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Author(s): Hänninen, Mikko M.; Välivaara, Juha; Cano, Joan; Sillanpää, Reijo; Colacio, Enrique

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Experimental and Computational Study of Unique Tetranuclear $\mu_1$-Chloride and $\mu$-phenoxo/chloro bridged Defective-Dicubane Cobalt(II) clusters

Mikko. M. Hänninen[a]*, Juha Välivaara[a], Joan Cano[b]*, Reijo Sillanpää[a], Enrique Colacio[c]

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Two tetranuclear Co(II) clusters $[\text{Co}_4(L)_2(\mu_1,\text{Cl})_2\text{Cl}_2]$ 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 properties 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, but also because of their aesthetic and fascinating structures. 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. 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, SMMs, 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.

[a] Department of Chemistry, University of Jyväskylä, P. O. Box 35, 40014 Jyväskylä, Finland
E-mail: mikko.m.hanninen@jyu.fi
[b] Instituto de Ciencia Molecular (ICMol) and Fundació General de la Universitat de València (FGUV), Universitat de València, E-46980 Paterna, València, Spain
[c] Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, Avda. Fuentenueva s/n, 18002 Granada, Spain
E-mail: ecolacio@ugr.es
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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. $\text{Co}^{3+}$ 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. 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. 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, $[\text{Co}_4(L1)_2(\mu_1,\text{Cl})_2\text{Cl}_2]2\text{CH}_2\text{CN}$ (1) and $[\text{Co}_4(L2)_2(\mu_1,\text{Cl})_2\text{Cl}_2]4\text{CH}_2\text{CN}$ (2) with novel diaminobisphenolate ligands (Scheme 1). It is worth mentioning that, among others,
amino/alcohol, amino/acid, amino/phenol/alcohol, pyridine/alcoholphenol, aza-macroyclic/acid, dipryridylketone, bidentate α-diamines and phenol/alcohol Schiff base ligands have been used to prepare “defective” dicycubane-like tetranuclear Co(II) and Co^{II},Co^{III} _{-2} clusters. All these complexes possess a μ_2-bridging (X = hydroxide, alkoxy, phenoxide or azide group) but to the best of our knowledge in only one case μ_2-halide bridges have been reported.7m

Results and Discussion

Complexes 1 and 2 were synthesized in good yields by dissolving two equivalents of CoCl_2·6H_2O into acetonitrile and adding one equivalent of the corresponding ligand (H_2L1 or H_2L2 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 H_2L1 (allyl substituents) was considerably slower compared to 2 with H_2L2 (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_2-bridging chloride ion and one ligand (the asymmetric unit of 2 contains two distinct molecules, 2a and 2b).

The molecular structures of 1 and 2 are presented in Figure 1. The tetranuclear complexes are formed from two [Co_2(L)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-dicycubane unit with two missing vertices which consists of four cobalt(II) ions with two μ_2-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 (τ = 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 H_2L2, the geometry of five-coordinated Co(II) cations is considerably more distorted from the perfect square pyramidal polyhedron.

![Figure 1](image-url)
The coordination mode of the ligands L1 and L2 in 1 and 2 resembles ones previously observed by us in mixed-valence manganese species \([\text{Mn(II)/Mn(III)}(\mu-OR)\text{Cl}]\) (L = L1 or L2, R = Me or Et and D = MeOH or EtOH). 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 CH–π interaction with adjacent allyl substituents of the phenol groups.

Finally, it is worth mentioning that complexes 1 and 2 represent the first examples of Co4 complexes with a defective dicubane structure containing two \(\mu_1\)-bridged chloride ions (inner bridges) and four \(\mu_1\)-bridged phenolate oxygen atoms (outer bridges). The other reported example having two \(\mu_1\)-bridged chloride ions, \(\text{[Co}_4(\mu_2\text{-Cl})(\mu_3\text{-Cl})\text{Cl}_4(\text{THF})_6]\) only contains chloride bridges between the Co\(^{III}\) ions.

![Figure 2](image-url)

**Figure 2.** Temperature dependence of \(\chi_M\) (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 \(\chi_M\) 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 \(\chi_M\) vs T plots \((\chi_M\) being the molar paramagnetic susceptibility of the compound). At room temperature, \(\chi_M\) were 12.07 (1) and 12.10 (2) \(\text{cm}^3\ \text{mol}^{-1}\ \text{K}^{-1}\), significantly larger than expected for four magnetically isolated high-spin Co(II) ions \((\chi_M = 7.5 \text{ cm}^3\ \text{mol}^{-1} \text{ K}^{-1})\) if \(g = 2\), which indicates that the orbital angular momentum of the metal ions is not quenched and therefore contributes significantly to \(\chi_M\). Thus, upon cooling, \(\chi_M\) decreased at an increasingly faster rate, reaching, however, a minimum value of 11.52 and 9.73 \(\text{cm}^3\ \text{K}^{-1}\) mol\(^{-1}\) at 22 K and 14 K for 1 and 2, respectively. Below these temperatures \(\chi_M\) 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 \(\chi_M\) 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 \(^4\text{F}\) 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 \(\text{cm}^{-1}\)) 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 \(\Delta\). 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 exhibit very large values of \(\Delta\) 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. 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-parametrization 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](image-url)

**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.

\[
\mathbf{H} = -J_1(\hat{S}_1\hat{S}_2 + \hat{S}_3\hat{S}_4) - J_2(\hat{S}_1\hat{S}_3 + \hat{S}_2\hat{S}_4) - J_3\hat{S}_1\hat{S}_4, \tag{1}
\]

Although the exchange pathways of \(J_1\) and \(J_2\) are similar and both involve an oxygen atom of a phenoxy group and a \(\mu_1\)-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 \(\mu_1\)-
chloride ligands. Thus, the whole spin Hamiltonian used in the simulations is built from equation 1 by adding the local terms \( \langle \hat{H}_{\text{local}} \rangle \) related to the Zeeman and magnetic anisotropy effects.

\[
\hat{H}_{\text{local}} = \sum_i \left\{ g_i \beta B \hat{S}_i + D_i \left( \hat{S}_i^2 - S(S+1)/3 \right) \right\}
\]  

(sites 3 and 4 corresponds to 1' and 2', respectively), where \( g, \beta, B \) and \( D \) are the g-factor, the Bohr magneton, the applied magnetic field and the axial magnetic anisotropy parameter, respectively, and \( g_1 = g_a, g_2 = g_b, D_1 = D_a \) and \( D_2 = D_b \). 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: \( g_1 = 2.546, \ g_2 = 2.521, \ D_1 = -60.2 \ \text{cm}^{-1}, \ D_2 = -36.9 \ \text{cm}^{-1}, \ J_1 = 4.08 \ \text{cm}^{-1}, \ J_2 = +0.3 \ \text{cm}^{-1}, \ J_3 = +2.0 \ \text{cm}^{-1} \) and \( F = 1.8 \times 10^{-2} \) for 1 and \( g_1 = 2.526, \ g_2 = 2.538, \ D_1 = -59.7 \ \text{cm}^{-1}, \ D_2 = -42.3 \ \text{cm}^{-1}, \ J_1 = -0.6 \ \text{cm}^{-1}, \ J_2 = +0.6 \ \text{cm}^{-1}, \ J_3 = +2.2 \ \text{cm}^{-1} \) and \( F = 1.2 \times 10^{-2} \) for 2. \( F \) is the agreement factor defined as \( \sum (\varphi_{\text{obs}} - \varphi_{\text{calc}})^2 / \varphi_{\text{calc}}^2 \). \( \varphi \) being the physical magnitude to fit (the \( g \) tensor 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 (\( D \), in cm\(^{-1}\) and \( E/D \) in parentheses) for 1 and 2.

<table>
<thead>
<tr>
<th>Site</th>
<th>( D ) (CAS)(^a)</th>
<th>( D ) (NEVPT2)(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complex 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 and 1'</td>
<td>-68.8 (0.27)</td>
<td>-</td>
</tr>
<tr>
<td>2 and 2'</td>
<td>+616.1 (0.29)</td>
<td>+49.3 (0.26)</td>
</tr>
<tr>
<td>Complex 2 Molecule A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 and 1'</td>
<td>-79.1 (0.24)</td>
<td>-61.3 (0.22)</td>
</tr>
<tr>
<td>2 and 2'</td>
<td>+58.3 (0.24)</td>
<td>+47.6 (0.22)</td>
</tr>
<tr>
<td>Complex 2 Molecule B</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 and 1'</td>
<td>-58.4 (0.29)</td>
<td>-44.1 (0.25)</td>
</tr>
<tr>
<td>2 and 2'</td>
<td>+56.7 (0.19)</td>
<td>+45.4 (0.16)</td>
</tr>
</tbody>
</table>

\(^a\) 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.\(^{10}\) 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.\(^{10}\) 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 \( \chi_T \) 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 contributed 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), 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.

<table>
<thead>
<tr>
<th>J(_i) Sites (ij)</th>
<th>( d_{\text{ag}}/\AA ) L</th>
<th>( d_{\text{ag}}/\lambda^a )</th>
<th>( d_{\text{ag}}/\beta^b ) M-L-M'</th>
<th>( J_{\text{iso}} )</th>
<th>( J_{\text{aniso}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Complex 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J(_1), (1, 1')</td>
<td>3.287</td>
<td>-0.69 (4)</td>
<td>-0.08 (4)</td>
<td>0.08</td>
<td>-0.08</td>
</tr>
<tr>
<td>J(_2), (1, 1')</td>
<td>3.044</td>
<td>-0.69 (4)</td>
<td>-0.08 (4)</td>
<td>0.09</td>
<td>-0.10</td>
</tr>
<tr>
<td>J(_1), (1, 1')</td>
<td>3.683</td>
<td>-0.69 (4)</td>
<td>-0.08 (4)</td>
<td>0.10</td>
<td>-0.10</td>
</tr>
<tr>
<td>Complex 2 Molecule A</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J(_1), (1, 1')</td>
<td>3.295</td>
<td>-0.69 (4)</td>
<td>-0.08 (4)</td>
<td>0.09</td>
<td>-0.10</td>
</tr>
<tr>
<td>J(_2), (1, 1')</td>
<td>3.273</td>
<td>-0.69 (4)</td>
<td>-0.08 (4)</td>
<td>0.10</td>
<td>-0.10</td>
</tr>
<tr>
<td>J(_1), (1, 1')</td>
<td>3.765</td>
<td>-0.69 (4)</td>
<td>-0.08 (4)</td>
<td>0.11</td>
<td>-0.11</td>
</tr>
<tr>
<td>Complex 2 Molecule B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>J(_1), (1, 1')</td>
<td>3.332</td>
<td>-0.69 (4)</td>
<td>-0.08 (4)</td>
<td>0.09</td>
<td>-0.09</td>
</tr>
<tr>
<td>J(_2), (1, 1')</td>
<td>3.271</td>
<td>-0.69 (4)</td>
<td>-0.08 (4)</td>
<td>0.10</td>
<td>-0.10</td>
</tr>
<tr>
<td>J(_1), (1, 1')</td>
<td>3.794</td>
<td>-0.69 (4)</td>
<td>-0.08 (4)</td>
<td>0.11</td>
<td>-0.11</td>
</tr>
</tbody>
</table>

\(^a\) 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 results 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 2) in the 92.20–95.38° range the observed ferromagnetic interaction is not unexpected. iv) As for the phenoxy/chloro pathways described by \( J_1 \) and \( J_2 \), the Co–Cl bond lengths are long and the Co-Cl-Co angles are acute (\( \gamma \) angles are found in the 79.23–84.17° range) and therefore a ferromagnetic interaction is expected through the Co-Cl-Co pathway. However, a moderate antiferromagnetic interaction is anticipated for the phenoxy exchange pathway with Co-O-Co angles (\( \beta \), in Figure 2) in the 110.09–112.93° range. For this pathway, antiferromagnetic couplings were found for Co-O-Co angles larger than \(~100°)\(^{21}\) 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 phenoxy 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 dianimobisphenolate ligands. Interestingly, the structures of these complexes are unique as they show unprecedented simultaneous presence of \( \mu_2 \)-Cl and \( \mu_2 \)-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 \( \mu_2 \)-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 = O, 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 \( \text{H}_3\text{L}1 \) and \( \text{H}_3\text{L}2 \) were synthesized according to the 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\( \alpha \) 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, [Co\(_2\)(L\(_1\))(\(\mu_2\)-Cl)\(_2\)]\(_2\)\(2\)CH\(_3\)CN (1): Complex was synthesized by dissolving 1.0 mmol (238 mg) CoCl\(_2\):6H\(_2\)O to 15 ml of acetonitrile and 0.5 mmol (242 mg) \( \text{H}_3\text{L}1 \) was added to the solution. 1.0
mmol (140 μl) 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_{6}H_{10}Cl_{2}Co_{2}N_{10}O_{10} (with 2 CH-CN) (1420.84): calcd. C 50.72, H 5.53, N 5.97; found C 50.89, H 5.46, N 5.97.

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-Kα 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-9228 program and full-matrix least squares refinement on F2 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 functional,30 the quadratic convergence approach and a guess function generated with the fragment method 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 six of one with 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 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 electron 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 TZVPP basis set proposed by Ahlrichs37 and the auxiliary TZV/C Coulomb fitting basis sets.38 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>
<thead>
<tr>
<th>Complex</th>
<th>1-2CH-CN</th>
<th>2-4CH-CN</th>
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<tr>
<td>Formula</td>
<td>C_{6}H_{10}Cl_{2}Co_{2}N_{10}O_{10}</td>
<td>C_{6}H_{10}Cl_{2}Co_{2}N_{10}O_{10}</td>
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<tr>
<td>Mf</td>
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<td>1398.77</td>
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</tbody>
</table>

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

Acknowledgments

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

Layout 1:

Unique mixed phenoxide/chloride bridged Co₄ clusters can be prepared using diaminobisphenolate ligands. The solid state structure and magnetic exchange interactions between Co(II) cations have been elucidated using a combination of experimental and computational techniques.


Experimental and Computational Study of Tetranuclear μ₃-Chloride Bridged Defective-Dicubane Cobalt(II) clusters

Keywords: Cobalt clusters / X-ray diffraction / Magnetic properties / DFT / Keyword 5