An anti-ferromagnetic terephthalate-bridged trigonal prismatic dinuclear manganese(II) complex: Synthon of rare anion $\cdots\pi$ interaction promoting dimensionality

SOMNATH CHOUBEY^a, SOUMI CHATTOPADHAYAY^a, KISHALAY BHAR^a,
SUBHASIS ROY^a, SUMITAVA KHAN^a, JOAN RIBAS^b and BARINDRA KUMAR GHOSH^{a,*}

^aDepartment of Chemistry, The University of Burdwan, Burdwan 713104, India

^bDepartament de Química Inorgànica, Universitat de Barcelona, Diagonal 647, 08028 Barcelona, Spain
e-mail: barin_1@yahoo.co.uk

MS received 26 December 2013; accepted 31 October 2014

Abstract. A dinuclear compound $[\text{Mn}_2(\text{L})_2(\mu\text{-tp})](\text{PF}_6)_2 \cdot 3.57\text{H}_2\text{O}$ (**1**) [$\text{L} = \text{N,N}'\text{-(bis(pyridin-2-yl)benzylidene)-1,3-propanediamine}$ and $\text{tp} = \text{terephthalate dianion}$] has been isolated and characterized on the basis of microanalytical, spectroscopic and other physicochemical properties. X-ray structural study showed interesting bis(bidentate) bridging motif of tp in the dicationic dinuclear unit $[\text{Mn}_2(\mu\text{-tp})]^{2+}$. Each manganese(II) centre adopts a rare distorted trigonal prismatic geometry with an MnN_4O_2 chromophore. Chelation of the tetradentate Schiff base (L) along with bis(bidentate) bridging of two O atoms of tp complete hexacoordination around each manganese(II) centre. The dinuclear units of **1** are associated through cooperative $\text{C-H}\cdots\text{F}$ hydrogen bonds and $\pi\cdots\pi$, $\text{C-H}\cdots\pi$ and rare anion $\cdots\pi$ interactions to promote the dimensionality in a graded manner. Variable temperature magnetic susceptibility measurement of **1** in the 2–300 K temperature range revealed weak anti-ferromagnetic interaction presumably due to long bridging arm of tp .

Keywords. Dinuclear manganese(II); N-donor schiff base; bis(bidentate) terephthalate bridge; anion $\cdots\pi$ interaction; magnetic behaviour

1. Introduction

The construction of diverse crystalline architectures^{1,2} is of current interest. In this regard non-covalent forces like hydrogen bonds, and $\pi\cdots\pi$ and $\text{C-H}\cdots\pi$ interaction^{3–5} are of great mention. Recently, anion $\cdots\pi$ interaction,^{6–8,37} has gained special recognition as a fundamental weak force with significant implications in chemical and biological processes. These different secondary interactions have great significance in systematic design of veritable metal-organic frameworks (MOFs) coupled with various functionalities.^{9–14} Carboxylates like terephthalate (tp) have now been extensively used to prepare a great diversity of molecular and crystalline architectures^{15–17} due to their versatile ligational behaviour (scheme 1) leading to interesting topologies and magnetic behaviour^{9,10,18} with paramagnetic 3d ions. Self-assembly¹⁹ using appropriate molar ratios of metal ions, organic ligands and tp is an efficient

approach to afford different MOFs^{15–17,20,21} with tunable properties. Schiff bases²² are useful organic ligands because of their ease of preparation, structural varieties and varied denticities. Currently, we are active^{23,24} in the isolation of different transition and post-transition metal complexes containing aliphatic/aromatic carboxylate bridges and N-donor spacers to understand the effects of the variation in molar ratios of metal ions, blocking ligands, bridging units and counter ions, that may lead to varied molecular and crystalline architectures and properties. Recently, we reported^{23a} the synthesis, structure and properties of a dinuclear manganese(II) carboxylate complex of the type $[\text{Mn}_2(\text{L})_2(\mu\text{-tp})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ [$\text{L} = \text{N,N}'\text{-(bis(pyridine-2-yl)-benzylidene)-1,3-propanediamine}$] (scheme 2). To establish the effect of counter anions on nucleation, crystal packing and magnetic behaviour, herein we report a new manganese(II)- tp compound of the composition $[\text{Mn}_2(\text{L})_2(\mu\text{-tp})](\text{PF}_6)_2 \cdot 3.57\text{H}_2\text{O}$ (**1**). The details of isolation, characterization, molecular and crystalline architectures, and thermal and magnetic properties of **1** with a different counter anion and varied crystallized solvent molecule are described.

*For correspondence

Scheme 1. Possible coordination modes of terephthalate (tp).

2. Experimental

2.1 Materials

High purity 1,3-propanediamine (Spectrochem, India), 2-benzoylpyridine (Lancaster, UK), terephthalic acid (Loba Chemie, India), piperidine (Loba Chemie, India), manganese(II) chloride (E. Merck, India) and ammonium hexafluorophosphate (Fluka, Germany) were purchased from respective concerns and were used as received. The Schiff base, *N,N'*-(bis-(pyridin-2-yl)benzylidene)-1,3-propanediamine (**L**) was prepared by condensation of 1:2 molar ratio of 1,3-propanediamine and 2-benzoylpyridine using the reported method.^{23a} Piperidinium terephthalate (ptp) was isolated by following a method described elsewhere.²⁵ All other chemicals and solvents used were AR grade.

2.2 Physical measurements

Elemental analysis was performed on a Perkin-Elmer 2400 CHNS/O elemental analyzer. Molar conductance was measured using a Systronics conductivity meter where the cell constant was calibrated with 0.01M KCl solution and dry DMF was used as solvent. IR spectrum (KBr discs, 4000–400 cm^{-1}) was recorded using a Perkin-Elmer FTIR model RX1 spectrometer. Thermal

Scheme 2. (N^P , N^i , N^i , N^P) donor set in **L**.

behaviour was examined with a Perkin-Elmer Diamond TG/DT analyzer heated from 35–740°C under nitrogen. Ground state absorption (in dry DMF) was made with a Shimadzu model UV-2450 UV-Vis spectrophotometer. The temperature-dependence magnetic susceptibility was measured on polycrystalline sample with a Quantum Design SQUID MPMS-XL susceptometer operating at a magnetic field 0.1 T over a temperature range 2–300 K. The diamagnetic correction was evaluated from Pascal's constants.

2.3 Isolation of the complex $[\text{Mn}_2(\text{L})_2(\mu\text{-tp})](\text{PF}_6)_2 \cdot 3.57 \text{H}_2\text{O}(\mathbf{1})$

Compound **1** was isolated following the similar procedure^{22a} as reported earlier but with a little modification. **L** (0.096 g, 0.24 mmol) in methanol (10 mL) was added dropwise to a light pink solution of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.048 g, 0.24 mmol) dissolved in the same solvent (10 mL). Ptp (0.040 g, 0.12 mmol) followed by NH_4PF_6 (0.0446 g, 0.2 mmol), each taken in methanol (5 mL), were added to the mixture. The final yellowish brown solution was left undisturbed in an open air for slow evaporation. After a week, yellow microcrystals of **1** that were deposited, were collected by filtration and dried *in vacuo* over silica gel indicator. Yield: 0.1154 g (75%). Anal. Calc. for $\text{C}_{62}\text{H}_{52}\text{N}_8\text{O}_{7.57}\text{F}_{12}\text{P}_2\text{Mn}_2(\mathbf{1})$: C, 52.07; H, 3.67; N, 7.84% Found: C, 52.14; H, 3.53; N, 8.01%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO}^-)$ 1560; $\nu_{\text{s}}(\text{COO}^-)$ 1389; $\nu(\text{C}=\text{N}) + \nu(\text{C}=\text{C})$ 1623, 1595; $\nu(\text{PF}_6^-)$ 843, 558. Λ_{M} (DMF, $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$): 238. UV-Vis (λ , nm): 277.

2.4 X-ray crystallographic analysis

Single crystal of **1** suitable for X-ray analysis was selected from those obtained by slow evaporation of methanolic solution of the reaction mixture at room temperature. Diffraction data was collected at 100(2) K on a Bruker APEX CCD area-detector diffractometer using graphite monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Intensity data were reduced using SAINT²⁶ and the empirical absorption corrections were performed with SADABS²⁷ program. The structure was solved by SHELXS-97²⁸ and refined by full-matrix least-squares methods based on $|F|^2$ using the program SHELXL-97.²⁸ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. One benzene ring (C17A, C18A, C19A, C20A, C21A, C22A/C17C, C18C, C19C, C20C, C21C, C22C atoms with 57/43% occupancy) and the

propylenic arm of L (C13A,14A,15A/C13C,14C,15C atoms with 57/43% occupancy) and O atoms of water molecules (O2C,O3C,O6C/O4C,O5C with 57/43%) are in positional disordered state. All the calculations were carried out using PLATON,²⁹ Diamond,³⁰ X-Seed³¹ and Mercury 3.1³² programs. The crystallographic data for the complex **1** are summarized in table 1.

3. Results and Discussions

3.1 Synthesis and formulation

Use of a 2:2:1:2 molar ratio of manganese(II) chloride tetrahydrate, tetradentate Schiff base (L), piperidinium terephthalate (ptp) and NH_4PF_6 in methanol at room temperature afforded Eq. (1) hexacoordinated dicationic dinuclear compound $[\text{Mn}_2(\text{L})_2(\mu\text{-tp})](\text{PF}_6)_2 \cdot 3.57 \text{ H}_2\text{O}$ (**1**) in good

yield. The compound was characterized using microanalysis, spectroscopic and thermal study. The microanalytical results are in good agreement with formulation of **1**. The air-stable compound is soluble in a wide range of common organic solvents such as MeCN, DMF and DMSO but is insoluble in water. In DMF solution, a 1:1 electrolytic nature³³ was observed for **1** (Λ_{M} : 238 $\text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$).

3.2 Spectroscopic studies

In IR spectrum, $\nu(\text{C}=\text{N})$ plus $\nu(\text{C}=\text{C})$ stretching vibrations of the metal-bound Schiff base are observed at 1623 and 1595 cm^{-1} . The stretching vibrations of tp are seen as strong $\nu_{\text{as}}(\text{COO}^-)$ stretch at 1560 cm^{-1} and $\nu_{\text{s}}(\text{COO}^-)$ band at 1389 cm^{-1} . The value for the difference between $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$ stretching frequencies (Δ) in the IR spectrum of the compound reflects bis(bidentate) bridging (**1**: $\Delta = 171$, ptp: $\Delta = 163$) motif of tp.³⁴ Additionally, presence of hexafluorophosphate stretches at 843 and 558 cm^{-1} (vide Experimental) are noticed indicating counter anionic view^{34b} with no metal coordination. X-ray study corroborates this hypothesis. Yellow DMF solution of **1** exhibits band at λ_{max} value 277 nm assignable to ligand-based charge transfer transition³⁵ since the free ligand, L also shows a strong band at 271 nm.

Table 1. Crystallographic data and structure refinement in **1**.

Compound	1
Formula	$\text{C}_{62}\text{H}_{52}\text{N}_8\text{O}_{7.57}\text{F}_{12}\text{P}_2\text{Mn}_2$
Formula weight	1430.06
Crystal size (mm^3)	$0.25 \times 0.25 \times 0.13$
Crystal system	Monoclinic
Space group	Cc
<i>a</i> (Å)	14.3910(17)
<i>b</i> (Å)	19.505(2)
<i>c</i> (Å)	23.966(3)
α (°)	90.00
β (°)	101.415(2)
γ (°)	90.00
<i>V</i> (Å ³)	6594.3(13)
λ (Å)	0.71073
ρ_{calcd} (g cm^{-3})	1.440
<i>Z</i>	4
<i>T</i> (K)	100(2)
μ (mm^{-1})	0.523
<i>F</i> (000)	2914
θ ranges (°)	1.73 to 28.01
<i>h</i> / <i>k</i> / <i>l</i>	−18, 18/ −25, 21/ −31, 30
Reflections collected	19739
Independent reflections	11585
Data/restraints/parameters	11585/14/815
Goodness-of-fit on F^2	1.025
T_{max} and T_{min}	0.9375 and 0.8803
R_{int}	0.027
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R = 0.0624$, $wR = 0.1664$
<i>R</i> indices (all data)	$R = 0.0740$, $wR = 0.1785$
Largest peak and hole (e Å^{-3})	1.168 and −0.707

Weighting scheme: $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$, $wR = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}}{[\sigma^2(F_o^2) + (0.1122P)^2 + 12.6515P]^{1/2}}$; where $P = (F_o^2 + 2F_c^2)/3$.

3.3 Molecular and crystalline structures of $[\text{Mn}_2(\text{L})_2(\text{tp})](\text{PF}_6)_2 \cdot 3.57 \text{ H}_2\text{O}$ (**1**)

Structural analysis reveals that compound **1** is made up of terephthalate (tp) bridged disordered dicationic dinuclear unit $[\text{Mn}_2(\text{L})_2(\text{tp})]^{2+}$ with a tetradentate Schiff base (L) as end-capping ligand, non-coordinated hexafluorophosphate counter anions and 3.57 units crystalline water molecules without hydrogen atoms. On the other hand, the perchlorate analogue $[\text{Mn}_2(\text{L})_2(\text{tp})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ ^{23a} of **1** with centrosymmetric environment has only one non-coordinated water molecule with hydrogen atoms. Perspective view of the dinuclear entity in **1** is shown in figure 1. Selected bond distances and angles are given in table 2. In the dication, the manganese(II) centres are bound by chelation of L and bis(bidentate) bridging motifs of tp with an M...M separation of 10.925 Å.

Figure 1. Molecular structure of $[\text{Mn}_2(\text{L})_2(\mu\text{-tp})]^{2+}$ in **1** with atom numbering schemes (50% probability ellipsoid for all non-hydrogen atoms).

Each manganese(II) centre adopts a rare distorted trigonal prismatic geometry³⁶ with an MnN_4O_2 chromophore. Each of the two trigonal faces of the prism (figure 2) is occupied by two N atoms of the Schiff base L and one O atom of bis(bidentate) tp bridging unit (O2A, N2A, N3A and O1A, N1A, N4A for Mn1A and O1B, N2B, N3B and O2B, N1B, N4B for Mn1B). The trigonal faces are away by a small distance than that expected for an ideal trigonal prismatic geometry.³⁶ A major reason for distortion from the trigonal prismatic geometry is the presence of two O atoms of tp (O1A, O2A/O1B, O2B for Mn1A/Mn1B) on the two opposite faces creating small bite angle $[58.69(13)/58.66(14)^\circ$ for Mn1A/Mn1B]. The mean planes of these two faces containing O2A, N2A,

N3A and O1A, N1A, N4A atoms for Mn1A and O1B, N2B, N3B and O2B, N1B, N4B atoms for Mn1B are slightly twisted from the ideal value of 0° creating angles of 7.97° (for Mn1A) and 8.54° (for Mn1B) with each other. The carboxylate group shows the expected trigonal geometry^{15a} with intracarboxylate bond angle O1A-C28A-O2A/O1B-C28B-O2B: $121.4(5)/120.2(5)^\circ$ for Mn1A/Mn1B (table 2). However, significant differences are observed in the values of the carbon-oxygen bond distance the value is $1.254(7)/1.271(6)$ Å (Mn1A), $1.296(6)/1.236(7)$ Å (Mn1B) for the symmetrical chelating carboxylato coordination. The Mn-N bond lengths are in the range $2.227(5)$ – $2.254(4)$ Å for Mn1A and $2.207(5)$ – $2.269(4)$ Å for Mn1B (table 2) and Mn-O distances are in the range $2.182(4)$ – $2.306(4)$ Å

Table 2. Selected bond distances (Å) and bond angles ($^\circ$) for **1**.

Bond distances for 1			Bond angles for 1		
Mn1A-N1A	2.230(4)	N1A-Mn1A-N2A	73.21(16)	N1B-Mn1B-N2B	73.05(16)
Mn1A-N2A	2.244(5)	N1A-Mn1A-N3A	133.31(16)	N1B-Mn1B-N3B	144.99(17)
Mn1A-N3A	2.254(4)	N1A-Mn1A-N4A	102.67(17)	N1B-Mn1B-N4B	103.11(16)
Mn1A-N4A	2.227(5)	N2A-Mn1A-N3A	82.93(17)	N2B-Mn1B-N3B	84.69(16)
Mn1B-N1B	2.221(5)	N2A-Mn1A-N4A	141.37(16)	N2B-Mn1B-N4B	134.08(16)
Mn1B-N2B	2.269(4)	N3A-Mn1A-N4A	72.43(17)	N3B-Mn1B-N4B	73.38(16)
Mn1B-N3B	2.207(5)	O1A-Mn1A-N1A	84.42(15)	O1B-Mn1B-N1B	112.86(16)
Mn1B-N4B	2.233(4)	O1A-Mn1A-N2A	130.91(16)	O1B-Mn1B-N2B	98.06(16)
Mn1A-O1A	2.306(4)	O1A-Mn1A-N3A	138.95(16)	O1B-Mn1B-N3B	96.48(16)
Mn1A-O2A	2.182(4)	O1A-Mn1A-N4A	85.39(16)	O1B-Mn1B-N4B	123.69(16)
Mn1B-O1B	2.196(4)	O2A-Mn1A-N1A	120.58(15)	O2B-Mn1B-N1B	84.55(15)
Mn1B-O2B	2.281(4)	O2A-Mn1A-N2A	96.30(16)	O2B-Mn1B-N2B	138.26(16)
C28A-O1A	1.254(7)	O2A-Mn1A-N3A	101.15(15)	O2B-Mn1B-N3B	128.56(17)
C28A-O2A	1.271(6)	O2A-Mn1A-N4A	117.03(15)	O2B-Mn1B-N4B	84.58(15)
C28B-O1B	1.296(6)	O1A-C28A-O2A	121.4(5)	O1B-C28B-O2B	120.2(5)
C28B-O2B	1.236(7)	O1A-Mn1A-O2A	58.69(13)	O1B-Mn1B-O2B	58.66(14)

Figure 2. Trigonal prismatic coordination environment of Mn1A and Mn1B in **1**.

(for Mn1A) and 2.196(4)–2.281(4) Å. The Mn–N and Mn–O bond distances are similar to those reported in literature.^{23a} The tetradentate Schiff base (L) is twisted around the manganese(II) centre such that the two planes containing the unsaturated chelate rings (Mn1, N1, C5, C6, N2) and (Mn1, N3, C16, C23, N4) are inclined to each other at 60.63/56.52° (Mn1A/Mn1B)

in **1**. The propylenic arm of L in the saturated six-membered chelate ring is to some extent puckered. The value of dihedral angle between O1A, C28A, O2A/O1B, C28B, O2B carboxylate group and benzene ring (C29A, 30A, C31A, C29B, C30B, C31B) of *tp* is 2.62°/7.15° which is indicative of quasi-planarity of the bridging unit on coordination.

Table 3. $\pi \cdots \pi$, C–H $\cdots \pi$, anion $\cdots \pi$ interactions and hydrogen bond parameters (Å, °) for **1**.

Cg-Cg	Cg-Cg distance	$\pi \cdots \pi$ interactions (Å, °)			Symmetry code
		Dihedral angle (<i>i</i> , <i>j</i>)	Perpendicular distances between baricentres (<i>i</i> , <i>j</i>)		
Cg10...Cg13	4.377(3)	2.1(3)	4.105(2) and 4.061(2)		1/2+x, 1/2+y, z
Cg13...Cg10	4.377(3)	2.1(3)	4.061(2) and 4.105(2)		−1/2+x, −1/2+y, z
Cg11...Cg12	3.978(3)	6.0(3)	3.829(2) and 3.902(2)		1/2+x, −1/2+y, z
Cg12...Cg11	3.978(3)	6.0(3)	3.902(2) and 3.829(2)		−1/2+x, 1/2+y, z
C-H π interactions (Å, °)					
D-H...A	D-H	H...A	D...A	D-H...A	Symmetry code
C14B-H14F...Cg16	0.989	2.70	3.651(7)	160	x, -y, −1/2+z
C14B-H14F...Cg19	0.989	2.77	3.710(8)	158	x, -y, −1/2+z
Anion... π interactions (Å, °)					
X-D...A	X-D	D...A	X...A	X-D...A	Symmetry code
P1A-F1A...Cg13	1.584(4)	3.107(5)	4.227(3)	125.4(2)	x, 1+y, z
P1A-F2A...Cg11	1.591(4)	3.198(5)	4.314(3)	125.1(2)	x, 1+y, z
P1A-F3A...Cg10	1.593(4)	3.134(5)	4.213(3)	122.7(2)	x, y, z
P1A-F3A...Cg11	1.593(4)	3.842(5)	4.314(3)	96.12(17)	x, 1+y, z
P1A-F4A...Cg12	1.603(4)	3.173(5)	4.216(3)	120.3(2)	x, y, z
Hydrogen bond parameters (Å, °)					
D-H...A	D-H	H...A	D...A	D-H...A	Symmetry code
C1B-H1B...F1B	0.9500	2.5400	3.375(8)	147.00	1/2+x, −1/2s+y, z
C2A-H2A...F3B	0.9500	2.4700	3.291(8)	144.00	1/2+x, 1/2-y, −1/2+z
C2A-H2A...F4B	0.9500	2.5400	3.428(8)	155.00	1/2+x, 1/2-y, −1/2+z
C26B-H26B...F6B	0.9500	2.4400	3.173(9)	134.00	1/2+x, −1/2+y, z
C12B-H12B...F3A	0.9500	2.5400	3.431(8)	156.00	x, −1+y, z

Cg(10): N(1A)–C(1A)–C(2A)–C(3A)–C(4A)–C(5A);

Cg(11): N(1B)–C(1B)–C(2B)–C(3B)–C(4B)–C(5B);

Cg(12): N(4A)–C(23A)–C(24A)–C(25A)–C(26A)–C(27A);

Cg(13): N(4B)–C(23B)–C(24B)–C(25B)–C(26B)–C(27B);

Cg(16): C(17A)–C(18A)–C(19A)–C(20A)–C(21A)–C(22A), and

Cg(19): C(17C)–C(18C)–C(19C)–C(20C)–C(21C)–C(22C).

In the crystalline state, individual dinuclear units of **1** are assembled through different types of C-H...F hydrogen bonds with $R_1^2(4)$ and $R_2^2(11)$ cyclic motifs in Etter's graph notation³⁷ along with C-H... π interactions (table 3) in a cooperative manner resulting in 1D chain structure parallel to crystallographic *c*-axis (figure 3a). The chains are further connected via anion... π interactions to form a flat 2D-sheet structure parallel to *bc*-plane (figure 3b). The dinuclear units of **1** are also associated to each other via π ... π interactions (table 3) between two closest pyridine rings (Cg10-Cg13 and Cg11-Cg12) of L affording a 2D sheet structure (figure 4a) parallel to *ab*-plane. Each 2D sheet is further stabilized by various types of anion... π interactions (table 3 and figure 4b) between F-atoms of the embedded hexafluorophosphate anions and pyridine rings (Cg10, Cg11, Cg12 and Cg13). To sum it up,

such cooperative C-H...F hydrogen bonds and π ... π , C-H... π and anion... π interactions promote the dimensionality of the dinuclear 0D unit to a 3D network structure (figure 5).

Here it is worth mentioning that instead of distorted trigonal prismatic structure of each manganese(II) centre in this hexafluorophosphate salt **1**, distorted octahedral geometry of each metal(II) centre is observed in the corresponding perchlorate analogue, $[\text{Mn}_2(\text{L})_2(\mu\text{-tp})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$.^{23a} So, an interesting change in coordination geometry and thereby molecular architecture of the hexacoordinated manganese(II) is revealed just by variation of counter anion from tetrahedral perchlorate to octahedral hexafluorophosphate. Again, in the crystalline state, **1** shows a rare anion... π interaction which is absent in the perchlorate analogue. The other non-covalent forces present are C-H...O and O-H...O

Figure 3. (a) 1D chain structure in **1** parallel to *c*-axis through cooperative C-H... π interactions and C-H...F hydrogen bonds with $R_1^2(4)$ and $R_2^2(11)$ cyclic motifs in Etter's graph notation; (b) formation of 2D sheet structure parallel to *bc*-plane through various anion... π interactions of the 1D chains.

Figure 4. (a) A view of 2D sheet structure in **1** formed through cooperative $\pi \cdots \pi$ and anion $\cdots \pi$ interactions parallel to *ab*-plane; (b) a segment of anion $\cdots \pi$ interactions involving pyridine rings and embedded PF_6^- anion

hydrogen bonds and $\pi \cdots \pi$ interactions in perchlorate salt, but the corresponding hexafluorophosphate salt contains C-H $\cdots \pi$ and $\pi \cdots \pi$ interactions along with only C-H $\cdots$ F hydrogen bond and with no O-H $\cdots$ O hydrogen bond, though both the salts contain crystallized water molecules. The anion $\cdots \pi$ interaction in **1** may presumably arise due to the presence of highly electronegative fluorine in hexafluorophosphate over relatively less electronegative oxygen in perchlorate that influences the packing in the long-range form in crystalline state. This reflects that these two counter anions in the dinuclear manganese(II) complexes have a pivot role in controlling molecular and crystalline architectures of these two compounds containing the same metal ion, blocking ligand and bridging unit.

3.4 Thermal study

To examine thermal stability of complex **1**, thermogravimetric analysis (TGA) was carried out between

35°C to 740°C in a static atmosphere of nitrogen. The TG curve shows (figure 6) the compound loses 3.57 units of crystalline water molecules (obs.: 2.172%, calcd.: 3.994%) in the temperature range 40–96°C and is stable up to 288°C. In the second step, it decomposes two Schiff base (L) units and one tp unit (obs.: 69.292%, calcd.: 68.048%) in the temperature range 288–724°C ultimately giving dirty brown amorphous solid, Mn_3O_4 (obs.: 23.238%, calcd.: 16.000%). In summary, the thermogravimetric analysis shows that **1** has reasonable thermal stability.

3.5 Magnetic property

Variable-temperature magnetic susceptibility measurement for **1** has been performed in the 2–300 K temperature range. The $\chi_M T$ vs. T plot (χ_M is for two Mn(II) ions) of complex **1** is shown in figure 7. The $\chi_M T$ value at 300 K is close to $9.1 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ which is as expected for two magnetically quasi-isolated spin

Figure 5. A view of 3D network structure in **1** formed through cooperative C-H...F hydrogen bonds, and $\pi \cdots \pi$, C-H... π and anion... π interactions.

doublets ($g \sim 2.00$). This remains practically constant up to 50 K, below which it decreases rapidly to $7.8 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K. The feature is characteristic of weak anti-ferromagnetic interactions. The reduced molar magnetization at 2 K (figure 7 inset) clearly corroborates that the anti-ferromagnetic coupling is small. The $M/N\mu_B$ value at 5 T tends to $10.0 N\mu_B$ and the curve does follow the Brillouin law. Complex **1** is with a dinuclear manganese(II) core. The fit of the susceptibility data has been carried out applying the corresponding formula for a dinuclear Mn(II) complex,^{9a} considering the Hamiltonian $H = -JS_1S_2$.

The best-fit parameters obtained are: $J = -0.083 \pm 0.001 \text{ cm}^{-1}$, $g = 2.03 \pm 0.01$ and $R = 1.1 \times 10^{-5}$. The small J value in **1** may presumably be due to weak interaction between the two metal(II) centres through intramolecular covalent tp bridging arm and intermolecular non-covalent forces such as hydrogen bonds, and $\pi \cdots \pi$, C-H... π and anion... π interactions of the same order of magnitude. In summary, the presence of long tp bridge is responsible for weak anti-ferromagnetism is revealed. The shape of the magnetization curve is in consonance with the Brillouin formula.

Figure 6. Thermal behaviour of **1**.

Figure 7. Plots of the $\chi_M T$ vs T and $M/N\mu_B$ vs H (inset, 2 K) for **1**. Solid line indicates the best fit obtained with the parameters (see text).

4. Conclusions

A new dinuclear terephthalate-bridged manganese(II) compound containing a tetradentate Schiff base has been isolated and characterized. The manganese(II) centres adopt a rare trigonal prismatic geometry connected by bis(bidentate) bridging motif of the aromatic dicarboxylate. Several weak non-covalent interactions such as hydrogen bonds and $\pi \cdots \pi$, C-H $\cdots$ π and anion $\cdots$ π interactions act in cooperative manner to promote dimensionality of the 0D dinuclear compound. The presence of unique anion $\cdots$ π interaction in **1** which is absent in the analogous perchlorate compound $[\text{Mn}_2(\text{L})_2(\mu\text{-tp})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ is noteworthy. The presence of octahedral hepta-atomic hexafluorophosphate counter anion over tetrahedral penta-atomic perchlorate may have a major role in such a unique interaction while embedding in the network. Variable-temperature magnetic susceptibility measurements show weak anti-ferromagnetic coupling between the metal centres mediated through long tp bridging. We are now extending this work using other 3d/4d metal ions in combination with different Schiff bases/polyamines and tailored polycarboxylates.

Supplementary Information

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic data centre No. 963133 (**1**). Copy of this

information can 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 <http://www.ccdc.cam.ac.uk>).

Acknowledgements

Financial support from the CSIR, New Delhi, India is gratefully acknowledged. The authors S. Choubey, S. Chattopadhyay, K. Bhar and S. Khan are grateful to CSIR and S. Roy to UGC, New Delhi, India for fellowships. Prof. J. Ribas thanks Spanish Government (GrantCTQ2012/30662) for financial support. The authors are also thankful to Prof. L. J. Barbour, Department of Chemistry, University of Stellenbosch, Stellenbosch 7600, South Africa for X-ray crystallographic study of the compound.

References

- (a) Lehn J M 1995 In *Supramolecular Chemistry: Concepts and Perspectives* (Weinheim: VCH); (b) Steed J W and Atwood J L 2009 In *Supramolecular Chemistry* (New York: Wiley)
- (a) Braga D, Grepioni F and Orpen A G 1999 In *Crystal Engineering: From Molecules and Crystals to Materials* (Dordrecht: Kluwer); (b) Tothadi S, Mukherjee A and Desiraju G R 2011 *Chem. Commun.* **47** 12080; (c) Desiraju G R 2013 *J. Am. Chem. Soc.* **135** 9952
- (a) Jeffrey G A 1997 In *An Introduction to Hydrogen Bonding* (Oxford: Oxford University Press); (b) Desiraju G R 2011 *Angew. Chem. Int. Ed.* **50** 59; (c) Reedijk J 2013 *Chem. Soc. Rev.* **42** 176
- (a) Tiekink E R T and Schpector J Z (eds.) 2012 In *The Importance of Pi-Interactions in Crystal Engineering: Frontiers in Crystal Engineering* (Chichester: John Wiley); (b) Kawase T and Kurata H 2006 *Chem. Rev.* **106** 5250
- (a) Nishio M, Hirota M and Umezawa Y 1998 In *The CH/ π Interaction* (New York: Wiley-VCH); (b) Hu M, Wang X, Jiang Y and Li S 2008 *Inorg. Chem. Commun.* **11** 85
- (a) Gamez P, Mooibroek T J, Teat S J and Reedijk J 2007 *Acc. Chem. Res.* **40** 435; (b) Mooibroek T J, Black C A, Gamez P and Reedijk J 2008 *Cryst. Growth Des.* **8** 1082; (c) Mooibroek T J, Gamez P, Reedijk J 2008 *CrystEngComm.* **10** 1501; (d) Schottel B L, Chifotides H T and Dunbar K R 2008 *Chem. Soc. Rev.* **37** 68; (e) Frontera A, Gamez P, Mascal M, Mooibroek T J and Reedijk J 2011 *Angew. Chem. Int. Ed.* **50** 9564; (f) Zhao Y, Domoto Y, Orentas E, Beuchat C, Emery D, Marada J, Sakai N and Matile S 2013 *Angew. Chem.* **125** 10124
- (a) Estarellas C, Frontera A, Quiñero D and Deyà PM 2011 *Angew. Chem. Int. Ed.* **50** 415; (b) Salonen L M, Ellermann M and Diederich F 2011 *Angew. Chem. Int. Ed.* **50** 4808; (c) Brooker S, White N G, Bauza A, Deyà P M and Frontera A 2012 *Inorg. Chem.* **51** 10334; (d) Wang D X, Wang M X 2013 *J. Am. Chem. Soc.* **135** 892;

- (e) Chifotides H T and Dunbar K R 2013 *Acc. Chem. Res.* **46** 894
8. (a) Seth S K, Saha I, Estarellas C, Frontera A, Kar T and Mukhopadhyay S 2011 *Cryst. Growth Des.* **11** 3250; (b) Manna P, Seth S K, Das A, Hemming J, Prendergast R, Helliwell M, Choudhury S R, Frontera A and Mukhopadhyay S 2012 *Inorg. Chem.* **51** 3557; (c) Seth S K, Manna P, Singh N J, Mitra M, Jana A D, Das A, Choudhury S R, Kar T, Mukhopadhyay S and Kim K S 2013 *CrystEngComm*. **15** 1285; (d) Mitra M, Manna P, Seth S K, Das A, Meredith J, Helliwell M, Bauza A, Choudhury S R, Frontera A and Mukhopadhyay S 2013 *CrystEngComm*. **15** 686 and references therein
 9. (a) Kahn O 1993 In *Molecular Magnetism* (New York: VCH); (b) Miller J S and Gatteschi D 2011 *Chem. Soc. Rev.* **40** 3053
 10. (a) Rowsell J L C and Yaghi O M 2005 *Angew. Chem. Int. Ed.* **44** 4670; (b) Czaja A U, Trukhanb N and Müller U 2009 *Chem. Soc. Rev.* **38** 1284; (c) Murray L J, Dinca M and Long J R 2009 *Chem. Soc. Rev.* **38** 1294; (d) Lee J Y, Farha O K, Roberts J, Scheidt K A, Nguyen S T and Hupp J T 2009 *Chem. Soc. Rev.* **38** 1450
 11. (a) Pashow K M L T, Rocca J D, Xie Z, Tran S and Lin W 2009 *J. Am. Chem. Soc.* **131** 14261; (b) Sumida K, Rogow D L, Mason J A, McDonald T M, Bloch E D, Herm Z R, Bae T H and Long J R 2012 *Chem. Rev.* **112** 724; (c) Wang C, Zhang T and Lin W 2012 *Chem. Rev.* **112** 1084
 12. (a) Rao C N R, Natarajan S and Vaidhyanathan R 2004 *Angew. Chem. Int. Ed.* **43** 1466; (b) Ye B H, Tong M L and Chen X M 2005 *Coord. Chem. Rev.* **249** 545; (c) LaDuca R L 2009 *Coord. Chem. Rev.* **253** 1759; (d) Lin Z, Tong M L 2011 *Coord. Chem. Rev.* **255** 421
 13. (a) Ma C B, Hu M Q, Chen H, Wang M, Zhang C X, Chen C N and Liu Q T 2010 *CrystEngComm*. **12** 1467; (b) Yuan W, Garay A L, Pichon A, Clowes R, Wood C D, Cooper A I and James S L 2010 *CrystEngComm*. **12** 4063
 14. (a) Sain S, Maji T K, Mostafa G, Lu T H and Chaudhury N R 2003 *Inorg. Chim. Acta* **351** 12; (b) Maji T K, Sain S, Mostafa G, Lu T H, Ribas J, Monfort M and Chaudhury N R 2003 *Inorg. Chem.* **42**, 709; (c) Ghosal D, Maji T K, Mostafa G, Lu T H and Chaudhury N R 2003 *Cryst. Growth Des.* **3** 9
 15. (a) Cano J, Munno G De, Sanz J L, Ruiz R, Faus J, Lloret F, Julve M and Caneschi A 1997 *J. Chem. Soc. Dalton. Trans.* 1915; (b) Palanisami N and Murugavel R 2011 *Inorg. Chim. Acta* **365** 430; (c) Deniz M, Rodríguez I H, Pasañ J, Fabelo O, Delgado L C, Yuste C, Julve M, Lloret F and Perez C R 2012 *Cryst. Growth Des.* **12** 4505
 16. (a) Ma C, Chen C, Liu Q, Liao D, Li L and Sun L 2003 *New J. Chem.* **27** 890; (b) Manna S C, Konar S, Zangrando E, Okamoto K I, Ribas J and Chaudhuri N R 2005 *Eur. J. Inorg. Chem.* 4646; (c) Liu J Q, Zhang Y N, Wang Y Y, Jin J C, Lermontova E Kh and Shia Q Z 2009 *Dalton. Trans.* 5365
 17. (a) Jiang Z Q, Zhao Z, Jiang G Y, Hou D C, Kang Y 2011 *Inorg. Chem. Commun.* **14** 1975; (b) Kumagai H, Sakamoto Y, Kawata S, Matsunaga S and Inagaki S 2012 *Bull. Chem. Soc. Jpn.* **85** 1102; (c) Gómez V, Corbella M, Mautner F A, Roubeau O, Teat S J, Bardia M F and Calvet T 2012 *Polyhedron* **45** 185
 18. (a) Hong C S and Do Y 1997 *Inorg. Chem.* **36** 5684; (b) Chen C, Huang D, Zhang X, Chen F, Zhu H and Liu Q 2003 *Inorg. Chem.* **42** 3540; (c) Hong C S, Yoon J H and You Y S 2005 *Inorg. Chim. Acta* **358** 3341
 19. (a) Chakrabarty R, Mukherjee P S and Stang P J 2011 *Chem. Rev.* **111** 6810; (b) Ward M D and Raithby P R 2013 *Chem. Soc. Rev.* **42** 1619
 20. (a) Stock N and Biswas S 2012 *Chem. Rev.* **112** 933; (b) Zhao D, Timmons D J, Yuan D and Zhou H C 2011 *Acc. Chem. Res.* **44** 123; (c) Qiu S and Zhu G 2009 *Coord. Chem. Rev.* **253** 2891
 21. (a) Li H, Eddaoudi M, O'Keeffe M and Yaghi O M 1999 *Nature* **402** 276; (b) Rosi N L, Eckert J, Eddaoudi M, Vodak D T, Kim J, O'Keeffe M and Yaghi O M 2003 *Science* **300** 1127; (c) Wang G H, Li Z G, Jia H Q, Hu N H and Xu J W 2008 *Cryst. Growth Des.* **8** 1932
 22. (a) Vigato P A and Tamburini S 2004 *Coord. Chem. Rev.* **248** 1717; (b) Vigato P A, Peruzzo V and Tamburini S 2012 *Coord. Chem. Rev.* **256** 953
 23. (a) Choubey S, Roy S, Bhar K, Ghosh R, Mitra P, Lin C H, Ribas J and Ghosh B K 2013 *Polyhedron* **55** 1; (b) Choubey S, Roy S, Khan S, Ghosh R, Bhar K and Ghosh B K 2013 *J. Indian Chem. Soc.* **90** 807; (c) Kundu S, Roy S, Choubey S, Bhar K, Ghosh P K, Mitra P and Ghosh B K 2013 *J. Mol. Struct.* **1051** 41
 24. (a) Roy S, Sarkar B N, Bhar K, Satapathi S, Mitra P and Ghosh B K 2013 *J. Mol. Struct.* **1037** 160; (b) Roy S, Choubey S, Bhar K, Khan S, Mitra P and Ghosh B K 2013 *J. Mol. Struct.* **1051** 328; (c) Roy S, Choubey S, Khan S, Bhar K, Mitra P and Ghosh B K 2013 *J. Chem. Sci.* **125** 715
 25. Verdager M, Gouteron J, Jeannin S, Jeannin Y and Kahn O 1984 *Inorg. Chem.* **23** 4291
 26. Sheldrick G M 1996 *SAINT, V4: Software reference manual, Siemens analytical X-ray systems* Madison, WI, USA
 27. Sheldrick G M 1996 *SADABS: Program for empirical absorption correction of area detector data*, University of Göttingen, Germany
 28. Sheldrick G M 2008 *Acta Crystallogr. Sect., A* **64** 112
 29. Spek A L 2009 *Acta Crystallogr. Sect., D* **65** 148
 30. Pennington WT 1999 *J. Appl. Crystallogr.* **32** 1028
 31. Barbour L J 2001 *J. Supramol. Chem.* **1** 189
 32. Macrae C F, Edgington P R, McCabe P, Pidcock E, Shields G P, Taylor R, Towler M and Streek J van de 2006 *J. Appl. Crystallogr.* **39** 453
 33. Geary W J 1971 *Coord. Chem. Rev.* **7** 81
 34. (a) Massoud S S, Mautner F A, Vicente R and Sweeney H N 2006 *Inorg. Chim. Acta* **359** 1489; (b) Nakamoto K 2009 In *Infrared and Raman Spectra of Inorganic and Coordination Compounds* Part B 6th ed. (New Jersey: John Wiley)
 35. (a) Lever A B P 1984 In *Inorganic Electronic Spectroscopy* 2nd ed. (New York: Elsevier); (b) Sole J G, Bausa L E and Jaque D 2005 In *An Introduction to the Optical Spectroscopy of Inorganic Solids* (New York: John Wiley)
 36. (a) Cremades E, Echeverr J and Alvarez S 2010 *Chem. Eur. J.* **16** 10380; (b) Mukherjee S, Patil Y P and Mukherjee P S 2012 *Inorg. Chem.* **51** 4888; (c) Choubey S, Roy S, Bhar K, Mitra P, Ribas J and Ghosh B K 2014 *Polyhedron* **74** 134
 37. Etter M C 1991 *J. Phys. Chem.* **95** 4601