Original Research Article

Syntheses, characterization, and X-ray crystal structure of Mn(III) coordination polymer of 2-((2-hydroxyethylimino)methyl)-6-methoxyphenol

ABSTRACT

The present investigation describes the synthesis of the ligand 2-((2-hydroxyethylimino)methyl)-6-methoxyphenol (H_2L) and its complex of Mn(III) cation. The structure of the compound were elucidated by spectroscopic study and X-ray diffraction for the complex formulated as $[\{Mn(\mu\text{–}HL)_2\}(C_2N_3)]_n$. The complex crystallizes in the monoclinic space group $P2_1/n$ with the following unit cell parameters: a = 5.8172 (3) Å, b = 11.8695 (7) Å, c = 17.2616 (11) Å, β = 96.565 (6)°, V = 1178.57 (12) $Å^3$, Z = 2, R_1 = 0.0603 and wR_2 = 0.1516. For this compound, the structure reveals that two monodeprotonated ligand interact with one Mn(III) in bidentate fashion while the third coordination site of the ligand interact with another Mn(III) of a neighboring unit. Thus, a polymeric coordination complex is obtained. The Mn(III) is hexacoordinated and the coordination environment can be described as slightly distorted octahedral geometry. Numerous hydrogen bonds link the molecules into three dimensional network.

Keywords: Schiff base; complex; octahedral; manganese; polymer.

1. INTRODUCTION

Manganese complexes have been widely studied over the past two decades, because to the easy preparation of ligands with hard donor sites and/or soft donor sites [1–5]. Given the possibility of manganese going into various oxidation states in the presence of a ligand possessing atoms such as oxygen or nitrogen, complexes possessing very diverse properties have been prepared [6–10]. Many complexes capable of mimicking enzymes with a manganese atom are synthesized in order to better understand the functioning of this type of enzymes such as superoxide dismutase and catalases in biological systems [11–13]. It has been reported that in these enzymes, manganese is involved in complex redox cycles with diverse oxidation states [14–17]. In coordination chemistry, many complexes in which manganese is found in various environments have shown good redox properties with oxidation states ranging from Mn^{2+} to Mn^{5+} [18–21]. These phenomena are very useful for understanding and modeling the functioning of active enzymes. Manganese complexes are also studied for their important catalytic properties [22, 23]. They are used as a catalyst in the epoxidation reaction of alkenes, in the oxidation and hydrogenation of ketones [24–28]. The involvement of manganese in these catalytic processes is due to the versatility of the metal which can have several oxidation states and several coordination numbers. The synthetic method used is essential to obtain a complex with specific properties. In this work, we used a one-pot method in which the ligand, manganese salt and sodium dicyanamide, which can act as a co-ligand, are mixed in ethanol solution. The ligand provides hard oxygen-binding sites and soft nitrogen-binding sites which made it possible to synthesize a polymeric coordination compound. Herein, the synthesis and the crystal structure of the polymeric coordination complex $[\{Mn(\mu\text{–}HL)_2\}(C_2N_3)]_n$ is reported.

2. EXPERIMENTAL DETAILS

2.1 Materials

2-hydroxy-3-methoxybenzaldehyde, aminoethanol, and manganese dichloride tetrahydrate were purchased from Sigma-Aldrich and used as received without further purification. All solvents used were of reagent grade. Elemental analyses of C, H and N were recorded on a VxRio EL Instrument. Infrared spectra were obtained on a FTIR Spectrum Two of Perkin Elmer spectrometer in the 4000-400 cm^{-1} region. The molar conductance of 1×10^{-3} M in DMSO solutions of the metal complex was measured at 25°C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibilities of the powdered samples were measured using a Johnson Mattey scientific magnetic susceptibility balance (Calibrant: $Hg[Co(SCN)_4]$).

2.2 Synthesis of the ligand 2-((2-hydroxyethylimino)methyl)-6-methoxyphenol (H_2L)

In a flask containing 20 mL of ethanol, (10 mmol, 1.52 g) of o-vanillin (2-hydroxy-3-methoxybenzaldehyde) is dissolved and (10 mmol, 0.61g) of aminoethanol, previously dissolved in 5 mL of ethanol, was added with two drops of acetic acid. The resulting mixture was refluxed for 2 hours. Finally, the solvent was evaporated to dryness using a rotary evaporator. The compound was recovered as oil. Anal. Found (Calcd.) for $C_{11}H_{15}NO_3$ (%):C, 63.14 (63.10); H, 7.23 (7.20); N, 6.69 (6.67). Main IR bands (cm^{-1}) : 3264, 1633, 1503, 1463, 1440, 1342,1217, 1168, 1069, 780, 734, 718. NMR ^1H (DMSO, 400 MHz, δ(ppm)) : 13.78 (s, 1H, Ph—O**H**) ; 8.55 (s, 1H, **H**C=N) ; 4.82 (S, 1H, —CH_2O**H**); 3.78 (T, 2H, CH_2—C**H**$_2$—O, 2H); 3.48 (T, 2H, CH_2—C**H**$_2$—N**);** 3.66 (S, 3H, O-C**H**$_3$); 6.72-7,14 (m, 3 H, H-Ph). NMR ^{13}C (DMSO, 400 MHz, δ(ppm)) : 124.0 (C_{Ph}) ; 154.1 (C_{Ph}) ; 147.3 (C_{Ph}) ; 118.2 (C_{Ph}) ; 114.9 (C_{Ph}) ; 117.2 (C_{Ph}) ; 166.70 (—**C**=N) imine ; 60.2 (—**C**H_2—N); 62.60 (—**C**H_2—O); 56.3 (O—**C**H_3).

2.3 Synthesis of the complex $[\{Mn(\mu–HL)_2\}(C_2N_3)]_n$

An ethanolic solution containing 1 mmol of $MnCl_2·4H_2O$ is introduced into a beaker and then (2 mmol) of a solution of $Na(N(CN))_2$ is added to the solution of metal salt. 10 min then filtered. 1 mmol of ligand (H_2L) contained in a 100 mL flask is added to this filtrate, stirred at room temperature for 2 hours. And filtered. The filtrate is subjected to slow evaporation. After a week, brown crystals of the $[Mn(HL)_2](N(CN))$ complex capable of being analyzed by X-ray diffraction are collected. The melting point of the compound is 247°C. Anal. Found (Calcd.) for $C_{22}H_{24}MnN_5O_6$ (%):C, 51.87 (51.85); H, 4.75 (4.72); N, 13.75 (13.71). Main IR bands (cm^{-1}) : 3099, 2268, 2215, 2148; 1610, 1551, 1469, 1447, 1226, 1076, 868, 782, 749.

2.4 Crystal structure determination

Crystals suitable for X-diffraction, of the reported compound, were grown by slow evaporation of MeOH solution of the complex. Details of the X□rays crystal structure solution and refinement are given in Table 1. Diffraction data were collected using a Rigaku XtaLAB PRO diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Using Olex2 [29] the structures were solved by intrinsic phasing methods with SHELXT [30] and SHELXL [31] was used for full matrix least squares refinement. The hydrogen atoms of water molecules and NH groups were located in the

Fourier difference maps and refined. Others H atoms were geometrically optimized and refined as riding model by AFIX instructions. Molecular graphics were generated using ORTEP-3 [32].

Table 1. Crystal data and structure refinement for $[\{Mn(HL)_2\}(C_2N_3)]_n$

Chemical formula	$C_{20}H_{24}MnN_2O_6 \cdot C_2N_3$
Mr	509.40
Crystal system	Monoclinic
Space group	$P2_1$
Temperature (K)	293
a (Å)	5.8172 (3)
b (Å)	11.8695 (7)
c (Å)	17.2616 (11)
β (°)	96.565 (6)
V (Å^3)	1178.57 (12)
Z	2
Radiation type	Mo Kα
D_{calc} (Mg/m^3)	1.435
Absorption coefficient (mm^{-1})	0.61
F(000)	528
Crystal size (mm)	0.03 × 0.02 × 0.02
T_{min}, T_{max}	0.825, 1.000
Index ranges	$-8 \leq h \leq 8$, $-16 \leq k \leq 14$, $-23 \leq l \leq 21$
Reflections collected	22110
Independent reflections	6384
Observed [$I > 2\sigma(I)$] reflections	5651
R_{int}	0.049
Goodness-of-fit on F^2	1.11
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0603$, $wR_2 = 0.1516$
R indices (all)	$R_1 = 0.0686$, $wR_2 = 0.1552$
No. of reflections	6384
No. of parameters	362
No. of restraints	141
Δρmax, Δρmin (e Å^{-3})	1.12, −0.56

3. RESULTS AND DISCUSSION

3.1 General study

The infrared spectrum of the ligand shows a strong band at 1603 cm^{-1} attributed to the $\nu_{C=N}$ imine vibration which confirms the condensation between the aldehyde and the amine. The wide band located at 3364 cm-1 is attributed elongation vibration of the alcoholic and phenolic hydroxyl groups. The bands pointed at 1217 cm^{-1} and 1346 cm^{-1} are attributed respectively to the C—O vibrations. The ^1H NMR spectrum of the ligand is recorded in chloroform. The singlet signal at 8.55 ppm is attributed to the imine proton. The two triplet signals at 3.48 ppm and 3.78 ppm are assigned to the methylene protons, respectively. The singlets at 3.66 ppm and 4.82 ppm are attributed to the methoxy group and the alcoholic proton. The three protons of the aromatic ring are pointed in the range 6.75-7.14 ppm. The signal of the phenolic proton appeared at 13.83 ppm. The ^{13}C NMR spectrum shows a characteristic signal at 166.60 ppm attributed to the carbon atom of the azomethine moiety.

Upon reaction of the ligand H_2L and manganese (II) chloride the spectrum of the resulting compound, shows a shift of *ca*. 23 cm^{-1} frequencies of the imine indicating a coordination of the ligand to the manganese ion which confirms the coordination of the ligand through the nitrogen azomethine atom. The broad band at 3099 cm^{-1} due to $\nu_{O—H}$ is indicative of the presence of non-deprotonated hydroxyl group in the complex. Additional bands pointed at 2268 cm^{-1}, 2215 cm^{-1} and 2149 cm^{-1} are indicative of the presence of uncoordinated dicyanamide anion. Molar conductivity is measured for freshly prepared complexes 10^{-3} M solution in DMF and after standing for two weeks. The conductance value of 87 $cm^2\ \Omega^{-1}\ mol^{-1}$ lies in the range observed for 1:1 electrolyte [33]. On standing for two weeks the conductance varies slightly indicating a stable complex in DMF solution. The electronic spectrum of the complex shows a strong band at $\lambda_{max} = 273$ nm attributed to an intraligand charge transfer (ILCT). The band at 373 nm is due to the azomethine and π—π^* transition. The band 430 nm arises from the ligand-to-metal charge transfer (LMCT) [34].

The room temperature magnetic moment value of 4.9 μ_B per ion in the complex is normal for high spin ($S = 2$) d^4 configuration of Mn(III) complex [35]. This value is comparable to the values reported for mononuclear octahedral Mn(III) complex [34]. The elemental analyses agree the formulation proposed for the compound. Crystals of $\{[Mn(HL)_2]\cdot(N(CN)_2\}$ suitable for X-ray diffraction were obtained by slow evaporation of corresponding methanol solutions. The details of the crystal structure determination for the Mn(III) compound are given in Table 1.

3.2 Structure of the polymeric complex

Suitable single crystals for X-ray diffraction of The manganese(III) complex were obtained by slow evaporation at room temperature of ethanol solution of the compound. Crystal data, collection and refinement parameters are listed in Table 1. Selected bond lengths and angles are summarized in Table 2. Hydrogen bond data for the complex are gathered in Table 3. The Mn(III) complex crystallizes in the monoclinic system with the space group $P2_1$. An ORTEP view of the structure is shown in Figure 1 and the packing diagram is presented in figure 2. The asymmetric unit contains two monodeprotonated ligand molecules and one Mn(III) ion. The ligand is coordinated to the Mn(III) cation in bidentate fashion through its phenolate oxygen atom and its azomethine nitrogen atom and one dicyanamide anion. For each ligand molecule, the oxygen atom of the methoxy group remains uncoordinated while the non-deprotonated oxygen atom of the alcoholic moiety is coordinated two a Mn(III) ion of a neighboring complex. Thus, each Mn(III) ion is coordinated to two phenolate oxygen atom, two alcoholic oxygen atoms and two imino nitrogen atoms, resulting in a six-coordinated cation. The environment around each Mn(III) cation is best described as a distorted octahedron. The best equatorial plane around Mn(III) is occupied by the two phenolate oxygen atoms and the two azomethine nitrogen atoms which are quite coplanar (rms 0.0172), with the metal ion 0.0079(2) Å out of the plane. The axial positions are occupied by the phenolic oxygen atoms from two neighboring molecules, O2_1^{i}—Mn1—O2_2^{ii}, 178.31 (18)°. The ranges of equatorial *cissoid* angles [88.8(2)°90.9(2)°] and the values of the *transoid* angles [178.4(2)° and 179.18(19)°] reflect the slightly distortion of the N_2O_4 environment from the ideal octahedral geometry. In each ligand molecule, the phenyl ring of the Schiff base lies in a plane including its phenolate oxygen (rms 0.0805 Å and 0.0212 Å). The coordination of the ligand molecules to the Mn(III) results in the formation of six membered rings of type MnOCCCN [Mn1/O1_1/C5_1/C4_1/C3_1/N1_1 and Mn1/O1_2/C5_2/C4_2/C3_2/N1_1] with bite angle values of 90.9(2)° and 90.6(2)°. These two means planes which share a vertex occupied by Mn1 are slightly twisted with dihedral angle of 5.723 (3)° and each of them forms dihedral angle with its related phenyl ring of 3.6669(4)° and 6.934(3)°, respectively. The bond distances Mn—O [1.863 (4) Å and 1.852(4) Å] and Mn—N [2.045(5) Å and 2.049(5) Å] in the basal plane are different as observed in similar complexes reported in the literature [34–36]. The distances Mn—O [2.237(4) Å and 2.232(5) Å] in the axial positions are longer than those in the equatorial plane and are comparable to those reported for the complex $[Mn(L)(CH_3OH)_2]ClO_4$ (H_2L = *N*,*N'*-bis(1-(1'-hydroxy-2- naphthyl)ethylidene)propane-1,3-diamine) [37]. This is indicative of Jahn Teller distortion expected for high spin manganese(III) complex [38, 39].

The uncoordinated dicyanamide cation is disordered with two sites occupancies of 0.672(10) and 0.328(10).

Table 2. Selected geometric parameters (Å, °).

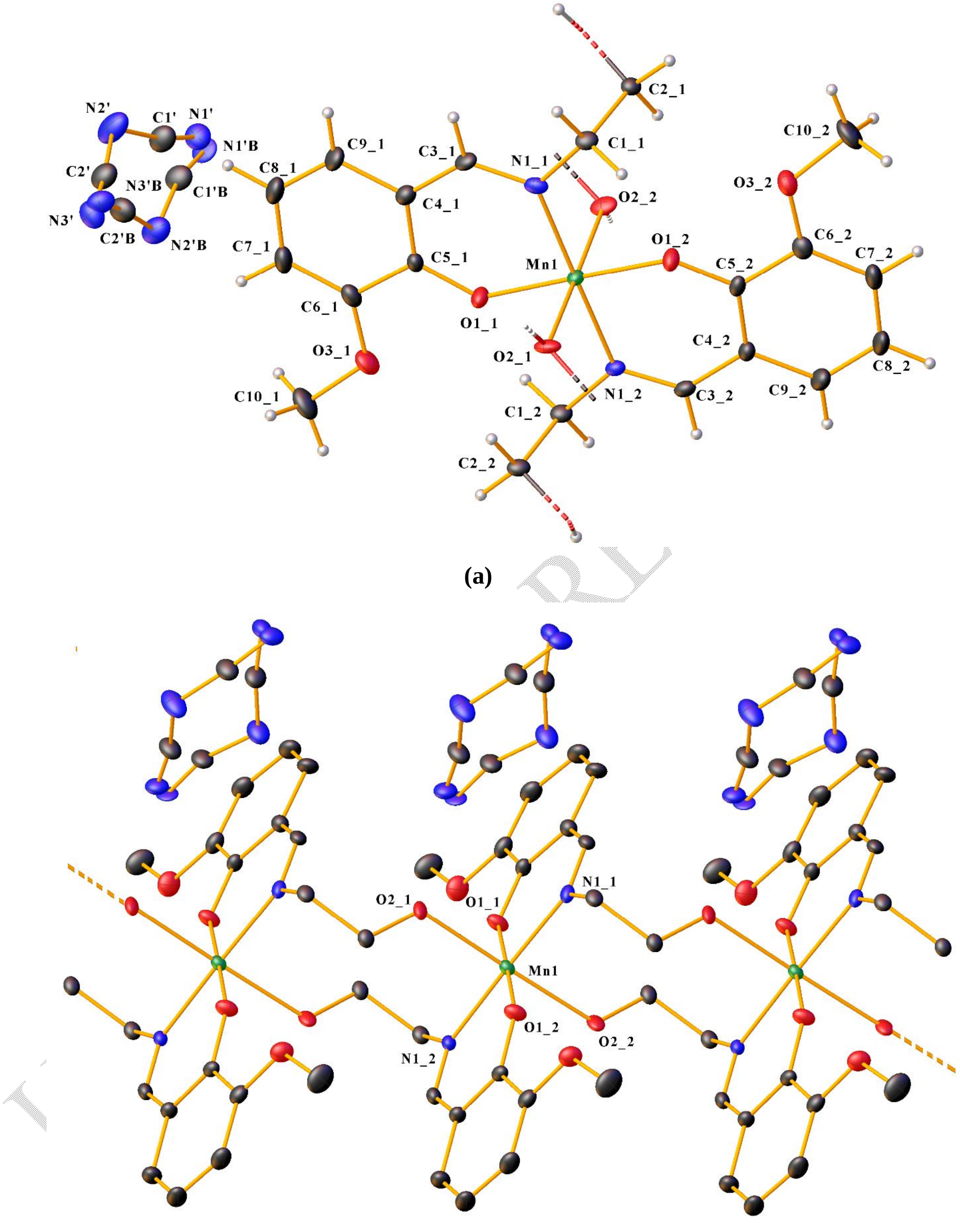
Mn1—N1_1	2.045 (5)	Mn1—O1_2	1.852 (4)
Mn1—O2_1^{i}	2.237 (4)	Mn1—O2_2ii	2.232 (5)
Mn1—O1_1	1.863 (4)	Mn1—N1_2	2.049 (5)
N1_1—Mn1—O2_1^{i}	87.93 (17)	O1_2—Mn1—O1_1	179.18 (19)
N1_1—Mn1—O2_2^{ii}	90.5 (2)	O1_2—Mn1—O2_2^{ii}	89.1 (2)
N1_1—Mn1—N1_2	178.4 (2)	O1_2—Mn1—N1_2	90.6 (2)
O1_1—Mn1—N1_1	90.9 (2)	O2_2^{ii}—Mn1—O2_1^{i}	178.31 (18)
O1_1—Mn1—O2_1^{i}	89.1 (2)	N1_2—Mn1—O2_1^{i}	93.67 (19)
O1_1—Mn1—O2_2^{ii}	91.5 (2)	N1_2—Mn1—O2_2^{ii}	87.94 (17)
O1_1—Mn1—N1_2	88.8 (2)	N1'—C1'—N2'	168 (2)
O1_2—Mn1—N1_1	89.7 (2)	C2'—N2'—C1'	121.9 (12)
O1_2—Mn1—O2_1^{i}	90.4 (2)	N3'—C2'—N2'	174 (2)

Symmetry codes: (i) *x*−1, *y*, *z*; (ii) *x*+1, *y*, *z*.

Table 3. Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2_1—H2_1···N1'^{i}	0.92(9)	1.87(9)	2.78(3)	174(7)
O2_1—H2_1···N1'B^{i}	0.92(9)	1.73(10)	2.64(5)	167(8)
C1_1—H1B_1···N2'B^{ii}	0.99	2.69	3.49(2)	138.0
C2_1—H2B_1···O1_2	0.99	2.61	3.162(7)	115.3
O2_2—H2_2···N3'^{iii}	0.58(9)	2.26(10)	2.78(4)	151(12)
O2_2—H2_2···N3'B^{iii}	0.58(9)	2.17(12)	2.71(8)	156(12)
C2_2—H2A_2···O1_1	0.99	2.56	3.111(7)	114.9

Symmetry codes: (i) −x+2, y−1/2, −z+1; (ii) −x+1, y−1/2, −z+1; (iii) −x, y+1/2, −z+1.



(a)

(b)

Figure 1. (a) Crystal structure of the Mn(III) complex. Displacement ellipsoids are drawn at the 30% probability level. (b) Drawing of the coordination polymer. H atoms are omitted for clarity.

The polymeric structure is consolidated by the presence of numerous hydrogen bonds. Intermolecular hydrogen bonds are observed between the alcoholic oxygen atoms and the nitrogen atoms of the uncoordinated dicyanamide anion: O2_1—H2_1···N1'^{i} and O2_1—H2_1···N1'B^{i} (i = −x+2, y−1/2, −z+1) and O2_2—H2_2···N3'^{iii} and O2_2—H2_2···N3'B^{iii} (iii = −x, y+1/2, −z+1). Weak intermolecular hydrogen bond of type C—H···N [C1_1—H1B_1···N2'B^{ii} ((ii) = −x+1, y−1/2, −z+1)] are present in the polymeric structure. Intramolecular hydrogen bond involving phenolate oxygen as acceptor and atoms and C—H as donor are present.

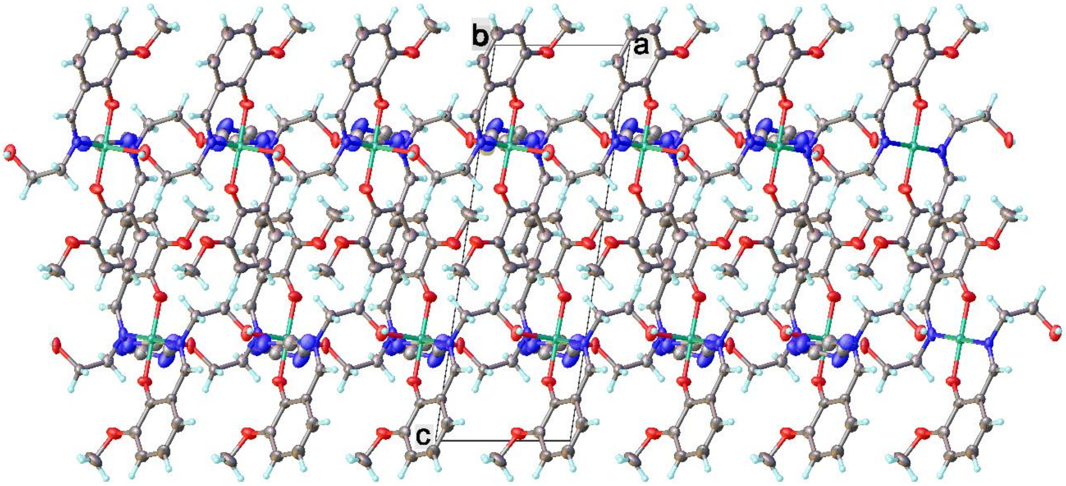


Figure 2. The packing of the compound in the crystal structure.

4. CONCLUSION

The reported work is concerned the synthesis of a manganese (III) polymer complex using the ligand 2-((2-hydroxyethylimino)methyl)-6-methoxyphenol and manganese (II) dichloride tetrahydrate in presence of sodium dicyanamide. In the resulting complex the ligand is monodeprotonated yielding a phenolate oxygen atom, while the alcoholic moiety remains undeprotonated. Each of the two ligand molecules acts in bidentate fashion in the coordination to Mn(III) through the phenolate oxygen atom and azomethine nitrogen atom. The alcoholic oxygen atom of the ligand is coordinated to a Mn (III) cation of a neighboring molecule complex yielding a polymeric structure. In the interesting polymer formulated as $[\{Mn(\mu\text{–}HL)_2\}(C_2N_3)]_n$ the manganese (III) ion occupied the inner N_2O_4 site, resulting in an octahedral geometry around Mn (III). Numerous hydrogen bonds connect the polymer chains in three dimensional network.

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