Inorganica Chimica Acta 443 (2016) 224–229

Contents lists available at ScienceDirect

Inorganica Chimica Acta

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

Manganese(II) coordination polymer having pyrazine and μ-phenolato bridging: Structure, magnetism and biological studies

Subrata K. Dey [a,*], Madhumita Hazra [a], Laurence K. Thompson [b], Animesh Patra [c]

[a] Department of Chemistry, Sidho-Kanho-Birsha University, Purulia 723 104, WB, India
[b] Department of Chemistry, Memorial University, St. John's, Newfoundland A1B 3X7, Canada
[c] Department of Chemistry, Midnapore College, Midnapore 721101, WB, India

ARTICLE INFO

Article history:
Received 30 May 2015
Received in revised form 26 November 2015
Accepted 6 January 2016
Available online 12 January 2016

Keywords:
Manganese (II) coordination polymer
Crystal structure
Magnetism
Antibacterial studies

ABSTRACT

The manganese(II) coordination polymer, {[Mn(L)(pyz)]ClO_4·2(H_2O)}*n*. (**1**) has been synthesized from a mixture of $Mn(ClO_4)_2$·6H_2O, Schiff base HL (derived from the condensation of 4-aminoantipyrine and salicylaldehyde) and pyrazine (pyz). Its molecular structure was determined by single crystal X-ray diffraction, which reveals that the polymeric structure consists of simultaneous Mn–Pyz–Mn and Mn–O (phenoate)–Mn bridges between the metal centers. Variable temperature magnetic studies give $g = 2.037(4)$, $J = -1.90(4)\ cm^{-1}$, $\vartheta = 0.5$ K values, using a simple dinuclear Mn–Mn model, and indicates that the major exchange pathway is via the two phenoxide bridges and the pyrazine has little influence. The coordination polymer also shows enhanced antibacterial activity compared with the standard antibiotic levofloxacin.

1. Introduction

The crystal engineering of solid-state materials is of ever increasing interest to chemists and material scientists alike [1]. The main goal has been to determine the topology (i. e. 1-, 2- or 3-dimensional structure) formed by a given set of components by the selection of metal nodes and multifunctional ligands [2–4]. Heterocyclic phenazones and their derivatives are known to act as monodentate, bidentate or tridentate ligands when coordinated to metal ions [5–7]. Transition metal complexes of Schiff bases are of growing importance in co-ordination chemistry, attributable to recent observations in antibacterial, antifungal and oxygen carrier properties and of those aminopyrines are commonly administered intravenously to detect liver disease [8] in clinical treatment. Also, they are particularly interesting as promising ligands for the building of polynuclear complexes as models to bioinorganic systems [9] as well as some interesting catalytic [10] and physicochemical properties [11], such as electrical conductivity [10] and magnetism [12]. The ability of pyrazine (pyz) to act as exo-bidentate ligands is well established [13–16]. It is a good candidate for designing and synthesizing oligomeric and polymeric complexes because of their good bridging ability [17]. Many examples exist where pyz acts as a linear rod-like spacer between metal centers to form 1-D chain and 2-D square-grid polymers with a wide variety of structural types with transition metals [17,18]. Crystal structure reports based on aminoantipyrine Schiff bases are very limited. Instead of many compounds in the literature including two monomeric Cu(II) [19] structure with aminoantipyrine based Schiff base ligand, our search on the CCDC shows no crystal structure of Mn(II) has been reported so far and the structures of those entire complexes are elucidated only with spectroscopic evidence except the above mentioned Cu(II) complexes. This report documents the first structurally characterized Mn(II) coordination polymer with an antipyrine based ligand, and also includes a discussion of its magnetic properties and antibacterial studies.

2. Experimental

2.1. Materials

All chemicals and solvents used for the synthesis were of analytical grade, and were purchased from E. Merck, India and used as received without further purification.

2.2. Synthesis of the ligand (HL) and the coordination polymer {[Mn(L)(pyz)]ClO_4·2(H_2O)}n (**1**)

1:1 equimolar methanolic solution (40 ml) of 4-aminoantipyrine (0.406 g, 2 mmol) and salicyaldehyde (0.19 ml, 2 mmol)

* Corresponding author. Tel.: +91 0947455 7873; fax: +91 3252 202419.
E-mail address: skdusask@yahoo.ca (S.K. Dey).

http://dx.doi.org/10.1016/j.ica.2016.01.013
0020-1693/

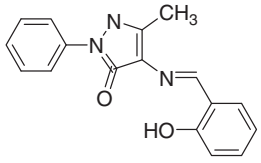
were mixed and refluxed at 45 °C for 2 h with constant stirring. The characteristic yellow precipitate obtained by Schiff base (Scheme 1) condensation was filtered out and kept for crystallization by dissolving in dichloromethane/methanol (1:1) mixture. Fine yellow crystals were obtained upon slow evaporation at room temperature after 12 h. Yield: 85%, ES [MSI] Calc for $C_{18}H_{17}N_3O_2$ (m/z + H +) = 308.34. Found = 309.46. *Anal.* Calc. for $C_{18}H_{17}N_3O_2$: C, 70.34; H, 5.57; N, 13.67. Found: C, 70.06; H, 5.59; N, 13.56%. A methanolic solution of $Mn(ClO_4)_2{\cdot}4H_2O$ (1 mmol, 0.33 g, 30 ml) was slowly added to a methanolic solution of HL (1 mmol, 0.308 g, 20 ml). The pH of the solution was adjusted to ~6 by adding a few drops of $NH_4OH/HClO_4$ (2/1). After stirring for 25 min in air, the mixture was placed into a round bottom flask containing pyrazine (1 mmol, 0.09 g, 10 ml) and refluxed in a temperature controlled oil bath at 80 °C for 24 h. The reaction mixture was cooled to room temperature, and filtered. Rectangle shaped light brown colored crystals of **1** suitable for X-ray diffraction were obtained after 10 days by slow evaporation of the filtrate and washed by dry methanol and air dried. Yield: 0.260 g (30%). Crystallinity of the bulk product was confirmed from the comparisons with powder X-ray data (Figs. S7–S9). *Anal.* Calc. for $[C_{22}H_{25}MnClO_8N_5]$: C, 45.72; H, 4.36; N, 12.12. Found: C, 46.12; H, 4.23; N, 13.11 (%).

2.3. Physical studies

Elemental analyses (carbon, hydrogen, nitrogen) were performed using a Perkin-Elmer 240 C elemental analyzer. FT-IR spectrum in KBr (4000–400 cm^{-1}) was recorded using a Perkin-Elmer RX I FT-IR spectrophotometer. Thermogravimetric analyses were carried out with a heating rate of 10 °C/min with a Mettler-Toledo Star TGA/SDTA-851^e thermal analyzer system in a dynamic atmosphere of N_2 (flow rate 80 mL min^{-1}), the sample was in an alumina crucible, and the temperature range was 25–550 °C. Variable-temperature magnetic data (2–300°K) were obtained using a Quantum Design MPMS5S SQUID magnetometer using a field strength of 0.1 T. Background corrections for the sample holder assembly and diamagnetic components of the complexes were applied.

2.4. X-ray data collection and structure refinement

Diffraction quality single crystal of compound **1** with dimension (0.18 × 0.15 × 0.12 mm) was mounted on a "Oxford Xcalibur" diffractometer equipped with a graphite monochromated fine focus Mo sealed tube ($\lambda_{Mo\ K\alpha}$ = 0.71073 Å). Data collection was performed at 293(2) K temperature using ω scan technique. Data collection and unit cell refinement were carried out using CrysAlisPro [20] while data reduction was performed using CrysAlis Red [21] programs. Multiscan absorption corrections were applied empirically to the intensity values (T_{max} = 0.877, T_{min} = 0.916) using CrysAlis RED [21]. The molecular structure was solved by direct methods using program SHELXS-97 [22] combined to Fourier difference synthesis and refined with full matrix least square technique based on F^2 using program SHELXL-97 [22]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Water hydrogen atoms were geometrically fixed and refined with isotropic thermal parameters. Molecular graphics, crystallographic illustrations, and publication materials were prepared using ORTEP [23], CAMERON [24], WinGX [25], software. Further crystallographic data and structure refinement parameters of the coordination polymer are summarized in Table 1. Selected bond distances and bond angles for the coordination polymer are given in Table 2. Powder X-ray data was recorded using a XRD, PW 1710, Philips, Holland (Cu Kα radiation, λ = 1.5406 Å) diffractometer.



Scheme 1.

2.5. Biological studies

The antibacterial activities of the Mn (II) coordination polymer have been studied by agar disc diffusion method. The antibacterial activities were done at 100 and 200 μg/mL concentrations of compound in DMF solvent by using two pathogenic gram negative bacteria (*Shigella flexneri* and *Proteus mirabilis*) and two gram positive pathogenic bacteria (*Bacillus cereus* and *Bacillus subtilis*). The bacteria were cultured for 24 h at 37 °C in an incubator. The agar medium was prepared and autoclaved at 121 °C for 15 min. The autoclaved medium was mixed well and poured onto a presterilized Petridis. Petri dishes containing nutrient Muller Hinton medium were seeded with 24 h culture of bacterial strains using sterile L-rod. Wells were punched using a sterile cork borer and the solution of Mn (II) coordination polymer was added from stock

Table 1
Crystal Structure parameters for **1**.

	1
Empirical formula	$C_{22}H_{21}MnClN_5O_6$
Formula weight	541.83
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	8.465(3)
b (Å)	9.980(4)
c (Å)	15.786(6)
α (°)	82.440(10)
β (°)	74.735(9)
γ (°)	65.166(9)
V(Å^3)	1167.3(7)
Z	2
T (K)	293(2)
$\lambda_{Mo\ K\alpha}$ (Å)	0.71073
D_c (g cm^{-3})	1.542
μ (mm^{-1})	0.729
F(000)	556
Total data	11 299
Unique data	4100
Observed data [$I > 2\sigma(I)$]	2081
R_{int}	0.0989
Goodness-of-fit (GOF) on F^2	1.005
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0719, wR^2 = 0.2284
R indices (all data)	R_1 = 0.1462, wR^2 = 0.1783

[a]$R = \Sigma(|F_o - F_c|)/\Sigma|F_o|$, [b]$R^w = \{\Sigma[w(|F_o - F_c|)^2]/\Sigma[w|F_o|^2]\}^{1/2}$.

Table 2
Bond lengths (Å) and bond angles (°) of **1**.

Mn(1)–O(6)	2.159(5)	Mn(1)–O(5)	2.089(5)	Mn(1)–N(1)	2.344(5)
Mn(1)–N(5)	2.278(6)	Mn(1)–N(3)	2.236(6)	Mn(1)–O(5)c	2.173(4)

O(6)–Mn(1)–O(5)	161.0(2)	O(6)–Mn(1)–N(1)	88.9(2)
O(6)–Mn(1)–N(5)	92.1(2)	O(6)–Mn(1)–N(3)	79.4(2)
O(6)–Mn(1)–O(5)c	99.32(18)	O(5)–Mn(1)–N(1)	93.76(19)
O(5)–Mn(1)–N(5)	106.9(2)	O(5)–Mn(1)–N(3)	81.75(18)
O(5)–Mn(1)–O(5)c	80.87(16)	N(1)–Mn(1)–N(5)	82.53(18)
N(1)–Mn(1)–N(3)	90.45(19)	N(1)–Mn(1)–O(5)c	169.1(2)
N(5)–Mn(1)–N(3)	169.11(19)	N(5)–Mn(1)–O(5)c	89.92(17)
N(3)–Mn(1)–O(5)c	98.10(18)		

Symmetry operations: x, y, z and −x, −y, −z.

solution. The inoculated plates were incubated for 24 h at 37 °C. After incubation, the diameter of the inhibition zone was measured and the results were recorded in millimeters (mm). The DMF solvent was used as a negative control whereas media with levofloxacin (standard antibiotic) was used as the positive controls. The experiments were performed in triplicate.

3. Result and discussion

3.1. Infrared studies

IR spectrum of the ligand displayed a medium intensity band around 1600 cm^{-1} due to $\nu_{C=N}$. The characteristic shifting to lower frequency region to the extent ~25 cm^{-1} in the coordination polymer, indicates that the nitrogen of the azomethine group is coordinated to the metal ion. The broad bands of coordination polymer in the range of 3150–3600 cm^{-1} indicate the presence of lattice water molecules [26]. A major band at 1095 cm^{-1} is in agreement with non-coordinated perchlorate. The ν_{C-O} (phenolic) stretching frequency of the ligand is observed around 1329 cm^{-1} and is shifted to lower frequency by ~35 cm^{-1} in the complex indicating coordination of phenolic oxygen. A band at 1654 cm^{-1} in the free ligand is due to $\nu_{C=O}$ stretching, which is shifted to lower frequency by ~43 cm^{-1} in the coordination polymer, suggesting the coordination of the ligand to the metal ion via the phenolic C–O group [27]. The two bands appearing in the low frequency range around 570 cm^{-1} and 500 cm^{-1} are due to ν_{Mn-O} and ν_{Mn-N} respectively [28]. The peaks observed at 475–490 cm^{-1}, are particularly diagnostic of bridging bidentate pyrazine ligand.

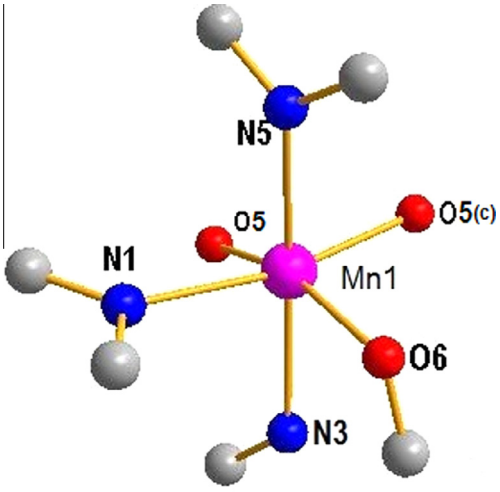


Fig. 1. Asymmetric unit of **1**.

3.2. Thermal studies

It is observed from the TGA curve (Fig. S6) that on heating under non-isothermal conditions complex **1** loses two molecules of water in the temperature range 90–110 °C. Then it undergoes decomposition and loses one molecule of pyrazine in the temperature range 145–210 °C. Upon further heating it was observed that the coordination polymer **1** is decomposed within the temperature range 250–515 °C. The decomposition residue (black) is identified as MnO_2, which is confirmed by a qualitative test (see Supplementary file, Fig. S5).

3.3. Crystal structure

Suitable crystals of compound **1** were grown from methanolic solution at room temperature. Single crystal X-ray diffraction showed that the compound **1** crystallizes in $P\bar{1}$ space group. Crystal structure determination of **1** shows that asymmetric unit (Fig. 1) altogether consists of a Mn(II) center possesses distorted octahedral geometry with N_3O_3 donor atoms coordinating from two Schiff base ligands and two different bridging pyrazine molecules (Fig. 2). The ligand binds to the Mn(II) ion in a tridentate fashion through one deprotonated phenolic oxygen, one coordinated oxygen from the antipyrine exocyclic five membered ring and one nitrogen of the azomethine group. The fourth coordination site of each Mn (II) ions is occupied by another deprotonated phenolic moiety coming from a second Schiff base ligand acting as a bridging phenolate group. The fifth and sixth coordination sites of each Mn(II)

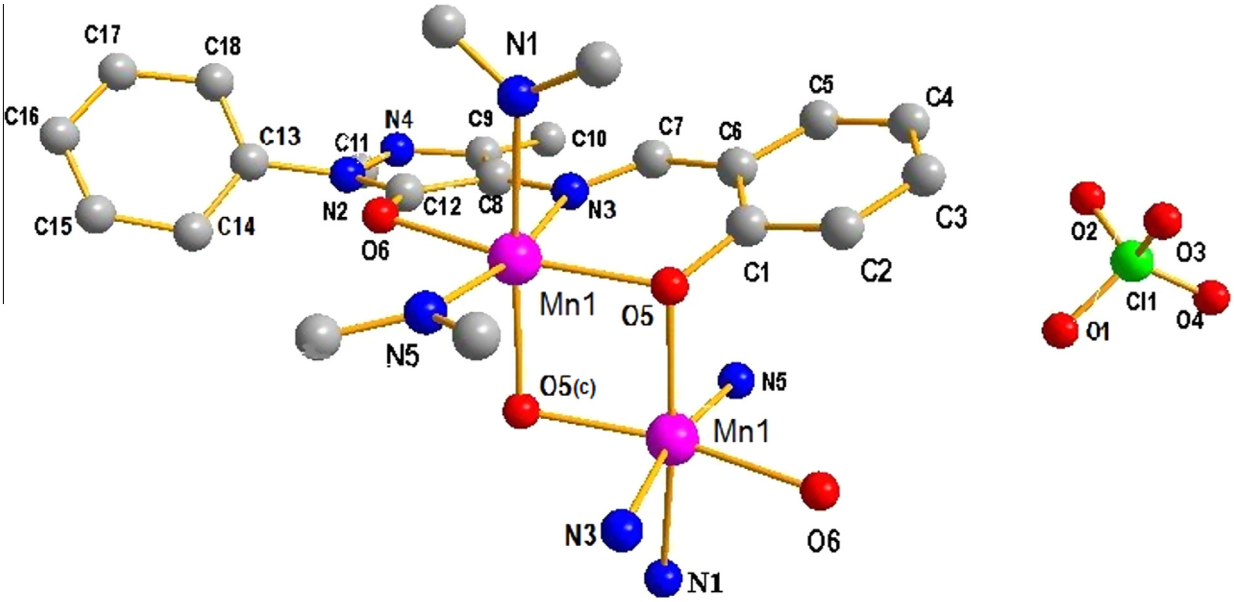


Fig. 2. Coordination modes of ligands to manganese(II) atoms in **1**.

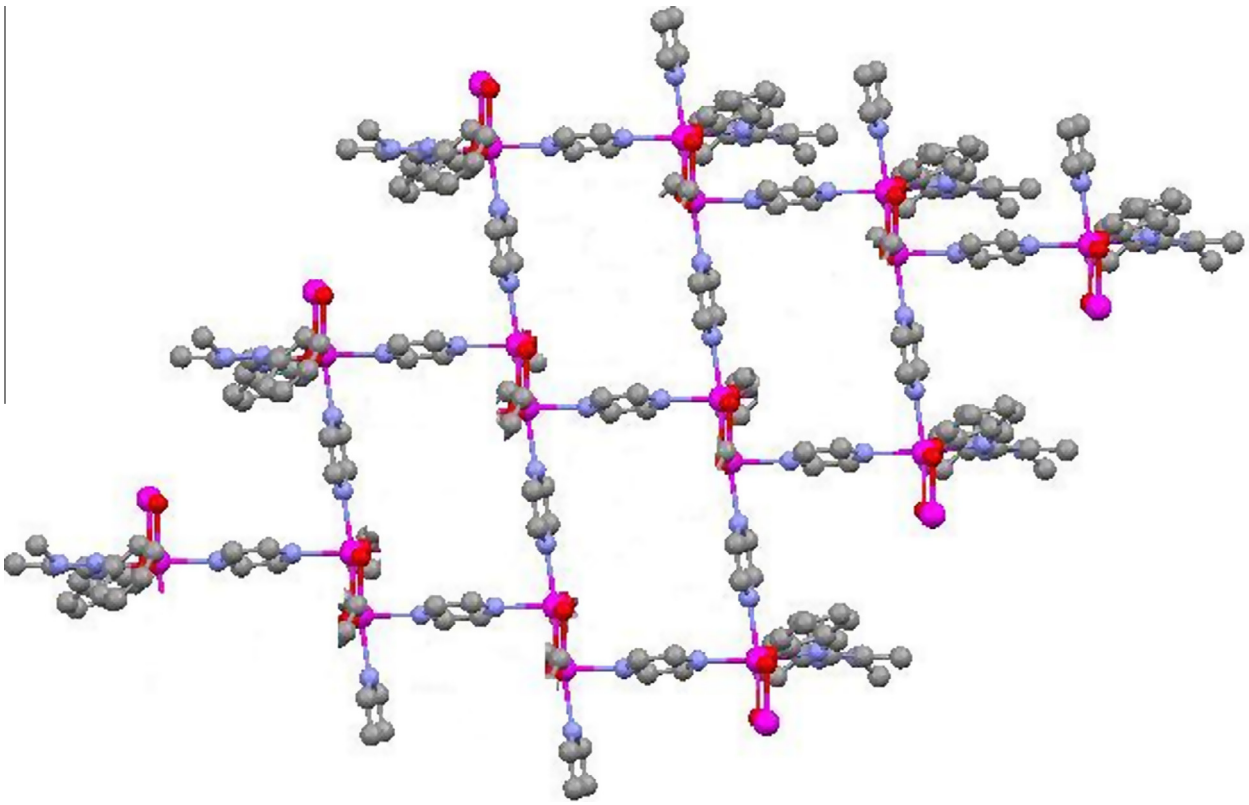


Fig. 3. Packing diagram of **1** viewed along *b* axis.

ions are occupied by two different bridging pyrazine molecules. One interesting point to be noted is that despite the rigidity and the steric strain imposed by the methyl substitution on the antipyrine moiety the ligand acts in a tridentate fashion. The extended structure of complex shows a rectangularly ordered hexa-manganese core bridged by two different types of bridging moiety, phenolate oxygen and pyrazine nitrogen atoms, with two arms (Mn···Mn separation) of 7.325 and 10.015 Å respectively and a Mn–Pyz–Mn and Mn–Mn–Mn angle of 176.99 and 134.29° respectively. In such manner it produces a polymeric grid like projection (Fig. 3), which shows the rigidity of the system. In the longest arm of the rectangular arrangement there are two different types of bridging, one with pyrazine and another with two phenolate groups from two different ligand moieties giving rise two different types of Mn–Mn distances, 3.244 Å and 7.245 Å respectively, a sum of 10.489 Å. The bridging phenolate oxygen produces the Mn–Mn distance of 3.244 Å and Mn–O–Mn angles of 99.12°, which are higher than normally seen in planar $[Mn_2(\mu\text{-}O)_2]^{+4}$ species, which usually have values of >2.7 Å and >97° respectively [29,30]. Bond valence sum calculations indicate that the oxidation states of all manganese atoms are Mn(II) [31]. The Mn–N distances (Mn1–N1, 2.334 Å, Mn1–N5, 2.278 Å, Mn1–N3, 2.237 Å) and Mn–O (Mn1–O6, 2.159 Å, Mn1–O5(c), 2.173 Å, Mn1–O5, 2.089 Å) are well within the range reported for related Schiff base complexes of Mn(II) [32].

3.4. Magnetic studies

Variable temperature magnetic data were obtained for **1** in the range 2–300 K, and are shown in Fig. 4 as plots of molar susceptibility and moment as a function of temperature. The characteristic drop in moment on lowering the temperature indicates intramolecular antiferromagnetic exchange. This is mirrored by

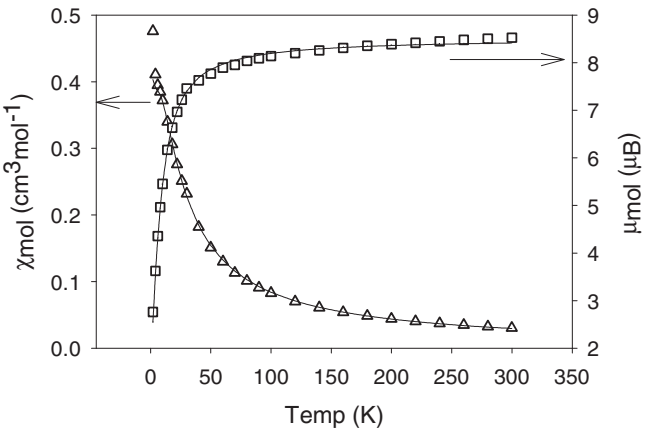


Fig. 4. Magnetic data of compound **1** recorded in the temperature range 2–300 K. The solid line corresponds to a fit with $g = 2.037(4)$, $J = -1.90(4)$ cm^{-1}, $\rho = 0.005$, $\theta = 0.5$ K, $10^2R = 1.62$ ($H_{ex} = -J\{S_1 \cdot S_2\}$; $S = 5/2$).

the slight shoulder in the susceptibility profile at low temperature. Examining the structure the dominant feature which would lead to such behavior is the repeating dinuclear $Mn_2(\mu_2\text{-}O)_2$ subunit, with a short Mn–Mn distance and a Mn–O–Mn angle of 99.1°. Such phenolate bridge angles typically lead to antiferromagnetic exchange [33]. Further bridging connections in the 2D structure from the pyrazine groups are expected to lead to weak, and perhaps insignificant exchange. Consequently the magnetic data were fitted to a simple model based on a dinuclear exchange Hamiltonian ($H_{ex} = -J\{S_1 \cdot S_2\}$; $S = 5/2$). A good fit was obtained with $g = 2.037(4)$, $J = -1.90(4)$ cm^{-1}, $\rho = 0.005$, $\vartheta = 0.5$ K, $10^2R = 1.62$ ($R = [\sigma\ (\chi_{obs} - \chi_{calc})^2/\sum\chi^2_{obs}]^{1/2}$; ρ = fraction paramagnetic impurity, ϑ = Weiss correction). Given the good fit extracting further exchange information from more elaborate models including longer range

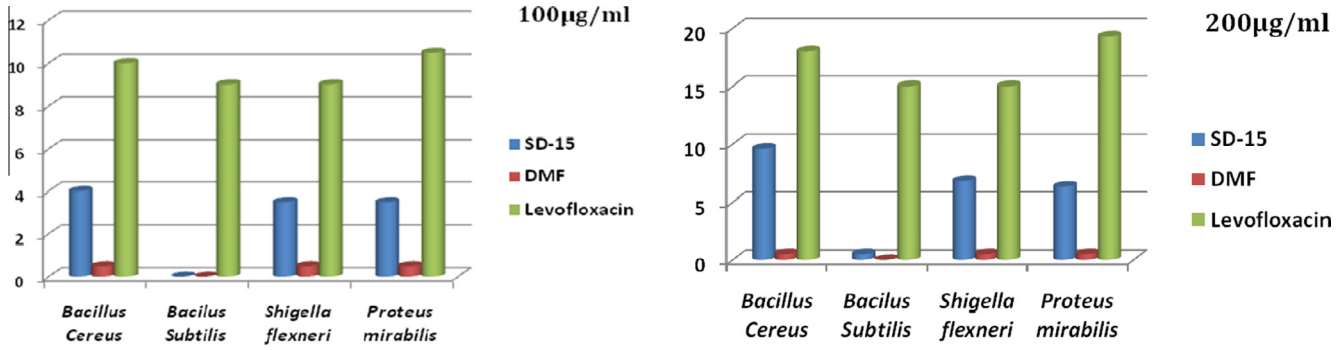


Fig. 5. Antibacterial activity of coordination polymer **1** at 100 and 200 µg/mL concentrations DMF solvent by using two pathogenic gram negative bacteria (*Shigella flexneri* and *Proteus mirabilis*) and two gram positive pathogenic bacteria (*Bacillus cereus* and *Bacillus subtilis*).

connections was not attempted. The Weiss correction (θ) implies possible weak ferromagnetic inter-dinuclear exchange behavior, presumably occurring via the long pyrazine connections.

3.5. Antibacterial activity

Antibacterial activity of the coordination polymer is given in Fig. 5. Antibacterial activity of Mn(II) polymer with respect to standard levofloxacin antibiotic against gram-positive (*B. cereus* and *B. subtilis*) and gram-negative (*S. flexneri* and *P. mirabilis*) bacteria were studied. The obtained results evidently showed that the coordination polymer have good antibacterial effects against the studied bacterial strains except *B. subtilis*. The activity of the metal chelates can be explained by overtone concept and the Tweedy chelation theory. The variation in the activity of coordination polymer against some different organisms depend either on the impermeability of the cells of the microbes or difference in ribosome of microbial cells. The lipid membrane surrounding the cell favors the passage of any lipid soluble materials and it is known that liposolubility is an important factor controlling antimicrobial activity. On chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of the positive charge of the metal ion with donor groups. Further, it increases the delocalization of π-electrons over the whole polymer and enhances the lipophilicity of the coordination polymer. This increased lipophilicity helps the penetration of the bacterial cell membranes and blocks the metal binding sites in enzymes of microorganisms and restricts further growth of the microorganisms. The Mn (II) coordination polymer shows no anti bacterial activity against *B. subtilis* due to lower impermeability of the bacterial cells.

4. Conclusion

Here, we present the synthesis, crystal structure, low-temperature magnetic study and antibacterial activity of one doubly bridged Mn(II) coordination polymer. From the forgoing discussion, it is found that the two phenoxo groups of two Schiff bases and two pyrazine groups coordinate to two manganese(II) centers. The coordination polymer shows moderate antiferromagnetic behavior and the magnetic interaction is dependent predominantly on the phenoxo bridges between the two manganese(II) centers. The coordination polymer also shows enhanced antibacterial activity compared with standard antibiotic levofloxacin.

Acknowledgements

We thank the CSIR, New Delhi, India for financial assistance to Dr. S. K. Dey (Ref. No. 01(2458)/EMR-II dt 16.05.2011). Thanks may also be extended to UGC, New Delhi, India for financial assistance.

Appendix A. Supplementary material

CCDC 1059136 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2016.01.013.

References

[1] (a) D. Braga, F. Grepioni, G.R. Desiraju, Chem. Rev. (1998) 1375;
(b) D. Braga, Acc. Chem. Res. 33 (2000) 601.
[2] (a) N.S. Persky, J.M. Chow, K.A. Poschmann, N.N. Lacuesta, S.L. Stoll, S.G. Bott, S. Obrey, Inorg. Chem. 40 (2001) 29;
(b) S. Subramanian, M.J. Zaworotko, Angew. Chem., Int. Ed. Engl. 34 (1995) 2127;
(c) M. Ward, Nature 374 (1995) 764.
[3] (a) D. Venkataraman, S. Lee, J. Moore, P. Zhang, Chem. Mater. 8 (1996) 2030;
(b) H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, Nature (London) 402 (1999) 276.
[4] (a) Y. Dong, M. Smith, R. Layland, H. Loye, Chem. Mater. 12 (2000) 1156;
(b) G. Guilera, J.W. Steed, Chem. Commun. (1999) 1563;
(c) O.H.S.L. Al-Obaidi, Bioinorg. Chem. Appl. (2012) 1.
[5] M. Sönmez, I. Berber, E. Akbas, Eur. J. Med. Chem. 41 (2006) 101.
[6] S.M.E. Khalil, H.S. Seleem, B.A. El-Shetary, M. Shebl, J. Coord. Chem. 55 (2002) 883.
[7] M. Weitzer, S. Brooker, Dalton Trans. 14 (2005) 2448.
[8] (a) I. Costova, L. Saso, Curr. Med. Chem. 20 (2013) 4609;
(b) D. Chiaramonte, J.M. Steiner, J.D. Broussard, K. Baer, S. Gumminger, E.M. Moeller, D.A. Williams, R. Shumway, Can. J. Vet. Res. 67 (2003) 183.
[9] (a) S. Kawata, H. Kumagai, K. Adachi, S. Kitagawa, J. Chem. Soc., Dalton Trans. (2000) 2409;
(b) A.N. Evstopov, V.E. Yavorovskaya, E.S. Vorobev, Z.P. Kudonogova, L.N. Gritsenko, E.N. Schmidt, S.G. Medevedeva, D.V. Filimonov, T.P. Prishchep, A.S. Saratikov, Pharm. Chem. J. 26 (1992) 426.
[10] (a) A. Togni, L.M. Venanzi, Angew. Chem., Int. Ed. Engl. 33 (1994) 497;
(b) R.A. Heinz, H. Zhao, X. Ouyang, G. Grandinetti, J. Cowen, K.R. Dunbar, Inorg. Chem. 38 (1999) 144.
[11] (a) M. Fujita, Y.J. Kwon, S. Washizu, K. Ogura, J. Am. Chem. Soc. 116 (1994) 1151;
(b) T.N. Sorrell, V.A. Vankai, M.L. Garrity, Inorg. Chem. 30 (1991) 207.
[12] J.S. Miller, A.J. Epstein, Angew. Chem., Int. Ed. Engl. 33 (1994) 385.
[13] (a) L. Carlucci, G. Liani, D.M. Proserpie, A. Sironi, J. Am. Chem. Soc. 117 (1995) 4562;
(b) C.R. Choudhury, S.K. Dey, S. Sen, B. Bag, S. Mitra, V. Gramlich, Z. Naturforsch. 57b (2002) 1191.
[14] L. Carlucci, G. Ciani, D.M. Proserpio, A. Sironi, Angew. Chem., Int. Ed. Engl. 34 (1995) 1895.
[15] I.G. Filippova, I.L. Malaestean, S.G. Baca, Z. Anorg, Allg. Chem. 640 (2014).
[16] (a) A. Das, I. Todorov, S.K. Dey, S. Mitra, Inorg. Chim. Acta 359 (2006) 2041;
(c) A.J. Blake, N.R. Chanpress, A.N. Khlobystov, S. Parsons, M. Schröder, Angew. Chem., Int. Ed. Engl. 39 (2000) 2317.
[17] B.Q. Ma, S. Gao, J. Yi, G.X. Xu, Polyhedron 20 (2001) 1255.
[18] K. Adachi, Y. Sugiyama, H. Kumagai, K. Inoue, S. Kitagawa, S. Kawata, Polyhedron 20 (2001) 1411.
[19] P.M. Selvakumar, E. Suresh, P.S. Subramanian, Polyhedron 26 (2007) 749.

[20] Agilent Technologies, CrysAlisPro Software System, Version 1.171.33.31. Aglient Technologies UK Ltd., Oxford, UK (2012).
[21] Agilent Technologies, Crysalis CCD and Crysalis RED Software System, Aglient Technologies UK Ltd., Oxford, UK (2012).
[22] G.M. Sheldrick, Acta Crystallogr. 64A (2008) 112.
[23] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 565.
[24] D.J. Watkin, C.K. Prout, L.J. Pearce, CAMERON, Chemical Crystallography Laboratory, University of Oxford, UK, 1996.
[25] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
[26] (a) A.A. Soliman, G.G. Mohamed, Thermochim. Acta 421 (2004) 151;
(b) L. Lindoy, W.E. Moody, D. Taylor, Inorg. Chem. 16 (1977) 1962.
[27] (a) T. Radmakrishnan, P.T. Joseph, C.P. Prabhakaran, J. Inorg. Nucl. Chem. 38 (1976) 2217;
(b) G. Shankar, R.R. Premkumar, S.K. Ramalingam, Polyhedron 5 (1986) 991.
[28] (a) K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, third ed., Interscience-Wiley, New York, 1978. p. 233;
(b) S.K. Dey, M.S. El. Fallah, J. Ribas, T. Matsushita, V. Gramlich, S. Mitra, Inorg. Chim. Acta 357 (2004) 1517;
(c) K.A. Kumar, K.L. Reddy, S. Satyanaryana, Spectrosc. Lett. 44 (2011) 27.
[29] L. Que, A.E. True, Prog. Inorg. Chem. 38 (1990) 97.
[30] N.A. Law, J.W. Kampf, V.L. Pecoraro, Inorg. Chim. Acta 297 (2000) 252.
[31] G.J. Palenik, Inorg. Chem. 36 (1997) 122.
[32] (a) B. Mabad, P. Casuoux, J.P. Tuchagues, D.N. Hendrickson, Inorg. Chem. 25 (1986) 1420;
(b) S.K. Dey, L.K. Thompson, L.N. Dawe, Chem. Commun. (2006) 4967.
[33] L.K. Thompson, S.K. Mandal, S.S. Tandon, J.N. Bridson, M.K. Park, Inorg. Chem. 35 (1996) 3117.