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Synthetic and magnetic studies of a dodecanuclear cobalt wheel

Euan K. Brechin,[a] Olivier Cador,[b] Andrea Caneschi,*[b] Cyril Cadiou,[a] Steven G. Harris,[c] Simon Parsons,[c] Michele Vonci[b] and Richard E. P. Winpenny*[a]

[a] *Department of Chemistry, The University of Manchester, Oxford Road, Manchester, UK M13 9PL. E-mail: richard.winpenny@man.ac.uk*

[b] *Laboratorio di Magnetismo Molecolare, Dipartimento di Chimica, Università degli Studi di Firenze, Polo Scientifico Universitario, Via Lastruccia n. 3, 50019, Sesto Fiorentino, Italy. E-mail: andrea.caneschi@unifi.it*

[c] *Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*

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The synthesis, structural characterisation and preliminary magnetic studies of a Co_{12} wheel are reported; the magnetic investigations reveal that the electronic ground state has a spin $S = 6$, which corresponds to ferromagnetic interactions between the twelve Co(II) ions.

Recently coordination chemists have reported a number of cyclic polynuclear wheels. Starting with the decanuclear yttrium ring reported by Hubert-Pfalzgraf and co-workers,[1] large metallocycles have been reported for 3d-metals as diverse as titanium[2] and nickel,[3] but remain rare. The nickel wheel, of formula $[Ni_{12}(chp)_{12}(O_2CMe)_{12}(H_2O)_6(THF)_6]$ **1**, (chp = 6-chloro-2-pyridonate) has an $S = 12$ ground state. A small negative zero-field splitting of this ground state results in this wheel being a single molecule magnet — *i.e.* it show hysteresis in a plot of magnetization against field.[4] Given the interesting physical properties we hoped this was the first dodecanuclear wheel of an extended family, and that similar wheels should be accessible for different metals and different ligands. This confidence has taken some years to be justified, however we now report a Co complex that leads us to hope other divalent metal centres might become involved in such structures. The magnetic properties of this wheel are highly unusual.

Hydrated cobalt acetate (6.8 mmol) is placed in a Schlenk tube and dried in vacuum for several days. Hchp (14.2 mmol) is then added and the mixture is heated under nitrogen to 130 °C for 15 min. The reaction mixture is then heated under reduced pressure, which removes acetic acid formed during reaction, and any unreacted Hchp. The resulting paste is then extracted with THF and crystallised by slow evaporation to give $[Co_{12}(chp)_{12}(O_2CMe)_{12}(H_2O)_6(THF)_6]$ **2** in 60% yield.† The reaction differs from the procedure to give **1** only in the prolonged drying of the cobalt acetate which is required prior to reaction. Although moisture is necessary to form both **1** and **2** it seems crucial that this is only present during crystallisation for **2**, and not earlier.

Structure solution‡ reveals a complex isostructural with **1** (Fig. 1). The compound lies on a crystallographic 3 axis, with two metal atoms in the asymmetric unit, each bound to six oxygen donors. These are derived from four types of ligands. Firstly, there are acetate ligands, which either lie within the cavity of the metallocycle and bind in a 3.21 mode (Harris notation[5]), bridging Co(1′) and Co(2) through one O-donor and binding to Co(1) through the second, or which are outside the ring and adopt the more common 2.11-mode. Secondly, the chp ligands are 2.20-bridging through the exocyclic O-donor only. Thirdly, there are water molecules that are 2.2-bridging and involved in H-bonds to the uncoordinated N-atoms of the chp units; the associated O…N distances are around 2.66 Å. Finally, there are terminal THF molecules attached to the Co(2) sites.

The metal coordination sites are close to octahedral, with the major distortion being one *cis*-angle which is compressed to 79.3(3)°. The Co···Co distances in **2** are 3.122 and 3.176 Å which compare with the Ni···Ni distances of 3.065 and 3.108 Å in **1**. This variation is similar to that found in trinuclear Co and Ni complexes.[6]

The magnetic properties of a powdered sample of **2** have been studied.§ The variation of the $\chi_M T$ product, where χ_M is the molar magnetic susceptibility and T the temperature, of **2** with temperature is represented in Fig. 2a. At 250 K $\chi_M T$ is equal to 38 emu K mol^{-1}. This value is much higher than what is expected for 12 isolated spin-only $S = 3/2$ ions (22.5 emu K mol^{-1} with $g_{Co} = 2$). It gives $g_{Co} = 2.6$ if we assume the ions are uncoupled. As T is lowered, first $\chi_M T$ decreases, reaches a minimum at $T_{min} = 35$ K with $\chi_M T = 34.5$ emu K mol^{-1}, then increases. The presence of a minimum is generally associated with ferrimagnetism (antiferromagnetic interactions between the spins with a noncompensation of the local magnetic moments) but the magnetism of Co(II) ion in molecular compounds is fairly complex because of the combined effects of spin-orbit coupling and the distortion of the octahedral crystal field. Normally this gives two low-lying Kramers doublets separated by a few tens of wavenumbers. The other Kramers doublets are much higher in energy. The consequence is that $\chi_M T$ shows strong deviation from the Curie law for an isolated Co(II) and it decreases with temperature.[7] At low temperature Co(II) can be treated with an effective spin $S'_{Co} = \frac{1}{2}$ and a very anisotropic g'_{Co} tensor.[8] We therefore consider that the decrease

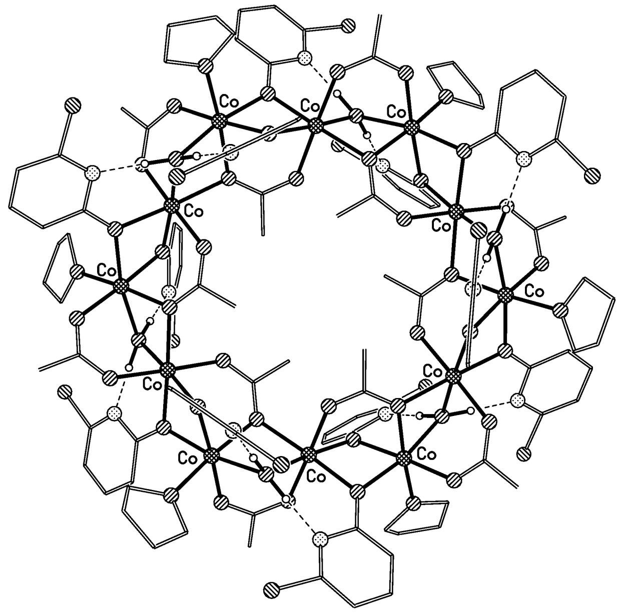

Fig. 1 The structure of **2** in the crystal. Bond length ranges for **2**: Co–O(chp) 2.073 to 2.100, Co–O(acetate), 2.036 to 2.100, Co–O(H_2O), 2.151 and 2.166, Co–O(THF), 2.108 Å (Av. esd 0.007 Å). H–bonds shown as dotted lines: N···O distances 2.636 or 2.696(14) Å. (Shading: Co, cross–hatched; N, dotted; O, diagonal bottom left–top right; Cl, diagonal top left–bottom right; C, line; H, open circles).

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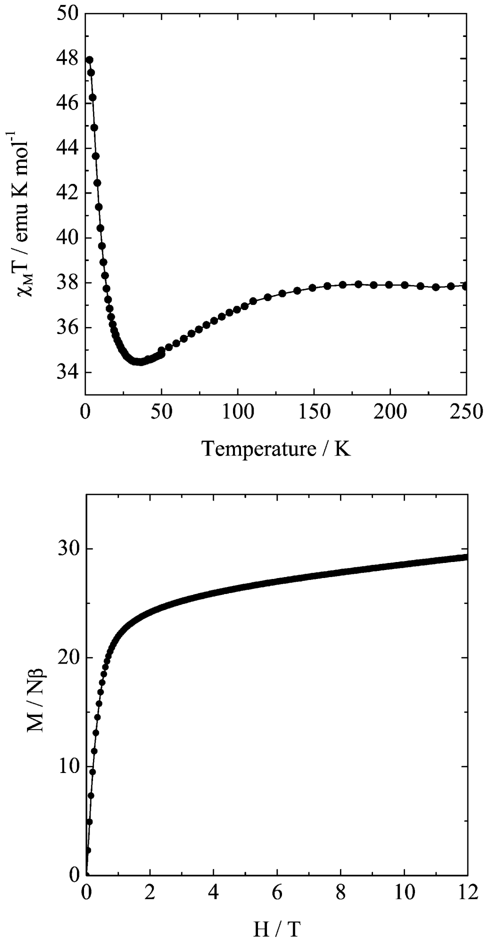

Fig. 2 a) Plot of $\chi_M T$ against T for **2** b) plot of the variation of the magnetization with the external field at $T = 2$ K.

of $\chi_M T$ above T_{min} is due to the magnetic anisotropy of Co(II) while the increase below T_{min} is due to ferromagnetic interactions between the effective spins S'_{Co}. In the low temperature limit the effective spin of the molecule S_T is equal to $12 \times ½ = 6$. We must stress that this is an over-simplified picture as the S_T classification is applicable only in the case of isotropic exchange.

We have investigated the variation of the magnetization *vs.* the magnetic field at 2 K for **2** (see Fig. 2b). The most striking feature is that the magnetization does not saturate. It increases almost linearly for higher fields than 4 T. This feature may be considered as the fingerprint of the magnetic anisotropy of the molecule. The value of the magnetization at 12 T is equal to 29 Nβ. In taking $S_T = 6$ we obtain $g = 4.83$, which is compatible with the powder average g value observed for the effective spin ½ of Co(II) at low temperature.[8]

A quantitative analysis of the magnetic properties of **2** is complicated by the high anisotropy of Co(II). Isotropic exchange interactions are not relevant, and both g and J anisotropy must be determined. Worse still, as there are two independent Co(II) sites in the crystallographic structure of **2** and two anisotropy tensors are required for both sites. The orientations of these tensors with respect to the crystallographic axis have to be determined in order to derive the spin configuration of the ground state. A solution would be to make a M_{12} wheel, with M(II) a diamagnetic ion, and dope this wheel with Co(II) so the anisotropy of each cobalt site can be identified and their respective influences on the magnetic properties of the 'pure' Co_{12} wheel quantified in the absence of exchange.

Magnetic anisotropy is vital for the molecule to become a single molecule magnet, but this condition is nevertheless not sufficient. The anisotropy must show an easy axis of magnetization to be able to trap the magnetic moment into two opposite, but equivalent, directions. Preliminary results show that **2** has a planar type anisotropy (*i.e.* D is positive) which prevents **2** behaving as a single molecule magnet.

Of the cyclic structures reported thus far, the most common are octanuclear cages where each metal–metal vector is bridged by two carboxylates and a single monoatomic bridge such as oxide, fluoride or hydroxide. Such M_8 wheels are found for the metals Ti,[2] V,[9] Cr,[10] Fe,[11] and Co.[12] M_{10} wheels are restricted to Fe(III)[13] and Cr(III),[14] and in these cages each metal–metal vector is spanned by one carboxylate and two μ-methoxides. The M_{12} wheels reported here have the same bridging motif — albeit with different sources of the μ_2-bridging groups — as the 'ferric wheels', but the metals are in the +2 oxidation state. If a pattern is emerging then we can predict that other M(II) centres, *e.g.* Fe(II), Mn(II) or Zn(II), may form M_{12} wheels isostructural with **1** and **2**.

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Notes and references

† A satisfactory elemental analysis was obtained for **2**.

‡ Crystal data for $C_{144}H_{208.3}Cl_{12}Co_{12}N_{12}O_{59.22}\cdot C_4H_8O_2$ **2**: rhombohedral, $R3c$, $a = 23.094(3)$, $c = 64.051(18)$ Å, $V = 29584(10)$ Å^3, $M = 4187.7$, $Z = 6$ (the molecule lies on a $\bar{3}$ axis), $T = 220.0(2)$ K, $\mu = 1.221$ mm^{-1}, no. of independent reflections = 4321 ($R_{int} = 0.00$), $R1 = 0.0895$. Data collection, structure solution and refinement were performed as detailed in ref. 4 using programs SHELXS-86[15] and SHELXL-93.[16] Solvent of crystallisation was treated in the manner described by van der Sluis and Spek.[17] CCDC 187800. See http://www.rsc.org/suppdata/cc/b2/b205721m/ for crystallographic data in CIF or other electronic format.

§ Variable temperature susceptibility was measured with a Cryogenic S600 SQUID magnetometer operating between 2 and 320 K. The magnetization studies were recorded with an Oxford Instruments Vibrating Sample Magnetometer (VSM) working between 0 and 12 T and in the 1.5–350 K temperature range.

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