Cluster Compounds

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Co^{II} Chemistry of 2,6-Bis(2-pyridylcarbonyl)-pyridine: An Icosanuclear Co Cluster Exhibiting Superparamagnetic Relaxation**

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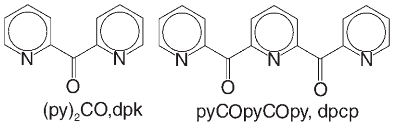
High-nuclearity transition-metal complexes (clusters) are of special interest in chemistry and physics because, both in terms of size and physical properties, they bridge the gap between the microscopic and macroscopic world, and between quantum and classical systems. In terms of size, the smallest classical nanoparticles fabricated today are the same size as the largest metal clusters that are synthesized by bottom-up methods.[1] In terms of physical properties, certain transition-metal clusters exhibit single-molecule magnetism[2] at low temperatures, that is, they retain their magnetization in zero field in a manner analogous to that of classical macroscopic magnets, but at the same time they exhibit quantum tunneling of magnetization (QTM),[3] clearly a quantum property. For these reasons transition-metal clusters are of great interest from the viewpoint of fundamental research, and applications have been proposed relating to memory devices[4] and quantum computing.[5] From the structural viewpoint, while the number of polynuclear 3d-metal complexes continues to grow rapidly, some nuclearities remain rare. Icosanuclear complexes are particularly uncommon.

A key factor in synthesizing such compounds is the proper use of ligands that can bind together a large number of metal ions. Di-2-pyridyl ketone ($(py)_2CO$ or dpk, Scheme 1) has afforded a host[6] of polynuclear clusters with a variety of transition-metal ions, including an Fe^{II} enneanuclear single-molecule magnet.[7] A metal-assisted nucleophilic attack by H_2O or ROH on the carbonyl group of this ligand yields its *gem*-diol or hemiacetal form, respectively. Subsequent deprotonation of the hydroxy groups gives the mono- or dianion (in the case of the *gem*-diol form), which can adopt a large number of coordination modes and bridge up to five metal ions.[7–10] We therefore supposed that a similar ligand with a second carbonyl group could be attacked on both carbonyl groups to provide additional donor atoms. The 2,6-bis(2-pyridylcarbonyl)pyridine ligand[11] (pyCOpyCOpy or dpcp, Scheme 1) has two carbonyl groups, each bonded to two 2-pyridyl units in a way similar to that in $(py)_2CO$. We thus thought that dpcp could have similar solvolysis, deprotonation, and coordination properties. Recent reports by Mak and co-workers on a series of Cu^{II},[12] Fe^{III},[13] and Cu^{I} and Ag^{I}[14] complexes verified this hypothesis.



Scheme 1. The $(py)_2CO$ and pyCOpyCOpy ligands.

Reaction of 4 equivalents of $Co(O_2CMe)_2{\cdot}4H_2O$ with 1 equivalent of dpcp in hot DMF and subsequent layering of the resulting solution with Et_2O led to deep purple crystals of $[Co_{20}(\mu_3\text{-}OH)_6(O_2CMe)_4(\mu_2\text{-}O_2CMe)_{12}(\mu_3\text{-}O_2CMe)_6(HL)_4(dmf)_2]{\cdot}2H_2O{\cdot}1.6dmf$ ($\mathbf{1}{\cdot}2H_2O{\cdot}1.6DMF$), where $HL^{3-} = pyC(O^-)(OH)pyC(O^-)_2py$ [Eq. (1)].

$$20\,Co(O_2CMe)_2\cdot 4H_2O + 4\,dpcp + 2\,DMF \xrightarrow{DMF,\ \Delta} [Co_{20}(OH)_6(O_2CMe)_{22}\{pyC(O)(OH)pyCO_2py\}_4(dmf)_2] + 66\,H_2O + 18\,MeCO_2H \quad (1)$$

The molecular structure[15] of **1** is shown in Figure 1. Complex **1** crystallizes in space group $P\bar{1}$. The asymmetric unit consists of a Co^{II}_{10} segment, and the other half of the molecule is generated by symmetry through an inversion

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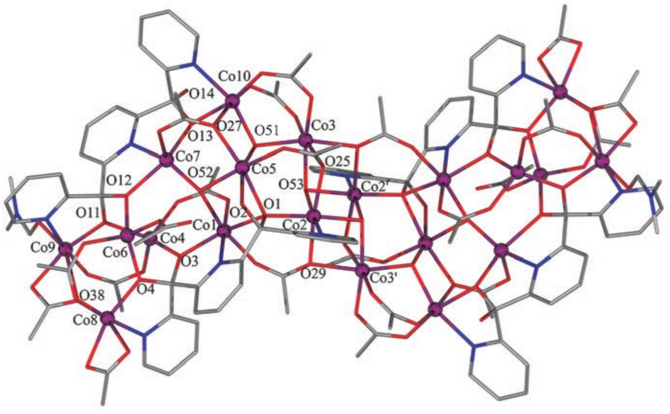
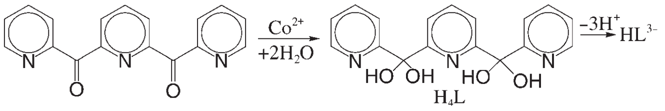


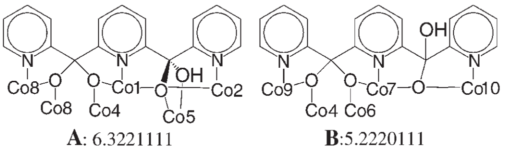
Figure 1. Molecular structure of **1**. For clarity, hydrogen atoms have been omitted and only Co atoms and monoatomic O bridges in one of the asymmetric units have been labeled. Color code: Co purple; O red; N blue. Distances [Å]: Co-$O_{hydroxo}$ 1.986–2.116, Co-N 2.055–2.147, Co-$O_{acetato}$ 1.965–2.593, Co-O_{alkoxo} 1.947–2.227.

center. The structure of **1** consists of a central double cubane with two missing vertices connected to two warped $\{Co_6O_6\}$ rings through two $\{Co_2O_4\}$ moieties (for a detailed discussion, see below).

The dpcp ligand has undergone hydrolysis of both carbonyl groups (Scheme 2), and both symmetry-independent ligands are present in their triply deprotonated bis(*gem*-diol) form (HL^{3-}). One of these (**A**) is sextuply bridging (μ_6), with a coordination mode that can be characterized as 6.3221111 in the Harris notation,[16] and the other (**B**) is quintuply bridging (μ_5, 5.2220111; Scheme 3). Both ligation modes are novel.



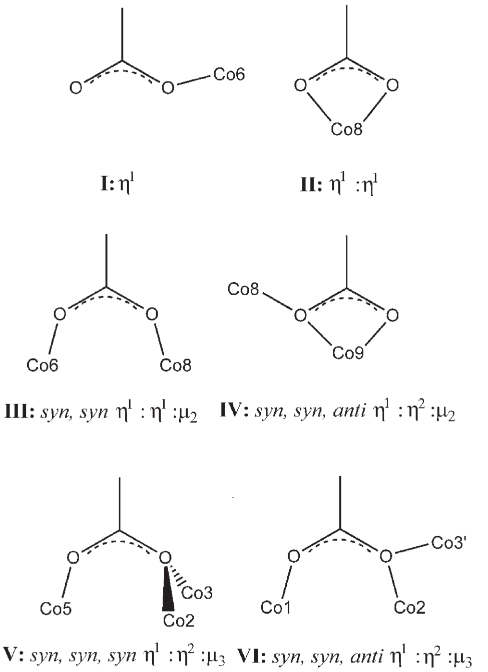
Scheme 2. Formation of the bis(*gem*-diol) form (H_4L) of dpcp and its triple deprotonation; note that H_4L and HL^{3-} do not exist as free species; they exist only as ligands in metal complexes.



Scheme 3. Crystallographically established coordination modes of the HL^{3-} ligands in **1** with Harris notations.

Of further interest are the six different coordination modes of the acetate ligands in the cluster (Scheme 4): one terminal monodentate (**I**), one terminal chelating (**II**), two doubly bridging (**III**, **IV**), and two triply bridging (**V**, **VI**).

The central incomplete double cubane comprises Co2, Co2′, Co3, and Co3′ (′ = −*x*, 2−*y*, 1−*z*), which exhibit distorted octahedral coordination spheres and are bridged solely by monoatomic bridges, two of which are μ_3-hydroxide ligands (O53 and O53′), and four are acetate oxygen atoms of type **V** (O25, O25′) and type **VI** (O29 and O29′) bridges (Figure 2).



Scheme 4. Crystallographically established coordination modes of the acetate ligands in **1**.

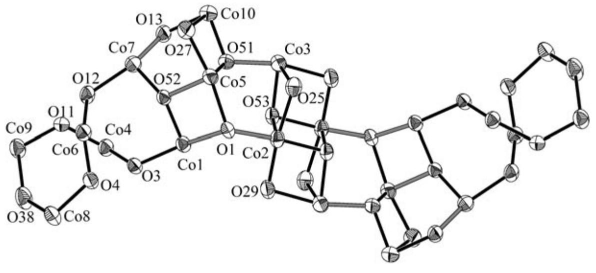


Figure 2. ORTEP plot of the central core of **1**. Only Co^{II} atoms and monoatomic O bridges are shown.

The external hexanuclear ring comprises Co1, Co7, Co6, Co8, Co9, and Co4. Of these, Co7 is pentacoordinate with a square-pyramidal geometry (trigonality index $\tau = 0.083$),[17] Co4 and Co6 are tetracoordinate with tetrahedral geometries, and the other metal ions are hexacoordinate with distorted octahedral geometries. The bridging of the ring is principally accomplished by six monoatomic bridges, that is, one μ_3-hydroxo (O52), four μ_2-alkoxo-type bridges (O3, O4, O11, O12) from the two trianionic ligands, and one oxygen atom (O38) from the μ_2-acetate ligand of type **IV**. Finally, the dinuclear moiety connecting the central incomplete double cubane subcore with the external ring through two alkoxo bridges (O14, O1) consists of atoms Co5 and Co10 bridged by one carboxylate and one hydroxide oxygen atom (O27 and O51, respectively).

The molecular structure is further stabilized by a series of intramolecular hydrogen bonds between the μ_3-hydroxide and acetate oxygen atoms (O52–H(O52)···O41, O2–H(O2)···O42, O51–H(O51)···O31) and between a hydroxy group of the ligand and an acetate oxygen atom (O14–H(O14)···O22). Concerning the formal charges of the Co ions, X-ray crystallography revealed the existence of one alcohol [H(O14)] and three hydroxide [H(O51), H(O52), H(O53)] hydrogen atoms per asymmetric unit, which were located from difference Fourier maps. Thus, charge-balance considerations require that all cobalt atoms are formally divalent.

Complex **1** is the first icosanuclear and second largest non-organometallic Co cluster synthesized to date, the largest being $[Co_{24}(\mu_3\text{-OH})_{14}(\mu\text{-OH})_4(\mu_3\text{-OMe})_2(\mu_3\text{-Cl})_2Cl_4(mhp)_{22}]$ (mhp^- = anion of 6-hydroxy-2-methylpyridine) reported by Winpenny and co-workers.[18] It is also one of the few structurally characterized non-organometallic, icosanuclear 3d-metal clusters with exclusively O and/or N ligation.[19] A handful of icosanuclear 3d-metal clusters involve S^{2-} or Se^{2-} bridges.[20] A space-filling plot of **1** (see Supporting Information) reveals that the molecule is approximately cylindrical in shape, with a length of about 3 nm and a diameter of about 1.5 nm.

Since cobalt(II) clusters are potential single-molecule magnets,[21] variable-temperature (2.0–300 K) magnetic susceptibility data (at 0.1 and 1 T) and a magnetization isotherm at 2 K (0–5.5 T) were recorded for **1** (Figure 3). The $\chi_M T$ product for **1** at 300 K (1-T field) of 51.23 $cm^3 mol^{-1} K$ is significantly higher than the spin-only value expected for 20 noninteracting ions with $S = 3/2$ (37.4 $cm^3 mol^{-1} K$). This is attributed to the orbital contribution of Co^{II}, which is known to be significant in an octahedral field. The continuous decrease in $\chi_M T$ with decreasing temperature is indicative of dominant antiferromagnetic interactions. The decrease is more pronounced below 10 K, and $\chi_M T$ reaches 6.90 $cm^3 mol^{-1} K$ at 2 K, due to the zero-field splitting of the ground state of the cluster, which is typically large for complexes containing high-spin, six-coordinate Co^{II} ions. In a 0.1-T field, however, this decrease is smoother (10.90 $cm^3 mol^{-1} K$ at 2 K) because of the weaker Zeeman splitting of the ground state. However, the nonzero value at 2 K and the continuous increase in χ_M on cooling indicate the existence of a magnetic ground state, or a diamagnetic ground state with low-lying magnetic excited states which are populated even at 2 K. This is also corroborated by the magnetization isotherm at 2 K, which does not show saturation up to a field of 5.5 T, possibly due to simultaneous population of numerous spin states.

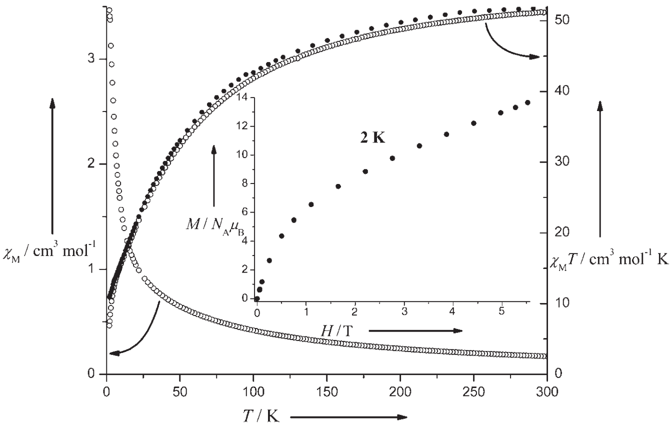


Figure 3. χ_M and $\chi_M T$ versus T plots for **1** in the range 2.0–300 K in fields of 1 T (○) and 0.1 T (●). The magnetization isotherm at 2 K between 0 and 5.5 T is shown in the inset.

To clarify this, and to probe the relaxation properties of **1**, zero-field ac susceptibility measurements between 1.9 and 10 K were carried out at frequencies of 50, 100, 500, 1000, and 1400 Hz (Figure 4). These showed frequency-dependent out-of-phase signals, which may be attributed to superparamagnetic relaxation of the magnetization of **1**. However, since no maxima were observable down to 1.9 K, quantitative estimation of the relaxation kinetics was not possible. The $\chi_M' T$ product extrapolates to about 11 $cm^3 mol^{-1} K$ at 0 K, which suggests an effective $S = 4$ ground state. Due to the size and complexity of the molecule, however, quantitative interpretation is not possible.

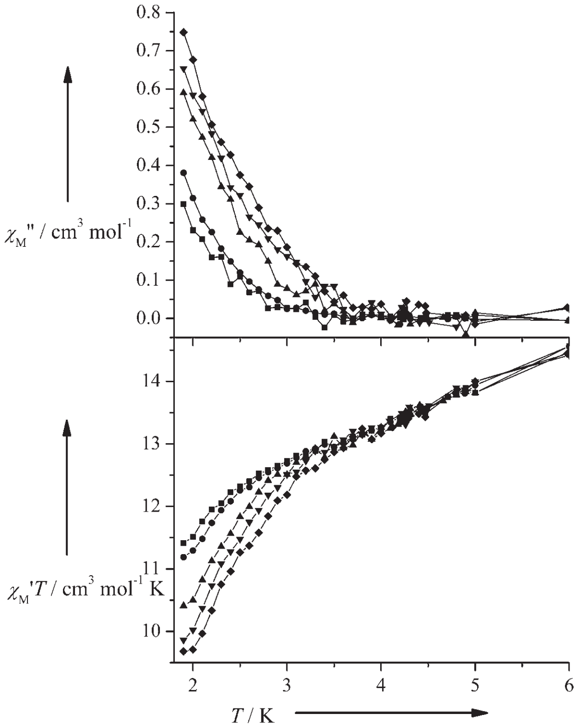


Figure 4. Frequency dependence of the in-phase $\chi_M' T$ product and the out-of-phase χ_M'' magnetic susceptibility versus T for **1** at frequencies of 50 (■), 100 (●), 500 (▲), 1000 (▼), and 1400 Hz (◆).

In summary we have isolated and characterized the first icosanuclear Co^{II} cluster, which is also a rare example of 3d-metal clusters with O and N ligation. Moreover, this work emphasizes the coordinative flexibility and versatility of the dpcp ligand and its synthetic utility in polynuclear metal chemistry.

Experimental Section

1: Solid dpcp (40.0 mg, 0.138 mmol) was added to a solution of $Co(O_2CMe)_2{\cdot}4H_2O$ (138 mg, 0.553 mmol) in DMF (15 mL). The color of the solution changed immediately from dark purple to deep wine red. The solution was heated for 10 min just below the boiling point of DMF, during which time a color change to very deep purple was observed. The solution was cooled to room temperature and layered with double the volume of Et_2O in a layering tube. Dark purple crystals formed after about one week. These were collected by decantation, repeatedly washed with Et_2O, and dried in vacuo (yield ca. 30%). The dried solid analyzed as **1**·0.2 DMF. Elemental analysis (%) calcd for $C_{118.6}H_{132.14}Co_{20}N_{14.2}O_{68.2}$: C 35.37, H 3.34, N 4.94; found: C 35.32, H 3.38, N 4.89. IR (KBr disk): $\tilde{\nu} = 3423$ (vs), 1664 (s), 1602 (vs), 1574 (vs), 1559 (vs), 1436 (vs), 1419 (vs), 1063 (m), 1027 (m), 827 (w), 797 (w), 761 (w), 663 (m), 617 cm^{-1} (w).

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[15] Crystal data for **1**·2 H_2O·1.6 DMF ($C_{122.8}H_{149.2}Co_{20}N_{15.6}O_{71.6}$): $M_r = 4167.98$, triclinic, $P\bar{1}$, $a = 16.643(7)$, $b = 17.733(8)$, $c = 21.976(8)$ Å, $\alpha = 105.03(1)$, $\beta = 111.18(1)$, $\gamma = 91.56(1)°$, $V = 5788(4)$ Å^3, $Z = 1$, $T = 298$ K, $F(000) = 2108$, $\rho_{calcd} = 1.196\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 1.457\ mm^{-1}$ ($\lambda = 0.71073$ Å), 11130 reflections measured, 10633 unique reflections ($R_{int} = 0.0302$), 1040 refined parameters, $R_1(F) = 0.0798$ and $wR_2(F^2) = 0.2207$ for 7068 reflections with $I > 2\sigma(I)$. CCDC-278700 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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