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A novel cyano-bridged pentanuclear complex: $[\{Mn_3(MAC)_3(H_2O)_2\}\{Fe(CN)_6\}_2]\cdot 6H_2O\cdot 2CH_3OH$—synthesis, crystal structure and magnetic properties (MAC = pentaaza macrocyclic ligand)

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Abstract

The reaction between $K_3[Fe(CN)_6]$ and $[Mn(MAC)(H_2O)_2]Cl_2\cdot 4H_2O$ (MAC = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo-[12.3.1]octadeca-1(18),2,12,14,16-pentaene) in a water/methanol mixture affords a pentanuclear complex with the formula $[\{Mn_3(MAC)_3(H_2O)_2\}\{Fe(CN)_6\}_2]\cdot 6H_2O\cdot 2CH_3OH$ (**1**), whose crystal structure has been solved. It consists of discrete $[Mn^{II}Fe^{III}Mn^{II}Fe^{III}Mn^{II}]$ entities. The three $\{Mn(MAC\}^{2+}$ moieties are connected by two $[Fe(CN)_6]^{3-}$ anions, each one involving two *cis* cyano bridging groups. The manganese ions display a distorted pentagonal–bipyramidal geometry, with the macrocyclic ligand forming the equatorial plane. The axial positions are occupied by two nitrogen atoms arising from the cyano bridges, for the central manganese atom, and by one aqua ligand and one nitrogen atom from the cyano bridge, for the terminal manganese atoms. The cryomagnetic properties of **1** have been investigated and reveal a new case of irregular spin-state structure.

Keywords: Crystal structure; Cyano-bridged complexes; Manganese complexes; Iron complexes; Macrocyclic ligands; Magnetic properties

1. Introduction

In the recent years, the hexacyanometalate anions, $[M(CN_6]^{n-}$, have been extensively employed as building-blocks for the design of cyano-bridged heterometallic complexes [1,2]. The synthesis of these systems consists in self-assembly processes involving the anionic bricks and various complex cations. These can be either hydrated cations, $[A(H_2O)_m]^{q+}$, or cationic complexes, $[A(L)_x(H_2O)_y]^{q+}$. In the first case, 3-D bimetallic assemblies of Prussian Blue type are obtained [1]. In the second one, since several coordination sites at the assembling cations are blocked by the polydentate ligands, L, a rich variety of bimetallic architectures, ranging from oligonuclear to high dimensionality systems, can be constructed [3]. Indeed, the ancillary ligands, through their denticity, charge, steric requirements, can strongly influence the nuclearity, the topology of the spin carriers, as well as the dimensionality of the resulting systems. Beyond their beauty and structural richness, such heterometallic systems exhibit spectacular magnetic [1–4] and photomagnetic [5] properties. The low nuclearity complexes play a key role in gaining insights into the magnetostructural correlation of the cyano-bridged heteropolynuclear systems. Particularly important, because of their spectroscopic and electrochemical properties, are the discrete heterodinuclear cyano-bridged complexes [6].

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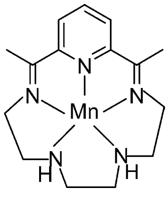
The formation of oligonuclear heterometal complexes is favored by the use of tetradentate or pentadentate ligands attached to the assembling cations. In these complex cations, the fifth or the sixth coordination site is occupied by a ligand, e.g. aqua, which can be easily substituted by the nitrogen atom from the hexacyanometalate template. So, the reactions between $[M(CN)_6]^{q-}$ bricks and $[M'L^5]^{2+}$ ($M' = Mn$, Ni, $L^5 =$ pentadentate ligand) or $[CuL^4]^{2+}$ ($L^4 =$ tetradentate ligand) lead to heptanuclear complexes, $[MM'_6]$ [7]. Other interesting oligonuclear complexes with various nuclearities have been obtained rather serendipitously [8].

A particular case is that of the macrocyclic ancillary ligands. The self-assembly process involving *trans*-$[M'(mac)(H_2O)_2]^{2+}$ and $[M(CN)_6]^{3-}$ ions yields 2-D $[M'_3M_2]$ networks (*mac* stands for a macrocyclic ligand). Within a layer, each $[M'(mac)]^{2+}$ moiety is linked to two $[M(CN)_6]^{3-}$ ions in *trans* positions, and each $[M(CN)_6]^{3-}$ ion is surrounded by three $[M'(mac)]^{2+}$ units. If the three $M'(mac)$ units adopt a facial configuration around the M ion, then layers with a stair-shaped honeycomb architecture are formed [9]. A meridional arrangement of the three $[M'(mac)]^{2+}$ moieties leads to flat brick wall-like layers [10]. Such 2-D $[M'_3M_2]$ systems have been obtained by using various nickel(II) complexes with macrocyclic ligands as assembling cations [9,10]. Aiming to obtain a $\{Mn^{II}_3Fe^{III}_2\}$ 2-D network, we have used as a precursor the manganese(II) complex with a pentaaza macrocyclic ligand, $[Mn(MAC)(H_2O)_2]Cl_2 \cdot 4H_2O$ (MAC = 2,13-dimethyl-3,6,9,12,18-pentaazabicyclo-[12.3.1]octadeca-1(18),2,12,14,16-pentaene—Scheme 1). Surprisingly, we have obtained a pentanuclear complex with a unique topology of the metallic ions. Its crystal structure and magnetic properties are described here.

2. Experimental

2.1. Synthesis

Chemicals were purchased from Aldrich and all manipulations were performed using materials as received. The manganese complex, $[Mn(MAC)(H_2O)_2]Cl_2 \cdot 4H_2O$, has been synthesized according to Ref. [11]. $[\{Mn_3(MAC)_3(H_2O)_2\}\{Fe(CN)_6\}_2] \cdot 6H_2O \cdot 2CH_3OH$ (**1**) has been obtained by slow diffusion, in H-shaped tubes, of two solutions, one of them containing $K_3[Fe(CN)_6]$ (1 mmol) dissolved in water (15 ml), and the other one the manganese complex, $[Mn(MAC)(H_2O)_2]Cl_2 \cdot 4H_2O$ (1.5 mmol), dissolved in methanol (15 ml). Brown crystals are obtained after 2 weeks. *Anal.* Found: C, 42.5; H, 5.2; Fe, 7.8; Mn, 11.1; N, 24.2. Calc.: C, 43.82; H, 5.80; Fe, 6.91; Mn, 10.19; N, 23.39%.



Scheme 1.

2.2. Physical measurements

The IR spectra (KBr pellets) were recorded with a BIO-RAD FTS 135 spectrophotometer. Variable-temperature (1.9–300 K) magnetic susceptibility measurements were carried out with MPMS-5 5T SQUID magnetometer. Diamagnetic corrections of the constituent atoms were estimated from Pascal constants.

2.3. Crystallography

X-ray diffraction measurements were performed at room temperature on a Enraf Nonius CCD diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). A total of 14391 reflections were collected all of them being unique [$R_{int} = 0.0000$]. The structure was solved by direct methods and the refinement of the structural data by least-squares method was based on F^2, using SHELX-97 package [12]. Final R indices: $R_1 = 0.0891$, $wR_2 = 0.2447$ [$I > 2\sigma(I)$] and $R_1 = 0.1095$, $wR_2 = 0.2618$ (all data). Largest difference peak and hole: 1.564 and -0.815 e Å^{-3} (Table 1).

3. Results and discussion

The mononuclear manganese(II) complex, $[Mn(MAC)(H_2O)_2]Cl_2 \cdot 4H_2O$ is a useful starting material for the synthesis of homo- and heteropolynuclear complexes with interesting magnetic properties [13]. It is

Table 1
Crystal data and structure refinement for crystal **1**

Empirical formula	$C_{59}H_{93}Fe_2Mn_3N_{27}O_{10}$
Formula weight	1617.12
Crystal system	monoclinic
Space group	*Cc*
a (Å)	41.8685(9)
b (Å)	10.1453(4)
c (Å)	20.0037(6)
β (°)	112.161(2)
V (Å^3)	7869.3(4)
Z	4
$F(0\,0\,0)$	3372
D_{calc} (g cm^{-3})	1.365
Absorption coefficient, μ (mm^{-1})	0.896
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0891$, $wR_2 = 0.2447$ [11601]
R indices (all data)	$R_1 = 0.1095$, $wR_2 = 0.2618$ [14391]
Goodness-of-fit	1.053

very robust and, in contrast with other manganese(II) complexes with aliphatic amines, it can be handled in air and aqueous solution, without getting oxidized.

By reacting $[Mn(MAC)(H_2O)_2]Cl_2$ with $K_3[Fe(CN)_6]$, we have obtained a novel pentanuclear complex with an unprecedented chain structure, Mn^{II}–NC–Fe^{III}–CN–Mn^{II}–NC–Fe^{III}–CN–Mn^{II}.

The crystal structure of **1** consists of non-centrosymmetric neutral pentanuclear entities and crystallization solvent molecules (Fig. 1). Selected bond distances and angles are collected in Table 2.

The three $\{Mn(MAC\}^{2+}$ moieties are connected by two $[Fe(CN)_6]^{3-}$ anions, each one involving two *cis* disposed cyano bridging groups, resulting in discrete $[Mn^{II}Fe^{III}Mn^{II}Fe^{III}Mn^{II}]$ molecules. The manganese ions display a distorted pentagonal–bipyramidal geometry, with the macrocyclic ligand forming the equatorial plane. The axial positions are occupied by two nitrogen atoms arising from the cyano bridges, for the central manganese atom, and by one aqua ligand and one nitrogen atom from the cyano bridge, for the terminal manganese atoms. The Mn–N(MAC) distances fall in the range 2.260(8) and 2.374(13) Å. The other Mn–N distances (N is the nitrogen atom arising from the cyano bridge) vary between 2.231(9) and 2.262(8) Å. The two Mn–O(aqua) distances for the terminal manganese ions are, respectively: Mn(3)–O(1) = 2.261(7) and Mn(4)–O(2) = 2.242(9) Å. The four Fe–CN–Mn linkages are non-linear: C(1)–N(1)–Mn(3) = 149.1(7)°; C(6)–N(6)–Mn(5) = 147.4(10)°; C(7)–N(7)–Mn(5) = 144.0(9)°; C(11)–N(11)–Mn(4) = 154.3(8)°. The distances between the metal ions are: Mn(3)–Fe(2) = 5.154 Å, Fe(2)–Mn(5) = 5.101 Å, Mn(5)–Fe(1) = 5.041 Å, Fe(1)–Mn(4) = 5.169 Å.

The analysis of the packing diagram (Fig. 2) shows no stacking interactions between the aromatic moieties of the organic ligands.

The infrared spectrum of **1** shows, apart the bands of the macrocyclic ligand, the characteristic bands of the CN^- groups: the band located at 2115 cm^{-1} is assigned to the bridging cyano ligands, while the other one (2066 cm^{-1}) is assigned to the terminal cyano ligands.

The most intriguing properties of the heteropolynuclear complexes concern the exchange interactions between the paramagnetic centers. The case of compound **1** is particularly complex: first, because of the low-spin Fe(III) ion, with a $^2T_{2g}$ ground state (the orbital contribution to the magnetic moment can be important); second, because of the low symmetry of the pentanuclear entities (there are four parameters describing the exchange interactions between the Mn(II) and Fe(III) ions). If, in a first approximation, we neglect the first-order orbital momentum associated with the low-spin Fe(III), and assuming all four Fe(III)–Mn(II) exchange pathways to be either antiferro- or ferromagnetic, then the following magnetic behaviors can be anticipated: (i) all $J_{MnFe} < 0$: $\chi_M T$ must decrease by lowering the temperature, then it must increase to the value corresponding to $S = 13/2$ (a case of irregular spin state structure); (ii) all J_{MnFe} values positive: $\chi_M T$ must increase by lowering the temperature. The $\chi_M T$ vs. T plot for compound **1** is given in Fig. 3. The value of $\chi_M T$ at room temperature (~ 14 cm^3 mol^{-1} K) corresponds to the expected value for a magnetically non-interacting 2Fe(III)-low-spin (l.s.). –3Mn(II) system (13.87 cm^3 mol^{-1} K, by neglecting the orbital contribution of Fe(III)-l.s.). As the temperature is lowered, $\chi_M T$ decreases more and more, reaches a value of 11.78 cm^3 mol^{-1} K at 8 K, then increases again to a value of 12.36 cm^3 mol^{-1} K at $T = 2$ K. This behavior suggests an irregular spin-state structure.

Having in mind the crystal structure of **1**, that is, its low symmetry, the magnetic susceptibility data must be analyzed through the following spin Hamiltonian (the orbital contribution of the low-spin Fe(III) is neglected):

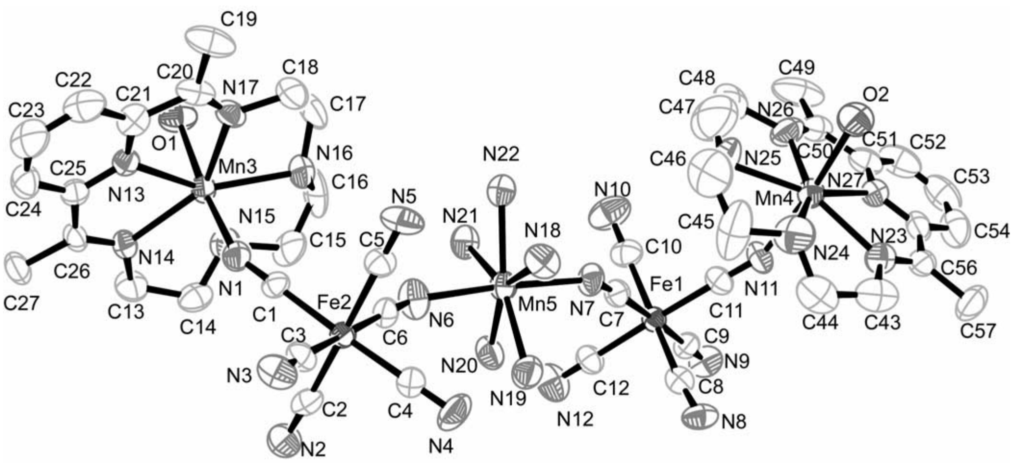


Fig. 1. Perspective view of the pentanuclear complex, **1**, with the atom numbering scheme. For the sake of clarity, the carbon atoms from the macrocyclic ligand coordinated to the Mn(5) have been removed.

Table 2
Selected bond lengths (Å) and angles (°) for **1**

Mn(3)–N(1)	2.245(9)
Mn(3)–N(14)	2.260(8)
Mn(3)–O(1)	2.261(7)
Mn(3)–N(13)	2.267(7)
Mn(3)–N(17)	2.290(8)
Mn(3)–N(16)	2.310(9)
Mn(3)–N(15)	2.340(9)
Mn(4)–N(11)	2.231(9)
Mn(4)–O(2)	2.242(9)
Mn(4)–N(27)	2.265(8)
Mn(4)–N(26)	2.267(12)
Mn(4)–N(23)	2.288(9)
Mn(4)–N(25)	2.307(13)
Mn(4)–N(24)	2.374(13)
Mn(5)–N(22)	2.242(9)
Mn(5)–N(7)	2.262(8)
Mn(5)–N(6)	2.269(9)
Mn(5)–N(20)	2.281(10)
Mn(5)–N(18)	2.295(10)
Mn(5)–N(21)	2.312(10)
Mn(5)–N(19)	2.324(10)
C(1)–N(1)–Mn(3)	149.1(7)
C(6)–N(6)–Mn(5)	147.4(10)
C(7)–N(7)–Mn(5)	144.0(9)
C(11)–N(11)–Mn(4)	154.3(8)
N(1)–Mn(3)–N(14)	90.4(3)
N(1)–Mn(3)–O(1)	174.5(3)
N(14)–Mn(3)–O(1)	95.0(3)
N(1)–Mn(3)–N(13)	92.3(3)
N(14)–Mn(3)–N(13)	69.4(3)
O(1)–Mn(3)–N(13)	88.4(3)
N(1)–Mn(3)–N(17)	90.2(3)
N(14)–Mn(3)–N(17)	138.6(3)
O(1)–Mn(3)–N(17)	84.9(3)
N(13)–Mn(3)–N(17)	69.2(3)
N(1)–Mn(3)–N(16)	84.1(3)
N(14)–Mn(3)–N(16)	148.4(3)
O(1)–Mn(3)–N(16)	92.0(4)
N(13)–Mn(3)–N(16)	141.7(3)
N(17)–Mn(3)–N(16)	72.7(4)
N(1)–Mn(3)–N(15)	94.9(3)
N(14)–Mn(3)–N(15)	72.8(3)
O(1)–Mn(3)–N(15)	88.0(3)
N(13)–Mn(3)–N(15)	141.6(3)
N(17)–Mn(3)–N(15)	148.2(3)
N(16)–Mn(3)–N(15)	76.7(4)
N(11)–Mn(4)–O(2)	173.3(4)
N(11)–Mn(4)–N(27)	92.5(3)
O(2)–Mn(4)–N(27)	90.2(4)
N(11)–Mn(4)–N(26)	89.7(4)
O(2)–Mn(4)–N(26)	85.5(4)
N(27)–Mn(4)–N(26)	69.4(4)
N(11)–Mn(4)–N(23)	90.5(3)
O(2)–Mn(4)–N(23)	96.2(3)
N(27)–Mn(4)–N(23)	69.6(3)
N(26)–Mn(4)–N(23)	139.0(4)
N(11)–Mn(4)–N(25)	82.2(6)
O(2)–Mn(4)–N(25)	92.1(6)
N(27)–Mn(4)–N(25)	144.9(5)
N(26)–Mn(4)–N(25)	75.8(6)
N(23)–Mn(4)–N(25)	144.6(5)
N(11)–Mn(4)–N(24)	92.0(4)
O(2)–Mn(4)–N(24)	89.8(5)
N(27)–Mn(4)–N(24)	140.7(4)
N(26)–Mn(4)–N(24)	149.6(5)
N(23)–Mn(4)–N(24)	71.3(4)
N(25)–Mn(4)–N(24)	74.4(6)
N(22)–Mn(5)–N(7)	90.3(3)
N(22)–Mn(5)–N(6)	93.6(4)
N(7)–Mn(5)–N(6)	176.1(4)
N(22)–Mn(5)–N(20)	141.7(4)
N(7)–Mn(5)–N(20)	84.4(3)
N(6)–Mn(5)–N(20)	99.9(4)
N(22)–Mn(5)–N(18)	69.3(3)
N(7)–Mn(5)–N(18)	89.0(4)
N(6)–Mn(5)–N(18)	91.9(4)
N(20)–Mn(5)–N(18)	148.1(4)
N(22)–Mn(5)–N(21)	69.4(3)
N(7)–Mn(5)–N(21)	91.1(3)
N(6)–Mn(5)–N(21)	90.7(4)
N(20)–Mn(5)–N(21)	72.7(4)
N(18)–Mn(5)–N(21)	138.7(4)
N(22)–Mn(5)–N(19)	142.2(4)
N(7)–Mn(5)–N(19)	91.2(3)
N(6)–Mn(5)–N(19)	85.4(4)
N(20)–Mn(5)–N(19)	75.9(4)
N(18)–Mn(5)–N(19)	73.1(4)
N(21)–Mn(5)–N(19)	148.2(4)

$$\boldsymbol{H} = -J_1\boldsymbol{S}_{\mathrm{Fe}_1}\boldsymbol{S}_{\mathrm{Mn}_4} - J_2\boldsymbol{S}_{\mathrm{Mn}_5}\boldsymbol{S}_{\mathrm{Fe}_1} - J_3\boldsymbol{S}_{\mathrm{Mn}_5}\boldsymbol{S}_{\mathrm{Fe}_2} - J_4\boldsymbol{S}_{\mathrm{Mn}_4}\boldsymbol{S}_{\mathrm{Fe}_2}$$

The equation describing the temperature dependence of the magnetic susceptibility has been obtained by full-matrix diagonalization of the above Hamiltonian and contains five parameters: J_1, J_2, J_3, J_4 and g_{av} [14]. Such an equation is charged by too many parameters and its use in fitting the magnetic data must be regarded with extreme caution. Least-squares fit to the magnetic data gives the following values: $g_{\mathrm{av}} = 2.03$; $J_1 = -2.6$ cm^{-1}, $J_2 = +0.3$ cm^{-1}, $J_3 = -1.6$ cm^{-1}, $J_4 = -1.5$ cm^{-1}, with $R = 2.5 \times 10^{-5}$ (R is the agreement factor defined as $\Sigma_{\mathrm{i}}[(\chi_{\mathrm{M}}T)_{\mathrm{obs}}(\mathrm{i}) - (\chi_{\mathrm{M}}T)_{\mathrm{calc}}(\mathrm{i})]^2/\Sigma_{\mathrm{i}}[(\chi_{\mathrm{M}}T)_{\mathrm{obs}}(\mathrm{i})]^2$). Although these values are not quite reliable, they suggest that one ferro- and three antiferromagnetic interactions between the Mn(II) and Fe(III) ions lead to a ground state with $S = 5/2$. The expected value of the $\chi_{\mathrm{M}}T$ product at low temperature ($T = 2$ K) is 4.37 cm^3 mol^{-1} K, much lower than the experimental one (12.36 cm^3 mol^{-1} K). This difference can be explained by analyzing the spectrum of the low-lying states of the pentanuclear complex (Fig. 4). Even at low temperature ($T = 2$ K), apart from the ground state ($S = 5/2$), the spin states $S = 7/2$, 9/2, 11/2 and 13/2, with the energies lower than $kT = 1.4$ cm^{-1}, are thermally populated. This diagram shows also that the spin state structure is not regular and accounts for the minimum observed on the $\chi_{\mathrm{M}}T$ vs. T curve. However, as already stated, the above results must regarded with caution, especially

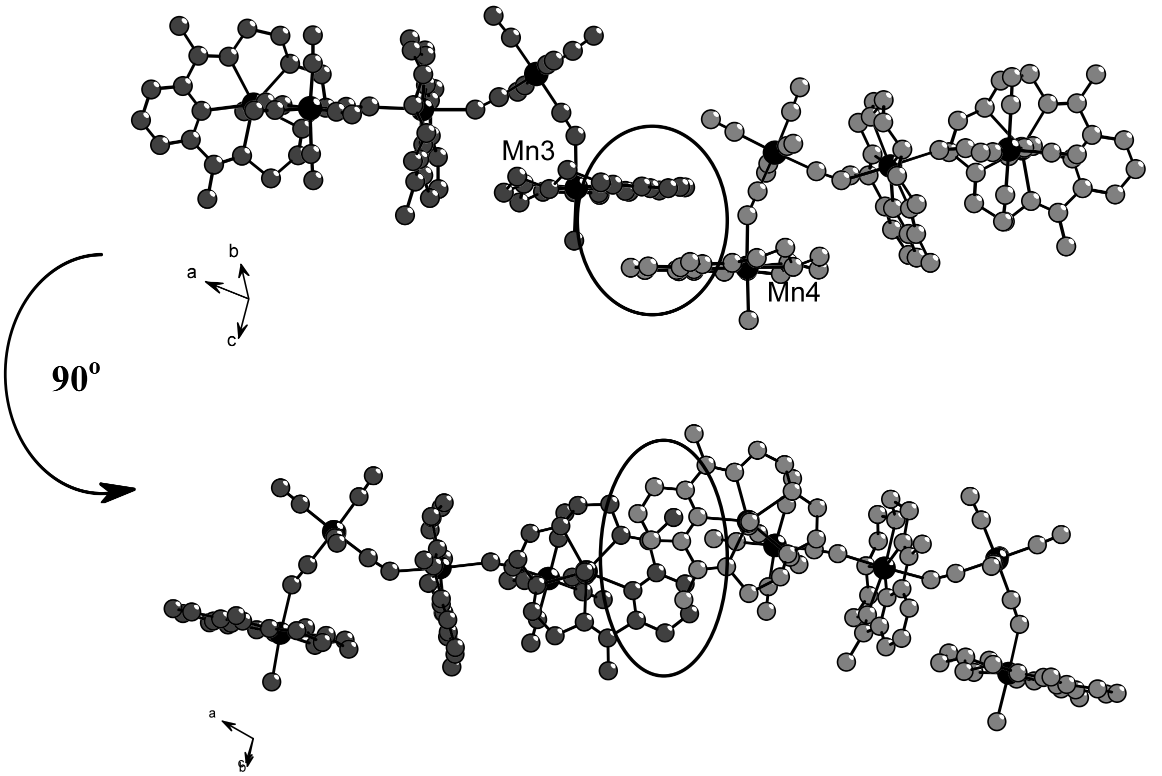


Fig. 2. Detail of the packing diagram for compound **1**, showing that no intermolecular stacking interactions occur between pyridyl moieties.

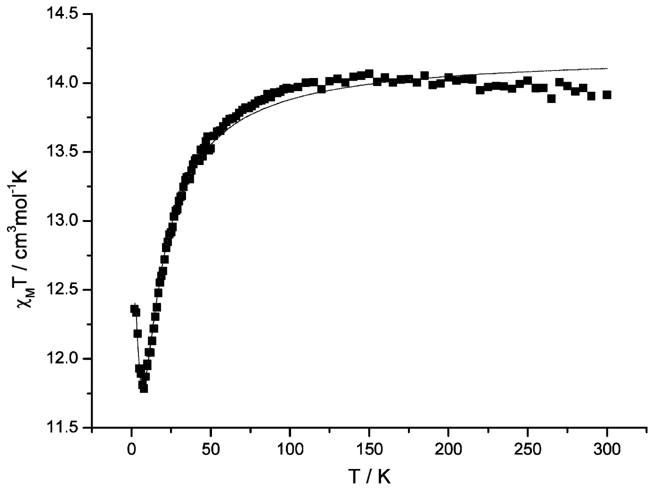


Fig. 3. $\chi_M T$ vs. T plot for compound **1**. The solid line represents the best fit curve.

because the Hamiltonian describing the exchange interactions neglects the contribution of the first order orbital momentum associated with the low-spin Fe(III) ion.

No magneto-structural correlation relating the sign and the magnitude of the J parameters with the Mn–NC–Fe angle is available in literature. Only recently the magnetic properties of the first discrete cyano-bridged Fe(III)–Mn(II) complex have been investigated, and the exchange interaction between the Fe(III) and Mn(II) ions was found to be antiferromagnetic ($J = -3.0$ cm^{-1}) [15]. Since in the case of our compound the four Mn–NC–Fe angles are not equal, their variation accounts for the different J values we found.

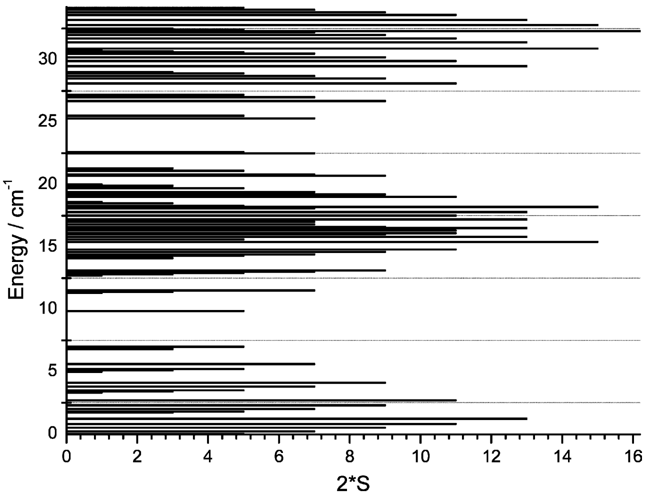


Fig. 4. The energy spectrum of the low-lying states for the pentanuclear complex **1**.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Data Centre, CCDC No. 177728. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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