Journal of Molecular Structure 1029 (2012) 169–174

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Single pot synthesis of pyridine-*N*-oxide based polymeric complexes of cadmium and manganese: Crystal structure and luminescence property

Sandip Mondal [a], Averi Guha [b], Eringathodi Suresh [c], Atish Dipankar Jana [d,*], Arpita Banerjee [e,*]

[a] Department of Chemistry, Behala College, Parnashree, Kolkata 700 060, India
[b] Department of Chemistry, University of Calcutta, 92, A.P.C. Road, Kolkata 700 009, India
[c] Analytical Science Discipline, Central Salt and Marine Chemicals Research Institute, G.B. Marg, Bhavnagar 364 002, India
[d] Department of Physics, Behala College, Parnashree, Kolkata 700 060, India
[e] Department of In Vitro Carcinogenesis and Cellular Chemotherapy, Chittaranjan National Cancer Institute, 37 S.P. Mukherjee Road, Kolkata 700 026, India

HIGHLIGHTS

- Two polymeric Cd^{II} and Mn^{II} with pyridine-*N*-oxide have been synthesized.
- Structural characterization reveals both complexes have 2D layer structure.
- Fluorescence study and thermal analysis has been performed.
- The observed luminescence is a consequence of LMCT.

ARTICLE INFO

Article history:
Received 9 May 2012
Received in revised form 3 July 2012
Accepted 4 July 2012
Available online 14 July 2012

Keywords:
Coordination polymer
Pyridine-*N*-oxide
Crystal structure
Thermal study
Luminescence property

ABSTRACT

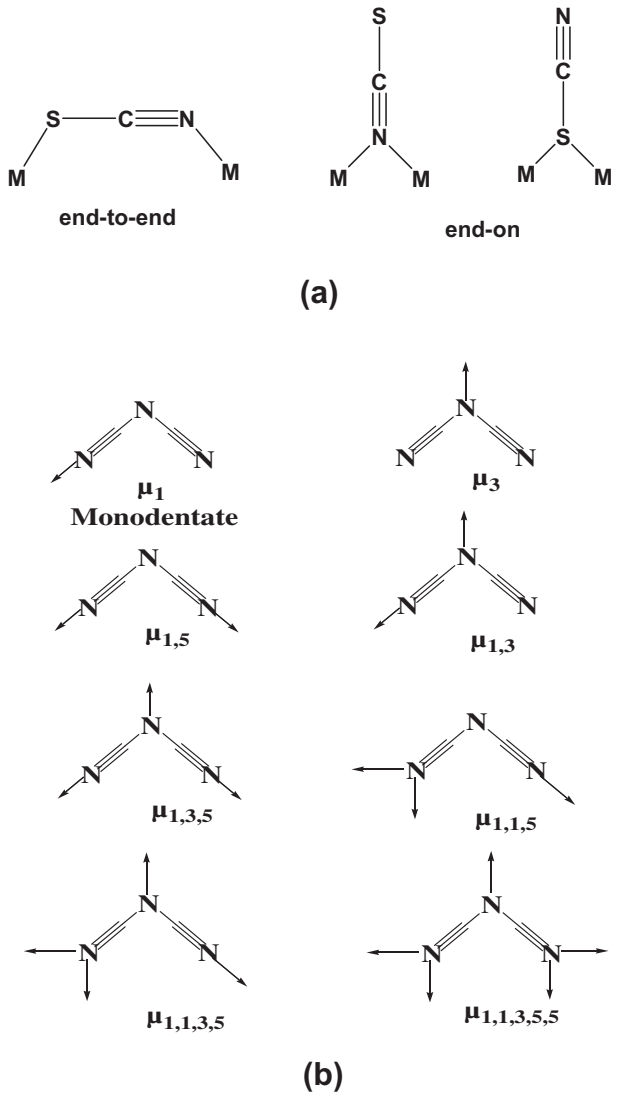
Two new polymeric complexes of cadmium(II) and manganese(II) with Pyridine-*N*-oxide (pyo) mediated by thiocyanate and dicyanamide (dca) anions have been synthesized and characterized by X-ray single crystal structure analysis. The structural analyses reveal that complexes $[Cd(pyo)_2(SCN)_2]_n$ (**1**) and $[Mn(pyo)_2(dca)_2]_n$ (**2**) [where, pyo = pyridine-*N*-oxide; dca = dicyanamide] are 2D coordination polymers. In complex **1** hexa-coordinated Cd(II) centers posses distorted octahedral coordination environments. Each Cd(II) is coordinated by four SCN^- in end to end fashion forming a zigzag chain and two pyo monodentate ligands bridge two adjacent Cd(II) centers leading to a two-dimensional sheet structure. In complex **2** hexa-coordinated Mn(II) centers posses octahedral coordination environments. The coordination polymer constitute a 2D polymeric sheet and has a (4, 4) grid network architecture Successive stacking of coordination polymeric sheets are enforced by inter layer OH···O and OH···N hydrogen bonding. The luminescence properties of these two polynuclear complexes in solid state were studied and complex **1** exhibits higher luminescence intensity than **2**.

1. Introduction

The construction of polymeric coordination network is an upcoming field of research [1,2]. Wide varieties of network topologies can be created through proper ligand selection and with the use of different transition metals. In particular the chemistry and applications of *N*-oxides received much attention due to their usefulness as synthetic intermediates and their biological importance [3]. Heterocyclic *N*-oxides are also useful as protecting groups, auxiliary agents, oxidants [3], ligands in metal complexes [4] and catalysts [3]. The N–O moiety of pyridine-*N*-oxides possesses a unique functionality which can act effectively as a push electron donor and as a pull electron acceptor group. On the other hand, pseudo halides like dicyanamide (dca, $N(CN)_2^-$) or thiocyanate (SCN^-) have long been known for their versatile coordination motifs which leads to coordination polymers of different dimensionality and polymer-based supramolecular entities. Dicyanamide, $[N(CN)_2]^-$ may be coordinated to metal ions in various modes viz, monodentate bonding through a nitrile nitrogen, end-to-end ($\mu_{1,5}$) bridging through two nitrile nitrogen atoms, tris monodentate ($\mu_{1,3,5}$) bridging of the three metal atoms, as well as unusual μ_4 coordination ($\mu_{1,1,3,3}$) where one nitrile nitrogen atom binds to two metal atoms and μ_5 bridge ($\mu_{1,1,3,5,5}$) with both nitrile atoms connected to two metal centers [5–19] and thiocyanate anion, exhibited ambidentate character of end-to-end or end-on coordination modes [20,21] (Scheme 1). These pseudohalides were expected to play a key role in the designing of poly-metallic coupling system. Interest in the structure and properties of complexes with thiocyanate, dicyanamide and aromatic

* Corresponding authors. Tel.: +91 9883010190.
E-mail address: banerjee_arpita@rocketmail.com (A. Banerjee).

0022-2860/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molstruc.2012.07.006



Scheme 1. Few possible coordination modes of (a) thiocyanate and (b) dicyanamide.

N-oxide as bridging ligands led us to synthesize and characterize complexes $[Cd(pyo)_2(SCN)_2]_n$ (**1**) and $[Mn(pyo)_2(dca)_2]_n$ (**2**) [where, pyo = pyridine-*N*-oxide; dca = dicyanamide]. As part of our investigation on polymeric coordination networks we are reporting herein two polymeric complexes of cadmium (II) and manganese (II) constructed through the dicyanamide and thiocyanate ligands with pyridine-*N*-oxide.

2. Experimental

2.1. Materials

High purity Pyridine-*N*-oxide purchased from Alfa Aesar, sodium dicyanamide and sodium thiocyanate were from Fluka; and Cadmium (II) chloride and Manganese (II) Chloride from Aldrich Chemical Company Inc. and they were used as received. All other chemicals were of AR grade.

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 240C elemental analyzer and cadmium (II) and Manganese (II) content were estimated gravimetrically. Infrared spectra were recorded on KBr disks (400–4000 cm^{-1}) with a Perkin-Elmer RXI FTIR spectrophotometer. UV–VIS spectra were measured on a Hitachi U-3501 spectrophotometer. Fluorescence spectra of the solid complexes were recorded in a Perkin-Elmer model LS 55 luminescence spectrometer. Thermal analyses (TG–DTA) were performed on a TGA/SDTA851 METTLER–TOLEDO thermal analyzer under a dynamic nitrogen environment (flow rate: 40 cc min^{-1}). All the samples were heated in platinum crucible at a rate of 10 °C min^{-1} from 30 to 700 °C.

2.3. Syntheses of the complexes

2.3.1. $[Cd(pyo)(SCN)_2]_n$ (*1*)

A methanolic solution (5 mL) of Pyridine-*N*-oxide (0.095 g, 1 mmol) was slowly added into a hot methanolic solution (10 mL) of cadmium(II) chloride (0.201 g, 1 mmol) and to it an aqueous solution of sodium thiocyanate (0.081 g, 1 mmol) was added dropwise. The resultant mixture was stirred for 2 h and filtered. The filtrate was kept in $CaCl_2$ containing desiccator and colorless single crystals suitable for X-ray analysis were obtained from the filtrate after a few days. Yield 93%. Anal. Calcd.: C_7 H_5 Cd N_3 O S_2; C, 25.97; H, 2.17; N, 12.98; Cd, 34.60; %. Found: C, 25.94; H, 2.17; N, 12.97; Cd, 34.45; %. IR data: ν = 3595 (s), 3106 (m), 2306 (s), 2171 (s), 1468 (s), 1363 (s), 1241 (m) cm^{-1}.

2.3.2. $[Mn(pyo)(dca)_2(H_2O)]_n$ (*2*)

It was synthesized adopting the same procedure as in case of **1** with Manganese(II) Chloride (0.125 g, 1 mmol) and sodium dicyanamide (0.089 g, 1 mmol) instead of cadmium(II) chloride and sodium thiocyanate respectively. The filtrate was kept in $CaCl_2$ containing desiccators. Off white single crystals suitable for X-ray analysis were obtained from the filtrate after a few days. Yield 92%. Anal. Calcd.: C_9 H_7 Mn N_7 O_2; C, 36.01; H, 2.34; N, 32.66; Mn, 18.36 %. Found: C, 35.99; H, 2.32; N, 32.38; Mn, 18.32%. IR data: ν = 3556(s), 3126 (w), 2314 (s), 2172(s), 1472 (m), 1362 (m), 1206 (w) cm^{-1}.

2.4. X-ray structure determination

Diffraction data for all the structures reported were collected at room temperature on a Bruker Smart CCD diffractometer equipped with graphite – monochromated Mo Kα radiation (λ = 0.71073 Å) at 150 K. Cell refinement, indexing and scaling of the data set were carried out using packages Bruker SMART APEX and Bruker SAINT package [22]. The structures were solved by direct methods and subsequent Fourier analyses [23] and refined by the full-matrix least-squares method based on F^2 with all observed reflections using SHELXL 97 [24] and SIR-92 [25] softwares. For all structures, all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were generated in idealized positions, riding on the carrier atoms, with isotropic thermal parameter and were refined riding on the carrier atoms with isotropic thermal parameters. All the calculations were performed using the WinGX System, Ver 1.80.05.[26], PLATON99 [27], ORTEP3 [28] programs. Crystal data and details of data collection and refinement for the structures reported are summarized in Table 1.

3. Results and discussion

The complexes were prepared by using Cadmium (II) chloride and Manganese (II) Chloride and the Heterocyclic *N*-oxides ligand (Pyridine-*N*-oxide) in presence of sodium thiocyanate (compound **1**) or sodium dicyanamide (compound **2**) maintaining a stoichiometric ratio of 1:1:1. All the syntheses were conducted in aqueous methanol medium.

Table 1
Crystallographic data and details of structure refinements for complexes **1** and **2**.

	1	2
Empirical formula	C_7 H_5 Cd N_3 O S_2	C_9 H_7 Mn N_7 O_2
Formula weight	323.69	300.16
Crystal system	Triclinic	Orthorhombic
Space group	*P*-1 (No. 2)	$P2_12_12_1$ (No. 19)
a (Å)	7.6502(10)	7.5118(9)
b (Å)	8.3613(11)	12.9507(16)
c (Å)	8.8582(11)	13.1305(16)
α (°)	62.799(2)	90.00
β (°)	87.299(2)	90.00
γ (°)	87.423(2)	90.00
Volume (Å^3)	503.22(11)	1277.4(3)
Z	2	4
D_{calcd} (mg m^{-3})	2.136	1.561
μ Mo Kα (mm^{-1})	2.551	1.043
F(000)	312	604
θ_{max} (°)	28.2	28.3
Reflns collected	4220	7599
Unique reflections	2240	1738
R_{int}	0.016	0.025
Observed $I > 2\sigma(I)$	2178	1690
Parameters	127	180
Goodness of fit (*F*2)	1.12	1.157
*R*1 ($I > 2\sigma(I)$)	0.0262	0.0590
*wR*2	0.0677	0.1490
$\Delta\rho$ (e/Å^3)	1.06, −0.97	1.85, −0.32

3.1. Crystal structures of complexes *1* and *2*

The X-ray crystallographic analysis of **1** reveals that a thiocyanate and pyridine-*N*-oxide (pyo) bridged 2D coordination polymeric sheet of Cd(II) (Fig. 1) constitute the *ab* crystal plane. Cd(II) ion occupies the centre of inversion and two crystallographically independent thiocyanate anion and a pyridine-*N*-oxide molecule is coordinated to it. The polymeric structure can be thought of as the network of dinuclear $Cd(II)_2(pyo)_2$ secondary building units (SBU) which are successively joined along two mutually perpendicular directions in the *ab* plane by thiocyanate anions [29].

The dinuclear $Cd(II)_2(pyo)_2$ secondary building units are the result of double bridging of adjacent Cd(II) centers by O atoms of two inversion symmetry related pyo molecules. The Cd–Cd distance in the SBU is 3.878 Å and Cd–O1–Cd* (* = 1 − *x*, 1 − *y*, −*z*) angle is 111.56°. The $Cd(II)_2(pyo)_2$ units are doubly bridged by thiocyanate anions both along the *a* and the *b* axis. The Cd–Cd separation along the *a* axis is 5.883 Å and that along the *b* axis is 5.946 Å. The Cd(II) centres posses distorted octahedral coordination environments. Terminal S atom of a thiocyanate anion, the N atom of its symmetry related counterpart along with two pyridine-*N*-oxide O atoms satisfies the equatorial coordination of the Cd(II) octahedron.

Two *trans* axial coordination sites are occupied by S atoms of two symmetry related thiocyanate anion. The S–Cd–S* [* = 1 − *x*, 1 − *y*, −*z*] angle in the equatorial plane is 112.10° and the O–Cd–O** [** = 1 − *x*, 2 − *y*, −*z*] angle is 68.44°. Cd–O, Cd–S and Cd–N distances and other bond distances and angle values fall in the usual range (Table 2) typical of Cd-SCN complexes. Successive coordination polymeric sheets are stacked along the crystallographic *c*-axis (Fig. 2). It is the S···S interaction [distance between nearest S and S$^{\#}$ on neighboring layers is 3.7401(12) Å, # = 1 − *x*, 1 − *y*, 1 − *z*] which is active between successive layers. Interestingly even though there was the possibility of π···π interaction among the pyo molecules on adjacent layers, it is the S···S interaction which

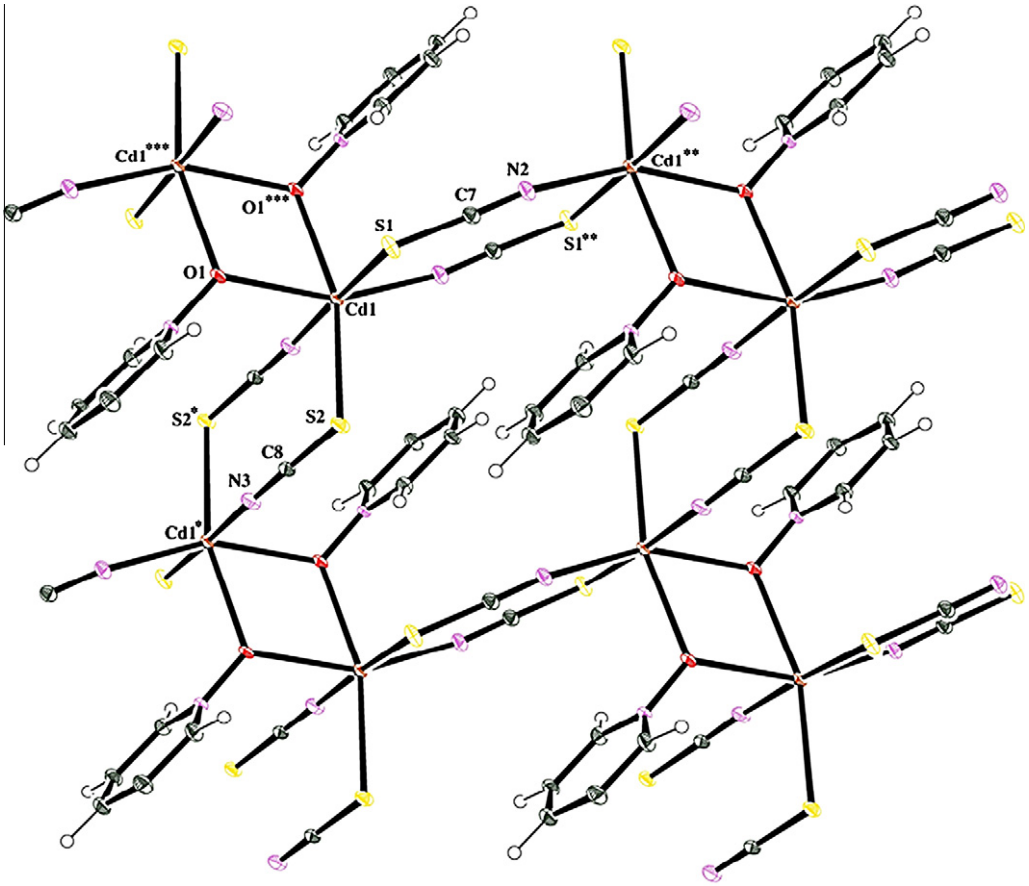


Fig. 1. ORTEP diagram of the complex **1** (30% ellipsoidal probability) with atom numbering scheme [* = 2 − *x*, 1 − *y*, −*z*; ** = 1 − *x*, 2 − *y*,−*z*; ***=1 − *x*, 1 − *y*, −*z*].

Table 2
Selected bond lengths (Å) and angles (°) for complex **1**.

Bond distances			
Cd1–S1	2.7340(9)	Cd1–N3_c	2.300(3)
Cd1–S2	2.6379(9)	S1–C7	1.650(4)
Cd1–O1	2.322(3)	O1–N1	1.343(4)
Cd1–O1_a	2.368(2)	N2–C7	1.153(4)
Cd1–N2_b	2.268(3)		
Bond angles			
S1–Cd1–S2	83.78(3)	O1–Cd1–N2_b	154.95(8)
S1–Cd1–O1	90.37(6)	O1–Cd1–N3_c	88.02(10)
S1–Cd1–O1_a	96.61(6)	O1_a–Cd1–N2_b	86.52(9)
S1–Cd1–N2_b	91.69(6)	N2_b–Cd1–N3_c	91.52(10)
S1–Cd1–N3_c	175.58(7)	Cd1–S1–C7	100.11(12)
S2–Cd1–O1	92.94(6)	Cd1–O1–N1	122.26(18)
S2–Cd1–O1_a	161.37(7)	Cd1–O1–Cd1_a	111.56(10)
S2–Cd1–N2_b	112.10(6)	Cd1_a–O1–N1	121.2(2)
S2–Cd1–N3_c	92.19(7)	Cd1_b–N2–C7	164.4(2)
O1–Cd1–O1_a	68.44(9)	Cd1_c–N3–C8	159.3(3)

Symmetry codes: $a = 1 - x, 1 - y, -z$; $b = 1 - x, 2 - y, -z$; $c = 2 - x, 1 - y, -z$

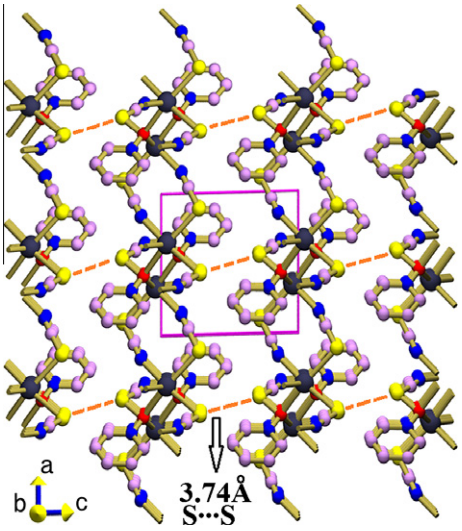


Fig. 2. Stacking of coordination polymeric layers of **1** along the crystallographic *c*-axis. Interlayer S···S interaction has been shown in broken lines.

Table 3
Selected bond lengths (Å) and angles (°) for complex **2**.

Bond distances			
Mn1–O1	2.210(4)	Mn1–N4_c	2.207(5)
Mn1–O2	2.243(4)	O1–N1	1.340(6)
Mn1–N2	2.185(5)	O2–H2D	0.92(7)
Mn1–N5	2.200(5)	O2–H2C	0.81(7)
Mn1–N7_a	2.211(5)	N1–C1	1.327(7)
Bond angles			
O1–Mn1–O2	87.22(18)	N2–Mn1–N4_c	94.6(2)
O1–Mn1–N2	90.43(18)	N5–Mn1–N7_a	93.36(18)
O1–Mn1–N5	83.96(17)	N4_c–Mn1–N5	92.3(2)
O1–Mn1–N7_a	176.39(17)	N4_c–Mn1–N7_a	90.5(2)
O1–Mn1–N4_c	92.0(2)	Mn1–O1–N1	121.0(3)
O2–Mn1–N2	86.28(18)	Mn1–O2–H2C	111(5)
O2–Mn1–N5	86.79(18)	Mn1–O2–H2D	123(4)
O2–Mn1–N7_a	90.21(18)	H2C–O2–H2D	116(7)
O2–Mn1–N4_c	178.9(2)	Mn1_d–N4–C7	163.4(5)
N2–Mn1–N5	171.28(19)	Mn1–N5–C8	155.0(5)
N2–Mn1–N7_a	91.95(19)	Mn1_b–N7–C9	166.3(5)

Symmetry codes: $a = -1 + x, y, z$; $b = 1 + x, y, z$; $c = 1 - x, -1/2 + y, 3/2 - z$; $d = 1 - x, 1/2 + y, 3/2 - z$

is preferred in the assembly. It was recently reported that S···S interaction involving SCN^- ions is a common phenomena and optimal S···S distance is 3.86 Å [30]. (See Table 3).

Literature survey unveils a Cd(II) complex of SCN^- and 4-methyl pyridine-*N*-oxide having an isomorphous structure with **1** which also crystallizes in the same space group.[31] In this complex the unit cell along the *c*-axis is distinctly lenthened (by 0.732 Å) compared to **1** due to the use of 4-methyl pyridine-*N*-oxide instead of unsubstituted pyridine-*N*-oxide. Methyl groups are directed away from the mean plane of the coordination polymer, and successive polymeric planes stack along the crystallographic *c*-axis. The increase in the cell dimension along the *c*-axis is the consequence of these additional methyl groups. There is also a Ni(II) complex of SCN^- and 4-methyl pyridine-*N*-oxide which is isomorphous to the Cd(II) complex and have nearly same cell lengths as that of the Cd(II) , SCN^- and 4-methyl pyridine-*N*-oxide complex. [29].

The X-ray crystallographic analysis of **2** reveals a di-cyanomido (dca) bridged 2D coordination polymer with Mn(II) centres acting as nodes (Fig. 3) Hexa-coordinated Mn(II) centres posses octahedral coordination environments. Terminal N atoms of three dicyanamide molecules and a O atom contributed by a pyridine-*N*-oxide molecule satisfy four equatorial coordination sites of Mn(II) centres. Trans *axial* sites of Mn(II) octahedral coordination environment are occupied by the terminal N atom of a fourth bridging dicyanamide molecule and O atom of a coordinated water molecule. Mn–N (dca) distances fall in the range 2.185(5) Å–2.210(4) Å and the Mn-O (pyridine-*N*-oxide) distance is 2.210(4) Å. The axial Mn–O (water) distance is 2.243(4) Å. Mn(II) occupies the centre of inversion and hence among four bridging dicyanamide molecules only two are crystallographically independent.

The coordination polymer constitute the *ab* crystal plane and has a (4, 4) grid network architecture. Mn-Mn separation along crystallographic *a*-axis is 7.512 Å and that along the *b*-axis is 8.451 Å. Successive coordination polymeric sheets are stacked along the crystallographic *c*-axis (Fig. 4). This stacking is enforced by inter layer OH···O and OH···N hydrogen bonding forces (Table 4) in which the coordinated water oxygen atom acts as donor.

Literature survey reveals a cobalt(II) complex having same set of ligands as in **2** but with different topology [32]. The reported cobalt complex is a 1D polymeric chain along crystallographic *b*-axis where the successive metal centers are doubly bridged by two dicyanamide ions ($\mu_{1,5}$ bridging). Co(II) centers are octahedrally coordinated to four N atoms from four different dicyanamide ions constituting the equatorial plane and the trans axial sites are occupied by two O-atoms of pyridine-*N*-oxide molecules. Pyridine moieties are aligned perpendicular to the chain axis and are so diposed that heterocyclic rings from adjacent chains interact through strong $\pi\cdots\pi$ interaction (pyridine ring centroid–centroid distance 3.9133(17) Å and dihedral angle is 0.0°). This lead to supramolecular 2D sheets in the (−101) plane. On the other hand in **2**, a 2D polymeric sheet is obtained where four dicyanamide ions connect successive Mn(II) centers in the crystallographic *ab* plane and hydrogen bonding interaction is operative instead of $\pi\cdots\pi$ interaction between successive polymeric sheets. The differences in the stoichiometric ratio during synthesis between Co(II) complex (Co:py:dca ratio is 1:2:2) [32] and **2** (Mn:pyo:dca stoichimetric ratio is 1:1:1) can be attributed to the differences in the differences in the topology of the coordination assembly respective metal complexes. Another colsely realed 2D coordination polymer of Cu(II) [33] based on 4-nitro-pyridine-*N*-oxide and dicyanamide (Cu:4-nitro-pyridine-*N*-oxide:dca stoichimetric ratio is 1:1:2) was repoted earlier where double layer structure of doubly-bridged dca dinuclear Cu(II) units joined via single bridged dca anions in $\mu_{1,5}$ mode. 4-pyridine-*N*-oxide molecules hanging on both sides of the layer where the O-atom of this ligand satisfy the axial site

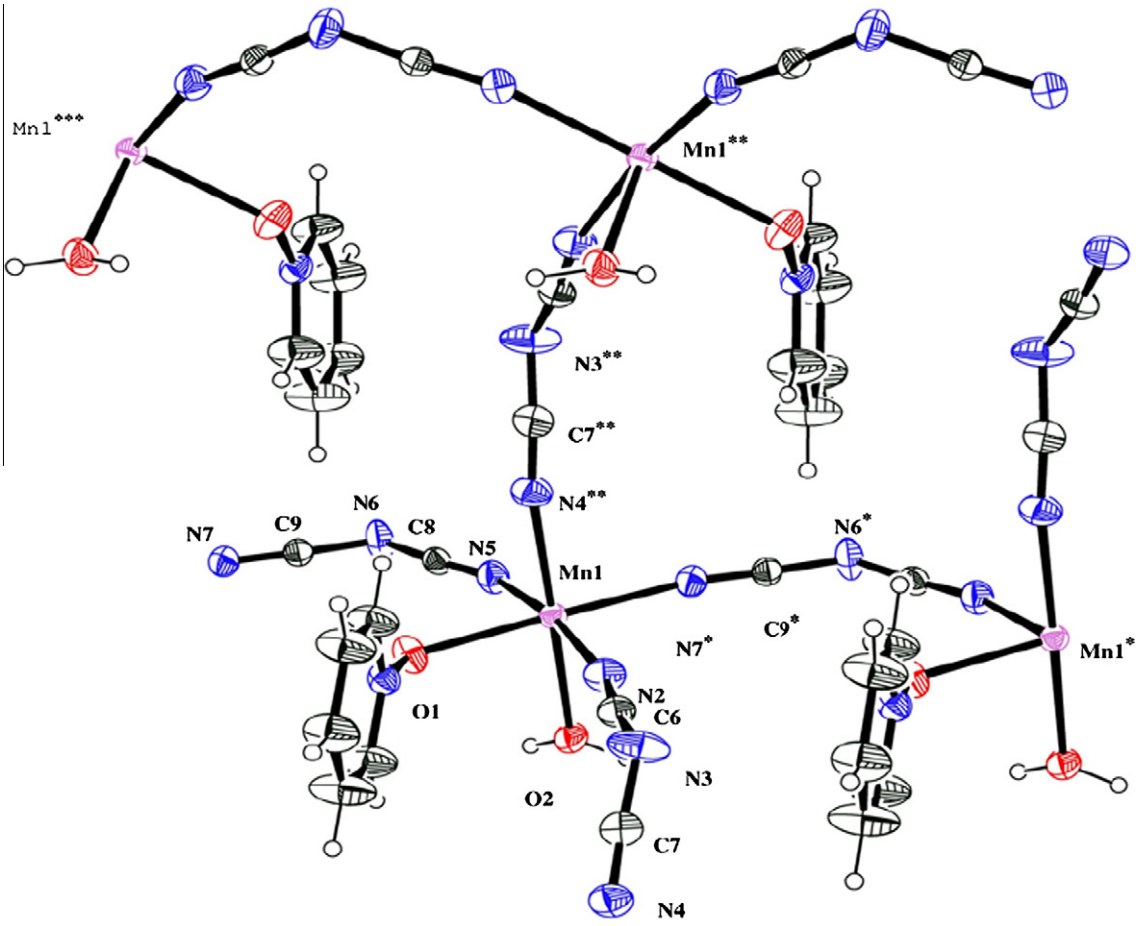


Fig. 3. ORTEP diagram of the complex **2** (30% ellipsoidal probability) with atom numbering scheme [* = −1 + *x*, *y*, *z*; ** = 1 − *x*, −1/2 + *y*, 3/2 − *z*; *** = 2 − *x*, −1/2 + *y*, 3/2 − *z*].

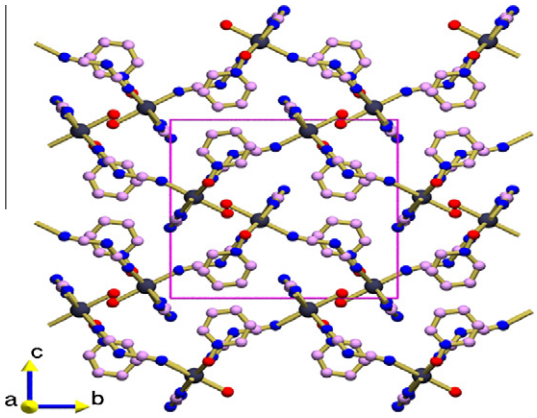


Fig. 4. Stacking of coordination polymeric layers of **2** along the crystallographic *c*-axis.

of Cu(II) square pyramidal coordination environemnt. Successive layers are stacked by N–O···π (O···π separation is 3.140 Å) interaction involving the nitrate group and the pyridine ring.

3.2. Absorption and fluorescence properties

Solid-state absorption spectra of the both the complexes were recorded at room temperature (SI File). The excitation wavelengths were selected at 415 and 457 nm which is corresponding to the λ_{max} (absorption) of complexes **1** and **2** respectively. Both **1** and **2** exhibit strong fluorescence emission in the solid state. The maximum emission peak is located at 580 nm and 616 nm for **1** and **2** respectively (Fig. 5). The broad and unstructured pattern of the emission bands might be attributed to a charge-transfer emission and probably it is LMCT (ligand-to-metal charge transfer) [34–38].

3.3. Thermal stabilities of complexes *1* and *2*

Thermo-gravimetric analyses were carried out to evaluate the solid state thermal properties of the compounds and to identify the end products. Thermal stability of the complexes **1** and **2** was found to be different (SI File). Complex **1** is thermally stable up to ~220 °C whereas **2** is only up to ~140 °C. On further heating complex **1** produces some unidentified product at the end at 650 °C, whereas complex **2** on most probably generates MnO (Calc.

Table 4
Hydrogen bond distances (Å) and angles (°) for **2**.

D–H···A	D–H (Å)	H–A (Å)	D–A (Å)	<D–H···A (°)	Symmetry
O2–H2C···N2	0.81(7)	2.42(7)	3.186(7)	160(6)	1/2 + *x*, 1/2 − *y*, 1 − *z*
O2–H2D···O1	0.92(7)	1.81(8)	2.717(6)	171(6)	−1/2 + *x*, 1/2 − *y*, 1 − *z*

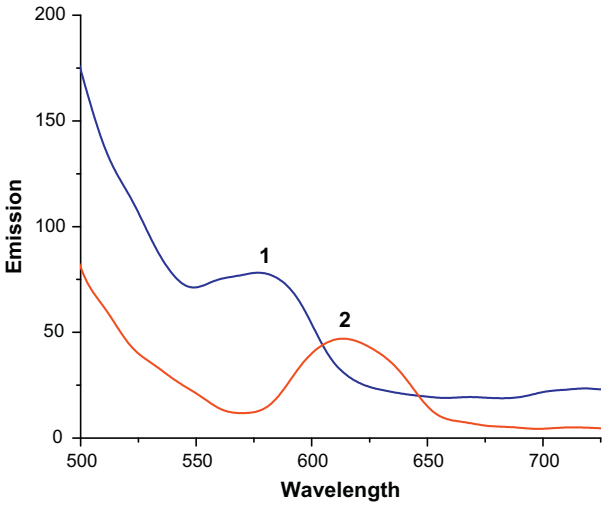


Fig. 5. Emission spectra of **1** and **2** at room temperature in solid state.

wt loss = 76.3% ; Expt. wt loss = 74.3%) as end product at around 650 °C.

4. Conclusion

Complexes **1** and **2** were synthesized using pyridine-*N*-oxide as an organic co-ligand in a single pot at room temperature. It has been found from crystal structure analysis that in **1** pyo acts as a bridging ligand between two cadmium centers, but in **2** pyo binds to manganese in mono-dentate fashion. Both the coordination polymers possess 2D sheet structures. Interestingly, in case of complex **1** only the S···S interaction seems to be operative between the adjacent sheets although the possibility of π···π interaction is very high. In case of complex **2** the stacking of successive 2D sheets are enforced by hydrogen bonding. Investigation of thermal property showed that complex **2** is less sable than **1**. The fluorescence properties of the two polymeric complexes were investigated in solid state. Both the complexes exhibited intense emission band at room temperature. Complex **2** has a lower fluorescent intensity than **1** and it has been assumed that the observed luminescence was a consequence of LMCT (ligand-to-metal charge transfer). The synthesized polymeric compounds have potentials to be applied as photoactive material as they demonstrates strong emission band at room temperature.

Acknowledgements

This work is supported by the UGC Major Research Project, (F.No. 34-308/2008 (SR) Dated: 31.12.2008). A.B is grateful to Dr. Debasis Das; Associate Professor in Chemistry, Department of Chemistry, University of Calcutta, for his valuable suggestions and constant encouragement.

Appendix A. Supplementary material

CCDC <858079, 858080> contain the supplementary crystallographic data for <**1**, **2**>. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, 287 Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2012.07.006.

References

[1] (a) S.R. Batten, R. Robson, Angew. Chem. Int. Ed. Engl. 37 (1998) 1460; (b) A.J. Blake, N.R. Champness, P. Hubberstey, W-S. Li, M. Schröder, M.A. Withersby, Coord. Chem. Rev. 183 (1999) 117.
[2] L. James, Chem. Soc. Rev. 32 (2003) 276.
[3] (a) A. Albini, S. Pietra, Heterocyclic N-Oxides, CRC Press, Boca Raton, 1991; (b) A. Albini, Synthesis 263 (1993).
[4] C.J. O'Connor, E. Sinn, R.L. Carlin, Inorg. Chem. 16 (1977) 3314.
[5] S.R. Batten, K.S. Murray, Coord. Chem. Rev. 246 (2003) 103.
[6] E. Colacio, I.B. Maimoun, F. Lloret, J. Suárez-Varela, Inorg. Chem. 44 (2005) 3771.
[7] G.A. Van Albada, S. Tanase, A. Mohamadou, I. Mutikainen, U. Turpeinen, J. Reedijk, Polyhedron 25 (2006) 2236.
[8] P. Alborés, E. Rentschler, Inorg. Chem. 47 (2008) 7960.
[9] H. Köhler, Z. Anorg, Allg. Chem. 331 (1964) 237.
[10] H. Köhler, B. Seifert, Z. Anorg, Allg. Chem. 344 (1966) 63.
[11] H. Köhler, H. Hartnung, A.M. Golub, Z. Anorg, Allg. Chem. 403 (1974) 41.
[12] H. Köhler, A. Kolbe, G. Lux, Z. Anorg, Allg. Chem. 428 (1977) 103.
[13] A.J. Civadze, H. Köhler, Z. Anorg, Allg. Chem. 510 (1984) 31.
[14] M. Hvastijová, J. Kohout, H. Wusterhausen, H. Köhler, Z. Anorg, Allg. Chem. 510 (1984) 37.
[15] S.R. Batten, P. Jensen, B. Moubaraki, K.S. Murray, R. Robson, Chem. Commun. 439 (1998).
[16] M.R. Pederson, A.Y. Liu, T. Baruah, E.Z. Kurmaev, A. Moewes, S. Chiuzbian, M. Neumann, K.L. Stevenson, D. Ederer, Phys. Rev. B 66 (2002) 014446.
[17] M. Kurmoo, C.J. Kepert, New J. Chem. 22 (1998) 1515.
[18] J.L. Manson, C.R. Kmety, Q.Z. Huang, J.W. Lynn, G.M. Bendele, S. Pagola, P.W. Stephens, L.M. Liable Sands, A.L. Rheingold, A.J. Epstein, J.S. Miller, Chem. Mater. 10 (1998) 2552.
[19] J.P. Costes, G. Novitchi, S. Shova, F. Dahan, B. Donnadieu, J.P. Tuchague, Inorg. Chem. 43 (2004) 7792.
[20] S.K. Dey, N. Mondal, M.S. El Fallah, R. Vicente, A. Escuer, X. Solans, M. Font-Bardia, T. Matsushita, V. Gramlich, S. Mitra, Inorg. Chem. 43 (2004) 2427.
[21] J.M. Shi, W. Xu, B. Zhao, P. Cheng, D.Z. Liao, X.Y. Chen, Eur. J. Inorg. Chem. 55 (2005).
[22] Bruker, (2000). SMART, SAINT. Software Reference Manual Bruker AXS Inc. Madison, Wisconsin, USA.
[23] G.M. Sheldrick, Acta Crystallogr. Sect. A. 64 (2008) 112.
[24] G.M. Sheldrick, SHELXL 97, Program for Crystal Structure Refinement; University of Gottingen, Germany, 1997.
[25] SIR-92 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Cryst. 27 (1994) 435.
[26] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
[27] A.L. Spek, PLATON, Molecular Geometry Program, University of Utrecht, The Netherlands, 1999.
[28] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
[29] J.M. Shi, Z. Liu, C.J. Wu, H.Y. Xu, L.D. Liu, J. Coord. Chem. 59 (2006) 1883.
[30] R. Ghosh, A.D. Jana, S. Pal, G. Mostafa, H.K. Fun, B.K. Ghosh, Cryst. Eng. Commun. 9 (2007) 353.
[31] J.M. Shi, Y.M. Sun, Z. Liu, L.D. Liu, Chem. Phys. Lett. 84 (2006) 418.
[32] D. Ghoshal, G. Mostafa, T.K. Maji, E. Zangrando, Tian-Huey Lu, J. Ribas, N.R. Chaudhuri, New J. Chem. 28 (2004) 1204.
[33] G.A. van Albada, I. Mutikainen, U. Turpeinen, J. Reedijk, Inorg. Chem. Commun. 9 (2006) 441.
[34] A.J. Lan, L. Han, D.Q. Yuan, F.L. Jiang, M.C. Hong, Inorg. Chem. Commun. 10 (2007) 993.
[35] S. Dalai, P.S. Mukherjee, G. Rogez, T. Mallah, M.G.B. Drew, N.R. Chaudhuri, Eur. J. Inorg. Chem. (2002) 3292.
[36] S. Dalai, P.S. Mukherjee, E. Zangrando, F. Lioret, N.R. Chaudhuri, Dalton Trans. (2002) 822.
[37] J. Tao, J.X. Shi, M.L. Tong, X.X. Zhang, X.M. Chen, Inorg. Chem. 40 (2001) 6328.
[38] N.N. Emmanuel, W. Liu, J.L. Zuo, X.Z. You, Trans. Met. Chem. 31 (2006) 837.