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Experimental and Computational Study of Unique Tetranuclear μ_3 -Chloride and μ -phenoxo/chloro bridged Defective-Dicubane Cobalt(II) clusters

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Two tetranuclear Co(II) clusters $[\text{Co}_4(\text{L})_2(\mu_3\text{-Cl})_2\text{Cl}_2]$ have been prepared using multidentate diaminobisphenolate ligands. The solid state structures of the complexes were determined by single crystal X-ray diffraction. The geometry of the core can be defined as two vertex deficient dicubane (pseudo dicubane). In the central unit, the cobalt(II) cations are bound together by phenoxide oxygens (outer bridges) and chloride anions (inner bridges) previously unprecedented in this type of cobalt clusters. The magnetic proper-

ties were studied by both experimental and computational methods. By using the combination of preceding techniques, we were able to determine the nature and strength of the intramolecular magnetic exchange coupling mediated by the different bridging fragments between the crystallographically differently cobalt(II) cations.

Introduction

During past decades, much attention has been devoted into design, preparation and study of polynuclear 3d complexes, not only due to their interesting catalytic, optical, photochemical, electronic, biological, absorption and magnetic properties,¹ but also because of their aesthetic and fascinating structures.² With regard to the magnetic properties, there has been great interest in understanding the structural, electronic and stereochemical factors governing the magnetic exchange coupling between metal ions transmitted through bridging ligands.³ This valuable information has allowed establishment of magneto-structural correlations, which, together with a judicious choice of ligands and metal ions, as well as a good knowledge of the self-assembly process of these building blocks leading to the final architecture, enable the design of polynuclear coordination compounds with desired magnetic properties. Among molecular magnetic materials based on polynuclear coordination compounds, single-molecule magnets, SMMs⁴ (systems exhibiting slow relaxation of the magnetization and magnetic hysteresis below the so-called blocking temperature, T_B), are being subject of an intense research activity, due to their intriguing physical properties and outstanding potential technological applications.⁵

Scheme 1. a) Tetranuclear core and common bridging groups of defective dicubane-like Co(II)-clusters and b) schematic presentation of the ligands H₂L1 and H₂L2.

The two main prerequisites to observe SMM behaviour are high spin ground state and, fundamentally, magnetic anisotropy. In view of this, high spin penta- and hexacoordinated cobalt(II) ions, which have large intrinsic magnetic anisotropy, are good candidates for anisotropic clusters with SMM behavior.⁶ Co^{II} aggregates with a variety of structural types and magnetic properties can be prepared from the self-assembly of polydentate ligands containing alcohol or phenol groups, which after deprotonation are able to bridge two cobalt ions, and ancillary neutral or anionic ligands, which either act as capping or bridging ligands.⁷ In this regard, aminobisphenol ligands are excellent building blocks for preparing polynuclear metal complexes since the versatility of these compounds provides great assortment of tools for modifying the structural and electronic environments around metal centers.⁸ The substituents and donor atoms in the aromatic rings and in the side chain attached to the central nitrogen can be varied extensively thus enabling a variety of coordination modes for the metal cations.

Herein, we report the synthesis, molecular structures and thorough experimental and computational magnetic studies of two new defective-dicubane tetranuclear Co(II)-complexes, $[\text{Co}_4(\text{L1})_2(\mu_3\text{-Cl})_2\text{Cl}_2] \cdot 2\text{CH}_3\text{CN}$ (**1**) and $[\text{Co}_4(\text{L2})_2(\mu_3\text{-Cl})_2\text{Cl}_2] \cdot 4\text{CH}_3\text{CN}$ (**2**) with novel diaminobisphenolate ligands (Scheme 1). It is worth mentioning that, among others,

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amino/alcohol, amino/acids, amino/phenol/alcohol, pyridine/alcoholphenol, aza-macrocyclic/acid, dipyritylketone, bidentate α -diimines and phenol/alcohol Schiff base ligands have been used to prepare “defective” dicubane-like tetranuclear Co(II) and $\text{Co}^{\text{II}}_2\text{Co}^{\text{III}}_2$ clusters. All these complexes possess a μ_3 -bridging (X = hydroxide, alkoxide, phenoxide or azide group)⁷ but to the best of our knowledge in only one case μ_3 -halide bridges have been reported.^{7m}

Results and Discussion

Complexes **1** and **2** were synthesized in good yields by dissolving two equivalents of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ into acetonitrile and adding one equivalent of the corresponding ligand ($\text{H}_2\text{L1}$ or $\text{H}_2\text{L2}$ respectively) to the solution. After addition of the ligand, triethylamine was added to neutralize the formed hydrochloric acid and X-ray quality crystal precipitated from the solutions during few days at room temperature or in a fridge. The effects of different aryl substituents were clearly visible already in preparation of the complexes, since the crystallization process of **1** with ligand $\text{H}_2\text{L1}$ (allyl substituents) was considerably slower compared to **2** with $\text{H}_2\text{L2}$ (methyl substituents) which crystallized overnight.

Crystal Structures. Complexes **1** and **2** crystallize in the orthorhombic (*Pbca*) and triclinic (*P*-1) space groups, respectively. Both **1** and **2** exhibit centrosymmetric structures in which the asymmetric unit is composed of two cobalt(II) cations, one μ_3 -bridging chloride ion and one ligand (the asymmetric unit of **2** contains two distinct molecules, **2a** and **2b**).

Figure 1. Top, molecular structure of **1**, symmetry operation: $\bar{c} = 1-x, -y, 1-z$. Bottom, molecular structure of **2** (only one of two similar molecules in the asymmetric unit is presented). Symmetry operation: $\bar{c} = -x, -y, 1-z$. Thermal ellipsoids have been drawn at 30% probability and the CH-hydrogens and solvent molecules are omitted for clarity.

The molecular structures of **1** and **2** are presented in Figure 1. The tetranuclear complexes are formed from two $[\text{Co}_2(\text{L})\text{Cl}_2]$ units which are bound together with two chloride and two phenoxide bridges. The central tetranuclear core in both complexes can be described as a pseudo-dicubane unit with two missing vertices which consists of four cobalt(II) ions with two μ_3 -bridged chloride ions (inner bridges) and four μ_2 -bridged phenolate oxygen atoms (outer bridges). Rest of the coordination sites are occupied by terminal chloride ions, amine nitrogens or by methoxy oxygen atoms from the aromatic rings. The central cobalt(II)-cations have slightly distorted octahedral coordination environment whereas the outermost ions have more evidently distorted square based pyramidal coordination. The deformation from square pyramidal to trigonal bipyramidal coordination can be estimated by the Addison's method ($\tau = 1$ for the trigonal bipyramidal and 0 for square pyramidal coordination).⁹ The τ value calculated for the centrosymmetric **1** is 0.16 while the values for **2** (two molecules in the asymmetric unit) are 0.30 and 0.37. The difference in τ values indicates, that with the ligand $\text{H}_2\text{L2}$, the geometry of five-coordinated Co(II) cations is considerably more distorted from the perfect square pyramidal polyhedron.

Table 1. Selected geometrical parameters of **1**·2CH₃CN and **2**·4CH₃CN.

	1 ·2CH ₃ CN	2 ·4CH ₃ CN (a) ^a	2 ·4CH ₃ CN (b) ^a
Co1-Co2	3.3037(4)	3.2733(5)	3.3322(5)
Co1-Co2'	3.2866(4)	3.2950(5)	3.2715(5)
Co1-Co1'	3.6827(4)	3.7653(5)	3.7944(5)
Co1-Cl1	2.4429(7)	2.4535(6)	2.4643(9)
Co1-Cl1'	2.6635(7)	2.6355(8)	2.7064(7)
Co1-O1	2.027(2)	2.020(2)	2.017(2)
Co1-O2	2.016(2)	2.011(2)	2.024(2)
Co1-N8	2.126(2)	2.150(2)	2.154(3)
Co1-N18	2.203(2)	2.241(2)	2.190(2)
Co2-Cl1	2.4863(7)	2.4872(9)	2.4878(9)
Co2-Cl2	2.2575(7)	2.2488(8)	2.2594(9)
Co2-O1	1.975(2)	1.966(2)	1.981(2)
Co2-O2'	1.985(2)	1.980(2)	1.967(2)
Co2-O3	2.211(2)	2.216(2)	2.207(2)
Co1-Cl1-Co1' (α)	92.20(2)	95.38(3)	94.30(3)
Co1-Cl1-Co2 (γ)	84.17(2)	82.98(2)	79.69(2)
Co1-Cl1-Co2'	79.23(2)	80.01(2)	82.69(3)
Co1-O1-Co2 (β)	111.27(7)	110.39(9)	112.93(9)
Co1-O2-Co2'	110.45(8)	111.32(9)	110.09(9)
τ^b	0.16	0.30	0.37

^a The asymmetric unit of **2**·4CH₃CN contains the halves of two distinct tetranuclear complexes denoted as a and b in the table. ^b see reference 9.

Selected geometrical parameters around cobalt(II)-ions are presented in Table 1. In general, the Co-O, Co-N and Co-Cl bond lengths and angles are in the range reported in previous studies. The inner Co-Cl-Co bridge is clearly asymmetric as pointed out by the Co1-Cl1 and Co1-Cl1' bond lengths, which differ by about 0.2 Å. The two outer bridges with heteronuclear bridging atoms (Cl and O) are not alike either. Furthermore, the Co-O_{bridge} and Co-Cl_{terminal} bond distances are in agreement with previous studies concerning phenoxide-bridged defective dicubane complexes.⁵

The coordination mode of the ligands **L1** and **L2** in **1** and **2** resembles ones previously observed by us in mixed-valence manganese species $[\text{Mn(II)Mn(III)}(\mu\text{-L})(\mu\text{-OR})\text{Cl}_2\text{D}]$ ($\text{L} = \text{L1}$ or L2 , $\text{R} = \text{Me}$ or Et and $\text{D} = \text{MeOH}$ or EtOH).^{8b} In these complexes, diaminobisphenolates act as bridging ligands between metal centers but this time producing dinuclear complexes instead of tetranuclear ones. In addition, only one of the methoxy substituents in phenyl rings is coordinated to metal center in similar fashion that in **1** and **2**. Hence, the lower nuclearity in the Mn(II)/Mn(III) complexes can be attributed to the intrinsic properties of the metal cations and/or different reaction conditions.

The intermolecular interactions between the tetranuclear complexes are minor. In **1** and **2** certain methylene, methyl (from methoxy group) and aromatic hydrogens have weak interactions with the chlorides and morpholine oxygens of neighboring complexes. Furthermore, methylene hydrogens around tripodal amine nitrogen (between the two aromatic rings) show very weak $\text{CH}\cdots\pi$ interaction with adjacent allyl substituents of the phenol groups.

Finally, it is worth mentioning that complexes **1** and **2** represent the first examples of Co_4 complexes with a defective dicubane structure containing two μ_3 -bridged chloride ions (inner bridges) and four μ_2 -bridged phenolate oxygen atoms (outer bridges). The other reported example having two μ_3 -bridged chloride ions, $[\text{Co}_4(\mu_3\text{-Cl})_2(\mu_2\text{-Cl})_4\text{Cl}_2(\text{THF})_6]$ only contains chloride bridges between the Co^{II} ions.^{7m}

Figure 2. Temperature dependence of $\chi_M T$ (circles) for **1** and **2** in black and grey colours, respectively. The solid lines correspond to the best fit. A zoom in the region of the minimum of $\chi_M T$ is shown in the inset.

Magnetic properties. Variable temperature magnetization measurements were performed on a powdered polycrystalline sample of **1** and **2** under a constant magnetic field of 0.1 T (300–50 K) and 0.05 T (50–2 K). The results are represented in Figure 2 as $\chi_M T$ vs T plots (χ_M being the molar paramagnetic susceptibility of the compound). At room temperature, $\chi_M T$ were 12.07 (**1**) and 12.10 (**2**) $\text{cm}^3 \text{K mol}^{-1}$, significantly larger than expected for four magnetically isolated high-spin Co(II) ions ($\chi_M T = 7.5 \text{ cm}^3 \text{K mol}^{-1}$ if $g = 2$), which indicates that the orbital angular momentum of the metal ions is not quenched and therefore contributes significantly to χ_M . Thus, upon cooling, $\chi_M T$ decreased at an increasingly faster

rate, reaching, however, a minimum value of 11.52 and 9.73 $\text{cm}^3 \text{K mol}^{-1}$ at 22 K and 14 K for **1** and **2**, respectively. Below these temperatures $\chi_M T$ quickly increased, which is related to the presence of predominant ferromagnetic interactions. However, whereas **1** behaved like that until 2 K, **2** showed a modest increase of $\chi_M T$ reaching at maximum at 4.5 K. This fact clearly indicates the presence of non-negligible antiferromagnetic couplings in this latter case.

It is known that in a purely octahedral symmetry, the ground term ^4F of a high-spin Co(II) ion is split into three states, $^4\text{T}_{1g}$, $^4\text{T}_{2g}$ and $^4\text{A}_{2g}$, of which the former is the ground state and is well separated (more than 8000 cm^{-1}) from the other two. Consequently, first order spin–orbit coupling splits the $^4\text{T}_{1g}$ ground state into a sextet, a quadruplet and a Kramer’s doublet. However, most genuine systems of Co(II) display distortions from the ideal octahedral geometry leading (for the case of an axial distortion) to a splitting of the triplet orbital state $^4\text{T}_{1g}$ into two other states, $^4\text{A}_{2g}$ and $^4\text{E}_g$, separated by an energy gap Δ . In such cases the T and P term isomorphism allows to analyze the magnetic behavior. Nevertheless, in **1** and **2**, cobalt(II) ions appear with coordination number of both five and six including some very long metal–ligand bonds. In consequence, these centers must exhibit very large values of Δ and may thus be treated as quartets ($S = 3/2$) subject to a moderate or even large ZFS (thus, as in the spin-only formalism) and also large g -factors.^{10a} This approach to the simulation of the magnetic behavior is more logical and, above all, it allowed limiting the number of parameters to fit. In the same sense, to avoid an over-parameterization and due to the geometrical parameters for the two distinct tetranuclear complexes (A and B) in the solid-state structure of **2**, it was considered as if only one complex was present as in **1**, resulting in an average value for each one of the fitted parameters.

Figure 3. Scheme of the magnetic exchange interactions present in complexes **1** and **2**.

Given the geometry of **1** and **2**, these systems require three different coupling constants for a description of their intramolecular magnetic exchange (see Figure 3), as represented in the Hamiltonian of equation 1.

$$\hat{H} = -J_1(\hat{S}_1\hat{S}_2 + \hat{S}_1'\hat{S}_2') - J_2(\hat{S}_1\hat{S}_2' + \hat{S}_1'\hat{S}_2) - J_3\hat{S}_1\hat{S}_1', \quad (1)$$

Although the exchange pathways of J_1 and J_2 are similar and both involve an oxygen atom of a phenoxide group and a μ_3 -chloride ligand, there are still some small geometrical differences in both pathways. To control possible unexpected influences on the magnetic coupling from small structural changes, these pathways were taken into account individually. On the other hand, J_3 represents a different exchange pathway made up with two μ_3 -

chloride ligands. Thus, the whole spin Hamiltonian used in the simulations is built from equation 1 by adding the local terms ($\hat{H}_{local}$, equation 2) related to the Zeeman and magnetic anisotropy effects.

$$\hat{H}_{local} = \sum_{i=1}^4 \{g_i \beta B \hat{S}_i + D_i [(\hat{S}_i^z)^2 - S_i(S_i + 1)/3]\} \quad (2)$$

(sites 3 and 4 corresponds to 1' and 2', respectively), where g , β , B and D are the g -factor, the Bohr magneton, the applied magnetic field and the axial magnetic anisotropy parameter, respectively, and $g_1 = g_4$, $g_2 = g_3$, $D_1 = D_4$ and $D_2 = D_3$. The experimental data was analyzed using this spin Hamiltonian by means of the VPMAG package.¹¹ The best fit (see Figure 2) was obtained with the following parameters; $g_1 = 2.546$, $g_2 = 2.521$, $D_1 = -60.2 \text{ cm}^{-1}$, $D_2 = -36.9 \text{ cm}^{-1}$, $J_1 = +0.08 \text{ cm}^{-1}$, $J_2 = +0.3 \text{ cm}^{-1}$, $J_3 = +2.0 \text{ cm}^{-1}$ and $F = 1.8 \times 10^{-5}$ for **1** and $g_1 = 2.528$, $g_2 = 2.538$, $D_1 = -59.7 \text{ cm}^{-1}$, $D_2 = -42.3 \text{ cm}^{-1}$, $J_1 = -0.6 \text{ cm}^{-1}$, $J_2 = +0.6 \text{ cm}^{-1}$, $J_3 = +2.2 \text{ cm}^{-1}$ and $F = 1.2 \times 10^{-4}$ for **2**. F is the agreement factor defined as $\sum [\varphi_{obs}(i) - \varphi_{calc}(i)]^2 / [\varphi_{obs}(i)]^2$, ϕ being the physical magnitude to fit (the $\chi_M T$ product here). The calculated curves for **1** and **2** (solid line in Figure 2) reproduced very well the magnetic data in the whole temperature range. The D values were considerably large because of the particular geometry of the coordination sphere of cobalt(II) ions, being greater for the ions with lower coordination number, as expected. The J values showed the presence of predominant moderate ferromagnetic couplings but also one weaker coupling, which turns into antiferromagnetic in **2**.

Table 2. Theoretical ZFS parameters (D_i in cm^{-1} and E/D in parentheses) for **1** and **2**.

Site	D (CAS) ^a	D (NEVPT2) ^b
Complex 1		
1 and 1'	-68.8 (0.27)	-----
2 and 2'	+61.6 (0.29)	+49.3 (0.26)
Complex 2 Molecule A		
1 and 1'	-79.1 (0.24)	-61.3 (0.22)
2 and 2'	+58.3 (0.24)	+47.6 (0.22)
Complex 2 Molecule B		
1 and 1'	-58.4 (0.29)	-44.1 (0.25)
2 and 2'	+56.7 (0.19)	+45.4 (0.16)

^a Calculated with CAS method and Orca 3.0.1 code. ^b Calculated with NEVPT2 method and Orca 3.0.1 code.

CAS and NEVPT2 calculations were carried out on molecules **1**, **2a** and **2b**. Since crystallographically different Co^{II} ions are present in the defective dicubane core, three of the Co^{II} cations were replaced by Zn^{II} in order to estimate the ZFS tensor and how it is orientated in the molecule for each Co^{II} cation (Table 2, Figures 4 and S1). We were not able to obtain theoretical D values for all Co^{II} ions from NEVPT2 calculations, but fortunately the missing data could be extracted from the CAS calculations. In general, the D values obtained from both methods give similar qualitative trends. In both cases, Co_1 and Co_2 sites present large ZFS. The values obtained from CAS methodology are slightly higher which is in agreement with an overestimation of CAS D values observed in previous studies.^{10b} The calculated E/D parameters, E being the rhombic contribution to the ZFS, are quite large, which is not uncommon overestimation even in mononuclear cobalt(II) complexes.^{10b} We would also like to point out that the D parameter

takes positive and negative values for the sites 1, (1') and 2, (2') (see Table 2), respectively, due to the different coordination environment of the Co^{II} ions. Although the sign of the D is not possible to extract from an analysis of the experimental thermal dependence of the magnetic susceptibility or its $\chi_M T$ product, theoretical and experimental values agree well even though certain approximations have been used. Finally, $|D_1|$ is larger than $|D_2|$ in **1** and **2a**, but they are very similar in **2b**. This fact shows that subtle changes in the geometry of the cobalt coordination sphere can modify the ZFS parameter by a change in the electronic structure and in the energy of the first quartet excited states, which contribute most significantly to the D parameter. Good agreement between the experimental and theoretical D values is likely because the z -axes of the ZFS tensors are nearly parallel in all Co^{II} ions (see Figures 4 and S1). For example, the angle between these axes calculated from NEVPT2 results on **2b** is 20.9° .

Table 3. Magnetic exchange coupling (J_i), bridging ligands (L), selected structural parameters (in Å and in degrees) and theoretical and experimental magnetic coupling constants (in cm^{-1}) for **1** and **2**.

J _i Sites {i,j}	d _{M-M} /Å	L	d _{M(i)-X} /Å ^a	d _{M(f)-X} /Å ^a	M-L-M/ ^o	J _{theo} ^b	J _{exp} ^c
Complex 1							
J ₁ {2, 1}	3.287	μ-OPh	1.985	2.016	110.4	−1.93(4)	+ 0.08
		μ-Cl	2.486	2.663	79.2		
J ₂ {2, 1'}	3.304	μ-OPh	1.975	2.027	111.3	+0.99(4)	+ 0.3
		μ-Cl	2.486	2.443	84.2		
J ₃ {1, 1'}	3.683	μ-Cl	2.443	2.663	92.2	+2.44(7)	+ 2.0
		μ-Cl	2.663	2.443	92.2		
Complex 2 Molecule A							
J ₁ {2, 1}	3.295	μ-OPh	1.980	2.011	111.3	−3.41(7)	− 0.6
		μ-Cl	2.487	2.636	80.0		
J ₂ {2, 1'}	3.273	μ-OPh	1.966	2.020	110.4	+0.55(7)	+ 0.6
		μ-Cl	2.487	2.453	83.0		
J ₃ {1, 1'}	3.765	μ-Cl	2.453	2.636	95.4	+2.01(12)	+ 2.2
		μ-Cl	2.636	2.453	95.4		
Complex 2 Molecule B							
J ₁ {2, 1}	3.332	μ-OPh	1.981	2.017	112.9	−3.20(4)	− 0.6
		μ-Cl	2.488	2.706	79.7		
J ₂ {2, 1'}	3.271	μ-OPh	1.981	2.024	110.1	+1.04(4)	+ 0.6
		μ-Cl	2.488	2.464	82.7		
J ₃ {1, 1'}	3.794	μ-Cl	2.464	2.706	94.3	+2.43(6)	+ 2.2
		μ-Cl	2.706	2.464	94.3		

^a Labels i and f are used to specify the initial and final metal atom in the magnetic coupling. ^b Calculated with Gaussian09 code. ^c Fitted values from the experimental data. The values in parentheses show the standard deviation in the evaluation the J values from DF calculations

DF study of the magnetic exchange

In order to support the experimental values of the magnetic exchange couplings for **1** and **2**, DF calculations were performed on the X-ray crystal structures. It is worth noting, that the experimental magnetic data is in good agreement with the DF study and the theoretical magneto-structural correlation. Experimental and theoretical results are summarized in Table 3.

Figure 4. Relative orientation of the D tensor on two Co^{II} ions in **2b** obtained from NEVPT2 calculations. Coloured rods represent the reference axis x (orange), y (yellow), and z (magenta) of the D tensor. For clarity, only the core of the polynuclear complexes is shown.

Theoretical methods based on density functional theory have been extensively used for some time to study the spin states of systems ranging from simple molecules¹² to polynuclear metal clusters.¹³ Such methodology allows for determining all the exchange coupling constants present in polynuclear transition metal complexes^{14–17} and it has been employed here to obtain an estimate of the magnetic interactions within complexes **1** and **2**. Furthermore, the results from this study have been used for the phenomenological simulation of the experimental magnetization data (see below) and have been rationalized in light of the structural features of the system. Using the Hamiltonian in equation 1 it was necessary to calculate the energy of at least four spin configurations,^{17, 18} chosen so that a system of three equations and three unknowns (the J constants) can be prepared and solved. In fact, in order to verify possible errors or shortcomings of the procedure, we studied the six electronic configurations that are allowed using the broken symmetry approach. These correspond to the following spin states (only spin down centers indicated, using the notation of Figure 3): one $S = 6$, five $S = 3$ ($[2]$ and $[1]$) and three $S = 0$ ($[2, 1']$, $[2, 2']$ and $[1', 2']$). The values of the three J_i constants resulting from these calculations are presented in Table 3 (see Figure 3 for notation) and validated by the low values of the standard deviations. These results allowed to draw the following conclusions; *i*) Regardless of the coordination sphere of the cobalt(II) ions, in all cases the coupling is from moderate to rather weak, because of some of the metal-ligand bond lengths involved in the exchange pathways are long (see Table 3), leading to the inefficiency of one or two paths present in each pathway; *ii*) Since the main geometrical parameters in the pathways are similar, the values of the magnetic coupling constants in all molecules are close to each other; *iii*) The bis-(μ -chloro) pathway (J_3) is the most efficient path to transmit ferromagnetic couplings. As far as we are aware, no magneto-structural correlation has been established for di- μ -chlorocobalt(II) complexes yet, probably due to the paucity in obtaining accurate J values for such systems containing large anisotropic metal ions. Nevertheless, the analogues di- μ -chloro copper(II) complexes show the change from ferromagnetic to antiferromagnetic interactions for M-Cl-M bridging angles close to 90° .¹⁹ In good agreement with this, the few examples of complexes containing di- μ -chloro²⁰ and di- μ_3 -chloro bridges^{7m} between the cobalt(II) ions present ferromagnetic coupling through these magnetic pathways for angles so high as 99° . In complexes **1** and **2** with Cl-Co-Cl bridging angles (α in

Figure 2) in the 92.20 – 95.38° range the observed ferromagnetic interaction is not unexpected. *iv*) As for the phenoxo/chloro pathways described by J_1 and J_2 , the Co–Cl bond lengths are long and the Co–Cl–Co angles are acute (γ angles are found in the 79.23 – 84.17° range) and therefore a ferromagnetic interaction is expected through the Co–Cl–Co pathway.^{7j} However, a moderate antiferromagnetic interaction is anticipated for the phenoxo exchange pathway with Co–O–Co angles (β , in Figure 2) in the 110.09 – 112.93° range. For this pathway, antiferromagnetic couplings were found for Co–O–Co angles larger than $\sim 100^\circ$,²¹ while smaller angles induced ferromagnetic coupling. Nevertheless, in the case of **1** and **2** this trend is not followed perfectly by the computational data (see Figure S2) and better correlation can be found between the J values and the Co–Cl–Co angle. This correlation groups the J values in two sets (see Figure S3) and takes into account the two different Co–Cl bond lengths. The resulting magnetic coupling described by J_1 and J_2 should be a balance between the interactions transmitted through Co–O–Co and Co–Cl–Co pathways, so that antiferromagnetic magnetic coupling through the phenoxide monoatomic pathway should be counterbalanced, at least partly, by the ferromagnetic interaction expected for the single-chloro exchange pathway. Therefore weak overall ferro- or antiferromagnetic interactions are expected for J_1 and J_2 pathways in good agreement with the experimental and theoretical results given in Table 3.

Conclusions

During the course of this study, we have prepared two novel tetranuclear Co(II) complexes with a defective dicubane structure using two different diaminobisphenolate ligands. Interestingly, the structures of these complexes are unique as they show unprecedented simultaneous presence of μ_3 -Cl and μ -Cl/phenoxo bridging fragments. The solid state structures of the complexes were determined by single crystal X-ray diffraction while the magnetic properties were investigated using combination of experimental and theoretical techniques. The exchange coupling mediated by the two μ_3 -bridging chlorides was shown to be ferromagnetic between the inner Co(II) cations of the pseudo dicubane fragment, whereas the mixed phenoxide oxygen/chloride bridges transmitted either weak ferro- or antiferromagnetic interactions, mostly depending on the Co–X and Co–X–Co ($X = \text{O}, \text{Cl}$) bond lengths and angles, respectively.

Experimental Section

All starting materials were reagent grade, purchased from Sigma Aldrich and used as received. Solvents were of HPLC grade and used without any additional drying. All syntheses were performed under ambient laboratory atmosphere. Ligands $\text{H}_2\text{L1}$ and $\text{H}_2\text{L2}$ were synthesized according to literature.²² Elemental analysis was performed by using a Vario El III elemental analyzer. Single-crystal X-ray measurements were performed by using an Enraf Nonius Kappa CCD area detector diffractometer with the use of graphite monochromated Mo-K α radiation. Variable-temperature (2 – 300 K) magnetic susceptibility measurements on polycrystalline samples were carried out with a Quantum Design Squid MPMSXL-5 device operating at 0.1 T from room temperature to 50 K and at 0.05 T from this latter temperature to 2 K. The experimental susceptibilities were corrected for the diamagnetism of the constituent atoms by using Pascal's tables.

Complex synthesis. $[\text{Co}_4(\text{L1})_2(\mu_3\text{-Cl})_2\text{Cl}_2] \cdot 2\text{CH}_3\text{CN}$ (**1**): Complex was synthesized by dissolving 1.0 mmol (238 mg) $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ to 15 ml of acetonitrile and 0.5 mmol (242 mg) $\text{H}_2\text{L1}$ was added to the solution. 1.0

mmol (140 μ l) of triethylamine was added to neutralize the formed hydrochloric acid and the mixture was let to crystallize at room temperature for four days after which blue X-ray diffraction quality crystal were separated by filtration. Yield 228 mg (68 %). Elemental analysis: $C_{60}H_{78}Cl_4Co_4N_6O_{10}$ (with 2 CH_3CN) (1420.84): calcd. C 50.72, H 5.53, N 5.91; found C 50.89, H 5.46, N 5.97.

[Co₄(L2)₂(μ_3 -Cl)₂Cl₂] $\cdot$ 4CH₃CN (2**):** Complex was synthesized by dissolving 1.0 mmol (238 mg) CoCl₂ $\cdot$ 6H₂O to 15 ml of acetonitrile and 0.5 mmol (215 mg) H₂L2 was added to the solution. 1.0 mmol (140 μ l) of triethylamine was added to neutralize the formed hydrochloric acid and the mixture was let to crystallize in fridge overnight after which blue X-ray diffraction quality crystal were separated by filtration. Yield 237 mg (76 %). Elemental analysis: $C_{50}H_{67}Cl_4Co_4N_5O_{10}$ (with 1 CH_3CN)²³ (1275.64): calcd. C 47.08, H 5.29, N 5.49; found C 47.16, H 5.25, N 5.37.

X-ray Crystallography. Crystals suitable for single-crystal X-ray measurements were obtained directly from the reaction vessels. The crystal data for compounds **1** (CCDC 1430995) and **2** (CCDC 1430996) are summarized in Table 4 along with other experimental details. The crystallographic data were collected at 123 K with an Enraf Nonius Kappa CCD area-detector diffractometer with the use of graphite-monochromated Mo-K α radiation (λ = 0.71073 Å). Data collection was performed by using ϕ and ω scans, and the data were processed by using DENZO-SMN v0.93.0.²⁴ SADABS²⁵ absorption correction was applied for all compounds. The data for **2** was also sorted and merged using SORTAV.²⁶ The structures were solved by direct methods by using the SHELXS-97²⁷ program or the SIR-97²⁸ program and full-matrix least squares refinements on F^2 were performed using the SHELXL-97²⁷ program. Figures were drawn with Diamond 3.²⁹ For all compounds the heavy atoms were refined anisotropically. The hydrogen atoms were included at the calculated distances with fixed displacement parameters from their host atoms (1.2 or 1.5 times of the host atom).

Computational details. Calculations were performed through the Gaussian09 package using the B3LYP functional³⁰, the quadratic convergence approach and a guess function generated with the fragment tool of the same program.³¹ Triple- ζ and double- ζ all electron basis sets proposed by Ahlrichs *et al.* were employed for the metal and for the other atoms, respectively.³² Contrary to what we have observed in other high-spin octahedral cobalt(II) complexes where non-negligible spin-orbit couplings are observed, any problems to reach the convergence criterion in the SCF process were not encountered. This can be explained by the fact that in our compound, we have two five-coordinated cobalt(II) cations while the other two cobalt centers have coordination number of six with one very large axial bond. For the former, we expect only negligible spin-orbit couplings and not very large for the latter ones either. Thus, in the former ones, a large value is expected for the parameter that evaluates the energy splitting between the lower states when the degeneracy of the triplet orbital state $^4T_{1g}$ is broken by a tetragonal or trigonal distortion.³³ In such cases, the ground state is separated enough to consider that the mixture with the excited states is poor leading to easier way to found the correct electronic structure for the cobalt(II) ion. More details about the use of the broken-symmetry approach to evaluate the magnetic coupling constants can be found in the literature.^{34,35} To evaluate the parameters that determines the axial (D) and rhombic (E) zfs , calculations based on a complete active space (CAS) methodology and a second order N-electron valence state perturbation theory (NEVPT2), applied on the CAS wave function previously obtained, were performed. These calculations were carried out with version 3.0 of the ORCA program³⁶ using the TZVP basis set proposed by Ahlrichs³⁷ and the auxiliary TZV/C Coulomb fitting basis sets³⁸. The 2nd order contributions to zfs from 10 quartet and 20 doublet excited states were generated from an active space with seven electrons in five d orbitals.

Table 4. Summary of crystallographic data for complexes **1** $\cdot$ 2CH₃CN and **2** $\cdot$ 4CH₃CN at 123K.

Complex	1 $\cdot$ 2CH ₃ CN	2 $\cdot$ 4CH ₃ CN
Formula	C ₆₀ H ₇₈ Co ₄ Cl ₄ N ₆ O ₁₀	C ₅₈ H ₇₆ Co ₄ Cl ₄ N ₅ O ₁₀
M_r	1420.8	1398.77
Crystal system	orthorhombic	triclinic
Space group (no.)	<i>Pbca</i> (61)	<i>P</i> -1 (2)
<i>a</i> (Å)	15.7503(2)	11.9709(2)
<i>b</i> (Å)	19.3529(3)	13.9647(2)
<i>c</i> (Å)	20.6324(2)	19.3538(3)
α (°)	90	75.610(1)
β (°)	90	82.642(1)
γ (°)	90	85.198(1)
<i>V</i> (Å ³)	6289.04(14)	3103.53(8)
<i>Z</i>	4	2
D_c (g cm ⁻³)	1.501	1.497
μ (MoK α) (mm ⁻¹)	1.268	1.284
Observed reflections	36601	42864
Unique reflections	6852	14572
R_{int}	0.0471	0.0451
Parameters	382	752
R_f^a	0.0584 (0.0383) ^b	0.0644 (0.0457) ^b
wR_2^c	0.0804 (0.0735)	0.1083 (0.1003)
Largest difference in peak and hole (e Å ⁻³)	0.418 – -0.395	0.805 – -0.574

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

Supporting Information (see footnote on the first page of this article): X-ray crystallographic data, additional figures and XYZ coordinates from the DFT calculations.

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Entry for the Table of Contents (Please choose one layout)

Layout 1:

Unique mixed phenoxide/chloride bridged Co_4 clusters can be prepared using diaminobisphenolate ligands. The solid state structure and magnetic exchange interactions between Co(II) cations have been elucidated using combination of experimental and computational techniques.

Cobalt clusters

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