Dalton Communications

Syntheses, Structures and Magnetic Studies of Homometallic Manganese and Heterometallic Iron–Sodium One-dimensional Polymers

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Two one-dimensional polymers involving pyridone ligands, $[\{Mn_2(chp)_2(O_2CMe)_2(MeOH)_2\}_n]$ and $[\{Fe(chp)_6Na_3(MeOH)_6\}_n]$ (Hchp = 6-chloro-2-pyridone), have been synthesised and structurally characterised, and their magnetic properties investigated.

During the last few years transition-metal co-ordination polymers have been the subject of a number of reports with future applications envisaged in the realm of new materials.[1] We have been interested in polynuclear complexes involving ligands derived from 2-pyridone (2-hydroxypyridine), and have shown a large structural variety with late 3d metals such as copper and nickel.[2–6] In attempting to extend this work we have now synthesised the first manganese and iron complexes of these ligands and shown by X-ray diffraction analysis that the compounds are one-dimensional polymers. Other than work on chromium complexes by Cotton[7] and Garner[8] and their co-workers and two cobalt complexes,[9,10] there are no compounds known for deprotonated pyridone ligands with 3d metals earlier than nickel.

Reaction of hydrated manganese(II) acetate (3.5 mmol) with Na(chp) (Hchp = 6-chloro-2-pyridone) (7.0 mmol) in ethanol (50 cm^3) gave a pale precipitate, which was crystallised by diffusion of diethyl ether vapour into a methanol solution.† Fast atom bombardment mass spectrometry indicated that a species of high nuclearity had formed; significant peaks were observed at m/z up to 1362, with other intense peaks at 1293, 1224, 1120, 1051, 980, 807, 738, 669 and 496. All these high mass peaks can be assigned to species of formula $[Mn_x(chp)_y(O_2CMe)_z(MeOH)_w]$, *e.g.* for m/z 1362, $x = 6$, $y = 5$, $z = 5$ and $w = 3$.

Structure determination ‡ showed that a polymeric complex of stoichiometry $[\{Mn_2(chp)_2(O_2CMe)_2(MeOH)_2\}_n]$ **1** had formed (Fig. 1). There are two unique Mn sites within the asymmetric unit; Mn(1) lies on a two-fold rotation axis and is bound to the O- and N-donors of two chelating chp units and to oxygen atoms from two acetate ligands. It is bridged to Mn(2) *via* the chp oxygen atom, which is μ-bridging, and by a 1,3-bridging acetate ligand. The atom Mn(2) lies on an inversion centre and its co-ordination sphere is completed by two molecules of MeOH. The co-ordination geometries of the two Mn atoms are quite distinct: Mn(2) has an octahedral array of six O atoms, while Mn(1) has two N- and four O-donors with a very distorted geometry. The closest Mn···Mn distance within the polymer is 3.7599(14) Å. The structure is consistent with the mass spectrum observed, although it is perhaps surprising that such large fragments of the polymer remain intact in the mass spectrometer.

An entry into the iron chemistry of these ligands is *via* reaction of the salt $[NEt_4]_2[Fe_2OCl_6]$[15] (0.83 mmol) with Na(chp) (6.66 mmol) in methanol (75 cm^3). This gives a red precipitate which redissolves in tetrahydrofuran (thf) to give a red solution which, after filtration, produces dark red crystals on standing. Structure determination ‡ revealed a one-dimensional heterobimetallic polymer of stoichiometry $[\{Fe(chp)_6Na_3(MeOH)_6\}_n]$ **2**, a portion of which is shown in Fig. 2. A crystallographic three-fold axis is coincident with the metallic 'back-bone' of this polymer; Fe(1) is on a crystallographic $\bar{3}$ axis, *i.e.* an S_6 site, and is bound to six symmetry-equivalent oxygen donors from chp ligands. Three of these chp oxygen atoms bridge to Na(2), which lies on a three-fold axis, and three to a symmetry-equivalent sodium; Na(2) is additionally bound

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† Satisfactory elemental analyses were obtained for all compounds.

‡ Crystal data. $C_{16}H_{18}Cl_2Mn_2N_2O_8$ **1**: $M = 547.1$, monoclinic, space group $P2/n$, $a = 8.791(2)$, $b = 10.797(2)$, $c = 11.826(3)$ Å, $\beta = 93.52(4)°$, $U = 1120$ Å^3 [from 2θ values of 28 reflections measured at $\pm\omega$ ($28 \leqslant 2\theta \leqslant 38°$), $F(000) = 552$, $\lambda = 0.710\,73$ Å], $Z = 2$ (the molecule is polymeric, the value given is for the stoichiometric unit), $D_c = 1.62$ g cm^{-3}, $T = 150.0(2)$ K, colourless lath ($0.58 \times 0.39 \times 0.16$ mm), $\mu = 1.41$ mm^{-1}.

$C_{36}H_{42}Cl_6FeN_6Na_3O_{12}\cdot1.2C_4H_8O$ **2**: $M = 1174.8$, trigonal, space group $P\bar{3}$, $a = 11.742(2)$, $c = 12.153(4)$ Å, $U = 1451$ Å^3 [from 2θ values of 31 reflections measured at $\pm\omega$ ($20 \leqslant 2\theta \leqslant 26°$), $F(000) = 605$, $\lambda = 0.710\,73$ Å], $Z = 1$ (the molecule is polymeric, the value given is for the stoichiometric unit), $D_c = 1.34$ g cm^{-3}, $T = 295$ K, red lath ($0.5 \times 0.4 \times 0.3$ mm), $\mu = 0.62$ mm^{-1}.

Data collection and processing. Stoë STADI-4 four-circle diffractometer with Oxford Cryosystems low-temperature device,[11] graphite-monochromated Mo-Kα X-radiation, ω–2θ scans. All data were corrected for Lorentz and polarisation effects and for absorption. The structure of **1** was solved by direct methods, **2** by heavy atom methods, using SHELXS-86.[12] Both structures were refined with all non-H atoms anisotropic to give: for **1**, with 166 parameters, $R1 = 0.0268$ for 1324 data with $F > 4\sigma(F)$, $wR2 = 0.0707$ for all 1479 independent reflections [$2\theta \leqslant 45°$]; for **2**, with 107 parameters, $R1 = 0.0981$ for 593 data with $F > 4\sigma(F)$, $wR2 = 0.3378$ for all 1275 independent reflections [$2\theta \leqslant 45°$]. All refinements used SHELXL-93.[13] Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

to three methanol ligands, which are shared with Na(1). As Na(1) also lies on a $\bar{3}$ axis its co-ordination sphere is completed by three further methanol ligands, which in turn bridge to a further sodium, which is again a symmetry equivalent to Na(2). Thus all chp and methanol ligands within the structure act as bridging ligands through μ-oxygen-donor atoms. There is an H bond between the chp nitrogen and methanol (N ··· O 2.75 Å). This presumably stabilises the structure, and also leads to some doubt as to whether the polymer should be formulated as $[\{Fe(chp)_6Na_3(MeOH)_6\}_n]$ or $[\{Fe(Hchp)_6Na_3(MeO)_6\}_n]$. As we have previously found that chp is stable in methanol, we favour the former formulation.

The magnetic properties of **1** and **2** have also been studied.* For **1** the variation of molar susceptibility with temperature shows a broad maximum at 13 K, typical of a classical Heisenberg linear chain. Extrapolation of the linear component of an inverse susceptibility–temperature plot gives an intercept of −26 K, indicative of antiferromagnetic exchange. The data were modelled as a linear-chain antiferromagnet using established procedures.[16] The susceptibility (χ_{LC}) is then given by equation (1), where $u = [T/2J \cdot S(S+1)] - \coth[2J \cdot S(S+1)/T]$. Although a moderate fit was achieved with g = 1.946 and $J = -1.14$ cm^{-1}, a large discrepancy is evident below 3.4 K where there is a steady rise in the observed susceptibility. In order to model this behaviour two further terms were introduced[17] to allow for a weak inter-chain interaction (J') between z nearest neighbours (here $z = 4$), and for the presence of uncoupled paramagnetic impurity (ρ = % paramagnetic impurity). The molar susceptibility is then given by equation (2). An excellent fit is found (Fig. 3) for

$$\chi_{LC} = \frac{Ng^2\beta^2(1-u)}{3kT(1+u)} \qquad (1)$$

$$\chi_M = \frac{\chi_{LC}}{[1-(2zJ'/Ng^2\beta^2)\chi_{LC}]}(1-\rho) + \rho\frac{Ng^2\beta^2}{3kT}S(S+1) \qquad (2)$$

$J' = 0.55$ cm^{-1} and $\rho = 0.16\%$ with the values for J and g as calculated for equation (1). The small exchange parameter is consistent with the Mn ··· Mn distance of 3.76 Å, but the presence of a weak ferromagnetic inter-polymer interaction is somewhat unexpected.

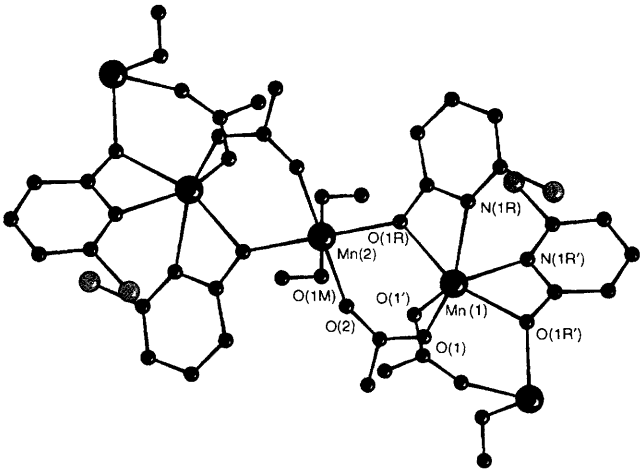

Fig. 1 A segment of the one-dimensional polymer $[Mn_2(chp)_2(O_2CMe)_2(MeOH)_2]$ **1** produced by CAMERON.[14] Selected bond lengths and angles: Mn(1)–O(1) 2.106, Mn(1)–O(1R) 2.191, Mn(1)–N(1R) 2.342, Mn(2)–O(1R) 2.127, Mn(2)–O(2) 2.171, Mn(2)–O(1M) 2.183 Å [av. estimated standard deviation (e.s.d.) 0.002 Å]; O(1)–Mn(1)–O(1R) 97.70, O(1)–Mn(1)–N(1R) 153.88, O(1)–Mn(1)–O(1') 93.95, O(1)–Mn(1)–O(1R') 96.73, O(1)–Mn(1)–N(1R') 99.48, O(1R)–Mn(1)–N(1R) 58.68, O(1R)–Mn(1)–O(1R') 158.79, O(1R)–Mn(1)–N(1R') 103.49, N(1R)–Mn(1)–N(1R') 77.74, O(1R)–Mn(2)–O(2) 86.52, O(1R)–Mn(2)–O(1M) 87.05, O(2)–Mn(2)–O(1M) 89.45° (av. e.s.d. 0.09°) (C, black; Cl, pink; Mn, green; N, blue; O, red)

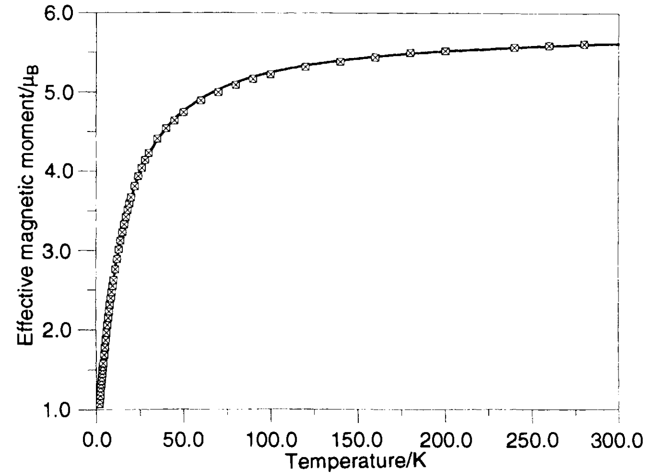

Fig. 3 Magnetic moment per Mn atom of **1** *vs.* temperature. Experimental data are shown as hatched squares and the full line is a simulation based on parameters given in the text

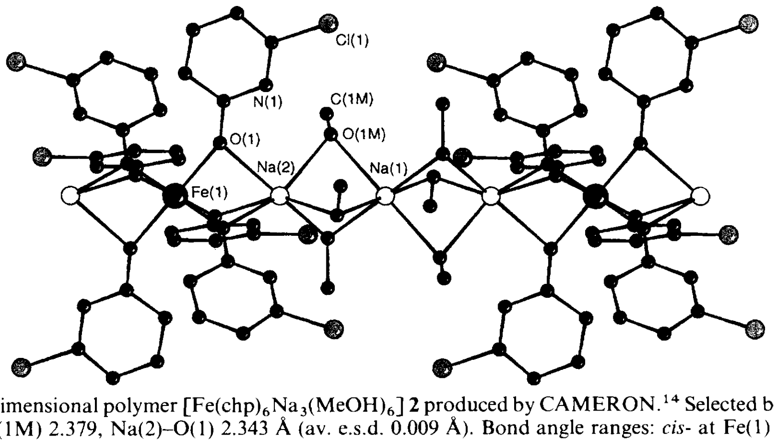

Fig. 2 A segment of the one-dimensional polymer $[Fe(chp)_6Na_3(MeOH)_6]$ **2** produced by CAMERON.[14] Selected bond lengths: Fe(1)–O(1) 2.000, Na(1)–O(1M) 2.381, Na(2)–O(1M) 2.379, Na(2)–O(1) 2.343 Å (av. e.s.d. 0.009 Å). Bond angle ranges: *cis*- at Fe(1) are 84.3 or 95.7; *cis*- at Na(1) 83.2 or 96.8; *cis*- at Na(2) 69.9 to 124.8; *trans*-angles at Na(2) 150.3° (av. e.s.d. 0.4°) (Colours as in Fig. 1, plus Fe, green; Na, yellow.)

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* Variable-temperature magnetic measurements on **1** and **2** in the region 1.8–300 K were made using a SQUID magnetometer (Quantum Design) with samples sealed in gelatine capsules. In all cases diamagnetic corrections for the sample holders were applied to the data. Diamagnetic corrections for the samples were determined from Pascal's constants and literature values. The observed and calculated data were refined using in-house software.

Compound **2** displays magnetic behaviour consistent with a paramagnet, with the magnetic moment constant at *ca.* 5.8 μ_B ($\mu_B \approx 9.274\,02 \times 10^{-24}$ J T^{-1}) from 300 K down to 40 K. Below this temperature there is a slight decline in the moment to 5.32 μ_B at 4 K. It is possible that this decline is due to a very weak antiferromagnetic interaction. Given the large Fe••• Fe distances in the structure (closest Fe••• Fe contact 12.15 Å) strong exchange interactions were not expected.

Acknowledgements

We thank the EPSRC for a studentship (to C. M. G.), a postdoctoral fellowship (to S. P.) and for funding for a diffractometer and SQUID susceptometer. We are also grateful to the Leverhulme Trust for a postdoctoral fellowship (to J. M. R. and G. A. S.).

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Received 25th *April* 1995; *Communication* 5/02634B