First Tetranuclear Co^{II} Cluster with Planar Triangular Pattern: Crystal Structure and Ferromagnetic Behavior

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The preparation, crystal structure and magnetic properties of the first tetrameric Co^{II} cluster with a unique planar triangular motif, $[Co_4L_3(H_2O)_2](ClO_4)_2{\cdot}2H_2O$ (**1**), based on a carboxylic-functionalized 1,5-diazacyclooctane (DACO) bridging ligand [1,5-bis(2-carboxyethyl)-DACO], are reported.

Introduction

The development of routes and strategies for the design and preparation of polynuclear clusters of 3d metals in moderate oxidation states is of great importance in bioinorganic chemistry, magnetochemistry, material chemistry and solid-state chemistry.[1] Tetranuclear systems have attracted particular interest since it was discovered that they are also the smallest aggregates that show single molecular magnet (SMM) behavior.[2] Of the relatively small number of reported tetracobalt(II) compounds, the majority have a dicubane/cubane rather than a square/rhombus-like core.[3] As described by us and others, diazamesocycles, especially 1,5-diazacyclooctane (DACO), modified by suitable functional pendants can be used as building blocks for constructing polymeric systems with unique structures and properties.[4,5] Very recently we have made an attempt to incorporate the carboxylic group, a versatile ligand with various coordination modes, on the backbone of DACO, and some fascinating chemistry of such ligands under self-assembly with metal ions were successfully achieved.[6] In the present contribution, we describe the preparation, crystal structure and magnetic properties of the first tetranuclear Co^{II} cluster $[Co_4L_3(H_2O)_2](ClO_4)_2{\cdot}2H_2O$ (**1**) [H_2L = 1,5-bis(2-carboxyethyl)-DACO; Scheme 1] exhibiting a unique planar-triangular Co_4 topology.

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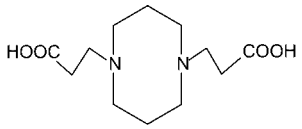

H_2L

Scheme 1

Results and Discussion

The crystal-structure determination of **1** reveals that it is a spontaneously resolved chiral crystal (each individual crystal is a single enantiomer).[7] Four Co^{II} centres are located on an exactly trigonal plane (see Figure 1) with a crystallographic twofold axis passing through Co1 and Co2. Three crystallographically independent Co^{II} ions have different octahedral coordination environments: the central Co1 bonds to six carboxylic oxygen donors, and the vertex Co^{II} ions are coordinated by DACO with unusual *chair*/*chair* configuration,[4] and four $O_{carboxylic}$ (for Co2), and three $O_{carboxylic}$ and one aqua ligand (for Co3). The carboxylato groups bridge the Co^{II} ions in two modes: μ-O,O-μ-O,O′$_{syn}$ (O5−C13−O6 and O3−C12−O4) and μ-O,O (O1−C1−O2) with Co···Co distances of 3.004(5) Å (Co1···Co2), 3.192(6) Å (Co1···Co3) and 4.939(3) Å (Co2···Co3), and Co−O−Co bridging angles of 99.9(2)° (Co1−O1−Co3), 89.3(1)° (Co1−O6−Co2) and 95.3(1)° (Co3−O3−Co1). The Co3···Co3A distance is 6.147(4) Å. The tetramers are well isolated, with the intermolecular contacts between the Co^{II} atoms above 7 Å.

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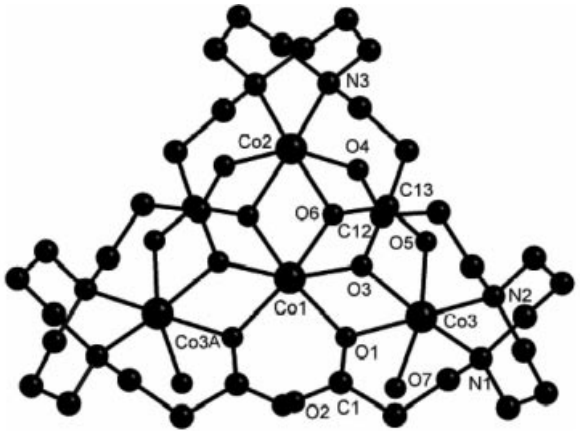


Figure 1. View of the $[Co_4L_3(H_2O)_2]^{2+}$ cation (H atoms omitted for clarity); symmetry code: $-x+1, y, -z+2$; selected bond lengths and angles: Co1−O1 2.070(4), Co1−O3 2.176(4), Co1−O6 2.109(4), Co2−N3 2.097(5), Co2−O4 2.099(4), Co2−O6 2.166(4), Co3−O5 2.119(4), Co3−N1 2.104(5), Co3−O7 2.102(5), Co3−O1 2.101(4), Co3−N2 2.127(5), Co3−O3 2.143(4), Co1−O(1)−Co3 99.9(2), Co1−O(3)−Co3 95.3(1), Co1−O(6)−Co2 89.3(1)

The magnetic properties of **1** in the form of $\chi_M T$ versus T plots (χ_M is the molar magnetic susceptibility for four Co^{II} ions) are shown in Figure 2 (A). The $\chi_M T$ value at 300 K is 11.87 $cm^3 \cdot mol^{-1} \cdot K$, which is larger than the spin-only value for four isolated Co^{II} ions (7.5 $cm^3 \cdot mol^{-1} \cdot K$, assuming artificially $g = 2.00$), indicating an important contribution from the orbital angular momentum typical for the $^4T_{1g}$ ground term. From 300 to 50 K the $\chi_M T$ value is almost constant (close to 12 $cm^3 \cdot mol^{-1} \cdot K$), and from 50 to 2 K it continuously increases (16.2 $cm^3 \cdot mol^{-1} \cdot K$ at 2.0 K). The shape of this curve indicates significant ferromagnetic interactions, because in the presence of spin-orbit interactions the $\chi_M T$ values for any Co^{II} ion tend to decrease with decreasing temperature.[8]

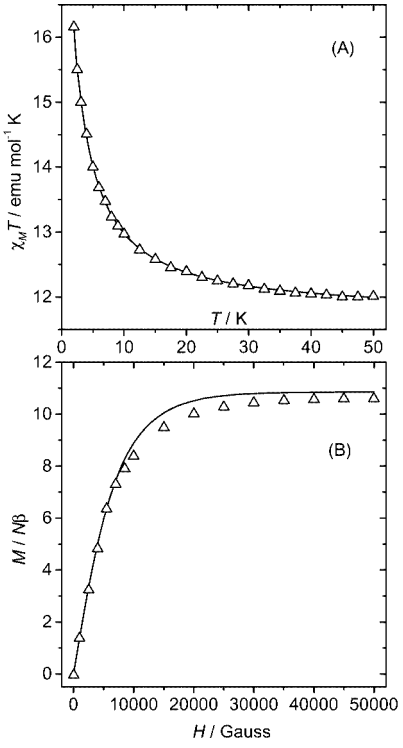
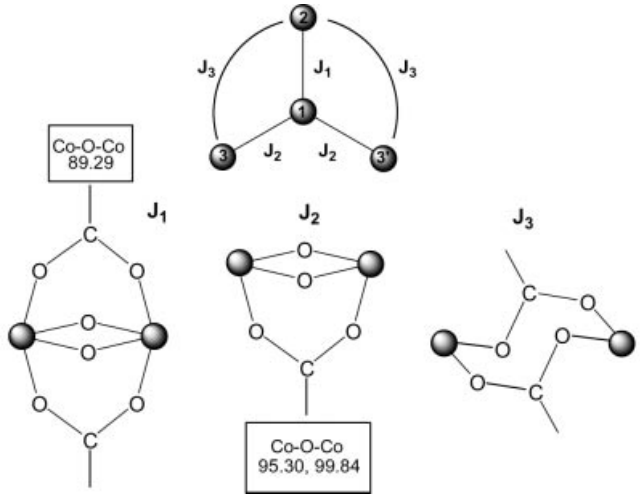


Figure 2. (A) Plot of the $\chi_M T$ vs. T from 50 to 2 K for **1** (the solid line is the best simulation with the following parameters: $J_1 = 2.15 \pm 0.08$ cm^{-1}, $J_2 = 0.40 \pm 0.03$ cm^{-1}, $J_3 = 0.12 \pm 0.02$ cm^{-1}, $g_{\parallel} = 7.3 \pm 0.2$ and $g_{\perp} = 3.5 \pm 0.1$; (B) plot of the reduced magnetisation at 2 K (the solid line is the simulation with J and g values obtained from the $\chi_M T$ vs. T curve)

For the interpretation of the magnetic measurements, the importance of the spin-orbit coupling of Co^{II} must be emphasized. The degeneracy of the $^4T_{1g}$ ground state of the octahedral Co^{II} ion prevents any possible fit in the whole temperature range, except for dinuclear complexes.[9] In the low-temperature region, the overall effect of low-symmetry crystal-field components and spin-orbit coupling produces up to six Kramers doublets and leads to a doublet ground state,[8] which should result in an anisotropic exchange coupling. This anisotropy has been clearly shown by inelastic neutron scattering (INS) studies in many polynuclear Co^{II} systems.[3b,10] For this reason, at low temperature ($< 40-50$ K), Co^{II} systems may be described as having an effective spin of 1/2 with large anisotropy. Thus, for not too complicated systems, it is possible to fit the low-temperature zone with special computational methods, such as the MAGPACK program,[11] as previously done for several di- to pentanuclear Co^{II} systems.[3b,10]

The exchange pathway connecting the Co^{II} ions is depicted in Scheme 2. In the case of tetramer **1**, the exchange Hamiltonian that describes the exchange interactions between the effective $S = 1/2$ spins is:

$$H = -2 \sum_{i=x,y,z} [J_{1i} S_{1i} S_{2i} + J_{2i}(S_{1i} S_{3i} + S_{1i} S_{3'i}) + J_{3i}(S_{2i} S_{3i} + S_{2i} S_{3'i})$$



Scheme 2. Spin topology for **1** assuming different J values

When the number of J values is only 1 or 2, it is possible to take into account axial anisotropy of J, since the number of final parameters is still sufficiently small. However, we had to assume here (even artificially) that $J_{x,y} = J_z$, simulat-

ing with an average J value, such as in an isotropic case. On the other hand, we assumed that $g_{\parallel}$ and $g_{\perp}$ for all four Co^{II} ions were equal. With this hypothesis, the best simulation was obtained with the following parameters: $J_1 = 2.15 \pm 0.08\ cm^{-1}$, $J_2 = 0.40 \pm 0.03\ cm^{-1}$, $J_3 = 0.12 \pm 0.02\ cm^{-1}$, $g_{\parallel} = 7.3 \pm 0.2$ and $g_{\perp} = 3.5 \pm 0.1$. The found g values are very reasonable for Co^{II} sites with distorted octahedral coordination.[12] Moreover, we have obtained the magnetisation vs. H curve at 2 K. At 5 T the $M/N\beta$ (reduced magnetisation) is 10.7. The simulation of the reduced magnetisation vs. H, with J and g values calculated from the susceptibility data, using the same MAGPACK program[11], is given in Figure 2 (B). There is reasonable agreement with the experimental curve.

Taking into account the difficulties for determining the exact J values, it will be interesting to compare this Co_4 cluster with the isostructural Ni_4 analogue.[6a] In the Ni^{II} case the J parameters were: $J_1 = 5.12\ cm^{-1}$, $J_2 = 0.35\ cm^{-1}$, $J_3 = 0.23\ cm^{-1}$ and $g = 2.17$. It was necessary to introduce the D parameter ($7.7\ cm^{-1}$) to explain the magnetic behavior at low temperatures. Thus, it is important to point out that in both cases the three J parameters are ferromagnetic and of the same order of magnitude: $J_1 >> J_2 > J_3$. As in the Ni_4 cluster, in **1** the Co−Co interactions between the corresponding spins are transmitted through the oxo and carboxylato bridges. From the magnetic point of view it is important to distinguish between these pathways. *Co−O−Co angles:* These angles lie close to 90° for J_1 and 95−100° for J_2; they are in the range in which ferromagnetic exchange pathways are dominant (90−100°); large superexchange angles lead to antiferromagnetic interactions while smaller ones induce ferromagnetic coupling.[13] *Acetato bridges*: The effect of the *syn*/*syn* acetato bridge is antiferromagnetic for Co^{II} and, actually, for any metal.[14] Thus, these bridges can mediate an additional exchange pathway and *significantly reduce* the ferromagnetic contribution from μ-oxo ligands. This effect has also been observed in the Ni_4 complex. *Comparison between J_1 and J_2*: J_1 is given by a planar Co−O−Co−O fragment (Scheme 2) with a Co−O−Co angle of 90°. This angle enhances the ferromagnetic coupling, but the presence of *two* carboxylato ligands (*syn*/*syn*) reduces this coupling. On the other hand, J_2 is given by a nonplanar Co−O−Co−O entity, with greater Co−O−Co angles, thus creating low ferromagnetic coupling, which is reduced by the presence of only *one* carboxylato group. Experimentally, both contributions are quasi-balanced, giving a J value that is positive but $< 1\ cm^{-1}$. *Study of J_3*: The carboxylato ligand bridges two Co^{II} ions in a *syn*/*anti* configuration; low antiferro- or ferromagnetic coupling is expected for this kind of coordination mode.[15] To the best of our knowledge, no magnetic studies for *syn*/*anti* carboxylato-bridged Co^{II} complexes have been reported so far.

Experimental Section

Materials and General Methods: H_2L was prepared by a literature method.[6] Other commercially available chemical reagents and solvents were of analytical grade and purified by standard procedures prior to use. FT-IR spectra were recorded with a 170SX (Nicolet) spectrometer at room temperature, and electronic absorption spectra were taken with a Hitachi UV-3010 spectrophotometer. Elemental analyses were carried out with a Perkin−Elmer 240C analyser. TG-DTA experiments were carried out with a Dupont thermal analyser from room temperature to 800 °C under N_2 at a heating rate of 10 °C/min. The variable-temperature magnetic susceptibilities were measured in the "Servei de Magnetoquímica (Universitat de Barcelona)" with a Quantum Design MPMS SQUID susceptometer operating at a magnetic field of 0.1 T between 2 and 300 K. The diamagnetic corrections were evaluated from Pascal's constants for all the constituent atoms.

Preparation of 1: Purple block crystals were obtained in 78% yield (199 mg) by slow concentration of the water solution containing $Co(ClO_4)_2 \cdot 6H_2O$ (300 mg, 0.8 mmol) and $H_2L \cdot 2HCl$ (200 mg, 0.6 mmol) in a 4:3 molar ratio by adjusting the pH to 5−6 with KOH. IR (cm^{-1}): $\tilde{\nu}$ = 1606 vs $\nu_{as}(COO^-)$, 1390 vs $\nu_s(COO^-)$, 1120 vs, 1108 vs and 625 s $\nu(ClO_4^-)$. $C_{36}H_{68}Cl_2Co_4N_6O_{24}$ (1275.6): calcd. C 33.90, H 5.37, N 6.59; found C 33.77, H 5.43, N 6.58. DTA (peak positions): 115, 293, 386 and 545 °C. UV (H_2O): $\lambda_{max.} = 491$ nm.

Crystallographic Study: $C_{36}H_{68}Cl_2Co_4N_6O_{24}$ (**1**), $M_r = 1275.58$, monoclinic, space group C_2, $a = 24.411(5)$, $b = 12.260(2)$, $c = 8.351(2)$ Å, $\beta = 98.738(4)°$, $V = 2470.4(8)$ Å^3, $F(000) = 1320$, $Z = 2$, $\mu = 1.518\ mm^{-1}$, $D_{calcd.} = 1.715\ g \cdot cm^{-3}$, Flack parameter = 0, 2989 reflections measured, 2669 unique ($R_{int} = 0.0186$). Final R, wR and S values are 0.0342, 0.0949 and 1.052, respectively. CCDC-176943 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/cons/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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