Structural diversity in supramolecular architectures of Mn(II) through non-covalent interactions

Ananta Kumar Ghosh, Debagyoti Ghoshal\textsuperscript{b, *}, Michael G B Drew\textsuperscript{c} & Nirmalendu Ray Chaudhuri\textsuperscript{b, *}

\textsuperscript{a} Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700 032, India
\textsuperscript{b} Department of Chemistry, Jadavpur University, Jadavpur, Kolkata 700 032, India
\textsuperscript{c} Department of Chemistry, University of Reading, Whiteknights, Reading RG6 6AD, UK

Email: icerc@iacs.res.in; debagyoti_g@yahoo.co.in

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Two mononuclear complexes of manganese(II), [Mn(OCN)\textsubscript{2}(phen)\textsubscript{2}] \textsuperscript{1} and [Mn(OCN)\textsubscript{2}(bpy)\textsubscript{2}] \textsuperscript{2} [1,10-phenanthroline (phen); 2,2'-bipyridine (bpy)], have been synthesized and characterized by single crystal X-ray analysis, infra-red spectroscopy and magnetic studies. The coordination structure of complex 2 is already reported. The cyanate anions are pendant in both the complexes. In 1, cyanate anion links manganese(II) through O-atom, whereas in 2 it coordinates through N-atom. The mononuclear fragments of 1 are built up to a supramolecular lamellar 3D architecture by π-π interactions only. On the other hand, mononuclear fragments of 2 are assembled to a 2D supramolecular brick-wall architecture by C-H···π interactions.

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Interest in the synthesis of metal-organic framework\textsuperscript{1} of desired architecture is growing due to their potential applications in the field of material science\textsuperscript{1}. It is important to know the controlling factors responsible for the building of higher dimensional supramolecular architectures\textsuperscript{2}. The covalent and non-covalent interactions\textsuperscript{3} are well-known driving forces for tuning the framework in crystal engineering\textsuperscript{4}. Among the non-covalent interactions, H-bonding\textsuperscript{5, 6} is the most useful for the packing of the crystal structure in the solid state. The role of π-π stacking and C-H···H-π interactions for the tuning\textsuperscript{7-9} of the supramolecular architecture has been paid less attention though such interactions can contribute up to 2-10 kJ mol\textsuperscript{-1} intermolecular attractive energy\textsuperscript{6}. The key factor for achieving higher dimensional network through weak interactions is the proper choice of the metal ion as well as ligand\textsuperscript{7}.

Syntheses and X-ray crystal structures of two supramolecular architectures having mononuclear fragments, [Mn(OCN)\textsubscript{2}(phen)\textsubscript{2}] \textsuperscript{1} and [Mn(OCN)\textsubscript{2}(bpy)\textsubscript{2}] \textsuperscript{2} are reported here. The coordination structure of 2 is already reported\textsuperscript{8}. Similar to the other pseudohalide, NCO/OCN anion can not only bridge the metal centers in various bridging modes\textsuperscript{9} (e.g., μ\textsubscript{1,1}; μ\textsubscript{1,2}; μ\textsubscript{1,1,3}) but also link metal ions either through N or O depending on the environment around the metal center\textsuperscript{9}. In complex 1, the cyanate ligand is linked to the Mn(II) center through O-atom, whereas in 2 this cyanate is ligated through N-atom. Among the planar chelating ligands, 1,10-phenanthroline and 2,2'-bipyridine\textsuperscript{10} are often used not only for their chelating ability but also for their ability to get involved in staking interactions in between the aryl rings. In solid state, complex 1 is extended to a supramolecular lamellar 3D architecture by π-π interactions whereas complex 2 is built up to a supramolecular brick-wall 2D structure by C-H···π interaction only.

Materials and Methods

High-purity (98%) 1,10-phenanthroline and 2,2'-bipyridine were purchased from the Aldrich Chemical Co. Inc. and were used as received. All other chemicals were of anar grade. Elemental analyses (C, H, N) were performed using Perkin-Elmer 240C elemental analyzer. IR spectra were measured from KBr pellets on Nicolet 520 FTIR spectrometer. The magnetic susceptibility was measured at 25°C using EG and G PAR 155 vibrating sample magnetometer, using [HgCo(SCN)\textsubscript{4}] as a reference material. Correction for sample holder was made by previous calibration and diamagnetic corrections were estimated from Pascal's tables\textsuperscript{11}.

Preparation of [Mn(OCN)\textsubscript{2}(phen)\textsubscript{2}] \textsuperscript{1}

A methanolic solution (5 mL) of 1,10-phenanthroline (0.396 g, 2 mmol) was mixed with an
aqueous solution (10 mL) of potassium cyanate (0.162 g, 2 mmol). Manganese chloride tetrahydrate (0.197 g, 1 mmol) in methanol (5 mL) was added to this solution dropwise with constant stirring. Thereby, a deep yellow compound separated out. Single crystals suitable for X-ray analysis were obtained by diffusing the methanolic solution (5 mL) of manganese chloride tetrahydrate on a water-methanol (2:1) layer (15 mL) of potassium cyanate and phen (2:2) in a corked tube. The deep yellow colored single crystals were deposited at the junction of the two solutions after a few weeks. Yield: 70%. Anal. Calcd for [Mn(OCN)](phen)2 (%): C, 62.48; H, 3.20; N, 16.82. Found: C, 62.42; H, 3.18; N, 16.78.

Preparation of [Mn(OCN)](bpy)2

It was synthesized by following a similar procedure adopted for complex 1 using 2,2'-bipyridine (0.312 g, 2 mmol) instead of 1,10-phenanthroline. Yellow colored single crystals of complex 2 suitable for X-ray diffraction were obtained by the diffusion process as adopted in the case of complex 1. Yield: 68%. Anal. Calcd for [Mn(OCN)](bpy)2 (%): C, 58.49; H, 3.54; N, 18.61. Found: C, 58.45; H, 3.52; N, 18.59.

Data collection, structure solution and refinement

The single crystal data collection of complex 1 was carried out at 293(3) K on a MAR research image plate system. Data analyses were made with the XDS program. The structure was solved by direct method, followed by successive Fourier and difference Fourier syntheses. Full matrix least square refinements on F2 were carried out using SHELXL-97 (ref. 13) with anisotropic displacement parameters for all non-hydrogen atoms. Data collection and structure refinement parameters for complex 1 are given in Table 1. All calculations were carried out using SHELXS 97 (ref. 14), SHELXL 97 (ref. 13), PLATON, ORTEP-32 (ref. 16) and the WinGX system, Ver. 1.64 (ref. 17). Crystallographic data are also provided in Table 1.

Results and Discussion

IR spectra of the complexes

Complex 1 shows one band at 2197 cm−1, corresponds to the ν(CN) stretching vibration indicating free CN group. The strong bands appearing at 1514 and 1425 cm−1 for 1 may be assigned as the ν(CO) stretching vibration of the cyanate ligand. The CO stretching frequency indicates that the cyanates are bound to the metal center through O atom, whereas complex 2 shows two intense bands at 2210 and 2194 cm−1 which are assigned as ν(CN) stretching vibration of the cyanate ligand. The CN stretching frequency indicates that the N-atom of cyanate is bonded to the metal center. It also shows very weak bands at 1595 and 1438 cm−1 which may be assigned as the ν(CO) stretching vibration. These stretching frequencies are comparable with the related complexes.

Description of crystal structures

Complex 1

The X-ray crystallographic data reveal that complex 1 is a mononuclear unit having composition of [Mn(OCN)](phen)2 (Fig. 1). The molecule possesses crystallographically imposed two-fold axial symmetry. Here, the Mn(II) center is six-coordinated with a distorted octahedral environment having MnO2N2 chromophore. The cyanate ligands are bound to the metal.
atom through O atom, which is not very common. The metal center is chelated by the two 1,10-phen ligands with independent Mn–N distances of 2.294(4) and 2.365(4)Å (Table 2). Two pendent OCN⁻ ligands are bonded to the metal center through O atom with Mn–O distance 2.156(4)Å, which are comparable to that of related complexes. The equatorial plane of the octahedron is formed by two N atoms of phen (N22, N22*) and two O atoms from the OCN⁻ (O31, O31*). The longer Mn–N bonds formed by the other N atoms (N11, N11*) of the chelated phen are in trans-axial position. The two OCN⁻ ligands are closely linear with Mn–O–C angles of 161.8(3)° and O–C–N angles of 177.2(6)°.

The crystal packing of 1 shows that the monomeric fragments are lined up (Fig. 2) alternately in such a way so that the aromatic rings of the phen ligand are arranged in face-to-face fashion to facilitate the formation of strong π–π interactions (Table 3) resulting a supramolecular three dimensional structure. The view along z-axis of this supramolecular architecture shows a honeycomb-like arrangement. The involvement of phen in π–π interactions delocalizes the electron cloud on the phen and thus lowers the electron density on the metal center making it more accessible towards O atom to form a bond rather than the N atom of the cyanate.

**Complex 2**

We have determined the crystal structure of complex 2 and found that all the parameters are same as those reported by Tsintsadze et al. In addition to the trivial crystal structure described in the aforesaid paper, some other interesting features related to the present studies are discussed here. The coordination structure of complex 2 is very similar to that of 1. Only difference is that bpy is used here as a chelating agent instead of phen (Fig. 3). But, complex 2 differs significantly from 1 in respect of coordination mode of the pendent NCO⁻ ligands. Here, the Mn(II) center has a distorted octahedral environment having MnN₆ chromophore. Two pendent NCO⁻ ligands are bonded to the metal center through N atom. The Mn–N bond distance is comparable with the other reported complexes. In the crystal packing of 2, each monomeric fragment is lined up alternately in such a way so that the aromatic ring of the phen ligand are arranged in face-to-face fashion to facilitate the formation of strong π–π interactions.
Table 3 — π-π (face-to-face) interactions in complex 1

<table>
<thead>
<tr>
<th>Ring(i) → Ring(j)</th>
<th>Dihedral angle (i,j) (°)</th>
<th>Slip angle (i,j) (°)</th>
<th>Distance of centroid(i) from ring(j) (Å)</th>
<th>Distance between the ring centroids of (i,j) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R(1) → R(1)'</td>
<td>0</td>
<td>18.75</td>
<td>3.514</td>
<td>3.711 (5)</td>
</tr>
<tr>
<td>R(2) → R(3)'</td>
<td>0.22</td>
<td>24.52</td>
<td>3.394</td>
<td>3.736(5)</td>
</tr>
<tr>
<td>R(3) → R(2)''</td>
<td>0.22</td>
<td>24.70</td>
<td>3.399</td>
<td>3.736(5)</td>
</tr>
</tbody>
</table>

Symmetry code: (i) = -x, -y, 1-z; (ii) = 1/2-x, 1/2+y, z; (iii) = 1/2-x, -1/2+y, z. R(i)/R(j) denotes the centroids of the i-th and j-th ring of phen: R(1) = N(11)-C(12)-C(13)-C(14)-C(15)-C(16); R(2) = N(22)-C(17)-C(18)-C(19)-C(20)-C(21); R(3) = C(15)-C(16)-C(17)-C(18)-C(24)-C(23).

Fig. 3 — Crystal packing of 2 (ref. 8) showing four adjacent C-H-π interacting monomeric fragments (dotted lines indicate C-H-π interactions) with atom labeling in one of the monomeric units (* = 1-x, 3/2-y, z).

clear unit of Mn(II) is surrounded by four mononuclear fragments joined to each other by C-H-π interactions (Table 4). The packing diagram (Fig. 3) shows, these C-H-π interactions are responsible for the formation of supramolecular two-dimensional architecture.

Magnetic study of the complexes

The room temperature (298 K) magnetic susceptibility measurements show that for complex 1, the \( \chi_M T \) value is 4.87 cm\(^3\) mol\(^{-1}\) K and that for complex 2, it is 5.30 cm\(^3\) mol\(^{-1}\) K. These values are in agreement with the typical value for one isolated Mn(II) ion (\( g = 2.00 \)). The calculated \( \mu_{eff} \) values are 6.27 and 6.54 BM for 1 and 2, respectively. The calculated \( \mu_{eff} \) values clearly indicate the presence of \( S=5/2 \) ground state of Mn(II) ion in both the complexes. In case of same metal ion, the bipyridine complex usually shows higher \( \chi_M T \) value than the phenanthroline complex.

Table 4 — C-H-π interactions in complex 2

<table>
<thead>
<tr>
<th>C-H → R(j)</th>
<th>H...R (Å)</th>
<th>&lt;C-H...R (°)</th>
<th>C...R (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C5-H5→R(1)'</td>
<td>3.096</td>
<td>109.56</td>
<td>3.519(5)</td>
</tr>
</tbody>
</table>

Symmetry code: (i) = 3/2-x, -1/2+y, z. R(i)/R(j) denotes the centroids of the i-th and j-th ring of bpy: R(1) = N(3)-C(7)-C(8)-C(9)-C(10)-C(11).

Sometimes, opposite trends are observed when extensive π-π interaction stabilizes the solid-state structure as extent of π-π interaction in phen complex is quite larger than that of the bpy complex. Here, the difference in \( \chi_M T \) value between the complexes is probably due to the supramolecular forces of the complexes as the mononuclear fragments of 1 are built up to a supramolecular 3D architecture by π-π interactions and the mononuclear fragments of 2 are assembled to a 2D supramolecular brick-wall architecture by the lower energy associated C-H-π interactions.
Conclusions
Two supramolecular architectures built by mononuclear unit comprising Mn(II), cyanate and chelated aryl ligands are reported here. In complex 2, cyanate ligand is bonded through N-atom to the metal center. But, in case of complex 1, cyanate is bonded through O atom which is rare. In crystal packing of 1, π–π interactions are responsible for the formation of solid state structure, but in 2 only C–H···π interactions are present. As the π–π interactions are more strong and directive than the C–H···π interactions, the aromatic electron clouds of phen (in case of 1) are more delocalized than that of bpy (in case of 2). This fact may be responsible for lowering of electron density on the Mn(II) center in 1 forming the rare Mn–O linkage by cyanate anion. Thus, it can be attributed that here π–π interactions play a significant role to control the coordination environment of Mn(II) by changing the donor site of the ancillary cyanate ligand, hence accounting its flexidentate behaviour.

Supplementary Data
X-ray crystallographic data in CIF format for 1 have been deposited with the Cambridge Crystallographic Data Center (CCDC number 275469). Copies of the data can be obtained free of charge at www.ccdc.cam.ac.uk/contents/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK Fax: (internet) +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

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References