamine was not added, the ligand itself (not a hydrochloride) served as a base leading to effective stoichiometry of UO_2^{2+} : $H_{n-1}L^-$ (1:1), which stoichiometry usually yielded a different complex than the 1:2 stoichiometry with the corresponding ligand. Thus, with base (triethylamine) it was possible to control the formation and stoichiometry of the uranyl complexes.

Immediately after addition of uranyl nitrate hexahydrate into a reaction solution, the colour of the solution turned red or orange indicating that the complexation had started. The resulting solutions were usually kept at room temperature, only in some cases in a freezer. Usually crystals formed in the reaction solutions, the time needed for their formation varying from a few hours to three weeks, albeit in most cases they formed within two days. The best crystallization solvent proved to be acetonitrile. The yields in the form of crystals were generally 60-80%, but after filtering off the crystals the filtrates were still coloured (red or orange) indicating that the crystallization was not complete. Judging from the colours of the reaction solutions all the prepared ligands formed uranyl complexes, but ligand **18** did not form a crystalline complex.

Altogether 20 new uranyl complexes were isolated in this study. From those crystals 19 structures were resolved (the crystal data of **25** were of poor quality and remained unsolved). Three ligands (**1**, **15** and **16)** formed a 1:1 complex, while all ligands, except **16** and **18**, formed a 1:2 complex with the uranyl ion. Most of the complexes contained also cocrystallized solvent molecules. These complexes are numbered and presented with their chemical formula and their unit cell symmetry in Table 1.

Table 1. Numbering and chemical formulae of the 20 new uranyl complexes, with their unit cell symmetry, prepared in this study.

No	Uranyl complex	Crystal system	Space group	Paper
19	$(UO_2)_2(H_2L1)_2(NO_3)_2$	Monoclinic	$P\,2_1/c$	I
20	$UO_2(H_2L1)_2 \cdot 2\,H_2O$	Monoclinic	$P\,2_1/c$	I
21	$UO_2(H_2L2)_2 \cdot 2\,CH_3CN$	Triclinic	$P\,\bar{1}$	I
22	$UO_2(H_2L3)_2$	Monoclinic	$P\,2_1/a$	I
23	$UO_2(H_2L4)_2$	Monoclinic	$P\,2_1/c$	I
24 a [a]	$UO_2(H_2L5)_2$	Triclinic	$P\,\bar{1}$	II
24 b [a]	$UO_2(H_2L5)_2 \cdot 2\,CH_3CN$	Triclinic	$P\,\bar{1}$	II
25	$UO_2(H_2L6)_2 \cdot CH_3CN$	Triclinic	$P\,\bar{1}$	II
26	$UO_2(H_2L7)_2 \cdot 2\,CH_3CN$	Triclinic	$P\,\bar{1}$	II
27	$UO_2(H_2L8)_2 \cdot 2\,CH_3CN$	Triclinic	$P\,\bar{1}$	II
28	$UO_2(H_2L9)_2 \cdot 4$ toluene	Monoclinic	$C\,2/c$	II
29	$UO_2(HL10)_2 \cdot 2\,CH_3CN$	Triclinic	$P\,\bar{1}$	III
30 [b]	$UO_2(HL11)_2$	Triclinic	$P\,\bar{1}$	III
31	$UO_2(HL12)_2 \cdot 2\,CH_3CN$	Triclinic	$P\,\bar{1}$	III
32	$UO_2(HL13)_2$	Monoclinic	$P\,2_1/c$	III
33	$UO_2(HL14)_2 \cdot 2\,MeOH$	Triclinic	$P\,\bar{1}$	III
34	$UO_2(HL15)(NO_3) \cdot CH_3CN$	Monoclinic	$P\,2_1/n$	V
35	$UO_2(HL15)_2$	Triclinic	$P\,\bar{1}$	V
36	$UO_2(HL16)(NO_3) \cdot 2\,CH_3CN$	Monoclinic	$P\,2_1/n$	V
37	$UO_2(HL17)_2 \cdot 2\,CH_3CN$	Triclinic	$P\,\bar{1}$	V

[a] Crystals of **24 a** and **24 b** were produced from the same preparation and thus they are referred as **24** in the text.
[b] **30** was originally isolated as $UO_2(HL11)_2 \cdot 2\,CH_3CN$. [III]

2.3 X-ray crystallography

Crystals suitable for single crystal X-ray measurements were obtained directly from the reaction vessels. The crystallographic data were collected at 173 K on an Enraf Nonius Kappa CCD area-detector diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). The data were collected using φ and ω scans and processed using a DENZO-SMN V 0.93.0.[86] SHELXA[87] or SADABS[88] absorption corrections were applied to the data of uranyl compounds. The structures were solved by direct methods using the SHELXS-97[89] or SIR-97[90] programs and full-matrix least-squares refinements on F^2 were performed using the SHELXL-97[89] program. For all compounds the heavy atoms were refined anisotropically. The CH hydrogen atoms were included at fixed distances using fixed displacement parameters from their host atoms while other H atoms were refined using fixed displacement parameters. Structure figures were drawn using ORTEP-3 for Windows.[91]

2.4 Uranyl extraction

Two-phase uranyl ion extraction studies from water to dichloromethane were performed at ambient room temperature (21-24°C) to determine the extraction ability of the prepared ligands (**1**-**18**). Generally, the experimental setup was as follows: into the bottom of a test tube was placed 3 ml of CH_2Cl_2 with ligand (0.210 mmol) and NEt_3 (0.210 mmol to neutralize HCl in case the ligand was hydrochloride, $H_nLm \cdot HCl$). At the top of the organic layer was placed 2 ml of water with uranyl nitrate (the usual amount being 0.0525 mmol). In the beginning of the extraction the ratio of uranyl ion in the water phase to ligand in the CH_2Cl_2 phase was 1:4. In every experiment one test tube with CH_2Cl_2 containing no ligand was prepared as control. The samples for ICP-OES were taken from the water layer over a 48-120 h period of time and were analyzed with inductively coupled plasma optical emission spectrometry (ICP-OES) at 385.958 nm using a Perkin Elmer Optima 4300DV instrument.[92]

As it has been shown that various ligands have different optimal extraction conditions,[93-97] the influence of the following factors on the extraction was studied:

1) The effect of the amount of the extractor solvent (i.e. the effect of the ligand concentration). This experiment was performed as described above, with the exception that the amount of CH_2Cl_2 was 6 ml, with ligands **5**, **9**, **11** and **13**.[III]

2) The effect of stirring the extractor solvent during the extraction. This experiment was performed as the first one (1) with the exception that the test tubes were stirred with a magnetic strirrer (300-500 rpm) throughout the experiment. Before the samples were taken, the stirring was interrupted and the solutions were allowed to settle for 5 min.[III]

3) The effect of the pH of the water solution. This was performed with ligands **6** and **11** under three different acetate buffer solutions with pH values 3.4, 4.3 and 5.2.[III]

4) The effect of the uranyl salt used. This experiment consisted of two measurements: the one presented above and the other, where the uranyl nitrate hexahydrate was replaced by uranyl acetate dihydrate. The ligands used were **1**, **5** and **9**.[III]

5) The selectivity of the ligands **3**, **9**, **11** and **15** towards several metal ions (UO_2^{2+}(aq), Fe^{3+}(aq), Co^{2+}(aq), Ni^{2+}(aq), Cu^{2+}(aq), Zn^{2+}(aq)) in an extraction process from the water layer at pH 1.8 to dichloromethane.[V]

6) The selectivity of the ligands **3**, **9**, **11** and **15** towards several metal ions (UO_2^{2+}(aq), Fe^{3+}(aq), Co^{2+}(aq), Ni^{2+}(aq), Cu^{2+}(aq), Zn^{2+}(aq)) in an extraction process from acetate buffer solution at pH 4.2 to dichloromethane.[V]

2.5 NMR studies of the prepared complexes

The ^1H and ^{13}C NMR spectra were measured for all the prepared ligands and their uranyl complexes either in $CDCl_3$, DMSO or pyridine. Two of the uranyl complexes, **24** and **31**, were analyzed with ^1H-^1H COSY, NOESY, ^1H-^{13}C HMQC and ^1H-^{13}C HMBC NMR techniques to find out the behaviour of the complexes in DMSO (complex **24**) and $CDCl_3$ (complex **31**). The choice of the NMR solvent for the particular complex was made on the basis of solubility: the complexes **19-28** and **34-37** were soluble in DMSO and the complexes **29-33** were soluble both in DMSO and $CDCl_3$. The complexes soluble in DMSO usually also dissolved into pyridine. The spectra measured in pyridine resembled those measured in DMSO with only slight differences in chemical shifts.

3 RESULTS AND DISCUSSION

3.1 Structural studies of the prepared ligands

3.1.1 Bis(5-*tert*-butyl-2-hydroxy-3-methylbenzyl)(6-hydroxyhexyl)ammonium chloride monohydrate as anion receptor

As a part of the search for new low molecular weight organic molecules for uranyl ion complexation, the compound 6-[bis[5-*tert*-butyl-2-hydroxy-3-methylbenzyl]-amino]hexan-1-ol (**9**) was prepared. This compound, as an ammonium cation, proved to function as a chloride ion receptor.[IV] Anion and cation receptors are important compounds in biological, environmental and supramolecular chemistry[98-101] because a large majority of substrates and cofactors engaged in biological processes are anions. Phosphate and chloride ions are of special interest among these anions because of their ubiquitous presence in biological systems.[102] A remarkable difference between anion and cation bond formation is that cations usually involve strong coordinate bonds. Conversely, anion binding is significantly weaker, often involving multiple hydrogen-bond formation acting in concert with electrostatic interactions.[98,103,104] The latter observation is valid also for the title compound, as can be seen from the crystal structure of **9** (as hydrochloride, Figure 3) made from the crystals obtained during the purification process.[IV]

Furthermore, the title compound has a potential of being an HCl co-transporter across bilayer membranes, as shown in an article by Gale *et al.*[105]

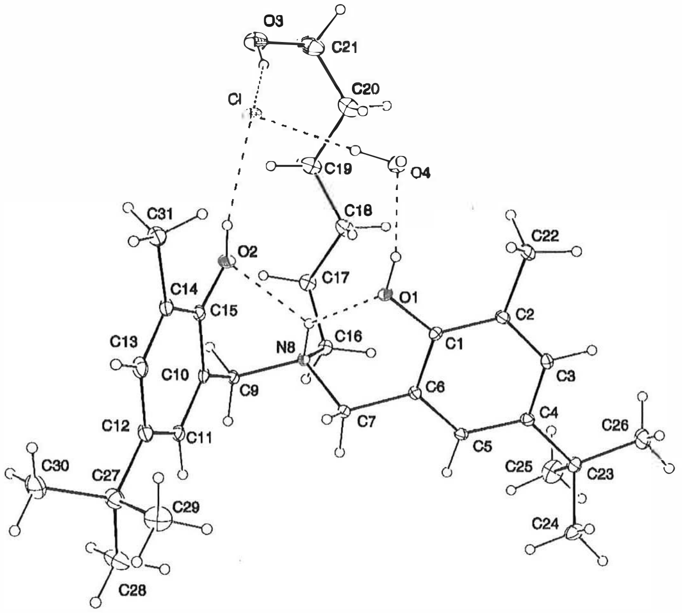


Figure 3. A view of the asymmetric unit of **9**·HCl with the atom-numbering scheme.[IV] The hydrogen bonds are shown as dashed lines.

The basic structural unit of **9**·HCl consists of a bis(5-*tert*-butyl-2-hydroxy-3-methylbenzyl)(6-hydroxyhexyl)ammonium cation, a chloride ion and a water molecule. The chloride ion is surrounded by the OH groups of the phenol, the alcoholic "tail" and the water molecule and it thus forms three strong intramolecular O-H···Cl hydrogen bonds ranging from 2.15(2) Å to 2.29(2) Å. In addition, the chloride ion forms one weak intermolecular C-H···Cl hydrogen bond, with a bond length of 2.66 Å, to hydrogen H9bC9 of the adjacent unit cell. The other H atom of the water molecule forms a hydrogen bond to the aliphatic alcohol atom O3 in an adjacent unit. Thus, the water molecule plays an important dual (intra- and intermolecular) role by acting as a bridge between the phenol H atom, the aliphatic alcohol O atom and the chloride ion, as can be seen in Figure 4. The H atom of the ammonium group does not form a hydrogen bond to the chloride ion but forms bifurcated intramolecular hydrogen bonds to two phenol O atoms. The values of the hydrogen-bond parameters are comparable to literature values.[106,107] Most of the polar part of the compound is located in the polar cavity; with the outer surface of the zwitterion being lipophilic this allows for an easy transport of the chloride ion into organic solvents.

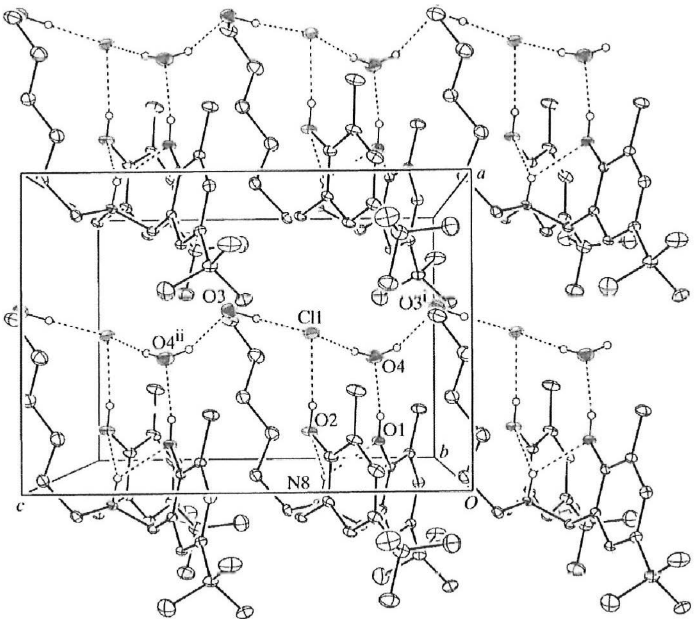


Figure 4. The crystal packing of **9**·HCl viewed in the *ac* plane, showing the hydrogen-bonding pattern as dashed lines.[IV]

3.1.2 Other structure results of the prepared ligands

In the course of the organic ligand preparations, the ligand **15** (which is a known compound but its crystal structure was published only recently[108,109]) crystallized out directly from the reaction solution with the method used in this study.[V] A single crystal X-ray analysis was done on one of these crystals and the results were in agreement with the literature[108,109].

Furthermore, another previously known ligand **18** (H_2L18) crystallized out from a recrystallization solution (acetonitrile) and its crystal structure was resolved by single-crystal X-ray analysis. This structure has not been published in the literature; it is now presented in Figure 5.

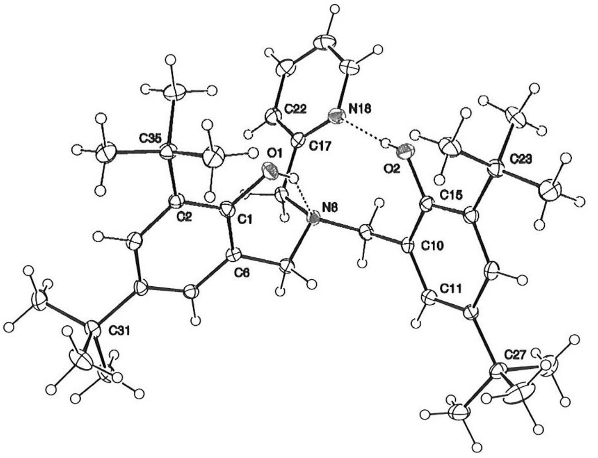


Figure 5. Previously unpublished crystal structure of the ligand **18** (H_2L18). The hydrogen bonds are shown as dashed lines.

The main structural features of compound **18** are the intramolecular hydrogen bonds, which lock the conformation of the molecule in the solid state.

3.2 Structural studies of the prepared uranyl complexes

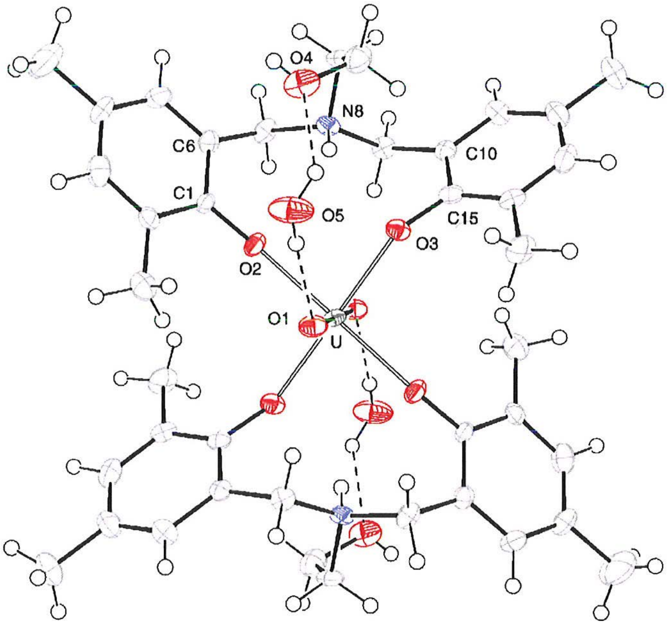
Altogether 20 new uranyl complexes were formed and of these 19 structures were solved. The solid-state structures of complexes **19**-**37** (except **25**) were verified by single-crystal X-ray analysis. 16 complexes are of the form $[UO_2(H_nLm)_2]\cdot kS$ (n = 1-2, m = 1-17, k = 0-4 and S = water, methanol, acetonitrile or toluene). Two of them are of the form $[UO_2(HLm)(NO_3)]\cdot kS$ (m = 15 or 16, k = 1 or 2 and S = acetonitrile). One of the compounds has a dinuclear structure, viz. $[(UO_2)_2(H_2L1)_2(NO_3)_2]$. In $[UO_2(H_nLm)_2]\cdot kS$ compounds there are four equatorial coordinating oxygen atoms leading to an octahedral coordination for U(VI). In $[UO_2(HLm)(NO_3)]\cdot kS$ compounds five equatorial donors (four oxygens and one nitrogen) lead to a pentagonal bipyramidal coordination for U(VI); finally, in the dinuclear complex, $[(UO_2)_2(H_2L1)_2(NO_3)_2]$, there are five equatorial oxygen donor atoms leading to a pentagonal bipyramidal coordination for both U(VI) ions. The crystal systems in all these uranyl complexes were either monoclinic or triclinic.

The selected and representative crystal structure figures, bond lengths and bond angles, for each of preceding three structure groups, are presented below.

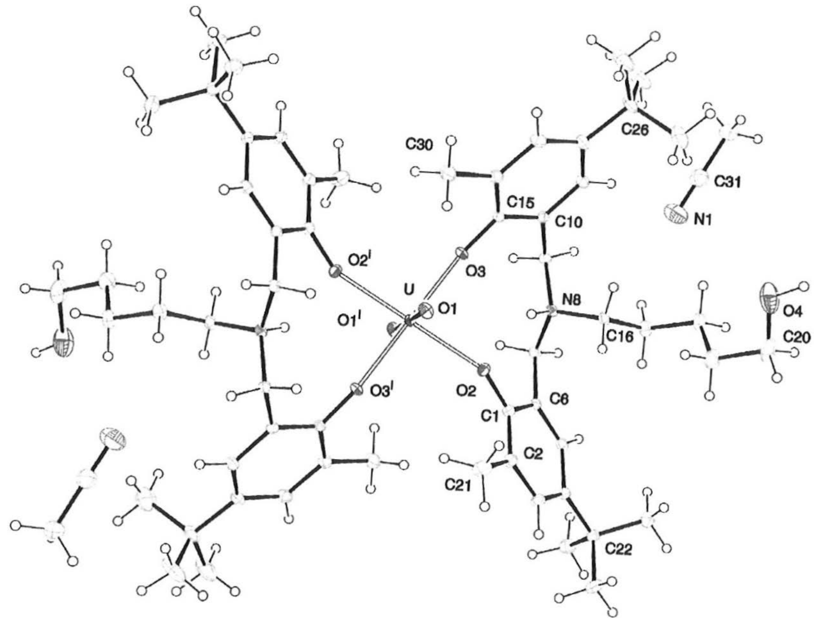
3.2.1 Structures of the $[UO_2(H_nLm)_2]$ complexes

Uranyl complexes of this type are formed most easily. In this group the common structural feature of the ligand is its zwitter ionic form. Although both phenol groups of the ligand are deprotonated, the ligand has only one negative charge as one of the phenolic protons is moved to the nitrogen atom.

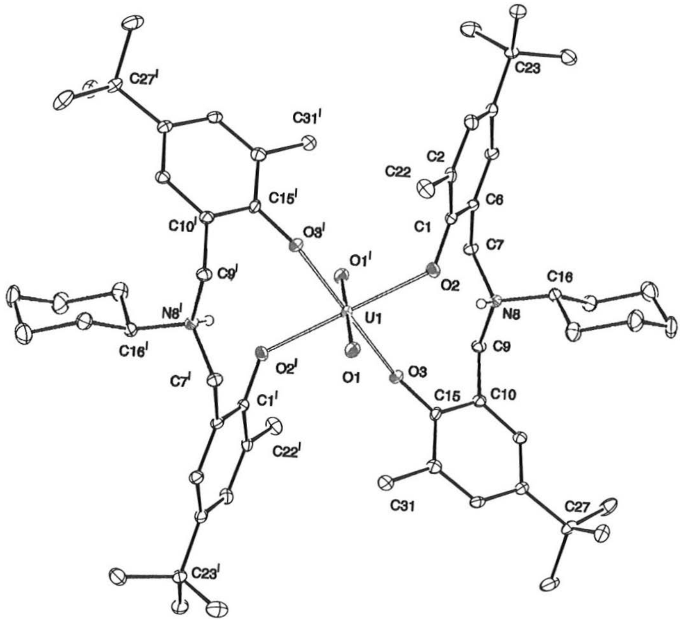
The triclinic unit cell is composed of one uranyl ion, two ligands and possibly up to two solvent molecules. The primitive monoclinic unit cell contains two $UO_2(H_nLm)_2$ molecules and the C-centered monoclinic unit cell for **28** contains four $UO_2(H_2L9)_2$ and sixteen toluene molecules. The uranium resides at the inversion center in all these complexes. The structural presentations with the atom numbering scheme can be seen in Figure 6 for the selected compounds (**20**, **27**, **32**, **35**) on pages 26-28. The superscript i on an atom label means that the coordinates of this atom are obtained by an inversion operation. In the complexes whose structures are not presented the atom numbering scheme follows similar principles.[I,II,III,V] In Table 2 the selected bond lengths and angles with the averages and standard deviations are presented for all the $UO_2(H_nLm)_2$ type complexes.



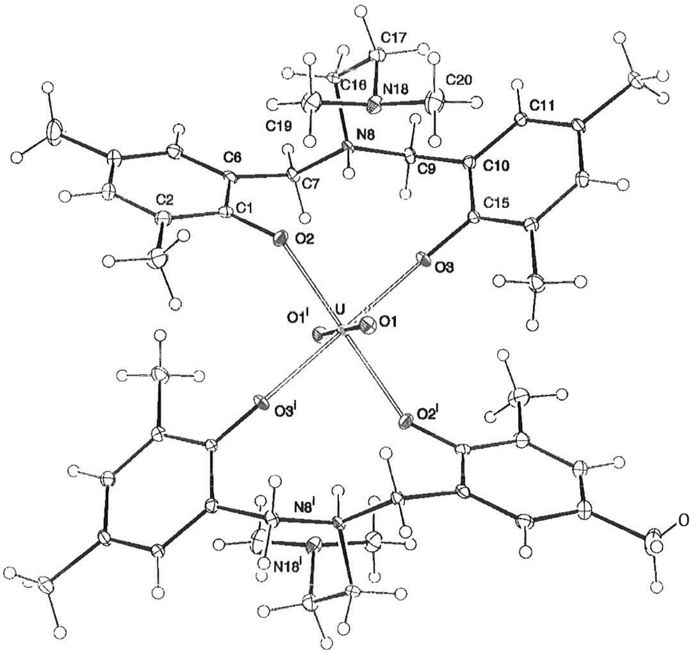
20


C30
C26
C31
C15
C10
N1
O2^{I}
O3
U
O1^{I}
O1
N8
O4
C16
C20
O2
C6
O3^{I}
C1
C2
C21
C22

27


C27^{I}
C23
C31^{I}
C2
C22
C6
C15^{I}
C10^{I}
C1
O3^{I}
C7
O1^{I}
C9^{I}
C16
O2
N8^{I}
N8
U1
C16^{I}
C9
O2^{I}
O1
O3
C7^{I}
C15
C10
C1^{I}
C22^{I}
C31
C27
C23^{I}

32



35

Figure 6. Four selected and representative structure figures (**20**, **27**, **32**, **35**) of the $UO_2(H_nLm)_2$ type new uranyl complexes synthesized in this study. In complex **20** the dashed lines represent hydrogen bonds.

Table 2. Selected bond lengths (Å) and angles (°) with averages and standard deviations for the complexes of the form $UO_2(H_nL_m)_2$. Superscript ^{i} denotes atoms generated by inversion.

No	Bond lengths (Å)			
	U=O1	U-O2	U-O3	
20	1.817(3)	2.228(3)	2.241(3)	
21	1.803(2)	2.236(2)	2.221(2)	
22	1.808(3)	2.214(3)	2.256(3)	
23	1.817(3)	2.232(3)	2.238(3)	
24 a	1.795(2)	2.242(2)	2.307(2)	
24 b	1.807(2)	2.202(2)	2.303(2)	
26	1.796(2)	2.250(2)	2.250(2)	
27	1.798(2)	2.266(2)	2.251(2)	
28	1.800(2)	2.245(2)	2.227(2)	
29	1.798(3)	2.258(3)	2.255(3)	
30	1.793(3)	2.255(3)	2.262(3)	
31	1.800(3)	2.260(2)	2.267(2)	
32	1.789(3)	2.311(3)	2.244(3)	
33	1.808(3)	2.251(3)	2.231(3)	
35	1.794(2)	2.260(2)	2.251(2)	
37	1.803(4)	2.296(3)	2.240(4)	
Average	1.802	2.250	2.253	
SD	0.008	0.026	0.023	
No	Bond angles (°)			
	O2-U-O3	O2-U-O3^i	C1-O2-U	C15-O3-U
20	84.97(12)	95.03(12)	162.7(3)	147.1(3)
21	85.89(8)	94.11(8)	173.4(2)	167.0(2)
22	82.38(11)	97.62(11)	174.0(3)	137.1(3)
23	84.43(10)	95.57(10)	160.3(3)	158.9(3)
24 a	84.96(7)	95.04(7)	151.9(2)	135.8(2)
24 b	82.52(8)	97.48(8)	175.5(2)	132.2(2)
26	82.72(9)	97.28(9)	167.2(2)	149.8(2)
27	84.54(8)	95.46(8)	150.9(2)	154.4(2)
28	84.03(10)	95.97(8)	159.7(2)	156.7(2)
29	85.07(11)	94.93(11)	165.8(3)	161.1(3)
30	84.83(12)	95.17(12)	160.2(3)	156.8(3)
31	84.76(9)	95.24(9)	155.1(2)	147.6(2)
32	84.47(11)	95.53(11)	132.0(3)	156.7(3)
33	84.60(10)	95.40(10)	158.5(3)	160.4(3)
35	84.52(8)	95.48(8)	140.6(2)	163.1(2)
37	83.04(13)	96.96(13)	131.6(3)	159.6(4)
Average	84.23	95.77	157.46	152.77
SD	0.990	0.990	13.1	9.98

The average U-O(phenolate) bond length of all U-O2 and U-O3 bonds of these 1:2 (U:HL) uranyl complexes is 2.252 Å. The lowest value is 2.202(2) Å (complex **24 b)** and the highest value is 2.311(3) Å (complex **32).** This average is close to the estimated "ideal" value of 2.2 Å found in U(VI) compounds with unrestricted, unidentate alkoxide ligands.[110-112] Similar results have been found also in U(VI) compounds with Schiff base ligands.[113] This suggests that the ligands prepared in this study bind to the UO_2^{2+}-ion quite effectively.

From the small standard deviations of the bond lengths of the U-O1, U-O2 and U-O3 and bond angles of O2-U-O3 and O2-U-O3^i it can be stated that the coordination spheres around uranium(VI) are quite similar in all these $UO_2(H_nLl)_2$ complexes.

From the values of the U-O-C(aromatic) angles and the corresponding U-O(phenolate) bond lengths in Table 2, the following trend can be observed: the smaller the U-O-C(aromatic) angle, the longer the U-O(phenolate) bond, e.g. for **37** the bond angle C1-O2-U is 131.6(3)° and the corresponding bond length U-O2 is 2.296(3) Å, while the respective values for **24 b** are 175.5(2)° and 2.202(2) Å. This correlation is presented as a graph in Figure 7. The possible explanation for this behaviour is that when the U-O-C(aromatic) angle is large, the outermost orbitals of uranium overlap better with the orbitals of phenolate oxygen, leading to increased π bond formation between uranium and oxygen atoms and thus to a shortening of the corresponding U-O(phenolate) bond.[37] Furthermore, on the basis of the large variations in C1-O2-U and C15-O3-U angles (from 131.6(3)° to 175.5(2)°), it seems that the ligands themselves can adopt slightly different conformations.

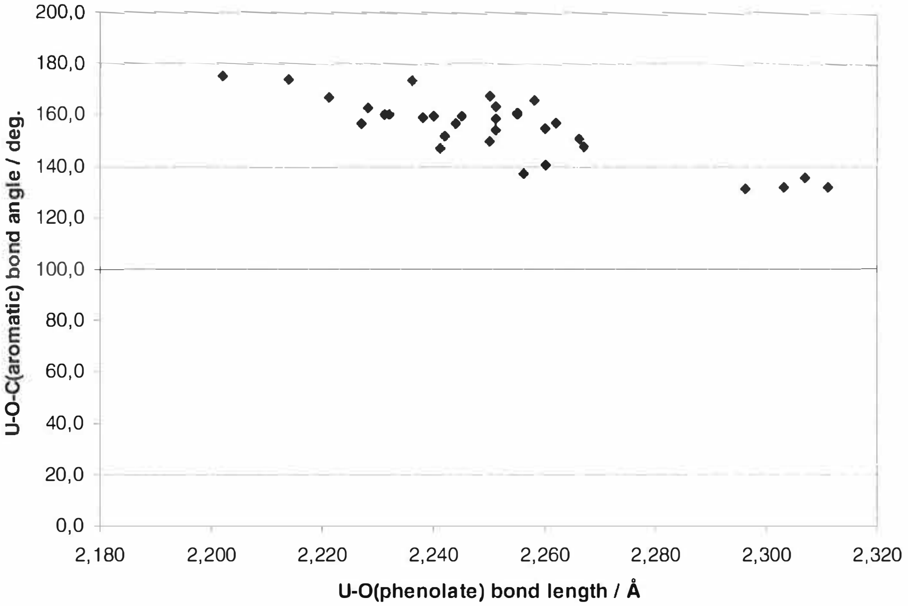


Figure 7. The correlation between the U-O-C(aromatic) bond angle and the corresponding U-O(phenolate) bond length in the $UO_2(H_nLm)_2$ type complexes prepared in this study.

Of the 16 asymmetric units of uranyl complexes of the formula $UO_2(H_nLm)_2$, one contained a water molecule (**20**), one contained a methanol molecule (**33**), one contained two toluene molecules (**28**), eight contained acetonitrile molecules (**21**, **24 b**, **26**, **27**, **29**, **30**, **31**, **37**) and five unit cells contained no solvent molecules at all (**22**, **23**, **24 a**, **32**, **35**). Thus, 11 out of 16 solid state structures contained solvent or water molecules indicating that in the solid state most of these structures contain "holes" that need to be filled for the proper crystal formation. When the crystals that contained solvent molecules (especially acetonitrile molecules) were taken out of the mother liquid, they rapidly decomposed as the solvent molecules evaporated. This indicates that usually the solvent molecules are weakly bonded inside the crystal through van der Waals interactions. In complex **20** two water molecules form two intermolecular bridges between uranyl oxo-oxygens and alcoholic "tail" oxygens by hydrogen bonds, as can be seen in Figure 6.

3.2.2 Structures of the $[UO_2(H_nLm)(NO_3)]$ complexes

Two complexes of the form $[UO_2(HLm)(NO_3)]\cdot kS$ (m =15 or 16, k = 1 or 2 and S= acetonitrile) were formed.[V] To prepare the crystals of this type of structure, the reaction conditions had to be dry (with no or very little presence of water molecules). This is presumably due to the fact that water molecules are stronger Lewis bases than nitrate ions and thus they replace the nitrate ion from the coordination sphere of the uranyl ion. A structural view of compound **36** is shown in Figure 8. Selected bond lengths and angles with averages and standard deviations are presented in Table 3.

These kinds of neutral mononitrate complexes of uranyl are rare. At the time of writing this thesis, to the best of our knowledge, only one example having a stoichiometry of $[UO_2(L)(NO_3)]$ (L= monoanionic ligand) has been reported,[1] while four examples with a stoichiometry of $[UO_2(L)(L')(NO_3)]$ (L= a monoanionic ligand and L´= a neutral ligand) have been described[114-117]. However, all these five uranyl complexes are dinuclear ones, although one nitrate ion is coordinated to uranyl ion in a η^2-fashion.

The interesting point in these complexes is that a ligand is also a zwitter ion, but the proton resides on the nitrogen atom N18 and not on N8, as in the 1:2 complexes. Now N8 can coordinate to the uranyl ion, as happened in these complexes. The uranyl coordination in complexes **34** and **36** is pentagonal bipyramidal and it resembles that of the anionic uranyl complex with a bis[2-(2-hydroxyphenoxy)ethane dianion.[118]

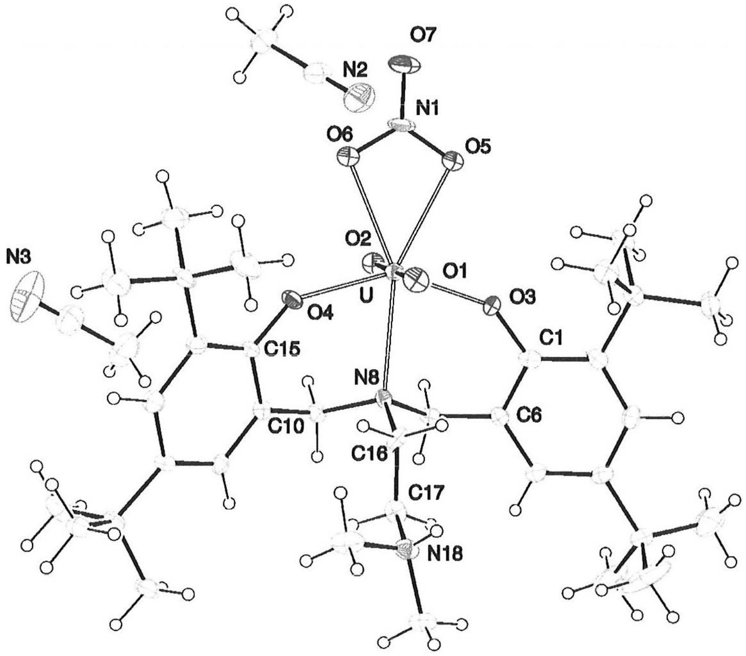


Figure 8. Perspective view of the $[UO_2(HL16)(NO_3)]\cdot 2CH_3CN$ uranyl complex (**36**) synthesized in this study.

Table 3. Selected bond lengths (Å) and angles (°) with averages and standard deviations for the complexes of the form $UO_2(H_nLm)(NO_3)$.

No	Bond lengths (Å)						
	U=O1	U=O2	U-O3	U-O4	U-O5	U-O6	U-N8
34	1.766(5)	1.796(5)	2.258(4)	2.165(5)	2.551(5)	2.518(4)	2.662(5)
36	1.788(5)	1.789(5)	2.202(5)	2.195(5)	2.546(5)	2.526(6)	2.614(7)
Average	1.785		2.205		2.535		2.638
SD	0.011		0.028	0.015	0.003	0.004	0.024

No	Bond angles (°)				
	O1=U=O2	C1-O3-U	C15-O4-U	O3-U-N8	O4-U-N8
34	174.8(2)	121.7(4)	148.3(4)	76.07(16)	71.18(16)
36	179.4(3)	142.9(5)	146.4(5)	74.61(19)	72.45(19)
Average	177.1	132.3	147.4	75.34	71.82
SD	2.30	10.6	0.95	0.73	0.64

The average of the U-O(phenolate) bond lengths of these 1:1 (U:HLm) uranyl complexes (**34** and **36**) is 2.205 Å while the average of U-O(nitrate) bond length is 2.535 Å. The average of the U-N bond lengths of these two complexes is 2.638 Å. From the preceding figures it can be seen that the U-O(nitrate) and the U-N bonds are 15 % and 20 % longer, respectively, than the U-O(phenolate) bonds, indicating that the nitrate oxygens and bridging amine nitrogens (N8) are more weakly bonded to the uranyl ion than the phenolate oxygens.

The average U-O(phenolate) bond length in these 1:1 complexes is slightly (2 %) shorter than the corresponding bond in the 1:2 complexes (2.205 Å compared to 2.252 Å) indicating that in the 1:1 complexes the phenolate oxygen atoms are more strongly bonded to the uranyl ion compared to the 1:2 complexes. The U-N bond length average (2.638 Å) of complexes **34** and **36** is close to the average bond length (2.616(7) Å) of monodentate nitrogen containing compound (pyridine) freely coordinated to uranyl as presented by Barnhart *et al.*[112], as well as close to the average U-N bond length (2.63(1) Å) in the [22]hexaphyrin(1.0.1.0.0.0) uranyl complex[23]. This indicates, along with the above-mentioned observations of other bonds, that the equatorial coordination sphere around uranium is not heavily constrained, albeit a third bonding donor (N8) forces the phenolate ligands closer to the uranyl ion.

In the $UO_2(H_nLm)(NO_3)$ compounds the oxo ligands of UO_2^{2+} ion are slightly bent as the O=U=O angles are 174.8(2)° in **34** and 179.4(3)° in **36**. Nonlinear O=U=O bonds are found generally in uranyl complexes with five nonsymmetrically bonding equatorial ligands.[I,112,114-121] The reason for the bending is presumably due to uneven π donation from the ligands to the UO_2^{2+} moiety, which results from the asymmetrical location of the donor atoms around the uranium caused by pentacoordination.[122]

As mentioned above, in these two compounds the bridging nitrogen atom (N8) between the two phenols coordinates to uranium. The ligand has still another nitrogen (ligands are diamines) to accommodate the phenolic proton, which is released in the complexation process. Thus, the existence of two nitrogens in the same ligand offers an option for the proton to choose between those nitrogens, and the choice seems to depend on the reaction stoichiometry between the uranyl ion, the ligand and the extra base. This was demonstrated in Paper V, in which it was shown that L15 formed a 1:1 (metal to ligand) complex (**34**) and a 1:2 complex (**35**) with the uranyl ion.

It is also interesting to note that complex **36** was the only one that we have been able to isolate with the uranyl ion, when the ligand contains a *tert*-butyl group at position 3 in the ligand. This shows the importance of the steric factors in the formation of these compounds.

3.2.3 Structure of the $[(UO_2)_2(H_2L1)_2(NO_3)_2]$ complex

A compound with the formula $[(UO_2)_2(H_2L1)_2(NO_3)_2]$ (**19**) was formed in the course of this study and its structure is presented in Figure 9. The formation of this dialkoxo-bridged dinuclear uranyl compound depends on the stoichiometry between the uranyl ion and the ligand. If the molar ratio of the uranyl ion to the ligand is 1:2 (or under 2 for the ligand) this dinuclear complex is obtained, but using the same molar ratio (1:2) in the presence of 2 moles of triethylamine results in the formation of complex **20**. If the molar ratio of the uranyl ion to ligand is 1:3 (or higher than 3 for the ligand) without extra base, only complex **20** is formed.

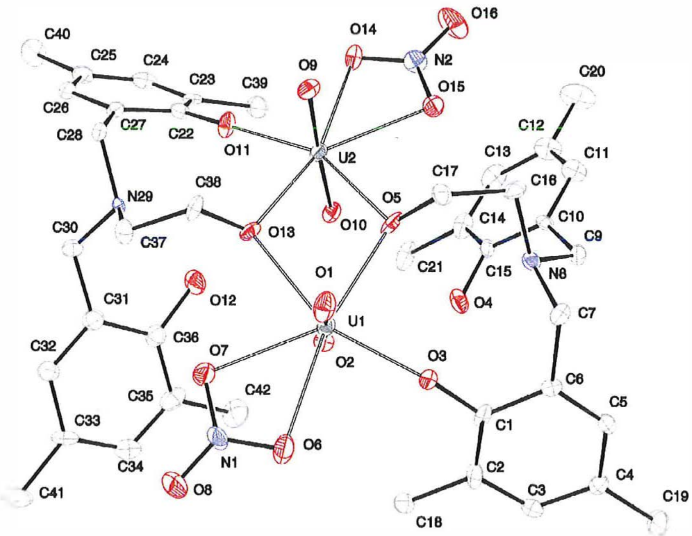


Figure 9. A perspective view of the $[(UO_2)_2(H_2L1)_2(NO_3)_2]$ uranyl complex (**19**) synthesized in this study.

Table 4. Selected bond lengths (Å) and angles (°) around both uranium centers, U1 and U2, in the complex of the form $[(UO_2)_2(H_2L1)_2(NO_3)_2]$ (**19**). The corresponding bond lengths and bond angles for both uranium centers are superimposed.

No	Bond lengths (Å)					
	U1-O1	U1-O3	U1-O5	U1-O6	U1-O7	U1-O13
19	1.786(6)	2.203(6)	2.360(6)	2.483(7)	2.499(6)	2.389(5)
	U2-O9	U2-O11	U2-O13	U2-O14	U2-O15	U2-O5
19	1.783(6)	2.184(6)	2.361(6)	2.503(6)	2.502(6)	2.381(6)

No	Bond angles (°)			
	O1-U1-O2	O5-U1-O3	O6-U1-O7	O5-U1-O13
19	177.5(3)	85.1(2)	51.1(2)	70.9(2)
	O9-U2-O10	O13-U2-O11	O15-U2-O14	O5-U2-O13
19	177.1(3)	85.7(2)	50.7(2)	71.0(2)

From the figures presented in Table 4 it can be seen that the coordination spheres around both uranium centers are very similar, as the corresponding bond lengths and bond angles have nearly the same values within the standard deviations. The largest difference in the bond lengths is between the U1-O3 (2.203(6) Å) and U2-O11 (2.184(6) Å) bonds, the difference being about 1 %.

In this structure the average of U-O(nitrate) bonds is 2.491Å, which is about 2 % shorter than the corresponding average of U-O(nitrate) bonds in complexes **34** and **36** (2.535 Å). This is probably due to the following two factors:

1) in this dinuclear complex there is only one phenolate oxygen coordinated to the uranyl, while in **34** and **36** two phenolate oxygens are coordinated,

2) the alcoholate oxygens, O5 and O13, are coordinated to both uranium centers, U1 and U2, which decreases their electron donation to one U-O(alcoholate) coordination bond (leading to the lengthening of the bonds in question compared to the U-O(phenolate) bond length, see Table 4).

Altogether, these two statements suggest that a subtle electron deficiency around the uranyl ion, compared to the cases of **34** and **36**, will arise, and this is compensated with a greater electron density donation from the nitrate oxygens leading to a shortening of the U-O(nitrate) bonds.

The U-O(phenolate) bond lengths in **19** are quite close to those in **34** and **36** (2.203 Å versus 2.205 Å, respectively). These bond lengths in part are similar to the lowest U-O(phenolate) bond length (2.202 Å) in 1:2 complexes, indicating that in the coordinated nitrate-containing complexes the phenolate oxygens are tightly bonded to the uranyl. The average of the U-O(alcoholate) bond lengths of this complex is 2.373 Å, which falls between the average of all U-O(phenolate) (2.244 Å) bond lengths and all U-O(nitrate) bond lengths (2.516 Å) presented in this study. This indicates that the order of the coordination strengths of these oxygens toward the uranium in all the complexes prepared in this study is U-O(phenolate) > U-O(alcoholate) > U-O(nitrate).

Similar to the nonsymmetrical pentacoordinated uranyl complexes **34** and **36**, in this structure (**19**) both O=U=O angles are bent (O1-U1-O2 being 177.5(3)° and O9-U2-O10 being 177.1(3)°). This observation is consistent with the explanation given in the last part of Chapter 3.2.2.

In the literature a number of reports can be found concerning aggregates, where uranyl groups lie parallel to one another as dimers, trimers, tetramers, hexamers, chains and even channels or helices (references 113, 114, 123-129 to mention a few). This aggregation of uranyl ions is achieved through bridging ligands or parts of ligands, such as complex **19**, where the alcoholic "tail" oxygen serves as a bridging atom between the two U(VI) ions.

3.2.4 General aspects of the prepared uranyl complexes

The U=O bond lengths in all the uranyl complexes prepared in this study vary from 1.766(5) Å (complex **34**) to 1.817(3) Å (complexes **20** and **23**), the average being 1.797 Å. The lengthening of the U=O bond in complexes **20** and **23**, compared to the average bond length, is due to a hydrogen bond from the bridging water molecule in **20**, and from the alcohol group from the adjacent molecule in **23**, to the uranyl oxido atom. A slight uranyl oxido bond lengthening is observed also in complex **33**, where the methanol molecule is hydrogen bonded to the uranyl oxido groups.

Generally, it can be seen that the shorter the U=O(oxido) bond in the $UO_2(H_nLm)_2$ complexes is, the longer the U-O(phenolate) bond will be and vice versa. This can be explained by the Lewis base strength of the donor atom. With the weaker donor atoms the electron density is more focused on the U=O bonds, leading to a shortening of the U=O bonds, and the electron density is decreased in the U-O(phenolate) bonds leading to their lengthening.

The observed U-O bond lengths are in agreement with those presented in the literature for similar type complexes[110-113], so that it can be said that the prepared ligands coordinate quite effectively to the uranyl ion.

In the 1:2 (U:H_nL1-L15) uranyl complexes the aliphatic nitrogen atom accepts a proton and thus it does not form a bond with the UO_2^{2+} ion. However, if the ligand is diaminobisphenol (**15** and **16**), it forms 1:1 complexes with the uranyl ion. In these complexes the proton is located on the nitrogen atom at the end of the alkyl chain. The NH^+ hydrogens form weak intramolecular hydrogen bonds to the one or two phenolate oxygens in 1:2 complexes and intermolecular H-bonds in 1:1 complexes with a phenolate oxygen in **34** and with an N atom of the acetonitrile in **36**. The Mannich bases are in general very active in forming hydrogen bonds, as shown in the literature.[130]

3.3 Extraction studies

3.3.1 Extraction studies with aminoalcoholbisphenol ligands

The decrease of the uranyl ion concentration in the water layer during the extraction studies at ambient temperature (22-23° C) with the ligands H_3L1-$H_3L9{\cdot}HCl$ is shown in Table 5.[I,II] The extraction was done without stirring the extraction system at the pH of the uranyl nitrate hexahydrate in water solution (around 3). The concentration ratio of the uranyl ion to the ligand was 1:4 during the extraction process. If the ligand was a hydrochloride, a stoichiometric amount of triethylamine was added to neutralize the hydrochloride. The concentration of the uranyl ion in the water layer of the control sample was constant during the 54 h follow-up.

Table 5. Decrease of the uranium concentration (%) in the water layer as a function of time during the extraction process with ligands H_3L1- $H_3L9{\cdot}HCl$.

Time (hours)	H_3L1	H_3L2	H_3L3	$H_3L4{\cdot}HCl$
0	100	100	100	100
1	80	73	64	66
2	62	69	42	61
3	65	-	27	59
4	62	63	23	55
6	68	62	21	52
24	38	40	10	29
30	36	39	9	26
48	29	37	9	19
54	26	37	8	17

Time (hours)	$H_3L5{\cdot}HCl$	$H_3L6{\cdot}HCl$	$H_3L7{\cdot}HCl$	$H_3L8{\cdot}HCl$	$H_3L9{\cdot}HCl$
0	100	100	100	100	100
1	54	53	45	75	62
2	30	37	31	67	61
3	23	28	25	61	47
4	21	25	20	48	49
6	12	24	17	39	44
24	8	14	9	13	10
30	8	13	9	10	8
48	7	10	7	8	6
54	7	9	7	6	6

From Table 5 it can be seen that the best extractor among these ligands was $H_3L9 \cdot HCl$, extracting 94% of uranyl ions from the water phase in 48 hours, although ligands H_3L5, H_3L7, H_3L8 were practically equally efficient.

With ligands H_3L1, H_3L3, $H_3L4 \cdot HCl$, $H_3L5 \cdot HCl$, $H_3L7 \cdot HCl$, $H_3L8 \cdot HCl$ and $H_3L9 \cdot HCl$ red or orange crystals were formed in the CH_2Cl_2 layer. Of these crystals, the ones formed with ligands H_3L1 and H_3L3 were of X-ray quality and consequently they were analyzed with single-crystal X-ray diffraction and they turned out to be complexes **20** and **22**, respectively. Especially with ligand H_3L3 the crystals were formed at the water/CH_2Cl_2 interface and after growing large enough they fell to the bottom of the CH_2Cl_2 phase. This indicates that the uranyl ion is extracted from water to the dichloromethane phase as 1:2 (U:H_nLm) complex by the ligands, and that the crystal formation is regulated by the solubility of these 1:2 (U:H_nLm) complexes into dichloromethane. However, there is also the possibility that the uranyl is extracted as a 1:1 (U:H_nLm) complex into dichloromethane and later on these form 1:2 complexes in dichloromethane. The solubility of the 1:1 complexes in organic solvents was generally quite good. This caused difficulties in their syntheses, especially if water was present.

3.3.2 Extraction studies with aminoalkylbisphenol ligands

The decrease of the uranyl ion concentration in the water layer during the extraction studies at ambient temperature (22-23° C) with the ligands $H_2L10 \cdot HCl$ - $H_2L14 \cdot HCl$ is shown in Table 6.[III] The extraction was performed as described in Chapter 3.4.1 for aminoalcoholbisphenol ligands.

Table 6. Decrease of the uranium concentration (%) in the water layer as a function of time during the extraction process with ligands $H_3L10 \cdot HCl$-$H_3L14 \cdot HCl$.

Time (hours)	$H_2L10 \cdot HCl$	$H_2L11 \cdot HCl$	$H_2L12 \cdot HCl$	$H_2L13 \cdot HCl$	$H_2L14 \cdot HCl$
0	100	100	100	100	100
3	72	72	73	64	64
24	53	54	55	49	57
48	38	33	34	32	48
120	11	7	29	14	45
480	8	5	6	5	43

From Table 6 it can be seen that the best extractors of aminoalkylbisphenol ligands were $H_2L11 \cdot HCl$ and $H_2L13 \cdot HCl$, extracting 95% of the uranyl ions of the water phase in 480 hours, although the ligands $H_2L10 \cdot HCl$ and $H_2L12 \cdot HCl$ were almost equally efficient. However, to reach the 95 % extraction level with these ligands, it took nine times longer (480 h versus 54 h) compared to the aminoalcoholbisphenol ligands. No crystals formed in the CH_2Cl_2 phase in the extraction process with these ligands, indicating that the uranyl complexes formed are more soluble in organic solvents than the uranyl complexes with aminoalcoholbisphenol ligands.

From the extraction experiments with aminoalcoholbisphenols and aminoalkylbisphenols the message is clear: the solubility kinetics controls the extraction process. If the ligand is not sufficiently polar, it does not properly dissolve in the water phase and the formation and transfer of the uranyl complexes into the organic solvent is slow.

3.3.3 Extraction studies with diaminobisphenol ligands

The extraction was performed as described in Chapter 3.4.1 for aminoalcoholbisphenol ligands and the results are presented in Table 7.[V]

Table 7. Decrease of the uranium concentration (%) in the water layer as a function of time during the extraction process with ligands H_2L15- H_2L18.

Time (hours)	H_2L15	H_2L16	H_2L17	H_2L18
0	100	100	100	100
3	81	61	81	76
24	76	80	74	79
120	72	77	72	67

As can be seen from the figures of Table 7, the diaminebisphenol ligands are not good extractors of uranyl; after 120 hours only about 30 % of uranyl ions were extracted from the water phase to dichloromethane.

3.3.4 Studies of the factors influencing the extraction process

1) The effect of the amount of the extractor solvent on the extraction rate with ligands **5**, **9**, **11** and **13** is presented in Table 8.[III]

Table 8. The decrease of the uranyl ion concentration (%) in the water layer (2 ml) in extraction experiments with two different amounts of extractor solvent (**A**: V(CH_2Cl_2) = 3 ml, **B**: V(CH_2Cl_2) = 6 ml).[III]

Time (h)	$H_3L5 \cdot HCl$ (**5**)		$H_3L9 \cdot HCl$ (**9**)		$H_2L11 \cdot HCl$ (**11**)		$H_2L13 \cdot HCl$ (**13**)	
	A	**B**	**A**	**B**	**A**	**B**	**A**	**B**
0	100	100	100	100	100	100	100	100
3	23	36	47	80	72	70	64	32
24	8	15	10	62	54	66	49	24
48	7	12	6	42	33	60	32	14

From the results presented in Table 8, after 48 h of extraction, it can be seen that increasing the amount of the solvent led to a slower extraction rate with ligands **5**, **9** and **11**; with the last two the decrease in the extraction rate was significant. With ligand **13** increasing the amount of the solvent led to a faster extraction rate. A possible explanation for the lower extraction rate with a lower ligand concentration is that the collision rate between the ligand and uranyl ions decreases. On the other hand, the amount of the complex formed may increase in CH_2Cl_2 as the amount of extractor solvent increases in cases where the CH_2Cl_2 solution is saturated with the formed uranyl complex. This phenomenon may be the reason for the increased extraction rate with the ligand **13**.

2) From the studies on the effect of stirring the extraction system during the process (published in Article III) it was observed that the stirring substantially shortened the time needed to reach an equilibrium state, but it did not improve the extraction percentage. Analogous results were also obtained as a side finding from other experiments, as e.g. the results in Table 9 show that the equilibrium is practically reached after 0.5 hours of extraction with stirring.

3) The effect of the pH of the water solution on the uranyl ion extraction percentage is presented in Table 9.

Table 9. The decrease of the uranyl ion concentration (%) in the water layer as a function of time and pH during the extraction process with stirring.[III]

Time (h)	$H_3L6{\cdot}HCl$ (**6**)			$H_2L11{\cdot}HCl$ (**11**)		
	pH 3.4	pH 4.3	pH 5.2	pH 3.4	pH 4.3	pH 5.2
0.0	100	100	100	100	100	100
0.5	21	15	10	22	10	10
1.0	20	14	8	22	10	7
3.0	20	13	8	22	11	7
6.0	20	14	8	23	12	8
24.0	23	15	8	22	12	9
48.0	20	15	7	22	13	11

From the results presented in Table 9 one can clearly see that the extraction efficiency improves as the pH is raised from 3.4 to 5.2 with both ligands **6** and **11**. This is probably due to the enhanced deprotonation of the phenolic proton of the ligand as the pH of the water solution is raised.

4) The effect of the uranyl salt used in the water phase on the extraction rates was also studied. The main points are that in water the pH of uranyl nitrate solution is ~2.9 and in uranyl acetate solution it is ~3.2. Also, acetate is a better ligand than nitrate. The results, after 48 h of extraction, are as follows:[III]

- 71 % of uranyl ions were extracted from the uranyl nitrate water solution compared to 92 % of uranyl ions extracted from the uranyl acetate water solution with ligand **1**,

- 93 % of uranyl ions were extracted from the uranyl nitrate water solution compared to 98 % of uranyl ions extracted from the uranyl acetate water solution with ligand **5**,

- 94 % of uranyl ions were extracted from the uranyl nitrate water solution compared to 97 % of uranyl ions extracted from the uranyl acetate water solution with ligand **9.**

From the above results it can be seen that all these ligands (**1**, **5**, **9**) extracted more uranyl ions from the uranyl acetate solution than from the uranyl nitrate solution. Especially with ligand **1** the improvement is remarkable. The reason for this distinction between the two uranyl salts is presumably the different effect these salts have on the pH equilibrium of the water solution.

3.3.5 Selectivity of the ligands toward uranyl ion in the presence of $Fe(aq)^{3+}$, $Co(aq)^{2+}$, $Ni(aq)^{2+}$, $Cu(aq)^{2+}$ and $Zn(aq)^{2+}$ ions

The selectivity tests were performed at pH's 1.8 and 4.2 while stirring the solutions during the extraction. The pH value of 1.8 was obtained after all the metal ions had been dissolved in water; a pH of 4.2 was obtained using acetate buffer. At pH 1.8 the following results were obtained after the 44 h of extraction using ligands **3**, **9**, **11** and **15** as representatives of the whole ligand family:[V]

- $Co(aq)^{2+}$, $Zn(aq)^{2+}$ and $Ni(aq)^{2+}$ ions were not extracted at all by any of the ligands **3**, **9**, **11** and **15**,

- the $UO_2(aq)^{2+}$ ion was extracted quite selectively by the ligands **3**, **9** and **11** (extracted 38 %, 41 % and 47 % of uranyl ions, respectively) while co-extracting only small amounts of $Fe(aq)^{3+}$ ions (10 %, 8 %, 20 % respectively) and no $Cu(aq)^{2+}$ ions at all,

- on the contrary the ligand **15** extracted 22 % of $Cu(aq)^{2+}$ ions, 20 % of $Fe(aq)^{3+}$ ions and only 10 % of $UO_2(aq)^{2+}$ ions.

The results of the selectivity test at pH 4.2, adjusted with an acetate buffer, after 3 h of extraction with ligands **3**, **9**, **11** and **15** are described in Figures 10-13.[V]

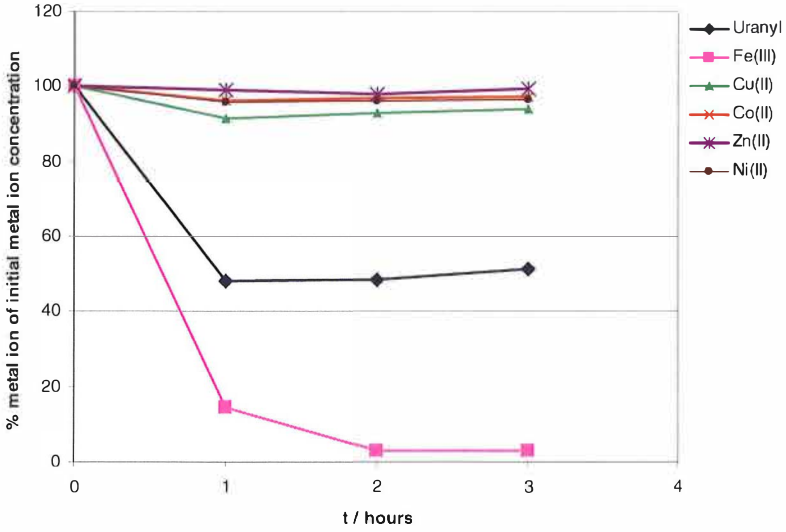


Figure 10. Decrease of the metal ion concentration (%) in the water layer as a function of time during the extraction process with ligand **3** at pH 4.2.

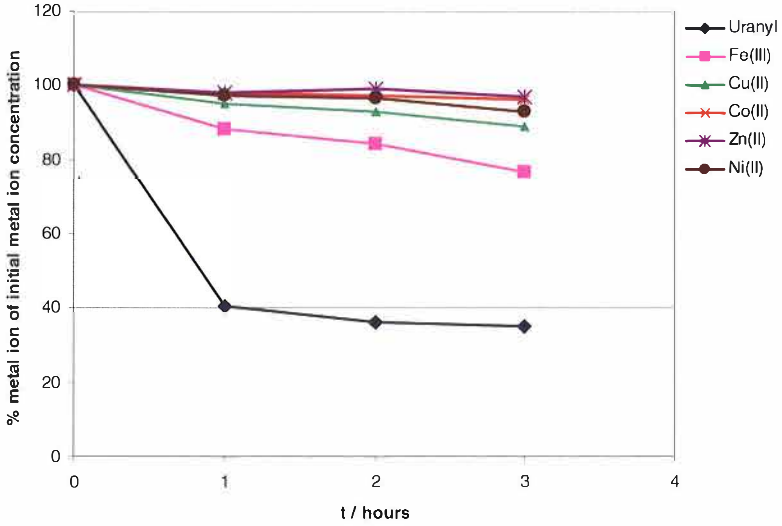


Figure 11. Decrease of the metal ion concentration (%) in the water layer as a function of time during the extraction process with ligand **9** at pH 4.2.

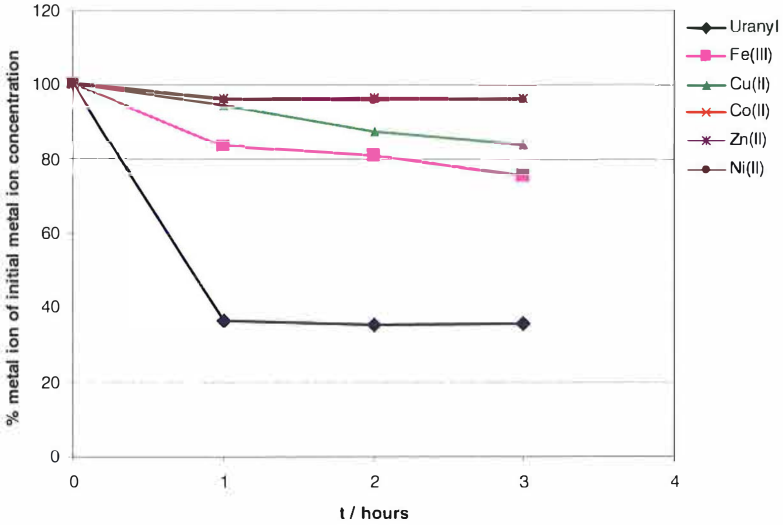


Figure 12. Decrease of the metal ion concentration (%) in the water layer as a function of time during the extraction process with ligand **11** at pH 4.2.

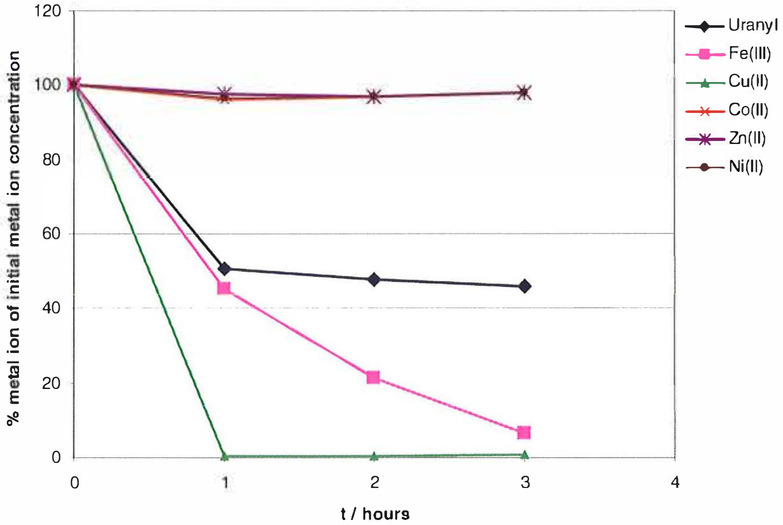


Figure 13. Decrease of the metal ion concentration (%) in the water layer as a function of time during the extraction process with ligand **15** at pH 4.2.

As can be seen from Figures 10-13 also at pH 4.2 the $Co(aq)^{2+}$, $Zn(aq)^{2+}$ and $Ni(aq)^{2+}$ ions were practically not extracted at all by any of the ligands **3**, **9**, **11** and **15**. The uranyl ion was extracted quite well by ligands **9** and **11** (65 % of the uranyl ions were extracted) with moderate amounts of Fe(aq) $^{3+}$ ions (about 25 % in both cases). The ligand **15** extracted Fe(aq)$^{3+}$ and Cu(aq)$^{2+}$ ions practically quantitatively, as did the ligand **3** for Fe(aq)$^{3+}$ ions. The simultaneous amount of uranyl ion extracted was about 50 % with both ligands.

As a conclusion of the selectivity tests for uranyl ion in the presence of several transition metal ions, one can conclude that the ligand **9** had the best selectivity for the uranyl ion over the other metal ions used in both solutions.

3.4 Uranyl aminobisphenol complexes in solutions

In order to get an idea of what happens when the prepared uranyl complexes are dissolved in polar or nonpolar solvents, and consequently how the ligands extract uranyl ions from a water solution to dichloromethane, several NMR experiments were done and the main points of the results obtained are presented below.

3.4.1 The 1 :1 (U :L) complexes

The complexes $[UO_2(HL15)(NO_3)]\cdot CH_3CN$ (**34**) and $[UO_2(HL16)(NO_3)]\cdot 2CH_3CN$ (**36**) are soluble in DMSO but they dissociate to some degree (20% for **34** and 33% for **36**), producing complexed and uncomplexed forms of the corresponding ligand. In the solid state these 1:1 complexes (**34** and **36**) have an extra proton located at nitrogen N18 (see Figure 8) and not in N8 as usual, and thus the N8 can form a bond with the uranyl ion. In a DMSO solution the structure of the complex remains similar to that in the solid state. In the free ligands formed by dissociation also the nitrogen N8 will receive a proton and now both nitrogens (N8 and N18) have a proton. These protons can form intramolecular hydrogen bonds to the phenolate oxygens in a way presented in Figure 5.

The dinuclear complex $[(UO_2)_2(H_2L1)_2(NO_3)_2]$ (**19**), which is formally 1:1 (U:L) complex, dissociated in DMSO, due to hydrolysis or autoprotonation or both, producing about 44 % of the free ligand. Originally in this complex only one phenolic oxygen (as phenolate) is coordinated to the uranyl ion, while the other phenolic oxygen of the same molecule is unprotonated and uncoordinated (see Figure 9). In a solution this singly deprotonated bisphenol can receive a proton from the solution (H_2O in DMSO) or from an other ligand. After receiving a proton the ligand dissociates from the complex. According to the ^1H NMR spectrum, the situation of complex **19** in DMSO is similar to the 1:2 (U:L) complexes in DMSO. See discussion in the next Chapter.

3.4.2 The 1 :2 (U :L) complexes

When the uranyl complex $[UO_2(H_2L5)_2]$ is dissolved in DMSO, it will break down to two components. This is shown by the ^1H NMR spectrum of complex **24** in DMSO in Figure 14.

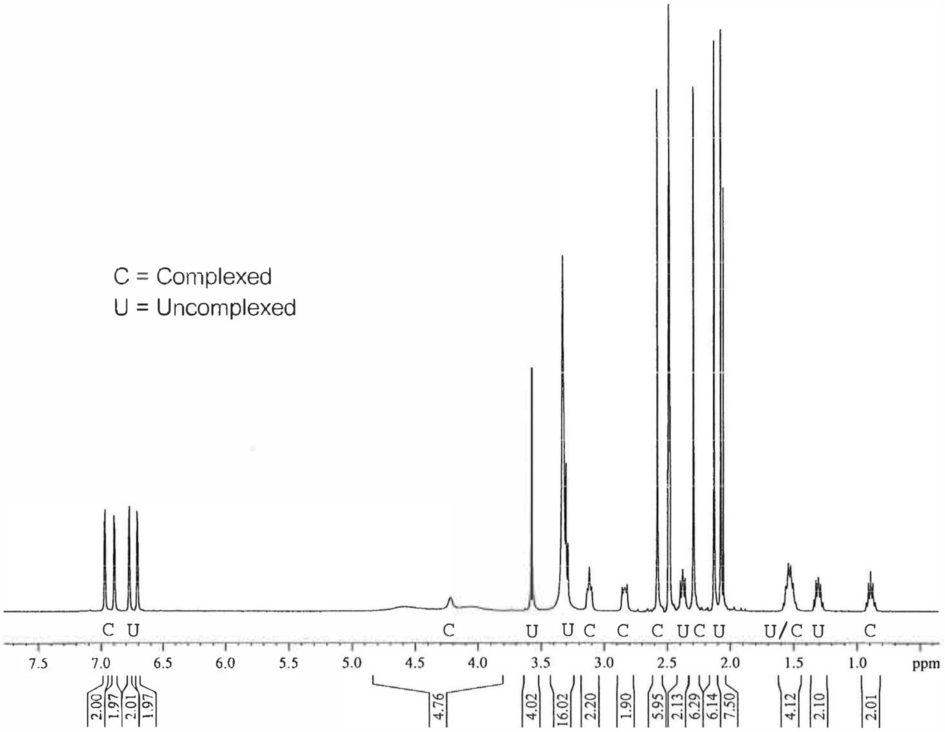


Figure 14. The ^1H NMR spectrum of complex **24** in DMSO.[II]

Two sets of peaks with equal integrals can be seen in this spectrum. These two peak sets indicate that the uranyl complex $[UO_2(H_2L5)_2]$ is dissolved in DMSO according to the reactions 1 or 2 (water is always present in DMSO solutions) or both:

$[UO_2(H_2L5)_2]$+ nDMSO →

$[UO_2(H_2L5)(DMSO)_x]^+ + H_2L5^- + (n\text{-}x)$ DMSO (1)

or

$[UO_2(H_2L5)_2]$+ H_2O + nDMSO →

$[UO_2(H_2L5)(OH)(DMSO)_y] + H_3L5 + (n\text{-}y)$ DMSO (2) where H_2L5^- in the $[UO_2(H_2L5)(DMSO)_x]$ and $[UO_2(H_2L5)(OH)(DMSO)_y]$ represents the complexed ligand (C) and the free H_2L5^- and H_3L5 the uncomplexed ligand (U). Ligands H_2L5^- and H_3L5 have almost indentical ^1H NMR spectra. The ratio of the complexed ligand (C) to the uncomplexed ligand (U) in reaction 1 (or 2) was 1:1 for the complex **24**. The complexes **19-33**, **35** and **37** behaved similarly in DMSO, with only the degree of dissociation varying slightly.

The uranyl complexes **29-33** dissolved also in non-coordinating solvents such as $CDCl_3$ but now in a molecular form, thus evoking only one peak set for the ligand (the complexed one), while some extra peaks appeared. The ^1H NMR measurements of **31** in $CDCl_3$ as a function of temperature from -60°C to +60°C with increments of 10°C was performed to verify the reason for the extra peaks. Some of these spectra are presented in Figure 15.

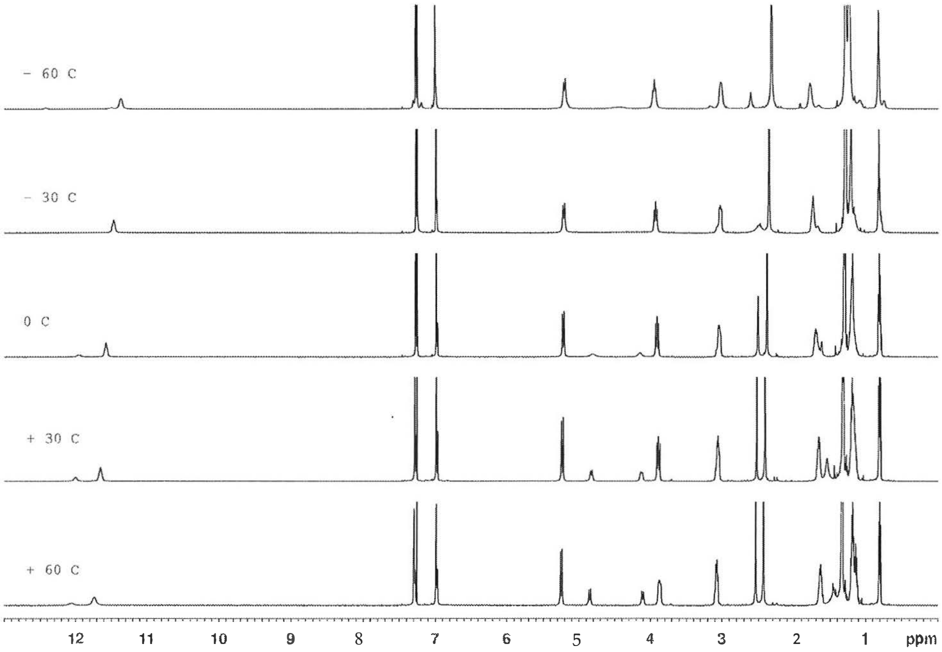


Figure 15. The ^1H NMR spectra of **31** in $CDCl_3$ as a function of temperature from -60°C to +60°C.[III]

The extra peaks are clearly seen between 4 – 5 ppm. The splitted signal pattern between 3.5 – 5.5 ppm is from the N-C*H*$_2$-aryl protons of the molecule. The splitting is due to the conformational changes of the N-CH_2-aryl joint. The ^1H signals of the aryl ring and the N-C*H*$_2$-aryl protons split in a ratio of 1:3 at 30°C for **29-31** and **33**, and in a ratio of 1:1 at 30°C for **32**. The reason for this difference is probably that in **32** the N-alkyl part of the molecule does not contain the flexible N-CH_2-alkyl joint present in the complexes **29-31** and **33**, and thus in **32** there are two conformers in equal amounts.

However, with the complex **35**, which is soluble in $CDCl_3$ and DMSO, it was realized that if the $CDCl_3$ solution of the complex $[UO_2(HL15)_2]$ (**35**) was allowed to stand at room temperature for several days, it started to hydrolyse according to the reactions 3, 4 and 5.[V]

$$[UO_2(HLm)_2] + xH_2O \rightarrow [UO_2(HLm)(H_2O)_x]^+ + HLm^- \tag{3}$$

$$[UO_2(HLm)(H_2O)_x]^+ + HLm^- \rightarrow [UO_2(HLm)(OH)(H_2O)_{x-1}] + H_2Lm \tag{4}$$

$$[UO_2(HLm)(OH)(H_2O)_{x-1}] \rightarrow [UO_2\,(OH)_2(H_2O)_{x-2}] + H_2Lm \tag{5}$$

If the NMR tube was not sealed, the hygroscopic uranyl complex absorbed water into the $CDCl_3$ solution of the complex from the atmosphere and in this case the reaction can go to an end (reaction 5). If the NMR tube was sealed, the hydrolysis reaction proceeded until all the water that the $CDCl_3$ contained prior to the sealing was consumed (reaction 4).

The hydrolysis reactions of the uranyl ion have been the subject of intensive study[54,131-135]. In this literature the solid state structures of uranyl hydroxide complexes reveal that polynuclear complexes can be formed. Two of them are presented in Figure 16.

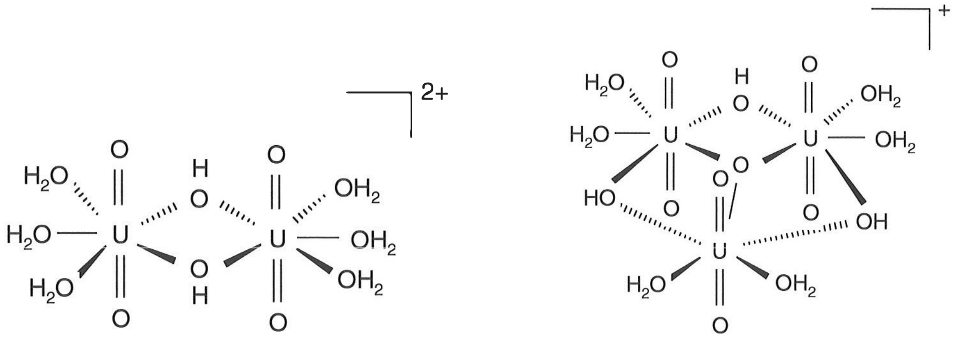


Figure 16. Examples of dimeric and trimeric solid state structures of uranyl hydroxide presented in the literature.[54,131-135]

According to these structures it is possible that the uranyl complexes prepared in this study, **19-37,** can dissolve respectively as monomeric, dimeric or even trimeric species into a DMSO solution, but it is impossible to identify the exact species in these solutions with NMR measurements. Obviously all three species exist, depending on the uranyl complex concentration. The structures of these possible polynuclear analogues of uranyl hydroxides (Fig. 16) are presented in Figure 17.

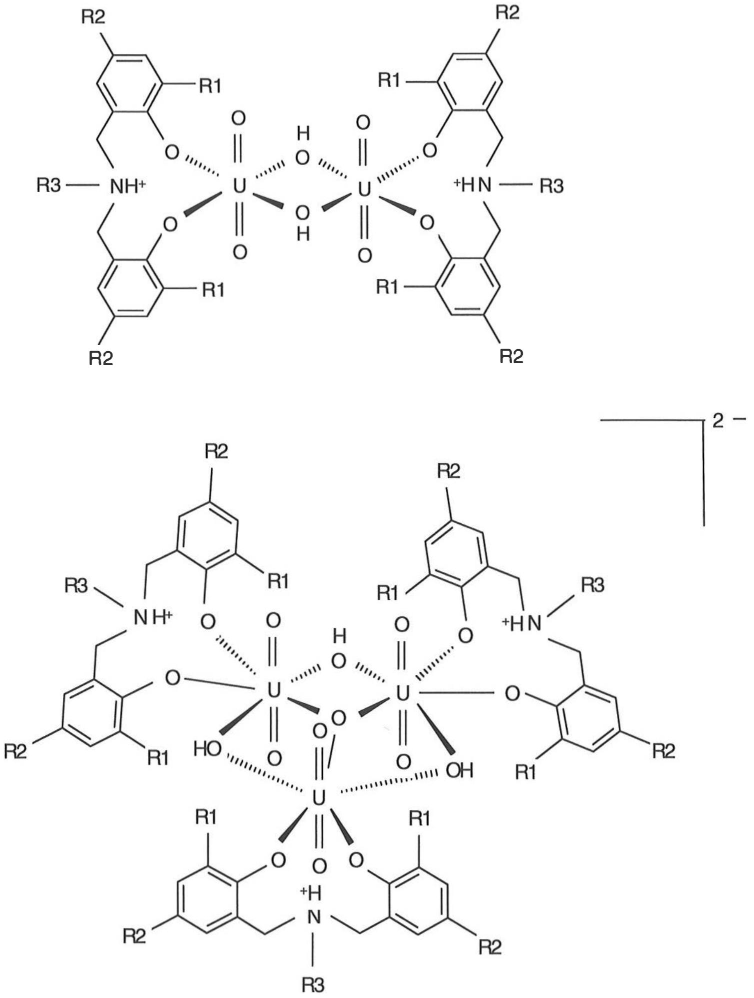


Figure 17. The possible polynuclear structures of the species formed by the uranyl complexes prepared in this study in DMSO or pyridine.

Furthermore, in polar solvents, such as DMSO and pyridine, an undefined number of solvent molecules can coordinate to the uranyl ion, which can lead to the formation of mononuclear units.

4 CONCLUSIONS

In this study 18 organic aminobisphenolate ligands, 12 of which are new ones, were synthesized with triethylamine catalysed Mannich condensation reaction. The separation of these ligands from the reaction mixture was achieved by treating them with concentrated HCl and thus changing the ligands to their hydrochlorides. The yields were generally 30-45 %. During the purification of these ligands, one of them, 6-[bis[5-*tert*-butyl-2-hydroxy-3-methylbenzyl]-amino]hexan-1-ol (**9**), crystallized as a hydrochloride. Its structure was solved and this is one of the few structural studies reported on aminoalcoholbisphenols or their hydrochlorides. Ligand **9** seems to act as a chloride ion receptor.

The prepared ligands were allowed to react with uranyl nitrate hexahydrate in acetonitrile, methanol or ethanol. The reaction was immediate, as could be seen from the change of colour of the solution from the yellow of uranyl nitrate hexahydrate to red. These solutions generally yielded red or orange crystals within a timescale of 1 h to three weeks. The uranyl complexes formed had the following structures: $[UO_2(H_nLm)_2]$, $[UO_2(H_nLm)(NO_3)]$ or $[(UO_2)_2(H_nLm)_2(NO_3)_2]$.

In the 16 structures of the type $UO_2(H_nLm)_2$, the zwitterionic (a proton at the N8-atom) ligand coordinated to the uranyl ion via two phenolate oxygens leading to an octahedral six-coordination around the uranium ion.

In the two $UO_2(H_nLm)(NO_3)$ type structures formed, the bridging nitrogen atom N8 between the two phenolic groups, also coordinated to the uranyl ion, leading to a tridentate coordination of the ligand and a pentagonal bipyramidal symmetry around the uranium ion. This phenomenon was found only with the diaminobisphenolate ligands. The reason for this is probably the two nitrogen atoms residing in the same ligand molecule. This situation provides a possibility for the proton, which becomes free in the complexation process, to attach to the "tail" nitrogen (N18), and consequently gives an opportunity for the nitrogen N8 to coordinate to the uranyl. The formation of the 1:1 or 1:2 (U:L) complexes with these diaminobisphenolate ligands was controlled by the reaction stoichiometry. In all the other bisphenolate complexes prepared in this work the proton resides at the bridging nitrogen (N8).

In the dinuclear structure $[(UO_2)_2(H_2L1)_2(NO_3)_2]$ the coordination sphere around both uranium centers was also pentagonal bipyramidal. The dinuclear structure is formed by two alkoxo bridges of the alcoholic "tail" part of the coordinated molecule.

In all the complexes prepared the coordinated atoms occupied equatorial positions perpendicular to the two axial uranyl oxido moieties. This feature, as well as the bond lengths and angles measured in the prepared uranyl complexes, were well in accordance with the data found in the literature.

A solid 1:2 (U:L) uranyl complex could not be crystallized from the solution with the di-*t*-butylphenol derivatives (ligands **16** and **18**). This may be due to steric constraints caused by the *t*-butyl group in 3 position (ortho to phenolic OH) in the phenolic ring. Steric constraints are known to control at least the formation of isomers in uranyl phenolate complexes.[136] Instead, a solid 1:1 (U:L) uranyl complex , $[UO_2(HL16)(NO_3)]\cdot 2CH_3CN$, could be crystallized.

For uranyl ion extraction from water phase to dichloromethane the aminoalcoholbisphenol and aminoalkylbisphenol ligands proved to be a good choice under the applied conditions. Generally, both the above ligand types extracted about 95 % of the uranyl ions in the water phase. The time needed to reach that extraction level without stirring the extraction solutions varied from about 30 hours to 120 hours, the aminoalcoholbisphenol ligands having the faster rates. By stirring the extraction solutions the time needed to reach the same extraction level (about 95 %) could be shortened to about two hours with both ligand groups. The presence of several uranyl(VI) ion complexes with water and nitrate in the water phase can also affect the complexation kinetics, and thus the extraction speed of the uranyl ions, as shown by Bühl *et al.*[137] The best uranyl ion extractor in applied chemical environments proved to be the aminoalcoholbisphenol ligand **9**.

Finally, a scenario for possible future studies of the prepared uranyl complexes (especially 1:1 complexes) is to study their applicability as catalysts, since there are a number of reports presenting the use of metal complexes resembling those made in this study as catalysts in various chemical reactions.[108,109,138-142]

5 REFERENCES

1. W.C. Holton, *Environmental Health Perspectives* **2005**, *113(11)*, A742.
2. M Yazzie, S.L. Gamble, E.R. Civitello, D.M. Stearns, *Chem. Res. Toxicol.* **2003**, *16*, 524.
3. M. Sawicki, J-M. Siaugue, C. Jacopin, C. Moulin, T. Bailly, R. Burgada, S. Meunier, P. Baret, J-L. Pierre, F. Taran, *Chem. Eur. J.* **2005**, *11*, 3689.
4. A.E.V. Gorden, J. Xu, K.N. Raymond, P. Durbin, *Chem. Rev.* **2003**, *103*, 4207.
5. J. Xu, K.N. Raymond, *Inorg. Chem.* **1999**, *38*, 308.
6. M. Baaden, R. Schurhammer, G. Wipff, *J. Phys. Chem. B* **2002**, *106*, 434.
7. A. Naylor, P.D. Wilson in Handbook of Solvent Extraction, T.C. Lo, M.H.I. Baird, C. Hanson (Eds.), John Wiley & Sons, New York, 1983, p. 783.
8. J.L. Sessler, A.E. Vivian, D. Seidel, A.K. Burrell, M. Hoehner, T.D. Mody, A. Gebauer, S.J. Weghorn, V. Lynch, *Coord. Chem. Rev.* **2001**, *216-217*, 411.
9. S. Shinkai, H. Koreishi, K. Ueda, T. Arimura, O. Manabe, *J. Am. Chem. Soc.* **1987**, *109*, 6371.
10. H. Singh, R. Vijayalakshmi, S.L. Mishra, C.K. Gupta, *Hydrometallurgy* **2001**, *59*, 69.
11. H.J. Schenk, L. Astheimer, E.G. Witte, K. Schwochau, *Sep. Sci. Technol.* **1982**, *17*, 1293.
12. J.P. Scanlan, *J. Inorg. Nucl. Chem.* **1977**, *39*, 635.
13. P.H. Koske, K. Ohlrogge, K.V. Peinemann, *Sep. Sci. Technol.* **1988**, *23*, 1929.
14. M. Carrière, L. Avoscan, R. Collins, F. Carrot, H. Khodja, E. Ansoborlo, B. Gouget, *Chem. Res. Toxicol.* **2004**, *17*, 446.
15. P.D. Beer, G.D. Brindley, O.D. Fox, A. Grieve, M.I. Ogden, F. Szemes, M.G.B. Drew, *J. Chem. Soc., Dalton Trans.* **2002**, 3101.
16. P. Thuéry, M. Nierlich, J. Vicens, B. Masci, H. Takemura, *Eur. J. Inorg. Chem.* **2001**, 637.
17. P. Thuéry, M. Nierlich, J. Vicens, H. Takemura, *Polyhedron* **2001**, *20*, 3183.
18. C. Dinse, N. Baglan, C. Cossonnet, J.F. Le Du, Z. Asfari, J. Vicens, *J. Alloys Compd.* **1998**, *271-273*, 778.
19. C. Drouza, V. Gramlich, M.P. Sigalas, I. Pashalidis, A.D. Keramidas, *Inorg. Chem.* **2004**, *43*, 8336.
20. N. Koshino, M. Harada, Y. Morita, T. Kiikuchi, Y. Ikeda, *Progr. Nucl. Energy* **2005**, *47*, 406.
21. L. Deshayes, N. Keller, M. Lance, A. Navaza, M. Nierlich, J. Vigner, *Polyhedron* **1994**, *13*, 1725.
22. R.D. Rogers, A.H. Bond, W.G. Hipple, A.N. Rollins, R.F. Henry, *Inorg. Chem.* **1991**, *30*, 2671.
23. J.L. Sessler, D. Seidel, A.E. Vivian, V. Lynch, B.L. Scott, D.W. Keogh, *Angew. Chem., Int. Ed.* **2001**, *40*, 591.
24. P. Thuéry, M. Nierlich, Z. Asfari, J. Vicens, *J. Chem. Soc., Dalton Trans.* **2000**, 1297.

25. P. Thuéry, Z. Asfari, M. Nierlich, J. Vicens, B. Masci, *Polyhedron* **2002**, *21*, 1949.
26. P.D. Wilson (Ed.), Nuclear Fuel Cycle: From Ore to Waste, Oxford Science Publications, Oxford, 1996, p. 373.
27. I. Korobkov, S. Gambarotta, G.P.A. Yap, *Organometallics* **2001**, *20*, 2552.
28. I. Korobkov, S. Gambarotta, G.P.A. Yap, L. Thompson, P.J. Hay, *Organometallics* **2001**, *20*, 5440.
29. L. Salmon, P. Thuéry, M. Ephritikhine, *Polyhedron* **2006**, *25*, 1537.
30. L. Salmon, P. Thuéry, S. Miyamoto, T. Yamato, M. Ephritikhine, *Polyhedron* **2006**, *25*, 2439.
31. J. Old, A.A. Danopoulos, S. Winston, *New J. Chem.* **2003**, *27*, 672.
32. P.C. Leverd, M. Nierlich, *Eur. J. Inorg. Chem.* **2000**, 1733.
33. D.E. Hobart, *Proc. Robert A. Welch Found. Conf. Chem. Res.* **1990**, *34*, 379.
34. W.R. Wadt, *J. Am. Chem. Soc.* **1981**, *103*, 6053.
35. R.G. Denning, *J. Phys. Chem. A* **2007**, *111*, 4125.
36. I.A.C. Infante, Computational Studies in Actinide Chemistry, Academic dissertation, Amsterdam, 2006, p. 52.
37. R.E. Connick, Z.Z. Hugus Jr., *J. Am. Chem. Soc.* **1952**, *74*, 6012.
38. M. Ephritikhine, *Dalton Trans.* **2006**, 2501.
39. M.J. Sarsfield, M. Helliwell, J. Raftery, *Inorg. Chem.* **2004**, *43*, 3170.
40. K.A. Venkatesan, V. Sukumaran, M.P. Antony, P.R.V. Rao, *J. Radioanalytical and Nucl. Chem.* **2004**, *260*, 443.
41. G. Schreckenbach, P.J. Hay, R.L. Martin, *Inorg. Chem.* **1998**, *37*, 4442.
42. P.B. Duval, C.J. Burns, W.E. Buschmann, D.L. Clark, D.E. Morris, B.L. Scott, *Inorg. Chem.* **2001**, *40*, 5491.
43. D.L. Clark, S.D. Conradson, R.J. Donahoe, D.W. Keogh, D.E. Morris, P.D. Palmer, R.D. Rogers, C.D. Tait, *Inorg. Chem.* **1999**, *38*, 1456.
44. G.H. John, I. May, M.J. Sarsfield, H.M. Steele, D. Collison, M. Helliwell, J.D. McKinney, *Dalton Trans.* **2004**, 734.
45. J-C. Berthet, M. Nierlich, M. Ephritikhine, *Chem. Commun.* **2003**, 1660.
46. A.R. de Aquino, G. Bombieri, P.C. Isolani, G. Vicentini, J. Zukerman-Schpegtor, *Inorg. Chim. Acta* **2000**, *306*, 102.
47. A.F. Wells, Structural Inorganic Chemistry, Clarendon Press, Oxford, 1995, chap. 28.
48. K.W. Bagnall in Comprehensive Coordination Chemistry, G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), Pergamon, Oxford, 1987, Vol. 3, chap. 40.
49. S. Sitran, D. Fregona, U. Casellato, P.A. Vigato, R. Graziani, G. Faraglia, *Inorg. Chim. Acta* **1987**, *132*, 279.
50. M.J. Sarsfield, M. Helliwell, D. Collison, *Chem. Commun.* **2002**, 2264.
51. N.W. Alcock, D.J. Flanders, D. Brown, *J. Chem. Soc., Dalton Trans.* **1985**, 1001.
52. N.W. Alcock, D.J. Flanders, M. Pennington, D. Brown, *Acta Cryst.* **1988**, *C44*, 247.
53. G. Paolucci, G. Marangoni, G. Bandoli, D.A. Clemente, *J. Chem. Soc., Dalton Trans.* **1979**, 459.

54. A. Navaza, F. Villain, P. Charpin, *Polyhedron* **1984**, *3*, 143.
55. N.C. Jayadevan, K.D. Singh Mudher, D.M. Chackraburtty, *Acta Cryst.* **1975**, *B31*, 2277.
56. T.S. Franczyk, K.R. Czerwinski, K.N. Raymond, *J. Am. Chem. Soc.* **1992**, *114*, 8138.
57. G.R. Choppin, L.F. Rao, *Radiochim. Acta* **1984**, *37*, 143.
58. G.R. Choppin, *Radiochim. Acta* **1983**, *32*, 43.
59. G.R. Choppin, P.J. Unrein in Transplutonium Elements, W. Muller, R. Linder (Eds.), North-Holland, Amsterdam, 1976, p. 97.
60. N.N. Greenwood, A. Earnshaw, Chemisty of the Elements, Pergamon Press, Exeter, 1984, pp. 1477-1479.
61. C.L. Christ, J.R. Clark, H.T. Evans Jr., *Science* **1955**, *121*, 472.
62. D. Apelman, *Bull. Geol. Soc. Am.* **1956**, *67*, 1666.
63. A. Coda, A. Della Giusta, V. Tazzoli, *Acta Cryst.* **1981**, *B37*, 1496.
64. D. Langmuir, *Geochimica et Cosmochimica Acta* **1978**, *42*, 547.
65. M. Gascoyne, Geochemistry of the actinides and their daughters, in Uranium-Series Disequilibrium: Applications to Earth, Marine and Environmental Sciences, M. Ivanovich, R.S. Harmon (Eds.), Clarendon Press, Oxford, p. 910.
66. J.D. Van Horn, H. Huang, *Coord. Chem. Rev.* **2006**, *250*, 765.
67. M.P. Wilkerson, C.J. Burns, H.J. Dewey, J.M. Martin, D.E. Morris, R.T. Paine, B.L. Scott, *Inorg. Chem.* **2000**, *39*, 5277.
68. R. Cea-Olivares, G. Canseco-Melchor, M.M. Moya-Cabrera, V. García-Montalvo, J.G. Alvarado-Rodríguez, R.A. Toscano, *Inorg. Chem. Commun.* **2005**, *8*, 205.
69. D.H. Busch, *Chem. Rev.* **1993**, *93*, 847.
70. R.D. Hancock, A.E. Martell, *Chem. Rev.* **1989**, *89*, 1875.
71. L. Karmazin, M. Mazzanti, C. Gateau, C. Hill, J. Pécaut, *Chem. Commun.* **2002**, 2892.
72. Y. Ikeda, E. Wada, M. Harada, T. Chikazawa, T. Kikuchi, H. Mineo, Y. Morita, M. Nogami, K. Suzuki, *J. Alloys Compd.* **2004**, *374*, 420.
73. W.J. Burke, M.J. Kolbezen, C.W. Stephens, *J. Am. Chem. Soc.* **1952**, *74*, 3601.
74. M. Arend, B. Westermann, N. Risch, *Angew. Chem. Int. Ed.* **1998**, *37*, 1044.
75. W. Notz, F. Tanaka, S. Watanabe, N.S. Chowdari, J.M. Turner, R. Thayumanavan, C.F. Barbas III, *J. Org. Chem.* **2003**, *68*, 9624.
76. I.H.S. Estevam, M.F. da Silva, L.W. Bieber, *Tetrahedron Letters* **2005**, *46,* 7601.
77. E.Y. Tshuva, I. Goldberg, M. Kol, *J. Am. Chem. Soc.* **2000**, *122*, 10706.
78. E.Y. Tshuva, I. Goldberg, M. Kol, Z. Goldschmidt, *Organometallics* **2001**, *20*, 3017.
79. D. Yuan, M. Zhang, Z. Pan, P. Ma, *Acta Cryst.* **2004**, *E60*, o1321.
80. W.J. Burke, R.P. Smith, C. Weatherbee, *J. Am. Chem. Soc.* **1952**, *74*, 602.
81. W.O. Siegel, M.S. Chatta, Eur. Pat. Appl. 276073, 1988.
82. A. Laobuthee, S. Chirachanchai, H Ishida, K. Tashiro, *J. Am. Chem. Soc.* **2001**, *123*, 9947.
83. W.J. Burke, J.L. Bishop, E.L. Mortensen Glennie, W.N. Bauer Jr., *J. Org. Chem.* **1965**, *30*, 3423.

84. J. Dunkers, H. Ishida, *Spectrochim. Acta* **1995**, *51A*, 855.
85. H. Ishida, C.M. Krus, *Macromolecules* **1998**, *31*, 2409.
86. Z. Otwinowski, W. Minor in Methods in Enzymology: Part A, vol. 276, C.W. Carter, R.M. Sweet (Eds.), Academic Press, London, 1997, pp. 307-326.
87. G.M. Sheldrick, SHELX-97 (Release 97-2): A Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1998.
88. G.M. Sheldrick, SADABS, University of Göttingen, Germany, 2002.
89. G.M. Sheldrick, SHELXS-97 and SHELXL-97: Programs for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
90. A. Altomare, M. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Pilodori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435.
91. L.J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.
92. D.W. Boomer, M.J. Powell, *Anal. Chem.* **1987**, *59*, 2810.
93. P.K. Mohapatra, V.K. Manchanda, *Talanta* **1998**, *47*, 1271.
94. V.K. Jain, S.G. Pillai, R.A. Pandya, Y.K. Agrawal, P.S. Shrivastav, *Talanta* **2005**, *65*, 466.
95. P. Metilda, J.M. Gladis, T.P. Rao, *Anal. Chim. Acta* **2004**, *512*, 63.
96. M.S. El Sayed, *Hydrometallurgy* **2003**, *68*, 51.
97. M.S. El-Shahawi, A.M. Othman, H.M. Nassef, M.A. Abdel-Fadeel, *Anal. Chim. Acta* **2005**, *536*, 227.
98. V. Amendola, M. Bonnizzoni, D. Esteban-Gómez, L. Fabbrizzi, M. Licchelli, F. Sancenón, A. Taglietti, *Coord. Chem. Rev.* **2006**, *250*, 1451.
99. A. Bianchi, K. Bowman-James, E. García-España (Eds.), Supramolecular Chemistry of Anions, Wiley-VCH, New York, Chichester, 1997.
100. D.P. Cormode, S.S. Murray, A.R. Cowley, P.D. Beer, *Dalton Trans.* **2006**, 5135.
101. P.A. Gale, R. Quesada, *Coord. Chem. Rev.* **2006**, *250*, 3219.
102. T.J. Jentsch, V. Stein, F. Weinreich, A.A. Zdebik, *Physiol. Rev.* **2002**, *82*, 503.
103. S. Goetz, P.E. Kruger, *Dalton Trans.* **2006**, 1277.
104. K. Wichmann, B. Antonioli, T. Söhnel, M. Wenzel, K. Gloe, K. Gloe, J.R. Price, L.F. Lindoy, A.J. Blake, M. Schröder, *Coord. Chem. Rev.* **2006**, *250*, 2987.
105. P.A. Gale, J. Garric, M.E. Light, B.A. McNally, B.D. Smith, *Chem. Commun.* **2007**, 1736.
106. T. Steiner, *Angew. Chem. Int. Ed.* **2002**, *41*, 48.
107. G.R. Desiraju, T. Steiner, The Weak Hydrogen Bond in Structural Chemistry and Biology, Oxford University Press, New York, 1999.
108. M. Velusamy, M. Palaniandavar, R.S. Gopalan, G.U. Kulkarni, *Inorg. Chem.* **2003**, *42*, 8283.
109. C. Lorber, F. Wolff, R. Choukroun, L. Vendier, *Eur. J. Inorg. Chem.* **2005**, 2850.
110. J. Harrowfield, *Gazz. Chim. Ital.* **1997**, *127*, 663.
111. P. Thuéry, M. Nierlich, J. Harrowfield, J. Vicens (Eds.), Calixarenes 2001, Kluwert Academic Publishers, Dordrecht, 2001.
112. D.M. Barnhart, C.J. Burns, N.N Sauer, J.G. Watkin, *Inorg. Chem.* **1995**, *34*, 4079.

113. D.J. Evans, P.C. Junk, M.K. Smith, *Polyhedron* **2002**, *21*, 2421.
114. J.H. Burns, *Inorg. Chem.* **1983**, *22*, 1174.
115. B. Kanellakopulos, E. Dornberger, R. Maier, B. Nuber, H.-G. Stammler, M. Ziegler, Z. *Anorg. Allg. Chem.* **1993**, *619*, 593.
116. G.A. Doyle, D.M.L. Goodgame, A. Sinden, D.J. Williams, *J. Chem. Soc., Chem. Commun.* **1993**, 1170.
117. A.R. de Aquino, P.C. Isolani, J. Zukerman-Schpector, L.B. Zinner, G. Vicentini, *J. Alloys Compd.* **2001**, *323-324*, 18.
118. P. Thuéry, M. Nierlich, B. Masci, *Acta Cryst.* **2002**, *C58*, m84.
119. B. Masci, P. Thuéry, *Acta Cryst.* **2005**, *E61*, m2278.
120. P. Thuéry, H. Takemura, *Acta Cryst.* **2003**, *C59*, m384.
121. M.S. Bharara, K. Strawbridge, J.Z. Vilsek, T.H. Bray, A.E.V. Gorden, *Inorg. Chem.* **2007**, *46*, 8309.
122. J.L. Sonnenberg, P.J. Hay, R.L. Martin, B.E. Bursten, *Inorg. Chem.* **2005**, *44*, 2255.
123. P.V. Rao, C.P. Rao, A. Sreedhara, E.K. Wegelius, K. Rissanen, E. Kolehmainen, *J. Chem. Soc., Dalton Trans.* **2000**, 1213.
124. P.D. Beer, M.G.B. Drew, D. Hesek, M. Kan, G. Nicholson, P. Schmitt, P.D. Sheen, G. Williams, *J. Chem. Soc., Dalton Trans.* **1998**, 2783.
125. P.G. Allen, J.J. Bucher, D.L. Clark, N.M. Edelstein, S.A. Ekberg, J.W. Gohdes, E.A. Hudson, N. Kaltsoyannis, W.W. Lukens, M.P. Neu, P.D. Palmer, T. Reich, D.K. Shuh, C.D. Tait, B.D. Zwick, *Inorg. Chem.* **1995**, *34*, 4797.
126. U. Turpeinen, R. Hämäläinen, I. Mutikainen, O. Orama, *Acta Cryst.* **1996**, *C52*, 1169.
127. P. Charpin, M. Lance, M. Nierlich, D. Vigner, J. Livet, C. Musikas, *Acta Cryst.* **1986**, *C42*, 1691.
128. D. Grohol, F. Gingl, A. Clearfield, *Inorg. Chem.* **1999**, *38*, 751.
129. M.A.G. Aranda, A. Cabeza, S. Bruque, D.M. Poojary, A. Clearfield, *Inorg. Chem.* **1998**, *37*, 1827.
130. B. Brzezinski, H. Maciejewska, G. Zundel, R. Krämer, *J. Phys. Chem.* **1990**, *94*, 528.
131. D.A. Palmer, C. Nguyen-Trung, *J. Solution Chem.* **1995**, *24 (12)*, 1281.
132. V. Eliet, G. Bidoglio, N. Omenetto, L. Parma, I. Grenthe, *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 2275.
133. I. Grenthe, J. Fuger, R.J.M. Konings, R.J. Lemire, A.B. Muller, C. Nguyen-Trung, H. Wanner, Chemical Thermodynamics of Uranium, Elsevier Science B. V., New York, 1992, Vol. 1.
134. M. Aberg, *Acta Chem. Scand., Ser. A* **1978**, *A32*, 101.
135. R.D. Rogers, L.K. Kurihara, M.M. Benning, *J. Inclusion Phenom.* **1987**, *5*, 645.
136. M.P. Wilkerson, C.J. Burns, D.E. Morris, R.T. Paine, B.L. Scott, *Inorg. Chem.* **2002**, *41*, 3110.
137. M. Bühl, R. Diss, G. Wipff, *Inorg. Chem.* **2007**, *46*, 5196.
138. S. Gendler, S. Groysman, Z. Goldschmidt, M. Shuster, M. Kol, *J. Polym. Sci. Part A: Polym. Chem* **2006**, *44*, 1136.

139. A.J. Chmura, M.G. Davidson, M.D. Jones, M.D. Lunn, M.F. Mahon, *Dalton Trans.* **2006**, 887.
140. Y. Kim, J.G. Verkade, *Organometallics* **2002**, *21*, 2395.
141. F.M. Kerton, A.C. Whitwood, C.E. Willans, *Dalton Trans.* **2004**, 2237.
142. Y. Huang, F. Yang, C. Zhu, *J. Am. Chem. Soc.* **2005**, *127*, 16386.

PAPER I

https://doi.org/10.1016/j.poly.2005.08.044

Reprinted from *Polyhedron*, **25**, H. Sopo, J. Sviili, A. Valkonen, R. Sillanpää, Uranyl ion complexes with aminoalcoholbis(phenolate) [O, N, O, O´] donor ligands, 1223-1232, Copyright (2006), reprinted with kind permission by Elsevier.

PAPER II

https://doi.org/10.1016/j.poly.2006.08.006

Reprinted from *Polyhedron*, **26**, H. Sopo, A. Väisänen, R. Sillanpää, Uranyl ion complexes with long chain aminoalcoholbis(phenolate) [O, N, O, O´] donor ligands, 184-196, Copyright (2007), reprinted with kind permission by Elsevier.

PAPER III

https://doi.org/10.1016/j.poly.2007.03.032

Reprinted from *Polyhedron*, **26**, H. Sopo, K. Goljahanpoor, R. Sillanpää, Aminoalkylbis(phenolate) [O, N, O] donor ligands for uranyl(VI) ion coordination: Syntheses, structures and extraction studies, 3397-3408, Copyright (2007), reprinted with kind permission by Elsevier.

PAPER IV

https://doi.org/10.1107/S0108270107023797

Reprinted from *Acta Crystallographica Section C* **63**, H. Sopo, R. Sillanpää, Bis(5-*tert*-butyl-2-hydroxy-3-methyl-benzyl)(6-hydroxyhexyl)ammonium chloride monohydrate, an anion receptor complex, o386-o388, Copyright (2007), reprinted with kind permission by International Union of Crystallography.

PAPER V

https://doi.org/10.1016/j.poly.2007.08.047

Reprinted from *Polyhedron*, **27**, H. Sopo, A. Lehtonen, R. Sillanpää, Uranyl(VI) complexes of [*O*, *N*, *O*, *N*′]-type diaminobis(phenolate) ligands: Syntheses, structures and extraction studies, 95-104, Copyright (2008), reprinted with kind permission by Elsevier.