

Available online at www.sciencedirect.com



Inorganica Chimica Acta 357 (2004) 25-32

Inorganica Chimica Acta

www.elsevier.com/locate/ica

Pyridine-2,6-dicarboxylate and perchlorate bridged hydrogen bonded 1D chains involving manganese(III)-cyclam moiety: synthesis, X-ray crystal structures and magnetic study ☆

Nizamuddin Shaikh^a, Anangamohan Panja^a, Pradyot Banerjee^{a,*}, Maria Kubiak^b, Zbigniew Ciunik^b, Malgorzata Puchalska^b, Janina Legendziewicz^{b,*}, Pavel Vojtíšek^c

^a Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, 2A&2B Raja S.C. Mullick Road, Kolkata 700 032, India ^b Faculty of Chemistry, University of Wroclaw, F. Joliot-Curie Str., 14, 50383 Poland ^c Department of Inorganic Chemistry, Universita Karlova, Albertov 2030, 128 40 Prague 2, Czech Republic

Received 4 February 2003; accepted 7 June 2003

Abstract

Two compounds H[Mn(cyclam)(pyridine-2,6-dicarboxylate)₂] \cdot H₂O (1) and [Mn^{III}(cyclam)Cl₂]ClO₄ (2) (where cyclam = 1,4,8,11-tetraazacyclotetradecane) have been synthesized and structurally characterized. The complex 1 crystallizes in the monoclinic space group P2(1)/c with a = 11.4328(11), b = 14.4275(14), c = 8.5782(9) Å, V = 1343.1(2) Å³, Z = 2, R = 0.0453. Complex 1 is octahedral in which [Mn(cyclam)]³⁺ unit occupies the basal plane having two pyridine-2,6-dicarboxylate anions in the axial positions. Molecular packing of the crystal is dominated by string of molecules along the *b*-axis. The strings are held together by extensive intermolecular hydrogen bonds involving N–H···O, N–H···N and O–H···O which impart it an infinite 1D chain. Complex 2 on the other hand crystallizes in the space group $P2_12_12_1$ (No. 19) of the orthorhombic system. Mn(III) ions occupy the center of a distorted octahedron and two chloride ions occupy the axial positions. The packing diagram of 2 reveals that the complex is percholrate-bridged hydrogen bonded 1D chain along *a*-axis. Cyclic voltammogram of complex 1 is characterized by an irreversible reduction wave at -0.25 V coupled to an oxidation wave at -0.05 V versus SCE in aqueous solution. The complex 2 is characterized by an irreversible reduction wave at -0.11 V versus SCE and is identical to that observed for [Mn^{III}(cyclam)Cl₂]Cl·5H₂O. The magnetic measurements in the temperature range 1.9–300 K have been carried out for complex 1 which exhibits a very weak ferromagnetic interaction at low temperature. Complex 2 shows room temperature magnetic moment value of 4.92 BM consistent with the high spin d⁴ electronic configuration.

Keywords: Manganese(III) complexes; Hydrogen bonding; 1D chains; Magnetic study

1. Introduction

Owing to their potential applications in various fields, e.g., molecular recognition [1–3], nonlinear optics [4,5], magnetism [6,7] and structural and functional analogues of inorganic zeolites [8–10], supramolecular architectures are gaining considerable attention from researchers. In the construction of such networks various type of interactions are being exploited; (a) coordinate covalent bonds connecting metal centers with appropriate ligands [11–13], (b) noncovalent hydrogen bonded interaction [14–16], (c) π – π stacking interaction [17,18], and (d) electrostatic interaction [19,20]. The use of transition metal ions to control assembly of molecular architectures has become a popular and rapidly growing discipline [21,22]. Infinite complexes involving macrocyclic frameworks are often assembled through metal coordinate coordinate control is bridging ligands [23].

The macrocyclic ligand, 1,4,8,11-tetraazacyclotetradecane (cyclam) is reported to yield *trans*-complexes with manganese(III), [Mn^{III}(cyclam)Cl₂]Cl · 5H₂O [24].

[★] Supplementary data associated with this article can be found, in the online version, at doi:10.1016/S0020-1693(03)00380-3.

^{*} Corresponding authors. Tel.: +91-33-2473-4971; fax: +91-33-2473-2805.

E-mail addresses: icpb@mahendra.iacs.res.in (P. Banerjee), jl@wchuwr.chem.uni.wroc.pl (J. Legendziewicz).

The binuclear di-µ-oxo-bis(cyclam)dimanganese(III,IV) ion has also been characterized through X-ray crystallography [25]. However, literature lacks any report for compounds utilizing manganese(III)-cyclam as a precursor molecule, partly due to its instability in aqueous solution as well as in different organic solvents. To meet the major current challenges to design coordination compounds with special structures, properties and/or functionalities, the two manganese(III)-cyclam complexes $H[Mn(cyclam)(pyridine-2, 6-dicarboxylate)_2] \cdot H_2O$ (1) and $[Mn(cyclam)Cl_2]ClO_4$ (2) have been prepared and characterized. The use of dicarboxylate spacers, e.g., terephthalate, oxalate, malonate and fumarate is a continuing field of study for the chemists [26–29]. We note that a pyridine-2,4-dicarboxylate coordination polymer with a bimetallic Zn^{II}-Cu^{II} assembly having a microporous network has appeared recently [30]. The crystal structures of both 1 and 2 and magnetic properties of 1 are reported herein.

2. Experimental

2.1. Materials and reagents

All the chemicals including manganous chloride, manganous acetate, methanol, sodium hydroxide, Na-ClO₄ and HClO₄ were of reagent grade. Pyridine-2,6dicarboxylic acid was purchased from Aldrich and used without further purification. Double distilled water was used throughout. The ligand cyclam (1,4,8,11-tetraazacyclotetradecane) was synthesized according to the literature procedure [31] and was checked by the elemental analysis and ¹H NMR spectroscopy. [Mn(cyclam)Cl₂]Cl was synthesized according to the reported method [24] and was checked as reported earlier [32].

2.2. Preparation of monosodium salt of pyridine-2,6dicarboxylic acid, Na(2,6-dipicH)

About 0.84 g (5 mmol) of pyridine-2,6-dicarboxylic acid (2,6-dipicH₂) was suspended in a minimum volume of water. To this mixture was added 0.1 g (2.5 mmol) of NaOH dissolved in 5 cm³ water. The mixture was stirred magnetically for 30 min at 50 °C. The solution was then filtered to remove any suspended material. To the filtrate was added dehydrated ethanol slowly thereby yielding the white micro-crystalline monosodium salt of dipicolinic acid, Na (2,6-dipicH).

2.3. Synthesis of H[Mn(cyclam)(pyridine-2,6-dicarb $oxylate)_2] \cdot H_2O(1)$

About 0.36 g (1 mmol) of $[Mn(cyclam)Cl_2]Cl$ was dissolved in 20 cm³ double distilled water to give a green solution. To this solution was added 0.21 g (1 mmol) of

Na(2,6-dipicH) dissolved in 20 cm³ of double distilled water. The color changed from deep green to light green. It was filtered to remove any suspended material and kept at room temperature for 3 days to produce green crystals of complex 1. It was filtered and washed first by cold water followed by acetone and then dried in air. Yield ca. 80%. *Anal.* Calcd. for $C_{24}H_{35}N_6O_{10}Mn$: C, 46.3; H, 5.6; N, 13.5. Found: C, 46.2; H, 5.7; N, 13.4%.

2.4. Preparation of $[Mn^{III}(cyclam)Cl_2]ClO_4$ (2)

To an aqueous solution (30 cm^3) of [Mn(cyclam)Cl₂]Cl·5H₂O was added an aqueous solution (5 cm³) of NaClO₄ in 1:1 ratio. (*Caution!* Although no problems have been encountered in this work, perchlorates are potentially explosive and should be handled with care and in only small quantities). The mixture was stirred for 20 min and filtered. The solution was kept for several days whereby deep green crystals of **2** were isolated in 75% yield. *Anal.* Calcd. for C₁₀H₂₄N₄Cl₃O₄Mn: C, 28.2; H, 5.6; N, 13.1. Found: C, 28.1; H, 5.5; N, 13.4%.

2.5. Physical measurements

Microanalysis (CHN) was performed in a Perkin– Elmer 240C elemental analyzer. Magnetic susceptibility measurement was carried out with SQUID magnetometer down to 1.9 K. IR spectra were obtained on a Nicolet, MAGNA-IR 750 spectrometer with samples prepared as KBr pellets. Cyclic voltammetry was performed at a planar EG&G PARC G0229 glassy carbon milli-electrode using an EG&G PARC electrochemical analysis system (model 250/5/0) in water under dry nitrogen atmosphere in conventional three electrode configurations with a scan rate of 0.05 V s⁻¹. Spectral measurements were performed in an UV–Vis Spectrophotometer (UV-2100, Shimadzu, Japan).

2.6. X-ray crystallography

The X-ray diffraction measurements were carried out on a KUMA KM4CCD diffractometer for 1 [33] and an Enraf-Nonious CAD4 diffractometer for 2, all using a graphite monochromated Mo Ka radiation. Intensity data were collected by ω scan technique. All data were corrected for Lorentz polarization effects [34]. Absorption corrections based on least-squares fitting against $|F_c| - |F_0|$ differences were also employed [35]. The structure was solved by direct methods (SHELXS 97) [36] and refined by full-matrix least-squares based on F^2 using SHELXL 97 [36]. Non-hydrogen atoms were refined with anisotropic thermal parameters, whereas the hydrogen atoms were included at calculated positions and refined isotropically. Informations concerning crystallographic data collection and refinement of the structures for 1 and 2 are compiled in Table 1.

Table 1

Crystal data and structure refinements for H[Mn(cyclam)(pyridine-2,6-dicarboxylate)₂]·H₂O (1) and [Mn(cyclam)Cl₂]ClO₄ (2)

Complex	1	2
Empirical formula	$C_{24}H_{35}N_6O_{10}Mn$	$C_{10}H_{24}Cl_2MnN_4ClO_4$
Formula weight	622.52	425.62
Temperature (K)	100(2)	293
Wavelength (Å)	0.71073	0.71070
Crystal system	monoclinic	orthorhombic
Space group	P2(1)/c	$P2_12_12_1$ (number 19)
a (Å)	11.4328(11)	6.5380(1)
b (Å)	14.4275(14)	13.2990(3)
c (Å)	8.5782(9)	19.8350(3)
β (°),	108.331(9)	880
$V(\dot{A}^{3})$	1343.1(2)	1724.63(5)
Ζ	2	4
μ (Mo K α) (mm ⁻¹)	0.560	1.3
F(000)	652	880
θ range for data collection (°)	3.39-28.52	2.0-27.5
Reflections collected	16573	3940
Independent reflections (R_{int})	3243 (0.0399)	3940
Final $R1$, $wR2$ indices $(I > 2\sigma I)$	0.0453, 0.0955	0.0307, 0.0804

3. Results and discussion

3.1. Structure of the complex, $H[Mn(cyclam)(pyridine-2,6-dicarboxylate)_2] \cdot H_2O(1)$

The anion of the complex **1** features a hydrogen bonded Mn(III) 1D chain as shown in Figs. 1 and 2. Important bond distances and bond angles appear in Table 2. The manganese ion lies on one inversion center. The geometry of manganese is *trans*-pseudo-octahedral with the four nitrogen atoms of the cyclam in equatorial position having an average Mn–N distance 2.033 Å which is very much comparable to that in *trans*- $[Mn(cyclam)Cl_2]^+$ reported earlier [24]. Two oxygen atoms of pyridine-2,6-dicarboxylate (dipic) ligand with the Mn–O distance 2.102 Å occupy the two axial positions. The metal ion is located in the plane of four nitrogen atoms. The hydrogen atoms bonded to N(2) and N(3) are above the four-nitrogen plane whereas those to N(1) and N(4) are below. The expected *trans*-III conformation as classified by Bosnich et al. [37] is thereby



Fig. 1. Molecular structure of $H[Mn(cyclam)(pyridine-2,6-dicarboxy-late)_2] \cdot H_2O(1)$ showing the atom labeling scheme.



Fig. 2. Packing diagram showing both intra- and intermolecular hydrogen bonding interaction of **1**.

Mn-N(2)#1	2.0332(16)	Mn–N(2)	2.0332(16)	
Mn-N(3)	2.0341(16)	Mn-N(3)#1	2.0341(16)	
Mn–O(2)	2.1020(13)	Mn-O(2)#1	2.1020(13)	
N(2)#1-Mn-N(2)	180.0	N(2)#1-Mn-N(3)	85.85(6)	
N(2)-Mn-N(3)	94.15(6)	N(2)#1-Mn-N(3)#1	94.15(6)	
N(2)-Mn-N(3)#1	85.85(6)	N(3)-Mn-N(3)#1	180.0	
N(2)#1-Mn-O(2)	91.36(6)	N(2)–Mn–O(2)	88.64(6)	
N(3)–Mn–O(2)	90.76(6)	N(3)#1-Mn-O(2)	89.24(6)	
N(2)#1-Mn-O(2)#1	88.64(6)	N(2)-Mn-O(2)#1	91.36(6)	
N(3)-Mn-O(2)#1	89.24(6)	N(3)#1-Mn-O(2)#1	90.76(6)	
O(2)-Mn-O(2)#1	180.0			

Table 2 Selected bond distances (Å) and angles (°) for H[Mn(cyclam) (pyridine-2,6-dicarboxylate)₂]·H₂O

achieved. The in-plane distortions are introduced by the ligand bite angles N(2)-Mn-N(3) of 85.85° and 94.15°. The complex is stabilized by intermolecular hydrogen bonds involving N-H \cdots O, N-H \cdots N and O-H \cdots O which control the overall chelate ring conformations. The O atoms of dipic and H₂O (water of crystallization) provide the potential hydrogen bond acceptor sites in addition to the amine N atoms of cyclam. Possible hydrogen bonds are listed in Table 3 with the widely accepted criteria that the hydrogen bonds should be less than the sum of the van der Waals radii of hydrogen and the acceptor atom. The molecular packing of the crystal is dominated by string of molecules along the b direction due to intermolecular hydrogen bonding. As can be seen from the packing diagram the 1D chain is formed by the hydrogen bonding between the -COOH of one $[Mn(cyclam)(dipic)_2]^-$ moiety to $-COO^-$ of another unit. The water of crystallization also participates in the hydrogen-bonding interaction to stabilize the crystal lattice. In the packing diagram two types of Mn-Mn bond distances were located. The bond distance along zaxis was found to be (Mn-MnA and Mn-MnB) 8.578 Å and that along the x- and y-axis (Mn–MnC, Mn–MnD, Mn-MnE and Mn-MnF) was found to be 8.363 Å.

3.2. Structure of $[Mn^{III}(cyclam)Cl_2]ClO_4$ (2)

The structure of complex **2** consists of the complex cation $[Mn(cyclam)Cl_2]^+$ and one perchlorate anion. The complex crystallizes in the space group $P2_12_12_1$

(No. 19) of the orthorhombic system with four formula units in the unit cell. Informations regarding crystallographic data collection and refinement of the structures are complied in Table 1. An ORTEP view of the isolated complex is shown in Fig. 3 and packing diagram showing intra- and intermolecular hydrogen bonding interaction appears in Fig. 4. The manganese atom lies on one inversion center. The principal bond lengths and angles are listed in Table 4. As in the trans-[Mn(cy $clam)Cl_2$ Cl \cdot 5H₂O reported earlier [24], as well as complex 1, complex 2 is roughly octahedral. The independent Mn-N bond lengths are 2.039(2), 2.045(2), 2.036(2) and 2.044(2) A. These values are shorter than those found for the corresponding bonds in the salts of $[Mn(cyclam)O]_2^{2+}$ which is probably indicative of the trans-influence of oxygen in the later ion [25]. The average Mn–N distance here (2.041 A) is, however, slightly higher than that (2.033 A) observed in trans-[Mn(cyclam)Cl₂]Cl · 5H₂O [24]. The axial Mn–Cl bond lengths of 2.532(1) and 2.521(1) Å are as expected, very long and comparable to reported values. This bond distance is much longer than that found in the similar cation $[Co(cyclam)Cl_2]^+$ where the Co–Cl distance is 2.252 A [38]. The cis N-Mn-N bond angles are 95.18(9)° and $93.70(8)^{\circ}$ with the smaller value being associated with the five-membered ring [Mn, N(11), C(10), C(9), N(8)] as expected. Similarly the bond distances and angles in the cyclam ligand are thoroughly consistent with those in the literature [39,40]. The metal ion is located in the plane of four nitrogen atoms. Hydrogen atoms bonded

Table 3 Hydrogen bonds for H[Mn(cyclam)(pyridine-2,6-dicarboxylate)₂]·H₂O (Å and °)

	,	2-()		
$D-H\cdots A$	d(D-H)	$d(\mathbf{H}\cdots\mathbf{A})$	$d(\mathbf{D}\cdots\mathbf{A})$	<(DHA)
$N(3)-H(12)\cdots N(1)#1$	0.81(2)	2.27(2)	3.071(2)	167(2)
$N(3)-H(12)\cdots O(3)#1$	0.81(2)	2.49(2)	3.003(2)	123(2)
$N(2)-H(14)\cdots O(1W)#2$	0.87(2)	2.02(2)	2.810(2)	151(2)
$O(1W) - H(01) \cdots O(4) #3$	0.88(4)	1.92(4)	2.801(2)	174(3)
$O(1W) - H(02) \cdots O(1)$	0.76(3)	2.04(3)	2.781(2)	166(3)
O(3)–H(03)···O(3)#4	1.2349(13)	1.2349(13)	2.470(3)	180.0
$O(3)-H(03)\cdots O(4)#4$	1.2349(13)	2.5204(14)	3.288(2)	118.12(7)

Symmetry transformations used to generate equivalent atoms: #1, -x, -y, -z; #2, x, y, z - 1; #3, x - 1, y, z; #4, -x + 1, -y, -z.



Fig. 3. An ORTEP plot of complex 2 showing atom labeling scheme. The thermal ellipsoids are represented at the 50% probability level.

to N(4) and N(8) are above the four nitrogen planes, whereas the hydrogen atoms bonded to N(11) and N(1) are below giving rise to the *trans-III* conformation. Extensive intra- and intermolecular hydrogen bonding occurs among the $[Mn(cyclam)Cl_2]ClO_4$ units. Intra-

molecular hydrogen bonding involves the coordinated Cl⁻ ions and the N–H hydrogen of cyclam. The intermolecular hydrogen bond involving the non-coordinated perchlorate anion and N–H hydrogen of the cyclam ligand leads to an endless 1D chain along *a*-axis (Fig. 4). Important hydrogen bonds are listed in Table 4. It is noticeable that in the *trans*-[Mn(cyclam)Cl₂] Cl · 5H₂O molecule, this type of chain does not exist. The solubility of **2** salt decreases significantly in NaClO₄ medium owing to larger ClO₄⁻ counter anion. Evolution of the one dimensional chain is facilitated through tetrahedral perchlorate anion which forms two O–H–N hydrogen bonds with adjacent [Mn(cyclam)Cl₂]⁺ units.

3.3. UV-Vis spectroscopy

The complex 1 is insoluble almost in all organic solvents. It is, however, sparingly soluble in water and, therefore, quantitative determination of extinction coefficient was not possible. The spectrum exhibits two sharp peaks at 203 and 271 nm with a weak maximum at about 354 nm. These bands are due to the ligand to metal charge transfer. The d-d transition band is very weak and appears as relatively broad in the 550-800 nm region. The spectrum is virtually identical with [Mn(cyclam)Cl₂]Cl [32] in aqueous medium which exhibits peaks at 630 ($\epsilon = 25$), 373 ($\epsilon = 1155$), 267 $(\varepsilon = 10, 941)$ nm. Complex 2 also exhibits similar spectral features having a broad weak band at 620 nm $(\varepsilon = 20)$ due to the d-d transition and characteristics of the manganese(III) complexes [41]. The intense bands at 370 ($\varepsilon = 1150$) and 267 nm (10,800) are similar to that observed for [Mn(cyclam)Cl₂]Cl [24].



Fig. 4. Molecular packing diagram of $[Mn(cyclam)Cl_2]ClO_4$ (2) showing intra- and intermolecular hydrogen bonding interaction giving rise to infinite 1D chain.

T 11

Table 4		
Selected bond distances (Å), a	ngles (°) and hydrogen bond distances (Å) for complex [Mn ^{III} (cyclam)Cl ₂]ClO ₄ (2)
Mn(1)–Cl(1)	2.5322(7)	Mn(1)–C(12)
Mn(1) N(1)	2.039(2)	Mn(1) N(4)

Mn(1)-Cl(1)	2.5322(7)	Mn(1)-C(12)	2.5205(7)
Mn(1)-N(1)	2.039(2)	Mn(1)–N(4)	2.045(2)
Mn(1)–N(8)	2.036(2)	Mn(1)–N(11)	2.044(2)
Cl(1)-Mn(1)-Cl(2)	178.99(2)	Cl(1)-Mn(1)-N(1)	87.52(6)
Cl(1)-Mn1-N(4)	92.17(6)	Cl(1)-Mn(1)-N(8)	92.11(6)
Cl(1)-Mn(1)-N(11)	87.54(7)	Cl(2)-Mn(1)-N(1)	91.54(6)
Cl(2)-Mn(1)-N(4)	88.12(6)	Cl(2)–Mn(1)–N(8)	88.84(6)
Cl(2)-Mn(1)-N(11)	92.19(7)	N(1)–Mn(1)–N(4)	85.89(9)
N(1)-Mn(1)-N(8)	179.43(10)	N(1)–Mn(1)–N(11)	95.18(9)
N(4)-Mn(1)-N(8)	93.70(8)	N(4)–Mn(1)–N(11)	178.88(8)
N(8)-Mn(1)-N(11)	85.23(9)		
$N(1)-H(1)\cdots Cl(2)$	3.265(2)	$N(4)-H(4)\cdots O(1)$	3.136(4)
$N(8)-H(8)\cdots Cl(1)$	3.239(2)	$N(11)-H(11)\cdots O(4)$	3.055(4)

3.4. IR spectroscopy

The complex **1** shows two distinct bands corresponding to the carboxylate stretching at 1643 and 1732 cm⁻¹. A broad band is also observed at 3476 cm⁻¹ due to the presence of H₂O molecule. Two separate bands at 1643 and 1732 cm⁻¹ indicate two types of carboxylate groups and are consistent with the free and coordinated carboxylates. In addition to these, the aromatic C–H stretching frequency is observed at 1605 cm⁻¹. For complex **2**, two intense unsplit bands at 1081 and 630 cm⁻¹ are observed at 3300–3350 cm⁻¹. Consistent with the structural features the bands at 3400–3500 cm⁻¹ region due to H₂O are not observed for **2**.

3.5. Electrochemistry

Complex 1 is insoluble in most of the organic solvents. It is, however, sparingly soluble in water and, therefore, electrochemistry was performed in aqueous medium as illustrated in Fig. 5. In aqueous solution [Mn(cyclam)Cl₂]Cl undergoes one electron irreversible reduction at -0.12 V versus SCE at pH 6.5 corresponding to Mn(III)/Mn(II) couple [32]. The corresponding peak in complex 1 was observed at -0.25 V versus SCE coupled to an oxidation wave at -0.05 V versus SCE ($E_{1/2} = 100 \text{ mV}, \Delta E_p = 200 \text{ mV}$). The larger negative shift of the redox potential in comparison to the parent complex might be due to the fact that coordination of dipic moiety renders the metal center less susceptible towards reduction. This is exemplified by the coordination of phosphate anion to the metal in $[Mn^{III}(cyclam)Cl_2]^+$ [32]. Carboxylato bridged dinuclear complex, $[Mn(salen)_2(pth)] \cdot 2H_2O$ (pth = terephthalic acid) also exhibits similar cyclic voltammetric pattern in aqueous solution [42]. Complex 2 exhibits cyclic voltammetric pattern, which is identical to that observed for $[Mn(cyclam)Cl_2]Cl$ with one reduction wave at -0.11



Fig. 5. Cyclic voltammogram of 1 at a scan rate of 50 mV/s⁻¹ in water at a platinum electrode. TEAP was used as supporting electrolytes.

V versus SCE at pH 7.0 [32]. No oxidation wave was observed for this complex in the range +1.0 to +1.5 V in aqueous solution.

3.6. Magnetic studies

The variable temperature magnetic susceptibility measurements for complex 1 were performed in the temperature range of 1.9–300 K. The room temperature effective magnetic moment value $(4.86\mu_{\rm B})$ agrees well to that observed for a high spin d^4 system (S = 2) [43–45]. The temperature dependence of the $\chi_{\rm M} T$ (3.41 cm³ mol⁻¹ K) shows a weak maximum at approximately 7 K and then decreases at lower temperature (see supplementary materials, Fig. S2a). The magnetic moment value increases with temperature and reaches a maximum $(5.24\mu_{\rm B})$ at approximately 7 K and then decreases (see supplementary materials, Fig. S2b). This feature indicates ferromagnetic ordering at lower temperature. The magnetic susceptibility obeys Curie-Weiss law and a plot of $1/\chi_{\rm M}$ versus T yields a straight line (Fig. 6) with $C = 2.89 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ and $\theta = +0.93$. The positive Weiss constant θ also suggests a very weak ferromagnetic in-



Fig. 6. χ_{M}^{-1} vs. *T* plot for complex **1**. Solid line indicates a fit of the data by Curie–Weiss law.

teraction between Mn(III) ions. The observed room temperature magnetic moment value of the complex **2** is 4.92 BM and is consistent with the high spin Mn(III) system having d^4 electronic configuration [43–45].

Recently Miyasaka et al. [46] have observed very weak intermolecular ferromagnetic interaction in an otherwise mononuclear Mn^{III} complex. The structural data of complex **1** shows no obvious pathway for the magnetic exchange. The observed ferromagnetic interactions are, therefore, might be due to intermolecular interaction. Such ferromagnetic interactions can be rationalized by considering the arrangement of Mn(III) ion d-orbitals. The electronic configuration of the Mn(III) ion in an elongated Jahn–Teller distortion is known to be $(d_{xy})^1$, $(d_{yz})^1$, $(d_{xz})^1$ and $(d_z 2)^1$ with a ⁵B₁ ground state [47]. The ferromagnetic exchange interaction between the Mn(III) ions could mainly be the result of the d_z^2 and the $d\pi$ (d_{xy} , d_{yz} and d_{xz} orbitals) orthogonality.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 195310 and 205949 for 1 and 2, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www.http:// ccdc.cam.ac.uk). Supplementary figures indicated in text are available from the corresponding authors.

Acknowledgements

Thanks are due to the Council of Scientific and Industrial Research, New Delhi, for financial support to AP and PB.

References

- [1] J.-M. Lehn, Supramolecular Chemistry, VCH, Weinheim, 1995.
- [2] G.M. Whitesides, J.P. Mathias, C.T. Seto, Science 254 (1991) 1312.
- [3] J. Rebek, Angew. Chem., Int. Ed. Engl. 29 (1990) 102.
- [4] S.M. LeCours, H.-W. Guan, S.G. DiMagno, C.H. Wang, M.J. Therien, J. Am. Chem. Soc. 118 (1996) 1497.
- [5] S.L. Darling, E. Stulz, N. Feeder, N. Bampos, J.K.M. Sanders, New J. Chem. 24 (2000) 261.
- [6] E.J. Brandon, R.D. Rogers, B.M. Burkhart, J.S. Miller, Chem. Eur. J. 4 (1998) 1938.
- [7] E.J. Brandon, D.K. Rittenberg, A.M. Arif, J.S. Miller, Inorg. Chem. 37 (1998) 3376.
- [8] Y. Diskin-Posner, S. Dahal, I. Goldberg, Angew. Chem., Int. Ed. Engl. 39 (2000) 1288.
- [9] Y. Diskin-Posner, I. Goldberg, Chem. Commun. (1999) 1961.
- [10] I. Goldberg, Chem. Eur. J. 6 (2000) 3863.
- [11] O.M. Yaghi, G. Li, H. Li, Nature 378 (1995) 703.
- [12] O.M. Yaghi, H. Li, J. Am. Chem. Soc. 117 (1995) 10401.
- [13] M. Fujita, H. Oka, K. Yamaguchi, K. Ogura, Nature 378 (1995) 469.
- [14] C.M.R. Juan, B. Lee, Coord. Chem. Rev. 183 (1999) 43.
- [15] G.R. Desiraju, Acc. Chem. Res. 29 (1996) 441.
- [16] T.N. Guru Row, Coord. Chem. Rev. 183 (1999) 81.
- [17] I. Unamuno, J.M. Gutiérrez-Zorrilla, A. Luque, P. Roman, L. Lezama, R. Calvo, T. Rojo, Inorg. Chem. 37 (1998) 6452.
- [18] M.-C. Tse, K.-K. Cheung, M.C.-W. Chan, C.M. Che, Chem. Commun. (1998) 3245.
- [19] D.S. Reddy, K. Panneerselvan, T. Pilati, G.R. Desiraju, J. Chem. Soc., Chem. Commun. (1993) 661.
- [20] Y.B. Dong, M.D. Smith, R.C. Layland, H.C. zur Loye, Inorg. Chem. 38 (1999) 5027.
- [21] C.J. Jones, Chem. Soc. Rev. 27 (1998) 289.
- [22] C. Bonnefous, N. Bellec, R.P. Thummel, Chem. Commun. (1999) 1243.
- [23] P.N.W. Baxter, in: J.M. Lehn (Ed.), Comprehensive Supramolecualr Chemistry, vol. 9, Pergamon, Oxford, 1996 (Chapter 5).
- [24] F. Letumier, G. Brocker, J.-M. Barbe, R. Guilard, D. Lucas, V. Dahaoui-Gindrey, C. Lecomte, L. Thouin, C. Amatore, J. Chem. Soc., Dalton Trans. (1998) 2233.
- [25] K.J. Brewer, M. Calvin, R.S. Lumpkin, J.W. Otvos, L.O. Spreer, Inorg. Chem. 28 (1989) 4446.
- [26] S.R. Batten, R. Robson, Angew. Chem., Int. Ed. Engl. 37 (1998) 1460.
- [27] L. Deakin, M.A. Arif, J.S. Miller, Inorg. Chem. 38 (1999) 5072.
- [28] S. Kitagawa, T. Okubo, S. Kawata, M. Kondo, M. Katada, H. Kobayashi, Inorg. Chem. 34 (1995) 4790.
- [29] S. Dalai, P.S. Mukherjee, E. Zangrando, F. Lloret, N. Ray Chaudhuri, J. Chem. Soc., Dalton Trans. (2002) 822.
- [30] S. Noro, S. Kitagawa, M. Yamashita, T. Wade, Chem. Commun. (2002) 222.
- [31] E.K. Barefield, F. Wagner, A.W. Herlinger, A.R. Dahl, in: F. Basolo (Ed.), Inorganic Synthesis, vol. XVI, McGraw-Hill, New York, 1976, p. 220.
- [32] N. Shaikh, M. Ali, P. Banerjee, Inorg. Chim. Acta 339 (2002) 341.
- [33] Kuma Diffraction KM4CCD system Software, Users Guide, Version 1.161; Kuma Diffraction Spolka Zoo, Wroclow, Poland, pp. 1195–1999.
- [34] P. Starynowicz, COSABS99. Program for Absorption Correction, University of Wroclaw, Wroclaw, Poland, 1999.
- [35] G.M. Sheldrick, SHELXS 97, Acta Crystallogr. A 46 (1990) 467.
- [36] G.M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
- [37] B. Bosnich, C.K. Poon, M.L. Tobe, Inorg. Chem. 4 (1965) 1102.
- [38] A. Bakac, J.H. Espenson, Inorg. Chem. 26 (1987) 4353.

- [39] M.E. Sosa-Torres, R.A. Toscano, Acta Crystallogr. C 53 (1997) 1585.
- [40] R.H. Blessing, Crystallogr. Rev. 1 (1987) 3.
- [41] A. Panja, N. Shaikh, S. Gupta, R.J. Butcher, P. Banerjee, Eur. J. Inorg. Chem. (2003) 1540.
- [42] N. Shaikh, A. Panja, P. Vojtíšek, S. Gao, P. Banerjee, unpublished works.
- [43] J.C Vites, M.M. Lynam, Coord. Chem. Rev. 131 (1994) 95.
- [44] K. Ramesh, D. Bhuniya, R. Mukherjee, J. Chem. Soc., Dalton Trans. (1991) 2917.
- [45] A. Panja, N. Shaikh, P. Vojtíšek, S. Gao, P. Banerjee, New J. Chem. 26 (2002) 1025.
- [46] H. Miyasaka, R. Clérac, T. Ishii, H.-C. Chang, S. Kitagawa, M. Yamashita, J. Chem. Soc., Dalton Trans. (2002) 1528.
- [47] M. Corbella, R. Costa, J. Ribas, P.H. Fries, J.-M. Latour, L. Öhrström, X. Solans, V. Rodriguez, Inorg. Chem. 35 (1996) 1857.