Ferromagnetic order in a μ-cyano Cr^{III}–Mn^{II} assembly with an unusual branched architecture

Arnaud Marvilliers,[a] Simon Parsons,[b] Eric Rivière,[a] Jean-Paul Audière[a] and Talal Mallah*[a]

[a] *Laboratoire de Chimie Inorganique, UMR CNRS 8613, Université Paris-Sud, 91405 Orsay, France.*
E-mail: mallah@icmo.u-psud.fr
[b] *Department of Chemistry, The University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ*

Received (in Cambridge, UK) 25th June 1999, Accepted 30th September 1999

Reacting hexacyanochromate(III) with a mononuclear Mn(II) complex chelated by a tetradentate ligand that leaves two coordination sites available in *cis* position leads to a new molecular ferromagnet (T_C = 17 K) with an unusual architecture.

Cyanide-bridged systems are generally obtained by reacting a hexacyanometalate with a mononuclear assembler complex where some of the coordination sites may be blocked by a chelating ligand. In the absence of such ligands or when the ligand is bidentate, three-dimensional cubic networks are obtained.[1,2] On the other hand, when the chelating ligands block more than two coordination sites around the assembler complex, different structures become accessible.[3–5] For example, when $Ni(tren)^{2+}$ [tren = tris(2-aminoethyl)amine is a tetradendate ligand that leaves two available coordination sites on Ni^{II} in *cis* position] is reacted with $[Fe(CN)_6]^{3-}$, a non-cubic three-dimensional compound that orders ferrimagnetically (T_C = 8 K) is obtained.[4] Using $Ni(bpm)_2{}^{2+}$ [bpm = bis(1-pyrazolyl)methane] instead of $Ni(tren)^{2+}$ affords a discrete pentanuclear complex $[Fe(CN)_6]_2[Ni(bpm)_2]_3{\cdot}H_2O$.[5] Magnetic ordering at T_C = 23 K is observed owing to intermolecular ferromagnetic interaction. The formation of a discrete μ-cyanide species in the latter and not in the former compound is probably due to the steric hindrance of the bidentate ligand bpm. We have shown as well that such a pentanuclear species is obtained with $Ni(IM2\text{-}py)_2{}^{2+}$ (IM2-py = 2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazolyl-1-oxy] where IM2-py is a bidentate ligand as bulky as bpm or bipy.[6]

Here we report on the structure and the preliminary magnetic properties of a new μ-cyano Cr^{III}–Mn^{II} polymeric compound obtained from the reaction of $Mn^{II}(bispicen)Cl_2$ and hexacyanochromate(III). $Mn^{II}(bispicen)Cl_2$ [bispicen = *N,N′*-bis(2-pyridylmethyl)-1,2-ethanediamine] was chosen because bispicen chelates the metal ion leaving the two chloride atoms in *cis*-position.[7] We reasoned that (i) this *cis* arrangement should be retained in the final compound where the two chloride atoms may be substituted by two nitrogen atoms of two $Cr(CN)_6$ units. and (ii) because the size of the manganese complex which is intermediate between that of $Ni(tren)^{2+}$ and $Ni(bpm)_2{}^{2+}$ [or $Ni(bipy)_2{}^{2+}$], a compound with a different dimension† should be obtained.

Yellow plates were obtained using the gel technique.[8], X-ray crystallography‡ reveals the formation of a one-dimensional neutral 3/2 : Mn/Cr polymer of formula $[Cr(CN)_6]_2[Mn(bispicen)]_3{\cdot}6H_2O{\cdot}0.5EtOH$ **1**. The asymmetric unit contains three crystallographically independent manganese and two crystallographically independent chromium ions [Fig. 1(a)]. The body of the one-dimensional assembly (along the *b* crystallographic axis) is made of Cr_2Mn_2 units sharing Cr(1) vertices; each chromium vertex is linked through one apical cyanide to a Mn(bispicen) complex which is itself connected to a terminal molecule of $Cr(CN)_6$. The pendant Mn(3)Cr(2) units are placed alternately below and above the body of the polymer. All the Mn^{II} complexes are surrounded by two $Cr(CN)_6$ entities in *cis* position as expected from the nature of the chelating ligand. The surroundings of the Mn^{II} metal ions is that of a distorted octahedron (see Fig.1 caption). The Mn–N–C angles, where NC is a bridging cyanide, vary from 161.5° to 177.7° for Mn(1) and Mn(2). The highest deviation from 180° is found for the Mn(3)–N(13)–C(13) angle (147.1°). Fig. 1(b) shows a H-bond network along the *a* axis involving four water molecules linking amine nitrogen atoms belonging to a pendant and to an in-body Mn

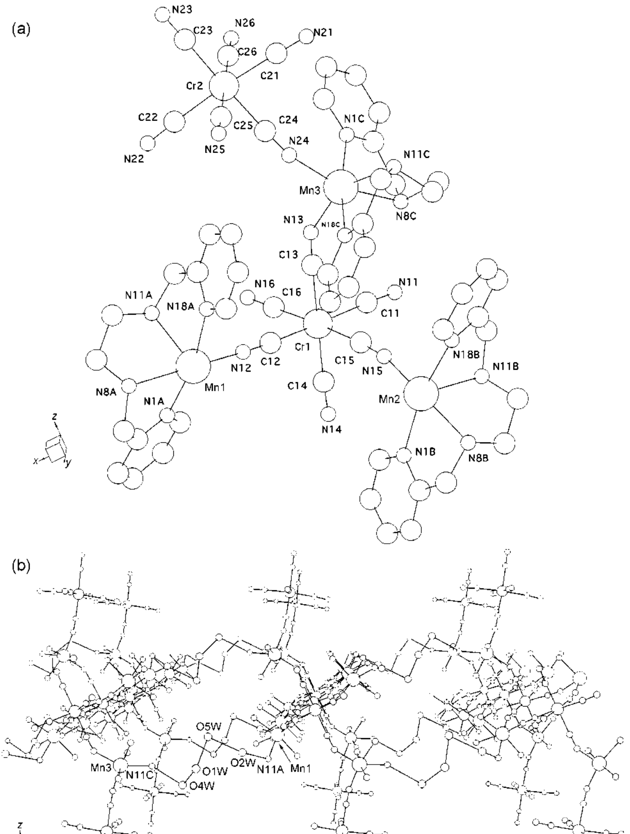

Fig. 1 (a) View of the asymmetric unit with atoms numbering. Selected bond distances and angles: Mn(1)–N(12) 2.162(6), Mn(1)–N(11) 2.173(6), Mn(1)–N(8A) 2.273(5), Mn(1)–N(1A) 2.282(5), Mn(1)–N(11A) 2.291(5), Mn(1)–N(18A) 2.315(5), Mn(2)–N(15) 2.180(6), Mn(2)–N(16) 2.182(6), Mn(2)–N(8B) 2.270(6), Mn(2)–N(1B) 2.276(6), Mn(2)–N(11B) 2.286(5), Mn(2)–N(18B) 2.288(6), Mn(3)–N(24) 2.137(6), Mn(3)–N(13) 2.174(6), Mn(3)–N(11C) 2.249(7), Mn(3)–N(18C) 2.268(6), Mn(3)–N(1C) 2.298(7), Mn(3)–N(8C) 2.330(7), Cr(1)–C(14) 2.045(7), Cr(1)–C(11) 2.055(7), Cr(1)–C(12) 2.055(7), Cr(1)–C(13) 2.056(7), Cr(1)–C(16) 2.068(7), Cr(1)–C(15) 2.078(7), Mn(1)–N(12)–C(12) 177.7(6); Mn(1)–N(11)–C(11) 163.6(5), Mn(2)–N(15)–C(15) 167.3(5), Mn(2)–N(16)–C(16) 161.5(5), Mn(3)–N(13)–C(13) 147.1(6), Mn(3)–N(24)–C(24) = 168.1(6). (b) View along the *b* axis showing the H-bond connections along the *a* axis between the amine nitrogen atoms of pendant and in-body Mn(bispicen) complexes belonging to two different polymers.

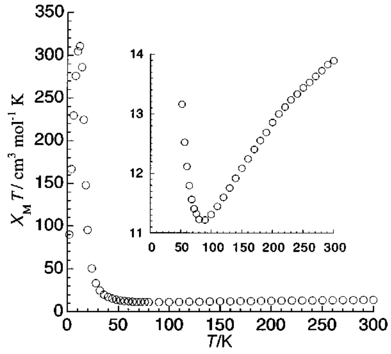

Fig. 2 $\chi_M T = f(T)$ plot performed at $H = 1$ kOe, the inset shows the decrease of $\chi_M T$ on cooling to $T = 84$ K.

complex of two different polymers. The other two water and the ethanol molecules do not participate in the extended two-dimensional network. No connection is observed along the *c* direction where the shortest metal–metal distance (11.08 Å) is between two pendant chromium ions of two neighbouring polymers.

Mixing two aqueous solutions of $[NBu^n_4]_3[Cr(CN)_6]$ and $Mn(bispicen)Cl_2$ in a 2:3 stoichiometric ratio leads to the immediate precipitation of a yellow powder. The IR spectrum of the powder was found to be identical to that of a collection of single crystals obtained by the gel technique. In the 2000–2200 cm^{-1} region, two bands centred at 2151 and 2130 cm^{-1} are present corresponding to bridging and non-bridging cyanides, respectively. TG analysis reveals a mass loss corresponding to six water molecules per unit formula.§

Magnetic studies were carried out on a powdered sample using a SQUID magnetometer. Fig. 2 shows the $\chi_M T = f(T)$ plot performed in an applied field of 1 kOe. On cooling from room temp., $\chi_M T$ (13.9 cm^3 mol^{-1} K) decreases, reaches a minimum at $T = 84$ K (insert of Fig. 2) then increases abruptly below $T = 30$ K and reaches a maximum value of 311 cm^3 mol^{-1} K at 11 K. The decrease of $\chi_M T$ on cooling indicates that the exchange interaction between Cr^{III} and Mn^{II} through the cyanide bridge is antiferromagnetic as has already been observed.[11] The abrupt increase of $\chi_M T$ at low temperature and the high value measured at 11 K may be due to a three-dimensional ordering leading to a molecular ferromagnet; the decrease below $T = 12$ K would in this case be due to the saturation of the susceptibility. In order to confirm this, magnetisation *vs.* field studies were performed at $T = 2$ K ; the curve shows that saturation is attained (Fig. 3) when a very small field of 400 Oe is applied. This is the signature of the occurrence of a magnetic ordering within the compound. The magnetisation value at $H = 55$ (8.9 μ_B) confirms the antiferromagnetic interaction between adjacent metal ions. Field cooled magnetisation curve obtained with an applied field of 30 Oe are in line with the presence of a magnetic ordering below a critical tempertaure $T_C = 17$ K (Fig. 3 insert).¶ The origin of the behaviour is not clear yet. The H-bond network may be responsible of a ferromagnetic interaction between the polymers along the *a* axis. However, since no connections are present in the third direction, only dipolar interactions along the *c* axis can account for the three-dimensional magnetic order.

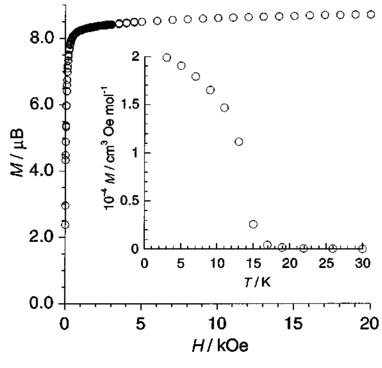

Fig. 3 $M = f(H)$ magnetisation curve at $T = 2$ K, inset: $M = f(T)$ at $H = 30$ Oe.

Magnetic studies on dehydrated samples and on oriented single crystals should bring insights on the origin of three-dimensional order and on the absence of coercive field and remnant magnetisation (curves not presented here) for powders below T_C.

This work was supported by the Franco–British joint program Alliance No. 96175 from the French Foreign Ministry and the British Council.

Notes and references

† We restrict the word dimension here to μ-cyanide bridges, *i.e.* a three-dimensional compound structurally is one where μ-cyanide bridges spread in the three directions of space while a compound containing discrete cyanide-bridged species is zero-dimensional.

‡ *Crystal data* for **1**: $C_{55}H_{63}Cr_2Mn_3N_{24}O_{6.5}$, $M = 1433.11$, monoclinic, space group $P2_1/n$ $a = 17.5085(10)$, $b = 15.5670(10)$, $c = 26.4406(17)$ Å, $U = 7128.6(8)$ Å^3, $\beta = 94.4330(10)$, $T = 150$ K, $Z = 4$, 31415 reflections measured, of which 10185 were unique ($R_{int} = 0.1055$). The structure was solved by direct methods (SIR92)[9] and refined with SHELXL-97.[10] The final conventional *R*-factor [based on *F* and 10185 data with $F > 4\sigma(F)$] was 0.0793. CCDC 182/1428.

§ Elemental analysis of a powder sample fits well with the proposed formula $Cr(CN)_6]_2[Mn(bispicen)]_3\cdot6H_2O$ which does not contain ethanol. Found (calc.) for $C_{54}H_{60}N_{24}O_6Mn_3Cr_2$: C, 45.98 (46.02); H, 4.30 (4.26); N, 23.83 (23.84); Mn, 11.39 (11.69); Cr, 7.25 (7.38)%. Only water is used as solvent when preparing the powder while the crystals are obtained using a gel containing a small amount of ethanol. Since, the crystallographic studies reveal that ethanol does not participate to an extended H-bond network, its absence should not have an influence on the magnetic properties (see below).

¶ Field-cooled magnetisation measurements ($H = 30$ Oe) were performed on a few single crystals embedded in the gel; below 17 K an abrupt increase confirms that the crystals order magnetically at the same temperature as the powder.

1 V. Gadet, T. Mallah, I. Castro and M. Verdaguer, *J. Am. Chem. Soc.*, 1992, **114**, 9213; T. Mallah, S. Thiébaut, M. Verdaguer and P. Veillet, *Science,*1993, **262**, 1554; W. R. Entley and G. S. Girolami, *Science*, 1995, **268**, 397; S. Ferlay, T. Mallah, R. Ouahès, P. Veillet and M. Verdaguer, *Nature*, 1995, **378**, 701; S. Ferlay, T. Mallah, R. Ouahès, P. Veillet and M. Verdaguer, *Inorg. Chem.*, 1999, **38**, 229.

2 M. Ohba, N. Usaki, N. Fukita and H. Okawa, *Angew. Chem., Int. Ed.*, 1999, **38**, 1795; T. Mallah, A. Marvilliers and E. Rivière, *Philos. Trans. R. Soc.* (*London*) A, 1999, **357**, in press.

3 G. O. Morpugo, V. Mosini, P. Porta, G. Dessy and V. Fares, *J. Chem. Soc., Dalton Trans.*, 1981, 111; M. Ohba, N. Maruono, H. Okawa, T. Enoki and J.-M. Latour, *J. Am. Chem. Soc.*, 1994, **116**, 11 566; H. Miyasaka, N. Matsumoto, N. Re, E. Gallo and C. Floriani, *Inorg. Chem.*, 1997, **36**, 670; S. Ferlay, T. Mallah, J. Vaissermann, F. Bartolomé, P. Veillet and M. Verdaguer, *Chem. Commun.*, 1996, 2481; E. Colacio, J. M. Dominguez-Vera, M. Ghazi, R. Kivekäs, F. Lloret, J. M. Moreno and H. Stoeckli-Evans, *Chem.Commun.*, 1999, 987.

4 S. El Fallah, E. Rentshler, A. Caneshi, R. Sessoli and D. Gatteschi, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1947.

5 K. Van Langenberg, S. R. Batten, K. J. Berry, D. C. R. Hockless, B. Moubaraki and K. S. Murray, *Inorg. Chem.*, 1997, **36**, 5006.

6 A. Marvilliers, Y. Pei, J. Cano Boquera, K. E. Vostrikova, C. Paulsen, E. Rivière, J.-P. Audière and T. Mallah, *Chem. Commun.*, 1999, 1951.

7 H. Toflund, E. Pedersen and S. Yde-Andersen, *Acta Chem. Scand. Ser. A*, 1984, **38**, 693.

8 S. Descurtins, H. W. Schmalle, P. Schneuwly, J. Ensling and P. Gütlich, *J. Am. Chem. Soc.*, 1994, **116**, 9521.

9 A. Altomare, G. Cascarano, Giacovazzo and A. Guagliardi, *J. Appl. Crystallogr.*, 1993, **26**, 343.

10 G. M. Sheldrick, Institüt für Angorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

11 A. Sculler, T. Mallah, A. Nivorozkhin, J.-L. Tholence, M. Verdaguer and P. Veillet, *New. J. Chem.*, 1996, **20**, 1.

Communication 9/05191K