The Synthesis, Structure and Magnetic Properties of a Cyclic Dodecanuclear Nickel Complex

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The synthesis and characterisation of the dodecanuclear nickel complex, $[\mathrm{Ni_{12}(O_2CMe)_{12}(chp)_{12}(H_2O)_6(THF)_6}]$ (where chp = the anion of 6-chloro-2-pyridone) is described; structure determination shows formation of a metallocycle, while magnetic studies indicate ferromagnetic coupling between the nickel(II) ions within the complex leading to a high spin multiplicity in the ground state.

There is much current interest in polymetallic coordination complexes,[1] and in particular in their magnetic properties.[2–5] Around ten years ago a dodecanuclear cobalt complex was reported featuring mixed acetate and pyridone bridging ligands.[6] When we recently synthesised a series of octanuclear copper complexes using the same mixture of bridging ligands,[7] we reasoned that the presence of mixed bridging ligands might be favouring the formation of high nuclearity assemblies. As a continuation of these studies we have now examined the reactivity of nickel acetate with 6-chloro-2-pyridone (Hchp), and produced in good yield a novel dodecanuclear metallocyclic complex, which furthermore possesses an unusual spin ground state.

Hydrated nickel acetate (6.8 mmol) was added to an excess of Hchp (14.2 mmol) and the mixture heated under nitrogen to 130 °C, causing the ligand to melt. The reaction was stirred for 1 hour, during which time the mixture became bright green. The resultant acetic acid and water, along with unreacted Hchp were then removed under reduced pressure. The residue was extracted with THF and crystallised by slow evaporation to give green blocks in 60% yield.[†]

Structure solution[‡] revealed a complex of stoichiometry $[\mathrm{Ni_{12}(O_2CMe)_{12}(chp)_{12}(H_2O)_6(THF)_6}]$ **1** (Fig. 1), crystallised as a THF solvate. The compound lies on a crystallographic $\bar{3}$ axis, with two nickel atoms in the asymmetric unit, each bound to six oxygen atoms in a distorted octahedral array. For Ni(1) three of these oxygens derive from acetate groups, two from chp ligands, and one from a water molecule. For Ni(2) there are two acetate oxygens, two chp oxygens, one oxygen from water and a sixth oxygen from a molecule of THF. All of these ligands, other than the THF, are involved in bridging between the metal atoms.

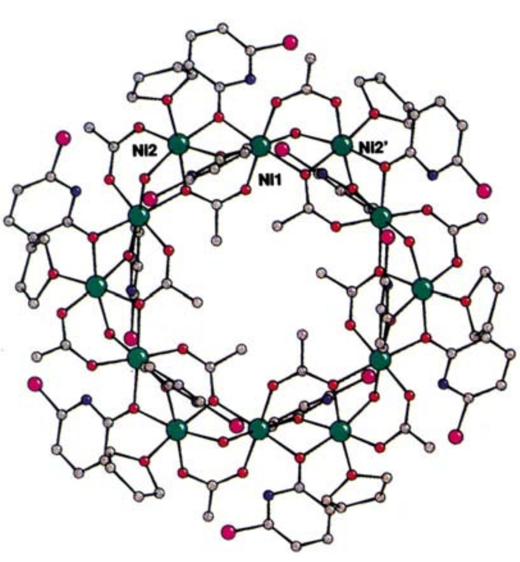

Fig. 1 The structure **1** in the crystal [Ni, green; O, red; N, blue; Cl, magenta; C, grey]. Bond length ranges: Ni–O (chp) 2.037–2.045; Ni–O (acetate), 1.977–2.067; Ni–O (water), 2.087–2.102; Ni–O (THF), 2.100 Å (av. esd. 0.009 Å). Bond angle ranges: *trans* at Ni, 169.2–177.4; *cis* at Ni, 78.8–106.5° (av. esd. 0.4°).

Ni(1) is bridged to Ni(2) by two μ_2-oxygen atoms, both derived from chp ligands, forming an $\mathrm{Ni_2O_2}$ ring. They are further bridged in a 1,3-fashion by an acetate ligand which lies inside the metallocycle. Ni(1) is also bridged to Ni(2′) [a symmetry equivalent of Ni(2) generated by the $\bar{3}$ axis] by two further μ_2-oxygens which are derived from the internal acetate and from a molecule of water. Ni(1) and Ni(2′) are also bridged in a 1,3-mode by an acetate molecule on the exterior of the ring. The structure therefore consists of a closed-chain of intersecting $\mathrm{Ni_2O_2}$ rings, with each ring being additionally strapped by an acetate ligand. The two crystallographically distinct acetate ligands have different bonding modes; the external acetate is binucleating, while the internal acetate is trinucleating. The methyl group of the internal acetate ligand efficiently fills the cavity of the macrocycle. There are no significant intermolecular interactions, but there are strong intramolecular H-bonds between the water molecule and chp ligands.

The structure of **1** in many ways resembles that of the decanuclear 'ferric wheel' $[\mathrm{Fe(OMe)_2(O_2CCH_2Cl)}]_{10}$[2] **2**. Both complexes feature intersecting $\mathrm{M_2O_2}$ rings additionally bridged by carboxylate ligands. They differ in that in **2** the carboxylate ligands are all exterior to the ring, whereas in **1** six of the acetates lie within the central cavity. This may be related to the greater steric requirements of chloroacetate ligands.

The magnetic properties of **1** were also studied.[§] The variation of the effective magnetic moment of **1** with temperature is illustrated in Fig. 2. At temperatures down to *ca.* 100 K the complex has an effective magnetic moment of *ca.* 11 BM, consistent with twelve non-interacting $S = 1$ centres (10.8 BM for $g = 2.2$). Below this temperature the magnetic moment rises rapidly, reaching 17.7 BM at 5 K. A plot of the inverse of the molar susceptibility against temperature gives a Weiss constant of +7 K, indicating ferromagnetic coupling between the $S = 1$ centres.

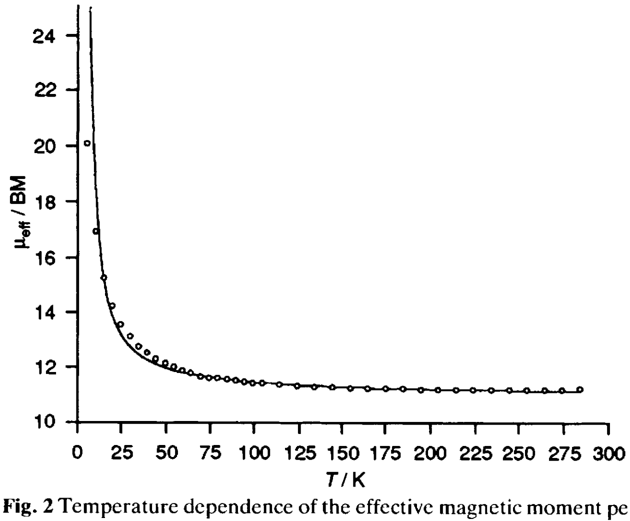

Fig. 2 Temperature dependence of the effective magnetic moment per formula unit for **1**. The experimental data are shown as circles, the best theoretical fit shown as a full-line.

To obtain an initial evaluation of the exchange interaction in the system we used a dipolar treatment[8] to estimate the magnitude of the exchange interaction term J in the Hamiltonian [eqn. (1)].

$$\mathcal{H} = -2J \sum_{i=1}^{i=12} \hat{S}_i \cdot \hat{S}_{i+1} \qquad (S_{13} \equiv S_1) \quad (1)$$

This produces a series of spin states with total spin, S_T, ranging from 12 to 0, and with multiplicities ranging from 1 to 15026. The energy of each spin state for the molecule can then be calculated from eqn. (2), where z = no. of nearest neighbours, n = no. of interacting centres and $S = 1$.

$$E(S_T) = zJ[S_T(S_T + 1) - nS(S + 1)]/n \quad (2)$$

By including the energy and multiplicity of each state in the Van Vleck equation,[8] we were able to simulate the magnetic behaviour of **1** using $g = 2.24$ and $J = 4.7$ cm^{-1} (Fig. 2). The ground state must have $S_T = 12$ to be consistent with ferromagnetic exchange between the Ni centres.

There is a well-known relationship for dihydroxy-bridged dicopper complexes, between the mean Cu–O–Cu bond angle at the bridging oxygen atoms and the sign and magnitude of the exchange interaction constant.[9] The relationship predicts that ferromagnetic coupling should occur for mean bond angles less than 97.5°, and the correlation has recently been extended to nickel(II) complexes.[10] In **1** the bridging arrangement is more complicated, but assuming that the magnetic interaction is dominated by super-exchange *via* the μ_2-oxygen atoms within the Ni_2O_2 ring then the mean Ni–O–Ni angle of 96.4 ± 1.5° in **1** is consistent with a small ferromagnetic coupling, and therefore the structure correlates well with the magnetic data.

Compound **1** is, to our knowledge, the largest polynuclear nickel complex with O-donor ligands, and again shows the immense structural diversity among pyridone complexes of the 3d metals.[6,7,11,12] Initial magnetic studies suggest ferromagnetic coupling between the Ni^{II} centres, leading to an $S = 12$ ground state. This is one of the highest spin ground states yet observed for molecular species.[4,5,13]

We thank the SERC for a studentship (to C. M. G.) and a postdoctoral fellowship (to S. P.), and for funding for both the diffractometer and SQUID magnetometer. We also thank the Leverhulme Trust for a post-doctoral fellowship (to J. M. R.).

Received, 25th July 1994; Com. 4/04560B

Footnotes

† A satisfactory elemental analysis was obtained for **1**.

‡ *Crystal data* for $C_{108}H_{132}Cl_{12}Ni_{12}N_{12}O_{48} \cdot 9\ C_4H_8O$ **1**: $M = 4146$, trigonal, space group $R\bar{3}c$, $a = 22.764(6)$, $c = 63.54(3)$ Å, $V = 28515$ Å^3 [from 2θ values of 27 reflections measured at ±ω ($15 \leqslant 2\theta \leqslant 23°$), $\lambda = 0.71073$ Å], $Z = 6$ (the molecule is disposed about a $\bar{3}$ axis), $D_c = 1.41$ g cm^{-3}, $T = 150.0(2)$ K, green block, $\mu = 1.41$ mm^{-1}.

Data collection and processing: Stoë STADI-4 four-circle diffractometer with Oxford Cryosystems low-temperature device (J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105), graphite-monochromated Mo-Kα X-radiation, ω scans [$2\theta_{max} = 40°$]. The structure was solved by direct methods using SHELXS-86 (G. M. Sheldrick, *Acta. Crystallogr. Sect. A*, 1990, **46**, 467). The bound THF molecule showed disorder, which was modelled with eight half-occupancy C atoms. The structure was refined using 324 parameters with all full-weight non-H atoms anisotropic to give $R1 = 0.0737$ for 1651 data with $F > 4\sigma(F)$ and $wR2 = 0.2534$ for all 2948 independent reflections. Refinement used SHELXL-93 (G. M. Sheldrick, University of Göttingen, Germany 1993).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue no. 1.

§ Variable temperature magnetic measurements in the region 5-300 K were made on a SQUID magnetometer (Quantum Design) in a field of 1000 Gauss, on samples sealed in gelatin capsules. In all cases diamagnetic corrections for the sample holders and samples were applied to the data. The observed and calculated data were modelled using in-house software (J. M. Rawson, The University of Edinburgh, 1994).

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