Magnetic behaviour in metal–organic frameworks—Some recent examples

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Abstract. The article describes the synthesis, structure and magnetic investigations of a series of metal–organic framework compounds formed with Mn^{+2} and Ni^{+2} ions. The structures, determined using the single crystal X-ray diffraction, indicated that the structures possess two- and three-dimensional structures with magnetically active dimers, tetramers, chains, two-dimensional layers connected by polycarboxylic acids. These compounds provide good examples for the investigations of magnetic behaviour. Magnetic studies have been carried out using SQUID magnetometer in the range of 2–300 K and the behaviour indicates a predominant anti-ferromagnetic interactions, which appears to differ based on the M–O–C–O–M and/or the M–O–M (M = metal ions) linkages. Thus, compounds with carboxylate (Mn–O–C–O–Mn) connected ones, $[\text{C}_3\text{N}_2\text{H}_5][\text{Mn}(\text{H}_2\text{O})\{\text{C}_6\text{H}_3(\text{COO})_3\}]$, **I**, $[\{\text{Mn}(\text{H}_2\text{O})_3\}\{\text{C}_{12}\text{H}_8\text{O}(\text{COO})_2\}]\cdot\text{H}_2\text{O}$, **II**, $[\{\text{Mn}(\text{H}_2\text{O})\}\{\text{C}_{12}\text{H}_8\text{O}(\text{COO})_2\}]$, **III**, show simple anti-ferromagnetic behaviour. The compounds with Mn–O/OH–Mn connected dimer and tetramer units in $[\text{NaMn}\{\text{C}_6\text{H}_3(\text{COO})_3\}]$, **IV**, $[\text{Mn}_2(\mu_3\text{-OH})(\text{H}_2\text{O})_2\{\text{C}_6\text{H}_3(\text{COO})_3\}]\cdot 2\text{H}_2\text{O}$, **V**, show canted-antiferromagnetic and anti-ferromagnetic behaviour, respectively. The presence of infinite one-dimensional $-\text{Ni}-\text{OH}-\text{Ni}-$ chains in the compound, $[\text{Ni}_2(\text{H}_2\text{O})(\mu_3\text{-OH})_2(\text{C}_8\text{H}_5\text{NO}_4)]$, **VI**, gives rise to ferromagnet-like behaviour at low temperatures. The compounds, $[\text{Mn}_3\{\text{C}_6\text{H}_3(\text{COO})_3\}_2]$, **VII** and $[\{\text{Mn}(\text{OH})\}_2\{\text{C}_{12}\text{H}_8\text{O}(\text{COO})_2\}]$, **VIII**, have two-dimensional infinite $-\text{Mn}-\text{O}/\text{OH}-\text{Mn}-$ layers with triangular magnetic lattices, which resemble the Kagome and brucite-like layer. The magnetic studies indicated canted-antiferromagnetic behaviour in both the cases. Variable temperature EPR and theoretical magnetic modelling studies have been carried out on selected compounds to probe the nature of the magnetic species and their interactions with them.

Keywords. Metal–organic frameworks; transition metals; magnetic interactions; ESR spectroscopy.

1. Introduction

Magnetism and magnetic materials have fascinated mankind for many centuries as the naturally occurring mineral, magnetite is magnetic which is present in the earth's crust.¹ Over the years, the family of compounds that exhibited magnetic behaviour continuously grew and many of the earlier magnetic materials are based on oxides.² During the last two decades or so, we begin to observe many new compounds that exhibit exotic magnetic behaviours. These include, single molecule magnets,³ purely organic magnets,⁴ dilute semiconductor,⁵ etc. Along with these discoveries, we also observed some important magnetic phenomena, viz. magnetic frustration,⁶ spin chirality,⁷ spin-crossover,⁸ etc. In addition, there is a constant demand to discover

materials that would combine magnetism along with other properties such as conductivity, ferroelectricity, etc. and such solids are classified as multiferroic materials.⁹

Recently, a new class of solids have been prepared by combining the coordination constraints of the central metal atoms and the functionality of the organic ligands and are known as metal–organic framework (MOF) compounds.^{10,11} These offer reasonable thermal stability (typically $\sim 400^\circ\text{C}$) and porosity and have been studied intensely during the last decade or so.^{10,12} When the central metal ion is a transition element, preferably the 3d ones, one might expect to observe magnetic behaviour that combines the porous nature of the solid. A magnetic porous solid could find interesting applications for air separation.¹³

The transition metal based MOFs have been prepared and characterized.^{10,12} It may be of importance

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Table 1. Synthesis conditions for compounds **I–VIII**.

Composition*	Temp (°C)	Time (h)	pH-initial (final)	Yields (%)	Product
0.25Mn(OAc) ₂ ·4H ₂ O + 1,3,5-BTC + imidazole + 2KOH + 444H ₂ O	75	24	6(5)	75	[C ₃ N ₂ H ₅][Mn(H ₂ O){C ₆ H ₃ (COO) ₃ }], I
Mn(OAc) ₂ ·4H ₂ O + 4,4'-OBA + imidazole + 2NaOH + 444H ₂ O	100	24	6(6)	70	[{Mn(H ₂ O) ₃ }{C ₁₂ H ₈ O(COO) ₂ }]·H ₂ O, II
Mn(OAc) ₂ ·4H ₂ O + 4,4'-OBA + imidazole + 2NaOH + 444H ₂ O	160	24	6(6)	75	[{Mn(H ₂ O)}{C ₁₂ H ₈ O(COO) ₂ }], III
Mn(OAc) ₂ ·4H ₂ O + 1,2,4-BTC + imidazole + 3NaOH + 444H ₂ O	220	24	8(5)	60	[NaMn{C ₆ H ₃ (COO) ₃ }], IV
2Mn(OAc) ₂ ·4H ₂ O + 1,2,4-BTC + imidazole + 2KOH + 444H ₂ O	110	24	6(5)	70	[Mn ₂ (μ ₃ -OH)(H ₂ O) ₂ {C ₆ H ₃ (COO) ₃ }]·2H ₂ O, V
Ni(OAc) ₂ ·4H ₂ O + 0.5 AIP + 4,4'-bipyridine + 278H ₂ O + 156CH ₃ OH	200	72	7(6)	67	[Ni ₂ (H ₂ O)(μ ₃ -OH) ₂ (C ₈ H ₅ NO ₄)], VI
Mn(OAc) ₂ ·4H ₂ O + 1,2,4-BTC + imidazole + 2KOH + 444H ₂ O	220	24	6(4.5)	70	[Mn ₃ {C ₆ H ₃ (COO) ₃ }] ₂ , VII
Mn(OAc) ₂ ·4H ₂ O + 4,4'-OBA + imidazole + 2NaOH + 444H ₂ O	220	24	6(4)	80	[{Mn(OH)} ₂ {C ₁₂ H ₈ O(COO) ₂ }], VIII

*1,3,5-BTC = 1,3,5-benzene tricarboxylate, 4,4'-OBA = 4,4'-Oxybis(benzoic acid), 1,2,4-BTC = 1,2,4-benzene tricarboxylate, AIP = 5-amino isophthalate

to note that the shorter and more conjugated the binding bridges between the metal centers are, the more efficient the magnetic interactions and overlap between them. In this context, it is preferable to have bridges such as M–O–C–O–M or M–O–M while using the carboxylates as the linker between the metal centers. One finds a reasonable variety and diversity in such structures in the literature.¹²

We have been interested in the study of the formation of MOF structures of 3d-transition metals using benzene-based aromatic polycarboxylic acids. In this paper, we present a few select examples of such MOF compounds, wherein we have isolated magnetic centers, magnetic dimers, one-dimensional chains and two-dimensional layers formed by the M–O–M linkages. The compounds, [C₃N₂H₅][Mn(H₂O){C₆H₃(COO)₃}], **I**, [{Mn(H₂O)₃}{C₁₂H₈O(COO)₂}]·H₂O, **II**, [{Mn(H₂O)}{C₁₂H₈O(COO)₂}], **III**, [NaMn{C₆H₃(COO)₃}], **IV**, [Mn₂(μ₃-OH)(H₂O)₂{C₆H₃(COO)₃}]·2H₂O, **V**, [Ni₂(H₂O)(μ₃-OH)₂(C₈H₅NO₄)], **VI**, [Mn₃{C₆H₃(COO)₃}]₂, **VII** and [{Mn(OH)}₂{C₁₂H₈O(COO)₂}], **VIII**, have been discussed here to illustrate the magnetic behaviour in MOFs.

2. Experimental

2.1 Synthesis

All the compounds were synthesized employing solvothermal reactions using water or a mixture of water and methanol as solvent. The synthesis conditions employed for the preparation of these compounds are presented in table 1. In a typical synthesis, for **I**, a mixture of Mn(OAc)₂·4H₂O (0.061 g, 0.25 mM), 1,3,5-benzene tricarboxylic acid (0.21 g, 1 mM), imidazole (0.068 g, 1 mM) and KOH (0.11 g, 2 mM) were dissolved in 8 ml of water and reacted in a PTFE-lined acid digestion vessel (23 mL) at 75°C for 24 h. The final product contained large quantities of crystals, which were filtered under vacuum, washed with a sufficient quantity of water and diethyl ether. In all the cases, the products were found to contain large quantities of single crystals. Thus, colourless rectangular (**I**), pale brown coloured block (**II**), colourless rectangular (**III**), light yellow coloured plate (**IV**), colourless rectangular (**V**), green coloured rod (**VI**), colourless rectangular (**VII**) and colourless plate (**VIII**) crystals were obtained. Elemental analysis: exptl (calcd): **I**, C 41.1

(41.24)%, N 8.31 (8.02)%, H 2.66 (2.86)%; **II**, C 43.6 (43.84)%, H 4.1 (4.18)%; **III**, C 50.95 (51.04)%, H 3.1 (3.03)%; **IV** C 37.5 (37.89)%, H 1.11 (1.05)%; **V** C 26.25 (26.6)%, H 2.98 (2.96)%; **VI** C 27.79 (27.57)%, N 4.14 (4.02)%, H 2.35 (2.60); **VII** 37.12 (37.30)%, H 1.11 (1.04)%; **VIII** 41.8 (41.98)%, H 2.44 (2.5)%. Powder X-ray diffraction (XRD) patterns were recorded on powdered samples in the 2θ range of $5\text{--}50^\circ$ using $\text{CuK}\alpha$ radiation (Philips X'Pert). The XRD patterns were found to be entirely consistent with the simulated XRD patterns generated from the structures determined by single crystal XRD studies, establishing the purity of the phases. All the compounds were characterized by the thermogravimetric analyses (TGA) and IR studies.

2.2 Single crystal structure determination

Suitable single crystal of **I–VIII** were carefully selected under a polarizing microscope and glued to a thin glass fibre. The single crystal data were collected on a Bruker AXS smart Apex CCD diffractometer at 293(2) K. The X-ray generator was operated at 50 kV and 35 mA using $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. Data were collected with ω scan width of 0.3° . A total of 606 frames were collected in three different setting of φ ($0, 90, 180^\circ$) keeping the sample-to-detector distance fixed at 6.03 cm and the detector position (2θ) fixed at -25° . The data were reduced using SAINTPLUS,¹⁴ and an empirical absorption correction was applied using the SADABS program.¹⁵ The structure was solved and refined using SHELXL9716 present in the WinGx suit of programs (Version 1.63.04a).¹⁷ All the hydrogen atoms of the carboxylic acids and the bound water molecules, were initially located in the difference Fourier maps, and for the final refinement, the hydrogen atoms were placed in geometrically ideal positions and refined in the riding mode. Restraints for the bond distances were used during the refinement for keeping the hydrogen atoms of the water molecules bonded with the oxygen atoms. Final refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares refinement against $|F_2|$ was carried out using the WinGx package of programs.¹⁷ Details of the structure solution and final refinements for **I–VIII** can be found elsewhere.^{18–20}

3. Results and discussion

3.1 Structure

The main structural feature of $[\text{C}_3\text{N}_2\text{H}_5][\text{Mn}(\text{H}_2\text{O})\{\text{C}_6\text{H}_3(\text{COO})_3\}]$, **I**, is the presence of isolated $\text{Mn}_2(\text{COO})_2$ units within the two-dimensional metal–organic framework. Here the octahedral Mn^{+2} ions are coordinated by five carboxylate oxygen atoms and one water molecule. Two Mn^{+2} ions are connected by the carboxylate group forming a Mn_2 dimer of the formula, $\text{Mn}_2(\text{COO})_2$. The $\text{Mn}_2(\text{COO})_2$ unit is also connected with six trimesate units giving rise to a two-dimensional anionic layer of the formula, $[\text{Mn}(\text{BTC})(\text{H}_2\text{O})]^-$ (figure 1). The protonated imidazole molecules present in between the two layers, act as the charge compensating cation. The two-dimensional layers are stabilized by hydrogen bond interactions between the coordinated water molecule, carboxylate oxygen atoms (intra-layer as well as inter-layer interactions) and the interactions between the imidazole molecules and the framework through $\text{N–H}\cdots\text{O}$ hydrogen bonds.

Structure of $[\{\text{Mn}(\text{H}_2\text{O})_3\}\{\text{C}_{12}\text{H}_8\text{O}(\text{COO})_2\}]\cdot\text{H}_2\text{O}$, **II**, has one-dimensional –Mn–O–C–O–Mn– connectivity. The structure of **II** consists of Mn^{+2} ions coordinated by three water molecules and three carboxylate oxygens forming an octahedral geometry. The connectivity between the carboxylate groups and $\text{Mn}(\text{H}_2\text{O})_3\text{O}_3$ octahedra gives rise to a one-dimensional structure, which are connected by the OBA units forming a two-dimensional layer structure (figure 2).

Figure 1. The two-dimensional layer structure of $[\text{C}_3\text{N}_2\text{H}_5][\text{Mn}(\text{H}_2\text{O})\{\text{C}_6\text{H}_3(\text{COO})_3\}]$, **I**, in the bc plane.

The structure of $[\{\text{Mn}(\text{H}_2\text{O})\}\{\text{C}_{12}\text{H}_8\text{O}(\text{COO})_2\}]$, **III**, is modified further from the structure of **II** by incorporation of an extra $\text{M}-\text{O}-\text{C}-\text{O}-\text{M}$ connectivity within the one-dimensional $-\text{Mn}-\text{O}-\text{C}-\text{O}-\text{Mn}-$ linkages forming infinite $-\text{M}-(\text{O}-\text{C}-\text{O})_2-\text{M}-$ connectivity. Here the Mn^{2+} ions coordinated by one water molecule and four carboxylate oxygen atoms forming a square pyramidal geometry. The Mn^{2+} ions are linked to the carboxylate units forming an 8-membered ring, which are connected through their corners forming a one-dimensional chain. The chains

Figure 2. The two-dimensional structure of $[\{\text{Mn}(\text{H}_2\text{O})_3\}\{\text{C}_{12}\text{H}_8\text{O}(\text{COO})_2\}]\cdot\text{H}_2\text{O}$, **II**, in the ac plane. Note that the isolated Mn-centers form $-\text{Mn}-\text{O}-\text{C}-\text{O}-\text{Mn}-$ connectivity.

Figure 3. The two-dimensional layer structure of $[\{\text{Mn}(\text{H}_2\text{O})_3\}\{\text{C}_{12}\text{H}_8\text{O}(\text{COO})_2\}]$, **III**. The Mn-centers are linked by two different carboxylate group to form $-\text{Mn}-(\text{O}-\text{C}-\text{O})_2-\text{Mn}-$ connectivity.

are bonded with the OBA units giving rise to the two-dimensional layer structure (figure 3).

The structure of $[\text{NaMn}\{\text{C}_6\text{H}_3(\text{COO})_3\}]$, **IV**, consists of Mn_2O_8 dimers, which are connected by the carboxylate groups $[(\text{COO})^-]$ forming a two-dimensional layer with a (4,4) net topology (figure 4a). Here the Mn^{2+} ions are trigonal bipyramidally coordinated by five carboxylate oxygen atoms and the Na^+ ions are trigonal prismatic coordinated by six carboxylate oxygen atoms. The MnO_5 units are connected via two μ_3 oxygens forming a simple Mn_2O_8 dimer. The NaO_6 units are connected together by two μ_3 oxygens to give rise to one-dimensional $-\text{O}-\text{Na}-\text{O}-$ chains. The connectivity between the Mn_2O_8 dimers and $-\text{O}-\text{Na}-\text{O}-$ chains gives rise to a two-dimensional layer (figure 4b).

Figure 4. (a) The figure shows the connectivity between the Mn_2O_8 dimers and one of the carboxylate groups of the 1,2,4-BTC in $[\text{NaMn}\{\text{C}_6\text{H}_3(\text{COO})_3\}]$, **IV**. Note the formation of (4,4) rhombus grid topology (light blue lines are a guide to the eye). The Na^+ ions are not shown for clarity. (b) The connectivity between Mn_2O_8 dimers and $\text{O}-\text{Na}-\text{O}$ chains forming a two-dimensional $-\text{MO}-\text{M}-$ ($\text{M} = \text{Mn}/\text{Na}$) connectivity in **IV**.

The two-dimensional $-\text{M}-\text{O}-\text{M}-$ ($\text{M} = \text{Na}, \text{Mn}$) layers are pillared by the trimellitate anions forming the three-dimensional structure.

The structure of $[\text{Mn}_2(\mu_3\text{-OH})(\text{H}_2\text{O})_2\{\text{C}_6\text{H}_3(\text{COO})_3\}]\cdot 2\text{H}_2\text{O}$, **V**, consists of tetranuclear clusters of formula $[\text{Mn}_4(\mu_3\text{-OH})_2(\text{H}_2\text{O})_4\text{O}_{12}]$ (figure 5a). The tetranuclear clusters, formed by two different manganese atoms that are related by the centre of symmetry, are connected by the trimellitate anions forming the three-dimensional structure with one-dimensional channel along the ‘*a*’ axis (figure 5b). The extra-framework water molecules occupy the channels. A careful analysis of the structural features of **V** shows that each Mn_4 cluster cations are connected with eight different trimellitate anions and each trimellitate anion is connected with four different Mn_4 cluster cations. This connectivity resembles the bonding observed in the fluorite (CaF_2) structure.

Figure 5. (a) The Mn_4 cluster, $[\text{Mn}_4(\mu_3\text{-OH})_2(\text{H}_2\text{O})_4\text{O}_{12}]$, with the coordination environment around the Mn^{2+} ions in $[\text{Mn}_2(\mu_3\text{-OH})(\text{H}_2\text{O})_2\{\text{C}_6\text{H}_3(\text{COO})_3\}]\cdot 2\text{H}_2\text{O}$, **V**. (b) Three-dimensional structure of **V** in the *bc* plane showing the connectivity between the Mn_4 clusters and the 1,2,4-BTC. Note that the channels are occupied by the water molecules.

The compound $[\text{Ni}_2(\text{H}_2\text{O})(\mu_3\text{-OH})_2(\text{C}_8\text{H}_5\text{NO}_4)]$, **VI**, contains infinite $-\text{Ni}-\text{O}-\text{Ni}-$ one-dimensional connectivity. Here two different types of octahedral Ni^{2+} ions are connected by $\mu_3\text{-OH}$ to form the one-dimensional $-\text{Ni}-\text{O}-\text{Ni}-$ linkages (figure 6a), which are connected by 5-amino isophthalate units give rise to a three-dimensional structure (figure 6b). The important point is that the one-dimensional chains have edge shared NiO_6 octahedrons (figure 6a).

The structure of $[\text{Mn}_3\{\text{C}_6\text{H}_3(\text{COO})_3\}_2]$, **VII**, contains $-\text{Mn}-\text{O}-\text{Mn}-$ linkages that form two-dimensional layers. The compound consists of two independent Mn^{2+} ions, and have a distorted trigonal

Figure 6. (a) View of the one-dimensional infinite $-\text{Ni}-\text{O}-\text{Ni}-$ chains in $[\text{Ni}_2(\text{H}_2\text{O})(\mu_3\text{-OH})_2(\text{C}_8\text{H}_5\text{NO}_4)]$, **VI**. (b) Figure shows connectivity between the $-\text{Ni}-\text{O}-\text{Ni}-$ chains by 5-amino isophthalate in **VI**.

prismatic $[\text{Mn}(1)]$ and octahedral geometry $[\text{Mn}(2)]$ with carboxylate oxygen atoms. The $\text{Mn}(2)\text{O}_6$ octahedral units are connected with two $\text{Mn}(1)\text{O}_6$ trigonal prismatic units via two different μ_3 carboxylate oxygen atoms and two $\text{Mn}(1)\text{O}_6$ units are connected via another μ_3 carboxylate oxygen atom forming a triangular lattice, which are connected through the corners to form a layer that resembles the Kagome arrangement (figure 7a). The Mn–Mn connectivity within the layer shows that each of the triangle of the distorted Kagome layer is formed by two $\text{Mn}(1)$ and one $\text{Mn}(2)$ species. The benzene carboxylate units connect the layers three-dimensionally (figure 7b).

Similar to VII, compound $[\{\text{Mn}(\text{OH})\}_2\{\text{C}_{12}\text{H}_8\text{O}(\text{COO})_2\}]$, VIII, also possess infinite $-\text{Mn}-\text{O}-\text{Mn}-$ layers. Here the Mn^{+2} ions have octahedral coordina-

tion by the three carboxylate oxygens and three $\mu_3\text{-OH}$. Three Mn^{+2} ions are connected by the $\mu_3\text{-OH}$ group forming a $[\text{Mn}_3(\mu_3\text{-OH})]$ triangular unit, which are connected by the carboxylate oxygens to form the two-dimensional layers (figure 8a). This layer closely resembles the brucite layer (replacing half the $-\text{OH}$ ions from the brucite by the carboxylate oxygen). The $-\text{Mn}-\text{O}-\text{Mn}-$ layers are connected by the OBA unit to form the three-dimensional structure (figure 8b).

4. Magnetic properties

4.1 Magnetic interaction pathways

From the structures described above, it is clear that the magnetic centers have either $-\text{M}-\text{O}-\text{C}-\text{O}-\text{M}-$

Figure 7. (a) The two-dimensional Kagome layer formed by the connectivity between $\text{Mn}(1)\text{O}_6$ and $\text{Mn}(2)\text{O}_6$ polyhedral units in $[\text{Mn}_3\{\text{C}_6\text{H}_3(\text{COO})_3\}_2]$, VII. (b) Figure shows the connectivity between the Kagome layer in VII by 1,2,4-BTC units.

Figure 8. (a) The two-dimensional brucite-related layer in $[\{\text{Mn}(\text{OH})\}_2\{\text{C}_{12}\text{H}_8\text{O}(\text{COO})_2\}]$, VIII. (b) Figure shows the connectivity between the brucite layers in VIII by OBA units.

or/and $-M-O-M-$ connectivity within the metal–organic framework structures. The magnetic behaviour of these compounds would depend on many factors including the site symmetry of the magnetic ions and the nature of the bridging modes/angles of the connectors (carboxylate group or carboxylate oxygen atoms/OH), etc. The magnetic exchanges between the transition metal ion centers of these compounds may be mediated through the super-exchange or super-super exchange interactions via the bridging ligands.

For the compounds having $-M-O-M-$ connectivity, the $M-O-M$ angle becomes an important parameter to understand the magnetic behaviour. According to the Goodenough and Kanamori postulations,²¹ for ideal ferromagnetic exchange, the $M-O-M$ angle is 90° and for an antiferromagnetic exchange, it is 180° . This exchanges ($M-O-M$), generally, occurs through the $2p$ orbital of the oxygen and the outer d orbitals of the transition metal ($d_M-p_O-d_M$) with appropriate site and spin symmetry of the respective orbitals. In carboxylate bridges ($O-C-O$), the exchanges occur via the $2p$ orbitals of the oxygen, $2p$ orbitals of the carbon and the metal d orbitals ($d_M-p_O-p_C-p_O-d_M$) with similar symmetry consideration of the participating orbitals. In addition, the exchanges through the carboxylate bridges, also may depend on the bridging modes of the carboxylate oxygens with the transition metal within the compound. The most commonly observed bridging modes of the carboxylate oxygen in these structures are syn–syn, syn–anti, and anti–anti arrangements. It has been observed that the carboxylate group with syn–syn and anti–anti bridging modes exhibit relatively stronger interaction compared to the syn–anti mode. Since the metal d orbitals are delocalized towards the oxygen $2p$ orbitals of the carboxylate bridges, the oxygen $2p$ orbitals would be more favourably oriented to have maximum overlap through the syn–syn and anti–anti modes rather than in the syn–anti mode. In addition, the oxygen $2p$ orbitals also overlap with the same carbon $2p$ orbital through the syn–syn and the anti–anti bridging modes and with different carbon $2p$ orbitals in the syn–anti bridging mode. This would result in an overlap that may not be strong for the syn–anti arrangement.

To understand the type of interactions (antiferromagnetic or ferromagnetic), we need to make a comparison between the same magnetic ions using the three different types of bridging modes in the

absence of other bridges. Of the $3d$ transition metal ions, Cu^{+2} ions have the largest number of complexes employing the three bridging modes described above when considering compounds that are formed without any other bridges.^{22–25} This creates impediment for a complete interpretation of the magnetic interactions that are formed by the carboxylate bridges.

It is well-known that the symmetry of the magnetic site is important to understand the magnetic interactions in extended systems like MOF, especially in the cases where the metal ions are bridged without any center of inversion. This aspect is proved to be quite important in many systems because it will allow antisymmetric interactions (Dzyaloshinsky–Moriya interaction, DM between the magnetic centers).²⁶ This helps in the canting of the interaction of spins because the coupling energy may be minimized when the two adjacent spins are perpendicular to each other. This DM interaction requires that the magnetically related spins do not possess the inversion center. Thus, canted antiferromagnetism or weak-ferromagnetism may be reasonably anticipated for many MOF compounds.

4.2 Magnetic behaviour in MOFs: Select examples

The X-band EPR spectra of **I** in the solid state was recorded at room temperature, which indicated a single resonance centered at $g \sim 2.004$, and confirmed that the manganese ions in this compound exist in $+2$ oxidation state (figure 9a). The temperature dependent magnetic susceptibility of **I** was studied using a wellground sample in the temperature range 2–300 K in a field using a SQUID magnetometer. The χ_M vs T plot per Mn^{+2} ion is shown in figure 9b. At room temperature, the observed effective magnetic moment (μ_{eff}) is $5.92 \mu_B$, which is comparable to the spin only value for Mn^{+2} ($S = 5/2$). The $\chi_M T$ versus T plot (figure 9b inset) shows a continuous decrease in the value of $\chi_M T$ from $4.38 \text{ emu mol}^{-1} \text{ K}$ at room temperature to $0.92 \text{ emu mol}^{-1} \text{ K}$ at 2 K, which is indicative of the presence of antiferromagnetic interactions. This may be expected from the syn–syn carboxylate bridges that connect the Mn^{+2} ions in the Mn_2 -dimer.²⁷ The high temperature magnetic susceptibility data (50–300 K) can be fitted to the Curie–Weiss behaviour with $C = 4.44 \text{ emu/mol}$ and $\theta_p = -2.74 \text{ K}$ (figure 9c). The magnetic behaviour was fitted using a dimer model.⁹ The spin Hamiltonian for the Mn^{+2} dimer

Figure 9. (a) EPR spectra of **I** at room temperature. Note the single resonance centered at $g = 2.004$ indicating Mn^{+2} ions. (b) The temperature variation of the molar susceptibility (χ_M) for **I** with the theoretical dimer model fit ($H = 0.1$ T). Inset shows the temperature dependence of the $\chi_M T$. (c) The temperature variation of the inverse molar susceptibility ($1/\chi_M$) for **I** along with Curie-Weiss fit ($H = 0.1$ T).

can be written in the form: $H = -2JS_1 \cdot S_2$. The susceptibility equation for the Mn^{+2} dimer can be obtained by substituting the values for the Mn^{+2} ion into the Van Vleck (1),²⁸ where N_A = Avogadro's number, g = gyromagnetic ratio (~ 2), μ_B = Bohr Magneton, k = Boltzmann constant, T = temperature, J = the coupling constant between the metal centres and $x = \exp[-J/(kT)]$.

$$\chi_M^{\text{dimer}} = \frac{N_A g^2 \mu_B^2}{kT} \frac{[55 + 30x^{10} + 14x^{18} + 5x^{24} + x^{28}]}{[11 + 9x^{10} + 7x^{18} + 5x^{24} + 3x^{28} + x^{30}]} \quad (1)$$

The best fit for the experimental data was obtained with $J = -0.346 \text{ cm}^{-1}$. This indicates weak anti-ferromagnetic interactions between the Mn^{+2} ions and the value is comparable with those observed in other similar carboxylate bridged manganese compounds.²⁹ Inter-dimer interactions, through the aromatic benzene ring was not considered, as the distances between the Mn_2 dimers are large to have any meaningful interactions.

The X-band EPR spectra of **II** and **III** shows a single resonance centered at $g \sim 2.00$ confirming that manganese ions are in $+2$ oxidation state (figures 10a and b). The temperature variation of the molar magnetic susceptibility (χ_M) of two related compound, **II** and **III** at 0.1 T is shown in figure 10c. At

room temperature, the observed effective magnetic moment is 5.55 and $5.61 \mu_B$, respectively for **I** and **II**, which are slightly less than the spin only value for Mn^{+2} ions ($5.92 \mu_B$). While the compound **II** does not show any magnetic ordering down to 2 K, compound **III** shows anti-ferromagnetic behaviour with $T_N = 12$ K. The $1/\chi_M$ vs T curves are shown in inset figure 10c. The high temperature magnetic susceptibility data (100 – 300 K) can be fitted to the Curie-Weiss behaviour with $C = 4.30$ and 2.42 emu/mol , and $\theta_p = -60.2$ and -14.2 K, respectively for **II** and **III**. The negative Weiss constant in both the compounds indicate antiferromagnetic behaviour. From the structural point of view, we can rationalize the anti-ferromagnetic behaviour in **II** and **III** by the bridging mode of the carboxylate groups. It can be noted that in both the compounds the Mn^{+2} ions are connected by the syn-syn $-\text{M}-\text{O}-\text{C}-\text{O}-\text{M}-$ bridges, which is favourable for antiferromagnetic exchanges.²⁷ The observation of the anti-ferromagnetic ordering ($T_N = 12$) in **III** is probably due to the presence four carboxylate bridges compared to the two carboxylate bridges in **II** for each Mn^{+2} ions.

The temperature dependence of $\chi_M T$ for the compound **IV** per Mn^{+2} ion is shown in figure 11a. At room temperature, **IV** shows a $\chi_M T$ value of $4.56 \text{ emu mol}^{-1} \text{ K}$. The $\chi_M T$ value decreases continuously with decreasing temperature and reaches a minimum of $4.36 \text{ emu mol}^{-1} \text{ K}$ at 45 K. On cooling

Figure 10. EPR spectra of at room temperature of (a) **II** and (b) **III**. (c). The temperature variation of the molar magnetic susceptibility (χ_M) for **II** and **III** ($H = 0.1$ T). Inset shows the $1/\chi_M$ vs T plot.

further the χ_M^T increases sharply suggesting that the magnetic behaviour at low temperature may be different from the room temperature one. The Curie–Weiss fitting of the high temperature region (100–300 K) gave values of $C = 5.43 \text{ emu mol}^{-1}$ and $\theta_p = -1.17 \text{ K}$. The small negative θ_p value suggests weak anti-ferromagnetic coupling between the Mn^{+2} species. The sharp change in the magnetic behaviour at lower temperature could be due to either a ferromagnetic or a canted antiferromagnetic behaviour. The observed differences in the field-cooled (FC) and zero-field-cooled (ZFC) susceptibilities measured at 0.1 T down to 2 K (inset of figure 11a), also suggest that the low-temperature magnetic interactions could be different. The field-cooled χ_{MT} values at different applied fields as a function of temperature shows a spontaneous increase around 40 K, which is more noticeable at lower field strengths (figure 11b). This feature suggest the possibility of a spin-canted antiferromagnetic behaviour,³⁰ in which a predominantly antiferromagnetic phase possesses a spontaneous magnetization originating from a small deviation between the antiparallel alignment of the spins. At 2 K, the field dependence of the magnetization shows a small hysteresis loop at low field strengths (inset of figure 11b). The magnetization value is $2.5 N\beta$ at 50 kOe, far from the saturation value of $5 N\beta$ for a Mn^{+2} ion ($S = 5/2$), which is also in agreement with an antiferromagnetic state. From the M vs H plot, we find a coercive field (H_c) of 745 Oe and a remnant magnetization (M_r) of 0.028

$N\beta$ (inset of figure 11b). This suggests spontaneous magnetization and consistent with the spin-canted antiferromagnetic behaviour. The canting angle is calculated to be ca. 0.32° , based on the equation $\psi = \tan^{-1}(M_r/M_s)$.³¹

Generally, the spin canting in a solid can arise from two contributions: (1) single-ion anisotropy and (2) the presence of an antisymmetric exchange.³² It is known that the presence of an inversion center between the adjacent spin centers would result in the disappearance of the antisymmetric exchange.²⁶ Several highspin Mn^{+2} complexes with inversion centers exhibiting spin-canted antiferromagnetic behaviour have been reported, which could be due to the weak single-ion anisotropy of the Mn^{+2} site or anisotropy of the whole crystal.³³ In **IV**, the adjacent Mn^{+2} ions are related structurally by a crystallographic inversion center and all the Mn_2 -units appear to be connected by the 2_1 axis. This structural arrangement of the Mn_2 dimers would create differences in the orientation of the Mn_2 -units, and can lead to antisymmetric exchanges resulting in the canting of the spins. Similar phenomena have also been observed in Mn^{+2} containing compounds that share similar space group with **IV**.³⁴ In addition, the distorted trigonal bipyramidal geometry of the Mn^{+2} ions can also enhance the antisymmetric exchanges,³⁵ and contribute to the total spin canting in **IV**. The X-band EPR spectra for compound **IV**, recorded in the temperature range 10–300 K, is shown in figure 11c. The spectra appear to remain un

Figure 11. (a) The temperature variation of $\chi_M T$ ($H = 0.1$ T) (FC) for **IV**. Inset shows the field cooled (FC) and the zero field cooled (ZFC) data ($H = 0.1$ T). (b) $\chi_M T$ vs T plot at various applied fields. Inset show M vs H Plot at 2 K. Note the spontaneous increase around 40 K. (c) The variable temperature X-band EPR spectra of compound **IV**. (d) Temperature dependence of the intensity (open circle) and the line width (closed circle) of the EPR signals for compound **IV**. Note the sudden increase at ~ 40 K.

changed up to 30 K, after which the signal broadens. The broadening of the spectra at lower temperatures could be due to the dipolar homogeneous broadening.³⁶ The g value remains unchanged at 2.028 during the entire temperature range, which confirms that the manganese is present in +2 oxidation state. The plot of the X-band intensity [calculated as $(\Delta H_{pp})^2 \cdot h_{pp}$, where ΔH = peak to peak linewidth, h_{pp} = peak to peak intensity] and the linewidth as a function of the temperature are shown in figure 11d.

As can be noted, the linewidth increases continuously with decreasing temperature, which suggests a stronger spin correlation between the Mn^{+2} species at lower temperature. The observed intensity, however, exhibits a small initial drop in the temperature range 300–150 K followed by sudden increase up to the lowest measured temperature ($T = 10$ K). The sharp increase in the signal intensity at low temperature ($T < 50$), could be due to the canting of the Mn^{+2} spins. This behaviour in the EPR study correlates

Figure 12. (a) The temperature variation of $\chi_M T$ ($H = 0.1$ T) (FC) for **V**. The continuous line is the theoretical fit from the model (see text). Inset shows the $1/\chi_M$ vs plot with Curie–Weiss fit ($H = 0.1$ T). (b) The various possible magnetic exchange pathways in the Mn_4 cluster in **V**. (c) The variable temperature X-band EPR spectra of compound **V**. (d) Temperature dependence of the intensity (open circle) and the line width (closed circle) of the EPR signals for compound **V**.

with our observation in the magnetic study, where a spin canted behaviour was observed at $T < 45$ K. Thus, the EPR studies appear to compliment the magnetic investigations of **IV**.

The temperature dependence of $\chi_M T$ for the compound **V** per Mn^{+2} ion is shown in figure 12a. At room temperature (RT), the $\chi_M T$ has a value of $4.5 \text{ emu mol}^{-1} \text{ K}$. The $\chi_M T$ value decreases continuously with decreasing temperature and reaches a minimum of $0.19 \text{ emu mol}^{-1} \text{ K}$ at 2 K (figure 12a).

This suggests a dominant antiferromagnetic interaction between the Mn^{+2} centers. The $1/\chi_M$ vs T curve was fitted to the Curie–Weiss law in the temperature range 100–300 K, which gave a value of $C = 5.26 \text{ emu mol}^{-1}$ and $\theta_p = -45.8 \text{ K}$ (figure 12a inset). The negative value for the θ_p suggests a predominantly antiferromagnetic coupling between the Mn^{+2} ions. Since the structure contains Mn_4 clusters, to understand the nature of the magnetic exchanges and to obtain the strength of the exchange interac-

tions, we have performed theoretical calculations by taking into account the structural features of **V**. From the structure of **V**, one can note that there are three distinct exchange pathways through the oxygen and the syn-syn carboxylate (O–C–O) bridges. The corresponding magnetic coupling constants for these interactions would be J_1 , J_2 and J_3 (figure 12b). The Mn–O–Mn bond angles of 101.7° (J_1), 101.8° and 89.8° (J_2) and 112.6° (J_3) suggests that J_1 and J_3 may be anti-ferromagnetic, while J_2 could have both the ferro- (89.8°) as well as the anti-ferromagnetic (101.8°) exchange interactions (figure 12b). Considering these structural features, we have modelled this system using the Hamiltonian,

$$H_1 = -J_1 \hat{S}_{\text{Mn}_{2a}} \cdot \hat{S}_{\text{Mn}_2} - J_2 (\hat{S}_{\text{Mn}_1} \cdot \hat{S}_{\text{Mn}_2} + \hat{S}_{\text{Mn}_{1a}} \cdot \hat{S}_{\text{Mn}_{2a}}) - J_3 (\hat{S}_{\text{Mn}_1} \cdot \hat{S}_{\text{Mn}_{2a}} + \hat{S}_{\text{Mn}_{1a}} \cdot \hat{S}_{\text{Mn}_2}), \quad (2)$$

$$H_2 = g\mu_B H \sum_{i=1}^4 \hat{S}_z^i - zJ' \langle \hat{S}_z \rangle \sum_{i=1}^4 \hat{S}_z^i, \quad (3)$$

$$H = H_1 + H_2, \quad (4)$$

where positive (negative) J corresponds to ferro-magnetic (antiferromagnetic) interactions and S 's are the usual spin operators. The three terms in the (2) are the exchange terms and the first term in (3) correspond to the Zeeman term and the second term corresponds to the intermolecular interactions. We have solved the model exactly and obtained eigenvalues, E_0 (S , M_s) of the unperturbed model Hamiltonian H_1 . We, then, use Hamiltonian H_2 as the perturbation over the unperturbed Hamiltonian H_1 , since, the Zeeman and intermolecular interaction terms are generally very weak when compared to the exchange interactions between the magnetic centers. Now, we can obtain the molar magnetic susceptibility from the relation,

$$\chi_M = \frac{Ng^2 \mu_B^2 F(J, T)}{[k_B T - zJ'F(J, T)]}, \quad (5)$$

where

$$F(J, T) = \frac{\sum_S \sum_{M_s} M_s^2 e^{-E_0(S, M_s)/k_B T}}{\sum_S \sum_{M_s} e^{-E_0(S, M_s)/k_B T}}. \quad (6)$$

We have fitted the experimental $\chi_M T$ vs T plot using the method described above. The best fits for the

experimental plot, shown in figure 12a, yields, $J_1 = -8.0$ K, $J_2 = 5.0$ K, $J_3 = -8.0$ K and $J' = -0.8$ K with $g = 2.06$. From these values, one can infer that of the three different magnetic interactions within the Mn₄ cluster, two are anti-ferromagnetic (J_1 and J_3) and other is ferromagnetic (J_2). The net total of all the three interactions result in a anti-ferromagnetic behaviour. The inter-cluster interactions (J') also appears to be anti-ferromagnetic and weak. Thus, it may be inferred that the overall magnetic behaviour of **V** would be anti-ferromagnetic. The X-band EPR spectra of **V** recorded in the temperature range of 4–300 K is shown in figure 12c. The spectra appear to remain unchanged upon cooling the sample from 300 to 70 K, but exhibit a systematic increase in the signal intensity. The spectra broadens considerably on lowering the temperature further, which may be due to the dipolar homogeneous broadening.³⁶ The g value, calculated for the Mn⁺² ion, does not change during the entire temperature range of the study and remained as 2.032 indicating that Mn species do not change in the spin state. A plot of the X-band intensity [calculated as $(\Delta H_{pp})^2 h_{pp}$, where ΔH = peak to peak linewidth, h_{pp} = peak to peak intensity] and the linewidth as a function of the temperature (figure 12d) shows some interesting features. As can be noted, the intensity keeps increasing on cooling up to 70 K, after which the intensity exhibits a sharp decrease up to 50 K. This could be due to the onset of anti-ferromagnetic interactions between the Mn⁺² ions in the system.³⁷ The intensity, however, starts to exhibit an increase again below 30 K, which probably be due to the significant increase in the line width. This behaviour further consolidates the anti-ferromagnetic behaviour observed in **V** in our magnetic studies. Similar behaviour has also been observed earlier in other Mn⁺² containing compounds.³⁸

The magnetic behaviour of **VI** is shown in figure 13. At room temperature, $\chi_M T$ value of **VI** is 2.86 emu mol⁻¹ K for the two Ni⁺² ion, which is slightly higher than the spin-only value (2 emu mol⁻¹ K). This increase could be due to the orbital contribution of the excited state of the Ni⁺² ions. The $\chi_M T$ versus T curve is shown in figure 13a. The $\chi_M T$ value decreases continuously and reaches a minimum at 44 K. On colling further, the $\chi_M T$ increases sharply, which suggests that the magnetic behaviour at low temperature may be either ferromagnetic or canted antiferromagnetic.³⁹ The $1/\chi_M$ vs T curve is shown in the inset of figure 13a. Above 100 K, the

Figure 13. (a) The temperature variation of the molar magnetic susceptibility (χ_M) for VI ($H = 0.1$ T) (FC). Inset shows the $1/\chi_M$ vs T plot. (b) Figure shows the field cooled (FC) and the zero-field cooled (ZFC) plots of χ_M vs T at $H = 0.1$ T. (c) The variation of the magnetization (M) as a function applied field (H) at 2 K.

magnetic behaviour can be fitted by the Curie–Weiss law, with $C = 6.21$ emu mol⁻¹ and $\theta_p = -328.9$ K. The large negative value for θ_p indicates the Ni⁺² ions are strongly coupled antiferromagnetically. The field-cooled (FC) and zero-field-cooled (ZFC) magnetization measured at 1000 Oe down to 2 K, shows a clear deviation at 25 K (figure 13b). This suggests that low-temperature behaviour could be ferromagnetic-like. This assumption is further supported by the observation of a small hysteresis loop at 2 K (figure 13c).

The magnetic behaviour of VII is shown in figure 14. At room temperature, the observed effective magnetic moment (μ_{eff}) is $6.01 \mu_B$, which is slightly higher than the spin only value for Mn⁺² ions ($5.92 \mu_B$). The $\chi_M T$ versus T curve is shown in figure 14a. The $\chi_M T$ value decreases continuously with decrease in temperature and reaches a minimum of 2.59 emu mol⁻¹ K at 23 K. On cooling further the $\chi_M T$ increases rapidly suggesting a change in the magnetic behaviour. It is likely that the magnetic behaviour at low temperature may be either ferromagnetic or canted antiferromagnetic.³⁹ The $1/\chi_M$ vs T curve is shown as the inset of figure 14a. The magnetic behaviour can be fitted to the Curie–Weiss law in the temperature range 100–300 K, with $C = 5.35$ emu/mol and $\theta_p = -46.1$ K. The negative value for the θ_p indicates a possible antiferromagnetic

coupling between the Mn⁺² ions. The field-cooled (FC) and zero-field-cooled (ZFC) studies measured using 50 Oe field down to 2 K show a deviation at 13 K (figure 14b), which suggest that the low temperature magnetic behaviour is different. In order to check the possible magnetic behaviour at low temperature, we have carried out AC magnetic susceptibility studies. The studies indicate (figure 14c and d) a sharp peak suggesting a magnetic transition with a critical temperature $T_c \approx 13$ K. Since the structure has triangular magnetic lattice with a distorted Kagome layers, it is expected that the system would show some degree of frustration. The degree of frustration, f , defined as θ_p/T_c ,⁴⁰ was found to be 3.55, which is much lower than those generally observed in classical Kagome lattice of iron jarosite.⁴¹ The field-cooled $\chi_M T$ values at different applied fields as a function of temperature also shows a spontaneous change in the values of $\chi_M T$ around 13 K, which is more noticeable for smaller field strengths (figure 14e). The drop in $\chi_M T$ values below 13 K could be attributed to the magnetic field saturation effect.³⁹ The field dependence of the magnetization M vs H (0–50 kOe) at 5 K (figure 14f), shows a behaviour that is typical of a canted antiferromagnet with sharp increase of the magnetization at low fields and a linear variation of M at $H > 20$ kOe.⁴² At 50 kOe the magnetizations value reaches $1.57 N\beta$, a value that

Figure 14. (a) The temperature variation of $\chi_M T$ ($H = 0.1$ T) (FC) for **VII**. Inset shows the $1/\chi_M$ vs T plot. (b) Figure shows the field cooled (FC) and the zero-field cooled (ZFC) plots of χ_M vs T at $H = 50$ Oe. The AC magnetic susceptibility at low temperature and different applied frequencies, (c) in phase response and (d) out of phase response. Note the sudden shift in the in-phase and out-of-phase response at $T \sim 13$ K (see text). (e) $\chi_M T$ vs T plot at various applied fields. Note the spontaneous increase around 15 K. (f) The variation of the magnetization (M) as a function applied field (H) at 5 K.

is far below the saturation value of $5 N\beta$ expected for a spin-only Mn^{2+} ion. This lack of saturation at high field confirms that the low temperature magnetic ground state is a canted anti-ferromagnetic one,⁴³ which may be due to the canting of spins caused by the antisymmetric Dzyaloshinsky–Moriya (DM) exchange.²⁶

In order to understand the DM exchanges in this compound and understand the small frustration, we carefully analysed the structure and the magnetic exchanges pathways. In this compound the Mn^{2+} ions are present in two different coordination environments, viz. trigonal prismatic and octahedral geometry. As discussed earlier, the antiferromagnetic

interactions between the Mn and O atom would occur through the super exchange process mediated through the metal d orbital and the oxygen p orbital. The octahedral geometry [Mn(2)] provides for favourable overlap between the p orbital of oxygen and $d_{x^2-y^2}$ and d_z^2 orbital of the Mn^{2+} ions. In the trigonal prismatic geometry [Mn(1)], the overlap needs to be between the d_{xz} and d_{yz} orbital of Mn^{2+} and the p orbitals of oxygen due to the differences in the crystal field splitting. This difference between the two Mn^{2+} species and its overlap with the oxygen p orbitals for the super exchange pathway can give rise to large antisymmetric DM interactions. This may be responsible for the canting of spins in

Figure 15. (a) The temperature variation of the molar susceptibility χ_M for **VIII** under FC and ZFC condition ($H = 0.1$ T). Inset shows the $1/\chi_M$ vs T plot (ZFC). (b) Temperature dependence of the field-cooled $\chi_M T$ at various magnetic fields. Note the spontaneous increase at ~ 40 K. The variation of the magnetization (M) as a function applied field (H) (c) at 2 K and (d) at 25 K.

our structure.²⁶ This geometric difference between the Mn^{2+} ions (in particular, the different Mn–Mn distances) reduces the frustrations within the triangular lattice. Simultaneously, the in-plane and the out-of-plane DM vectors would also be non-zero in this compound. It is likely that the in-plane component of the DM vector may induce canted spin moments in the out-of-plane directions, which results in long range magnetic ordering in **VII**. The

large inter layer distance of ~ 8 Å is suggestive of the fact that the magnetic interactions are confined within the layers.

The magnetic behaviour of **VIII** is summarized in figure 15. At room temperature, the observed effective magnetic moment is $5.66 \mu_B$, which is slightly less than the spin only value for Mn^{+2} ($5.92 \mu_B$). As can be noted, the χ_M value increases steadily upon cooling to reach a maximum at $T \sim 40$ K, which in-

indicates the onset of long-range magnetic ordering is achieved (figure 15a). The χ_M value starts to decrease upon cooling further up to 8 K, beyond which it increases again. The $1/\chi_M$ vs T curve is shown as the inset of figure 15a. The high temperature magnetic susceptibility data (100–300 K) could be fitted to the Curie–Weiss law, which gave values of $C = 4.37$ emu/mol and $\theta_p = -66.7$ K. This suggests that the dominant exchange interactions between the Mn^{+2} ions are anti-ferromagnetic. In addition, the large Weiss constant along with the reasonably high ordering temperature indicates that there is a good overlap between the metal and the oxygen orbitals through the super exchange interactions. The field-cooled $\chi_M T$ vs T studies at different applied dc fields suggests that there is an onset of spontaneous magnetization below 42 K, though the effect is appreciable at lower field strengths. The spontaneous increase in $\chi_M T$ values at low fields suggests that the low temperature behaviour could be due to a canted anti-ferromagnetism (figure 15b). The field cooled (FC) and the zero-field-cooled (ZFC) susceptibility values at low temperature indicate that there could be some ferromagnet-like correlations.⁴⁴ The abrupt jump of $\chi_M T$ below 42 K along with the divergence in the susceptibility values between ZFC and FC curve at $T \sim 40$ K suggests a long range ordering in **VIII** with a T_C around 42 K.⁴⁵ This behaviour is also supported by the M vs H studies at 2 K which shows a small hysteresis loop (figure 15c). It may be noted that the M vs H studies at 25 K (figure 15d), do not show any hysteresis behaviour indicating that the compound experiences only weak ferromagnetic polarizations at very low temperatures. Structurally, a closer look at the Mn–O–Mn angles could give some idea about the origin of canting in **VIII**. Here the Mn–O–Mn angles have large variation being in the range of 96.03 – 125.03° , which could create distortions within the $[Mn_3(\mu_3-OH)]$ triangles. This could result in antisymmetric (DM) exchanges between the Mn^{+2} spins and lead to spontaneous spin canting.

4. Concluding remarks

The synthesis, structure and magnetic studies of a series of metal–organic framework compounds have been presented. Structurally, the compounds show a remarkable diversity in their structures having two- and three-dimensional connectivity. The magnetic centers also show considerable variety in their

arrangement such as isolated dimers, one-dimensional chains and two-dimensional layers bound by the carboxylate units. The presence of magnetically active transition elements in diverse environments provide for a careful evaluation of the exchange pathways, geometry and also possible mechanism of the magnetic interactions. The magnetic studies reveal that the compounds generally show anti-ferromagnetic interactions. Spontaneous magnetizations have been observed when the magnetic centers are closer or the coupling between them are favourable. Though it would be a little premature to suggest that the magnetic exchanges in MOFs would only be anti-ferromagnetic from the present studies, it is abundantly clear that these compounds hold a lot of promise. Further work and careful study are required to evaluate and understand magnetism in these compounds. It is also likely that the use of more strongly binding ligands could lead to better exchanges between the magnetic ions paving the way for a truly magnetic porous solids. A beginning towards this direction is being attempted by many researchers, especially by employing stable free-radical based carboxylic acid.⁴⁶ Under these circumstances, one could hope that the best is yet to come in this area of magnetic porous network structured compounds.

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