



Fabrication of two supramolecular self-assemblies of Mn(II)-dicarboxylates with *trans*-4,4'-azobispyridine: Analysis of H-bonding interactions with Hirshfeld surfaces and DFT calculations



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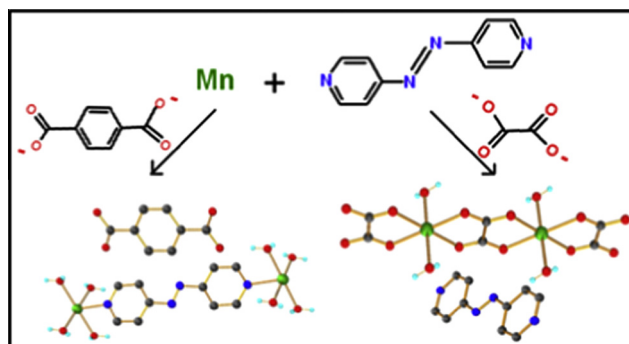
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HIGHLIGHTS

- Qualitative and quantitative determination of hydrogen bonding.
- The hydrogen bonding interaction recognizes two different dicarboxylates.
- The supramolecular interactions directs the formation of coordination structure.

GRAPHICAL ABSTRACT

Two new supramolecular self assembly of Mn(II) have been designed with an aliphatic as well as an aromatic dicarboxylate in combination with an N,N' donor ligand. The variation in the use of different dicarboxylates, creates a huge variation in the co-ordination modes of the metal ion as well as in their supramolecular structure.



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ABSTRACT

Reactions with an aliphatic dicarboxylate (*oxalate*) as well as an aromatic dicarboxylate (*terephthalate*) in combination with an N,N' donor ligand (*trans*-4,4'-azobispyridine) results two new coordination polymer of divalent manganese, namely $\{[\text{Mn}(\text{azbpy})(\text{H}_2\text{O})_4] \cdot (\text{bdc}) \cdot (\text{H}_2\text{O})_2\}_n$ (**1**) and $\{[\text{Mn}(\text{ox})(\text{H}_2\text{O})_2] \cdot (\text{azbpy}) \cdot (\text{H}_2\text{O})_2\}_n$ (**2**). Both the coordination polymers have one dimensional structure and extended to two-dimension by means of H-bonding. Interestingly, in solid state structure, the hydrogen bonding interaction recognizes the dicarboxylate (*bdc*) in case of **1** and N donor ligands (*azbpy*) in **2**. The variation in the use of dicarboxylates, creates here a huge variation in the co-ordination modes of the metal ion as well as in the supramolecular structure within the crystal of **1** and **2**. The contribution of various types of non-covalent forces are quantitatively explained in the light of Hirshfeld surface analysis, which justifies the role of hydrogen bonding in the recognition of the above organic linkers. A DFT calculation of NBO also gives a quantitative understanding of the formation of the solid state structure by H-bonding. A thermogravimetric analysis, solid state fluorescence spectra and EPR spectroscopic study of the complexes have also performed which also nicely corroborated their crystal structures.

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Introduction

In last two decades, chemists have made significant progress on understanding the fundamental rules of self-assembling processes

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[1–3] involving non-covalent interactions [4–7]. Owing to the directionality and specificity, hydrogen bonds are found very useful for the design of self-assembly from smaller molecular components to generate supramolecular ensembles with predefined structural features [8–10]. The correct choice of subunits and linkers appear to be the most important criteria for the success of constructing these supramolecular self assemblies [11,12]. In the design of metal organic frameworks, the combinational use of negative and neutral ligand has become the most popular technique, where both the ligands are coordinated to the metal centre [13–16]. The use of such mixed ligand system can also be useful to produce excellent supramolecular self-assemblies by exploiting the non-covalent forces [17,18]. In this context, the interplay of covalent and non-covalent interaction for the generation of such assemblies will be an attractive area to explore by both the synthetic as well as the theoretical chemists.

Here we have synthesized two Mn(II) complexes, using an aliphatic dicarboxylate (*oxalate*) as well as an aromatic dicarboxylate (*terephthalate*) in combination with an N,N' donor ligand [17–19] *trans*-4,4'-azobispyridine (*azbpy*) which gives a nice understanding on the interplay of covalent and non-covalent interactions. Here in one case, the H-bonding forces interacted with the dicarboxylates (*bdc*) and in another case, with the N, N donor ligands (*azbpy*). The oxalate can be more easily coordinated with the metal center compared to terephthalate, due to the absence of any electron withdrawing aromatic ring, which is present in case of terephthalate. On the other hand, the electronegativity of oxygen is greater than that of nitrogen, and hence the binding capability of dicarboxylates should much higher than that of *azbpy*. Following these aspects, keeping the metal ion and N,N' donor ligand [17–19] (*azbpy*) fixed, we have changed the dicarboxylate ligands (terephthalate and oxalate) which results a significant difference in the metal–ligand coordination as well as in the solid-state structure (Scheme 1).

In complex **1**, $\{[Mn(azbpy)(H_2O)_4](bdc)(H_2O)_2\}_n$, *azbpy* is directly coordinated to the metal centre to create a one dimensional chain and the terephthalate anions, present in the lattice. The coordinated water molecules present in the chain and the lattice water molecule are linked to each other with the lattice terephthalate anion by intra-molecular H-bonding to create a supramolecular 2D sheet. Whereas in complex **2**, $\{[Mn(ox)(H_2O)_2](azbpy)(H_2O)_2\}_n$ the oxalate is directly co-ordinated to the metal centre and the *azbpy* ligands are not involved in the bonding, but remain in the crystal lattice. There are intra-chain H-bonding between the oxygen atom of oxalate and the coordinated water molecules. The chains are further linked to each other with the lattice *azbpy* and the lattice water molecule by intra-molecular H-bonding to create a supramolecular 2D arrangement. The formations of solid-state structures are also explained with the help of theoretical calculations in a quantitative manner. A thermogravimetric study of the

complexes, the solid state fluorescence spectra and EPR study also corroborate their structures.

Experimental

Materials

Trans 4,4'-azobispyridine (*azbpy*) was synthesized following a slightly modified procedure reported earlier, by oxidative coupling of 4-aminopyridine [20]. High purity Manganese (II) chloride tetrahydrate was purchased from the Aldrich Chemical Company Inc. and used as received. All other chemicals were of AR grade and were used as received.

Physical measurements

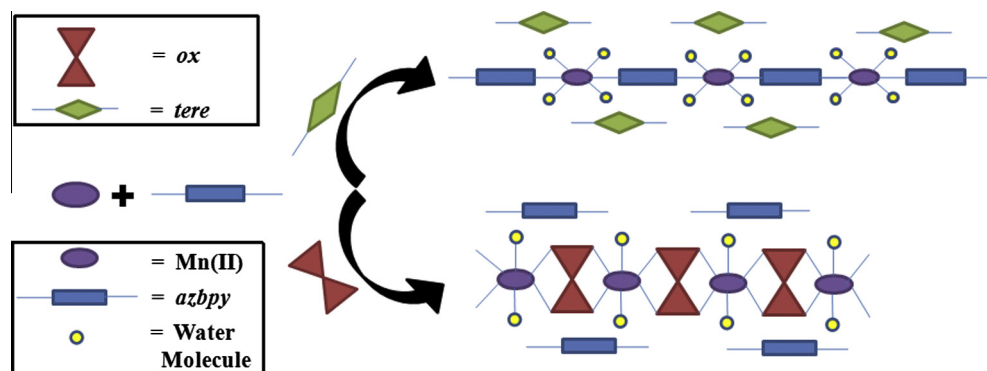
Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Heraeus CHNS analyzer. Infrared spectra ($4000\text{--}400\text{ cm}^{-1}$) were taken on KBr pellets, using a PerkinElmer Spectrum BX-II IR spectrometer. TGA was carried out on a Shimadzu DT-30 thermal analyzer under dinitrogen (flow rate: $30\text{ cm}^3\text{ min}^{-1}$). Emission spectra were recorded on a HORIBA Jobin Yvon (Fluoromax-3) fluorescence spectrophotometer. EPR spectra of powder samples have collected in JEOL JES-FA 200 Q-band ESR spectrophotometer. X-ray powder diffraction (PXRD) pattern of the powder sample of both the complexes were recorded on a PANalytical X'Pert PRO XRD instrument using Cu K α radiation.

Synthesis of complex $\{[Mn(azbpy)(H_2O)_4](bdc)(H_2O)_2\}_n$ (**1**)

An aqueous solution (4 ml) of manganese chloride tetrahydrate (0.0247 g, 0.125 mmol) was dissolved and it was taken in a layer tube of 20 ml capacity. Then 5 ml of buffer mixture (1:1 of water and MeOH) was added. After that, a methanolic solution (3 ml) of *trans*-4,4'-azobispyridine (0.023 g, 0.125 mmol) was added to an aqueous solution (3 ml) of disodium terephthalate (0.0263 g, 0.125 mmol) and the mixture was stirred for 20 min to mix it well. The ligand mixture was then slowly layered on the Mn(II) solution. After four days, an orange compound was formed at the bottom of the tube. Shiny orange single crystals suitable for X-ray diffraction analysis were obtained at the wall of the tube after one week (yield 69%). *Anal. Calc.* (%) for $C_{18}H_{24}N_4O_{10}Mn$: C, 42.27; H, 4.73; N, 10.95. *Found*: C, 42.24; H, 4.72; N, 10.93. IR spectra (in cm^{-1}): $\nu(\text{O--H})$, 3435–3270; $\nu(\text{C=C})$, 1600–1420; $\nu(\text{C--O})$, 1320–1210; $\nu(\text{C=O})$, 1655; $\nu(\text{CH--Ar})$, 3100–2900 and $\nu(\text{N=N})$ 1420.

Synthesis of complex $\{[Mn(ox)(H_2O)_2](azbpy)(H_2O)_2\}_n$ (**2**)

This has been synthesized using the same procedure as that of **1** using disodium oxalate (0.0167 g, 0.125 mmol) instead of disodium terephthalate. After ten days, an orange compound was



Scheme 1.

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