

Synthesis, crystal structure and magnetic properties of a mixed-valence pentanuclear cobalt complex†

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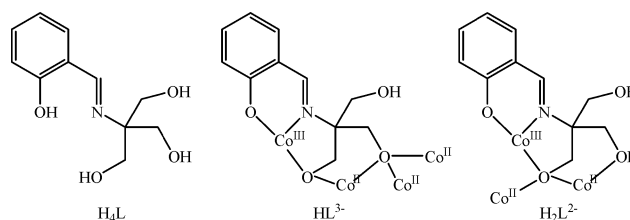
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Solvothermal reaction of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ with H_4L ($\text{H}_4\text{L} = 2-((2\text{-hydroxybenzylidene)amino})-2\text{-hydroxymethylpropane-1,3-diol}$) in MeCN gave a mixed-valence pentanuclear cobalt complex $[\text{Co}_5(\text{HL})_2(\text{H}_2\text{L})_2(\text{OAc})_2] \cdot 2.5\text{H}_2\text{O}$. Crystal structural analysis revealed that two $\text{Co}(\text{III})$ ions were linked to a central triangular $\text{Co}(\text{II})$ core through HL^{3-} and H_2L^{2-} hydroxyl groups. Magnetic measurements showed interesting magnetic properties that were assigned to spin-orbital coupling and ferromagnetic exchange interactions.

Polynuclear paramagnetic clusters (PMCs) have recently attracted considerable attention, not only due to their intriguing structures and magnetic properties but also to their potential application in functional molecule-based materials. The discovery of single-molecule magnets (SMMs)¹ and their potential applications in high density information storage have immensely prompted the investigation of PMCs in quest of SMMs with high blocking temperature and slow magnetization relaxation. The synthetic approaches towards novel PMCs usually involve the one-pot reaction of metal salts with polydentate ligands or the ligand-substitution/modification of PMC precursors,² in which metal ions with magnetic anisotropy (Mn^{3+} , Co^{2+} , Fe^{3+} , Tb^{3+} , Dy^{3+} , etc.) are mostly introduced due to the possibility of the formation of PMCs showing interesting magnetic properties. Among of them, PMCs containing $\text{Co}(\text{II})$ ions are of particular interest because of their complicated magnetic properties, which are affected not only by large single-ion magnetic anisotropy, but also by strong spin-orbital coupling as well as magnetic dipole-dipole interactions. Especially at low temperature, the splitting of the ground state makes the magnetic properties of $\text{Co}(\text{II})$ clusters more complicated than those of other metal clusters. Up to now, various polynuclear $\text{Co}(\text{II})$ oligomers³ have been reported to show interesting magnetic properties, however two triangular $\text{Co}(\text{II})$ trimers have been only recently synthesized and in one trimer cobalt ions were bridged by end-on μ_2 - and μ_3 - N_3^- and $\eta^1:\eta^1:\mu\text{-OAc}^-$ and ferromagnetically coupled.⁴

In order to synthesize new polynuclear $\text{Co}(\text{II})$ clusters, we have recently begun to employ the Schiff-base ligand 2-((2-hydroxybenzylidene)amino)-2-hydroxymethylpropane-1,3-diol (H_4L , Scheme 1), which contains a pentadentate $\{\text{NO}_4\}$ donor set and a tripodal alcohol unit that possesses chelating and bridging capabilities. We believe that the five potential incorporable sites



Scheme 1 H_4L and the coordination modes in **1**.

and multiple coordination modes will make the ligand a good candidate for the achievement of new polynuclear complexes. Indeed, H_4L was once successfully used in the assembly of several trinuclear and tetranuclear copper, manganese and nickel complexes.⁵ Here, we present the solvothermal synthesis, structure and magnetic properties of a novel mixed-valence pentanuclear cobalt complex, namely $[\text{Co}_5(\text{HL})_2(\text{H}_2\text{L})_2(\text{OAc})_2] \cdot 2.5\text{H}_2\text{O}$ (**1**, $2.5\text{H}_2\text{O}$). It should be mentioned here that although polynuclear mixed-valence $\text{Co}(\text{II,III})$ complexes have been widely reported,⁶ no pentanuclear $\text{Co}(\text{II,III})$ complex has been found and this is the first one with triangular $\text{Co}(\text{II})$ core.

$\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.075 g, 0.3 mmol) was added with stirring to a MeCN (8 mL) solution containing H_4L (0.046 g, 0.2 mmol). The resulting dark brown suspension was further stirred for 30 min and then placed in a Teflon-lined autoclave and heated for 1 d at 110 °C. After cooling to room temperature, red-brown block crystals suitable for single crystal X-ray diffraction were obtained in a yield of about 38% (based on ligand).

Complex **1**· $2.5\text{H}_2\text{O}$ crystallized in the triclinic space group $P\bar{1}$. The structure of **1** is shown in Fig. 1a.† The complex contains a mixed-valence $[\text{Co}^{\text{III}}_2\text{Co}^{\text{II}}_3(\mu_2\text{-O})_2(\mu_3\text{-O})_4]$ cluster comprising three edge-shared $[\text{Co}_3\text{O}]$ triangles, in which the three central divalent Co ions (Co3, Co4 and Co5) are ligated exclusively by oxygen atoms to form an isosceles triangle with the $\text{Co} \cdots \text{Co}$ distances of 2.859(1) Å, 2.855(1) Å, 3.124(1) Å and with the $\text{Co} \cdots \text{Co} \cdots \text{Co}$ angles of 56.79(2)°, 56.93(2)° and 66.28(3)°, respectively (Fig. 1b). The $\mu_3\text{-O3}$ and $\mu_3\text{-O11}$ atoms from two HL^{3-} alcohol groups sit 1.24 Å above the triangular plane in each side. The remaining two peripheral $\text{Co}(\text{III})$ ions (Co1 and Co2) lie above and below the plane of the central three $\text{Co}(\text{II})$ ions and possess N_2O_4 ligand sets. The oxidation states of all cobalt ions are evidenced by charge-balance considerations and the typical bond lengths for oxygen- and nitrogen-bound $\text{Co}(\text{II})$ and $\text{Co}(\text{III})$ ions. The bond distances around the central trinuclear cobalt ions (Co3, Co4, Co5) vary from 2.007(3) to 2.231(3) Å, while which of the peripheral cobalt ions (Co1, Co2) from 1.872(4) to 1.942(3) Å. All five cobalt ions adopt distorted octahedral geometries with the coordination spheres completed by two HL^{3-} ligands, two H_2L^{2-} ligands and two acetate ligands. The two acetate ligands bind to the three

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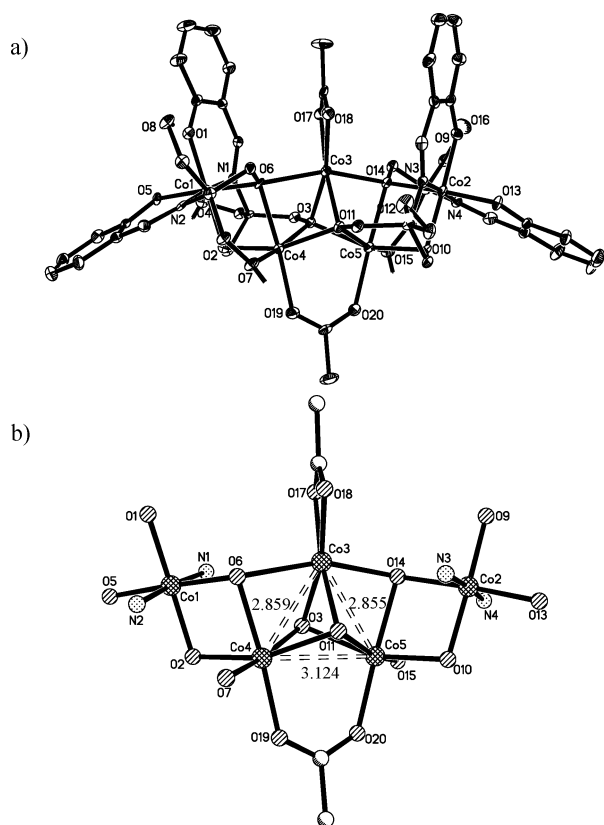


Fig. 1 ORTEP drawing at 50% probability of **1** (a) and a perspective view of the pentanuclear unit (b) with atom labels. Selected Co–O–Co bond angles ($^{\circ}$): Co3–O3–Co5 86.3(1), Co3–O3–Co4 84.8(1), Co4–O3–Co5 94.7(1), Co3–O11–Co4 87.4(1), Co3–O11–Co5 84.2(1), Co4–O11–Co5 94.7(1).

Co(II) ions in different modes, e.g. *syn-syn* $\eta^1:\eta^1:\mu$ -OAc for Co4 and Co5 and $\eta^1:\eta^1$ -OAc for Co3, respectively. The H_4L ligands in **1** are partially deprotonated to give HL^{3-} and H_2L^{2-} (Scheme 1), respectively, and display different coordination modes: for HL^{3-} , one alkoxide oxygen atom is μ_3 -bridged to the three central Co(II) ions and the second one is μ_2 -bridged to a Co(II) ion and a Co(III) ion. While for H_2L^{2-} , only one alkoxide oxygen atom acts as μ_3 -bridging mode to link two Co(II) ions and one Co(III) ion, and the second one is protonated and binds only with one Co(II) ion. Both HL^{3-} and H_2L^{2-} possess a free alcohol group that is involved in the formation of intra- and intermolecular hydrogen bonds, and the second ones lead to the formation of 2D hydrogen-bonded sheets.

The magnetic properties of **1**·2.5 H_2O are attributed to the three octahedrally coordinated Co(II) ions, which are arranged in an isosceles triangular $\{Co_3\}$ fashion as shown in Fig. 1b (dashed open line). At room temperature, the $\chi_M T$ value (Fig. 2a) is 9.98 emu K mol $^{-1}$ ($\mu_{\text{eff}} = 5.16 \mu_B$ per Co(II)), which is considerably larger than the spin-only value of 5.63 emu K mol $^{-1}$ calculated for three high-spin Co(II) ions ($S = 3/2$, $g = 2$) due to the orbital contribution from single octahedral Co(II) ions. Upon lowering the temperature, $\chi_M T$ smoothly decreases to a minimum value of 7.83 emu K mol $^{-1}$ ($\mu_{\text{eff}} = 4.57 \mu_B$ per Co(II)) at 18 K, resulting from the depopulation of the higher energy Kramers doublets associated with the high-spin Co(II) single ions. Thus, between room temperature and 18 K, $\chi_M T$ is dominated by single-ion

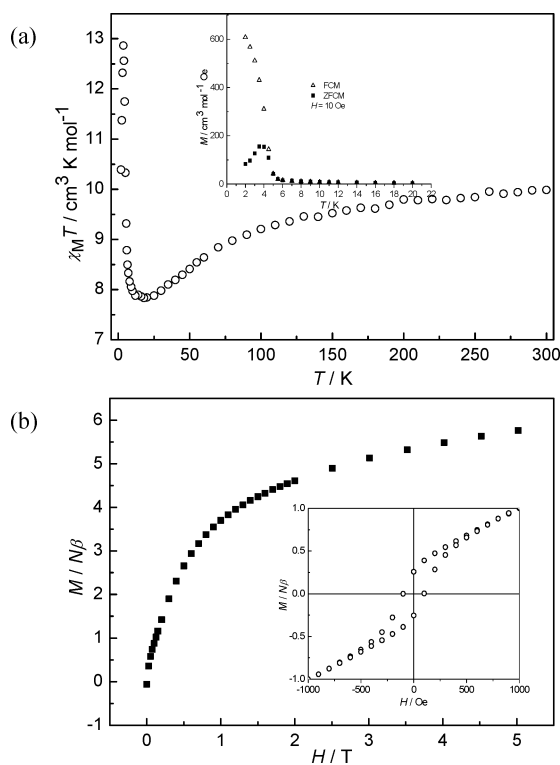


Fig. 2 (a) The temperature-dependent susceptibility of **1**·2.5 H_2O measured under applied field of 1000 Oe; inset: ZFCM and FCM plots under applied field of 10 Oe. (b) Magnetization and the hysteresis loop (inset) at 2 K.

properties of three uncoupled Co(II) ions. When the temperature continues to decrease from 18 K, the $\chi_M T$ value abruptly increases to reach a maximum of 12.87 emu K mol $^{-1}$ at 3.5 K, indicating the presence of intramolecular ferromagnetic interactions between the Co(II) ions mediated by the alkoxide bridging oxygen atoms. Finally, the $\chi_M T$ value suddenly decreases on further cooling to reach a value of 10.39 emu K mol $^{-1}$ at 2 K, which may be due to long-range magnetic ordering. The magnetization *versus* field plots at 2 K also confirm the observed ferromagnetism. At 5 T, complex **1**·2.5 H_2O reaches a saturation value of magnetization (MS) of 5.76 $N\beta$, that is 1.92 $N\beta$ per Co(II) ion, which is smaller than the expected value of 3 $N\beta$, for a spin quartet Co(II) with $g = 2$. The fact is that the spin–orbit coupling splits the ground $^4T_{1g}$ term of each octahedral Co(II) ion into doublet Γ_6 , quartet Γ_7 and sextet $\Gamma_7 + \Gamma_8$ states,⁷ and that only the ground Kramers doublet is populated at low temperature ($T < 20$ K), where Co(II) ion can be treated as an effective spin $S_{\text{eff}} = 1/2$ system with large anisotropic g -tensor (3.8–4.3). As a result, MS can be 1.9–2.15 $N\beta$ per Co(II) ion at 2 K. Attempts to fit the magnetic susceptibility by spin-Hamiltonian with the Kambe or Lines methods⁸ failed, because six-coordinate Co(II) ions present considerable first-order orbital momentum, so the spin-Hamiltonian must be supplemented by the orbitally dependent exchange interactions and spin–orbit coupling effects.⁹

Complex **1**·2.5 H_2O shows a clear bifurcation in the field-cooled (FC) and zero-field-cooled (ZFC) magnetization plots (Fig. 2a, inset), which gives clear evidence for long-range order. The FCM curve increases sharply below about 6 K and ZFCM curve shows a maximum at $T_c = 3.5$ K, thus suggesting the onset of a long-range

ferromagnetic transition. The transition is further confirmed by a small hysteresis loop at 2 K (Fig. 2b, inset), which is characteristic of a soft ferromagnet with coercive field of 100 Oe and remnant magnetization of $0.26 N\beta$.

The AC data were collected at three frequencies and χ' curves show rapid increases below 5 K with maxima at 4.3 K, then deeply decrease to reach non-zero values at 2 K. This and the appearance of peaks in χ'' curves can be assigned to the dynamics of magnetic domains in the ordered phase.

In a small applied field of 100 Oe (Fig. 3b), the $\chi_M T$ value increases sharply at T_c , reaching a value much higher than anticipated for short-range order, confirming the long-range ferromagnetic order revealed by ZFC and ZFCM. The unusual temperature dependence of $\chi_M T$ at different fields comes from the effect of spin-orbit coupling and low-symmetry ligand field splittings on single-ion $^4T_{1g}$ states combined with weak intracluster ferromagnetic coupling. The exchange coupling is not strong enough to overcome single-ion effects and yield the long-range order as displayed by a 3D ferromagnet α -Co(dca) $_{10}$ and a layered, hard ferromagnet $\text{Co}^{II}_5(\text{OH})_8(\text{dca})_2 \cdot 6\text{H}_2\text{O}$ (dca = dicyanamide).¹¹ The long-range ferromagnetic order may be propagated through intralayer cluster-cluster hydrogen bonds.

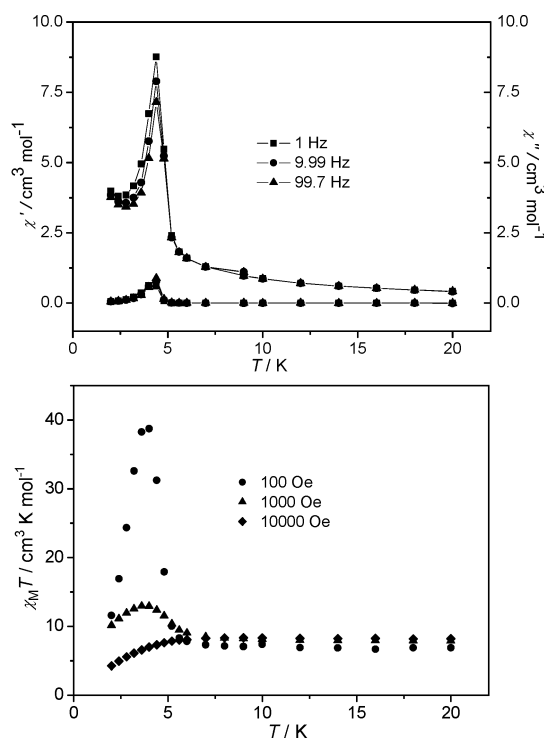


Fig. 3 (a) AC data of 1-2.5H₂O determined in an oscillating field of 2 Oe. (b) Plots of magnetic susceptibilities of 1-2.5H₂O in fields of 100 Oe, 0.1 T and 1 T.

In summary, a new pentanuclear mixed-valence cobalt(II,III) complex with a triangular $\{\text{Co}^{II}_3\}$ center has been synthesized by using a pentadentate Schiff-base ligand. Magnetic measurements reveal the existence of intramolecular ferromagnetic coupling and long-range ferromagnetic order.

Acknowledgements

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Notes and references

‡ Anal. calcd. (%) for $[\text{Co}_5(\text{HL})_2(\text{H}_2\text{L})_2(\text{OAc})_2] \cdot 2.5\text{H}_2\text{O}$ (1-2.5H₂O), C₄₈H₆₁N₄Co₅O_{22.5}: C, 42.75; H, 4.56; N, 4.15. Found: C, 41.90; H, 4.73; N, 4.28. IR data (cm⁻¹): 3420 (s), 2926 (m), 2869 (w), 1629 (s), 1600 (s), 1566 (s), 1446 (s), 1343 (w), 1305 (w), 1202 (w), 1147 (w), 1028 (m), 925 (w), 763 (w), 686 (w), 665 (w), 609 (m), 533 (m), 445 (w). The crystal data for 1-2.5H₂O were collected on a Oxford CCD diffractometer at 173(2) K using Mo-K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods¹² and refined on F^2 .¹³ The calculated hydrogen atoms were included in the final refinement. Crystal data for 1-2.5H₂O: dark red-brown blocks (0.5 mm \times 0.16 mm \times 0.1 mm), C₄₈H₆₁N₄Co₅O_{22.5}, $M = 1348.66$, triclinic, space group $P\bar{1}$ (no. 2), $a = 9.5216(2)$ Å, $b = 11.6982(3)$ Å, $c = 23.8356(6)$ Å, $\alpha = 92.693(2)^\circ$, $\beta = 92.320(2)^\circ$, $\gamma = 97.910(2)^\circ$, $U = 2623.82(11)$ Å³, $Z = 2$, $T = 173$ K, 19 332 reflections measured, 10 915 unique reflections ($R_{\text{int}} = 0.0518$), refinement with 721 parameters converged with agreement factors R_1 ($I > 2\sigma$) = 0.0647, wR_2 (all data) = 0.1308, GOF = 1.005, $2\theta \leq 54^\circ$. CCDC reference number 694931. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b812113c

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