

Synthesis and Characterization of the 2-(-(2-(-2-hydroxy-3-methoxybenzylideneamino)propylimino)methyl)-6-methoxyphenol dimanganese(III) Complex containing $\mu(O,O')$ -nitrito-aqua Ligands

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Abstract

Single crystal of new nitrito bridged Mn(III) dinuclear compound $\{[\text{Mn}(\text{L})(\text{H}_2\text{O})](\mu\text{-NO}_2)[\text{Mn}(\text{L})(\text{H}_2\text{O})]\} \cdot (\text{ClO}_4)$ has been synthesized in the absence of nitrite source. The compound was characterized by elemental analysis, IR spectroscopy and single crystal X-ray diffraction. The compound crystallizes in the triclinic system in the space group P-1 with $a = 12.4175(3)\text{Å}$, $b = 13.6360(4)\text{Å}$, $c = 12.8207(5)\text{Å}$, $\alpha = 74.876(3)^\circ$, $\beta = 89.064(2)^\circ$, $\gamma = 85.361(2)^\circ$, $V = 2159.39(11)\text{Å}^3$, $Z = 9$, $D_c = 1.489\text{Mg m}^{-3}$. Each of the two ligand molecules encapsulates one Mn(III) ion in tetradentate fashion through two phenolate oxygen atoms and two azomethine nitrogen atoms. The two methoxy oxygen atoms of each ligand molecule remain uncoordinated. In the structure, each manganese(III) ion is situated in a N_2O_4 inner. The environment around each Mn(III) cation is best described as a distorted square pyramidal geometry, in which the equatorial plane is occupied by the atoms from the ligand molecule and the axial positions are occupied by one oxygen atom of a coordinated water molecule and one nitrito oxygen atom. The two Mn(III) ions are bridged though one $\mu_{1,3}$ -nitrito group. Numerous intermolecular hydrogen bonds, established between water molecules as donors and phenoxo or methoxy oxygen atoms as acceptors, connect the dinuclear units into three-dimensional network.

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1. Introduction

In the two past decades, o-vanillin is widely used as source of Schiff bases owing to its capacity to react rapidly with primary amine compounds to yield compound with multiple donor sites. The chelating agents formed from this keto-precursor contain generally donor sites such N, O or S. Their abilities to form coordination compounds are used for the synthesis of complexes with original physico-chemical properties [1–5]. Original structure such as open cubane or honeycomb are obtained [6–8]. Compounds with magnetic [9], optical [10], electrochemical [11] and, catalytical properties [12]. Metal complexes containing o-vanillin derivatives exhibit a variety of biological activities [13]. These kind of ligand can be used in presence of auxiliary ambidentate ligand such as NO_2^- , a versatile ligand which can acts in different fashions such as $\mu_{1,1^-}$, $\mu_{1,2^-}$, $\mu_{1,3^-}$, $\mu_{1,2,3^-}$, $\mu_{1,1,2^-}$, $\mu_{1,2^-}$, $\eta^1\text{-O}$, $\eta^1\text{-N}$ [14–16]. In certain cases, anions NO_2^- can appears in the complex's formula despite the absence of NO_2^- source. The reduction of NO_3^- by the formamide (DMF) solvent is one of the ways [17]. The formation of nitrite from nitrate is common in the presence of bacteria [17,18].

As part of our ongoing research on metal transition complexes, the Schiff base 2-(2-(2-hydroxy-3-methoxybenzylideneamino)propylimino)methyl)-6-methoxyphenol (H_2L), is prepared from the condensation of o-vanillin and 1,2-diaminopropane. The manganese compound $\{[\text{Mn}(\text{L})(\text{H}_2\text{O})](\mu\text{-NO}_2)[\text{Mn}(\text{L})(\text{H}_2\text{O})]\} \cdot (\text{ClO}_4)$, was obtained as unexpected product, which represents a rare example of $\mu_{1,3}$ -nitrite manganese(III) complex. In this paper, we report its synthesis, infrared characterization, and X-rays structure.

2. Experimental Part

2.1. Starting materials and instrumentation

Propane-1,2-diamine, 2-hydroxy-3-methoxybenzaldehyde and manganese perchlorate hexahydrate 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 $4000\text{-}400\text{ cm}^{-1}$ region. The molar conductance of $1 \times 10^{-3}\text{ M}$ in DMSO solution of the metal complex was measured at $25\text{ }^\circ\text{C}$ 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 Matthey scientific magnetic susceptibility balance (Calibrant: $\text{Hg}[\text{Co}(\text{SCN})_4]$).

2.2. Synthesis 2-(-(2-(-2-hydroxy-3-methoxybenzylideneamino)propylimino)methyl)-6-methoxyphenol

3.04 g (20 mmol) of 2-hydroxy-3-methoxybenzaldehyde was dissolved in methanol and then 0.9 mL (10 mmol) of 1,2-diaminopropane was added. The orange-yellow mixture obtained is stirred and heated under reflux for 4 hours, then filtered and air-dried. The yellow-orange precipitate, which is obtained, was washed thoroughly with diethyl ether. The compound was thoroughly washed with ether and dried over P_4O_{10} . Yield: 65.5 %. $C_{19}H_{22}N_2O_4$: Elemental Anal. Found (Calcd.) (%): C, 66.65 (66.63); H, 6.48 (6.45); N, 8.18 (8.15). IR (cm^{-1}): 3196, 3190, 2931, 1625, 1466-1358, 1249. RMN 1H [DMSO- d_6 , 300 MHz, (δ , ppm)]: 13.65 (s, 2H, Ar-OH), 8.30 (s, 2H, HC=N), 6.92-6.75 (m, 6H, Ar-H), 3.86 (d, 2H, CH₂), 3.79 (qd, 1H, CH), 3.71 (s, 6H, -CH₃), 1.40 (d, 3H, -CH₃-CH). RMN ^{13}C [DMSO- d_6 , 75 MHz, (δ , ppm)]: 20.25, 55.9, 64.49, 65.20, 118.00, 118.28, 123.14, 148.08, 151.40, 154.60.

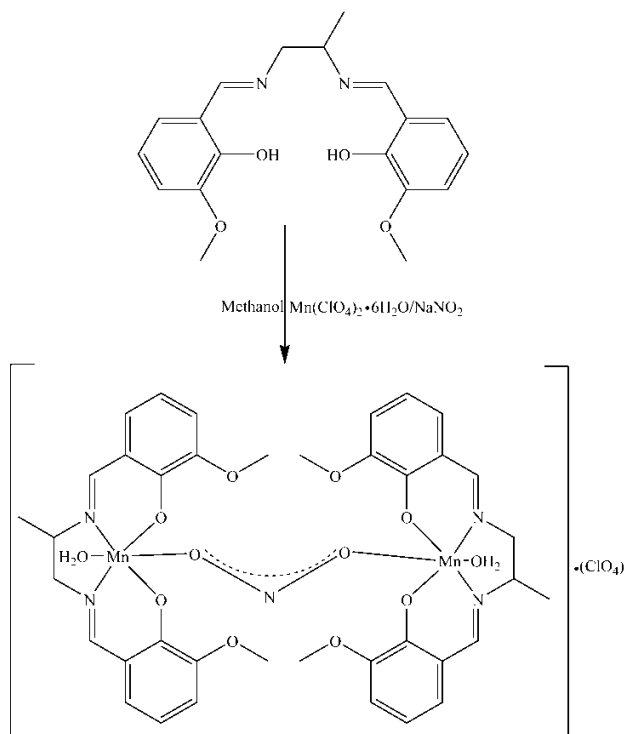
2.3. Synthesis of the complex $\{[Mn(L)(H_2O)](\mu-NO_2)[Mn(L)(H_2O)]\} \cdot (ClO_4)$

In a 100 mL round-bottomed flask, 0.1 g (0.3 mmol) of the H₂L ligand was dissolved in DMF (10 mL). 10 mL of methanolic solution of 0.85g (0.3 mmol) of manganese perchlorate hexahydrate $Mn(ClO_4)_2 \cdot 6H_2O$ and 0.026 g of sodium nitrate (0.3 mol) were added. The mixture is stirred for 2 hours at room temperature. The dark brown solution obtained was filtered and the filtrate was left to slow evaporation. One month after, brown colored crystals suitable for X-ray diffraction were obtained. IR (cm^{-1}): $\nu(C=N) = 1600\text{ cm}^{-1}$; $\nu(Ar-C-O) = 1220\text{ cm}^{-1}$, $\nu(ClO_4^-) = 1100\text{ cm}^{-1}$. $\mu_{\text{eff}} (\mu_B) : 5.22 \cdot \Lambda (\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}) : 93$.

2.4. X-ray crystallography

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 SuperNova Rigaku Oxford Diffraction with graphite monochromatized Cu $K\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Complex scattering factors were taken from the program package *SHELXTL* [20]. The structures were solved by direct methods which revealed the position of all non-hydrogen atoms. All the structures were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms [21]. The hydrogen atoms were geometrically optimized and refined

as riding model by AFIX instructions. Molecular graphics were generated using ORTEP-3 [22].



Scheme 1. Chemical diagrams for $\{[\text{Mn}(\text{L})(\text{H}_2\text{O})](\mu\text{-NO}_2)[\text{Mn}(\text{L})(\text{H}_2\text{O})]\} \cdot (\text{ClO}_4)$.

3. Results and Discussion

3.1. General study

The preparation of ligand H_2L was achieved in one step procedure by condensation of *o*-vanillin and 1,2-diaminopropane in 2:1 ratio in quantitative yield. The IR spectrum of H_2L shows a strong band at 1625 cm^{-1} assigned to the $\text{C}=\text{N}$ vibration. Two broad bands pointed at 3500 cm^{-1} and 3190 cm^{-1} are due to the phenolic $\text{O}-\text{H}$ groups. The band at 1249 cm^{-1} is attributed to the $\nu_{\text{C}-\text{O}}$ vibration. The bands observed in the range 2800 and 2935 cm^{-1} are attributed to the methylene groups. The bands in the region 1466 – 1358 cm^{-1} are characteristic of phenyl rings. The ^1H NMR spectrum of H_2L was recorded in $\text{DMSO}-d_6$. The singlets at 3.71 and 13.65 ppm represent respectively the $\text{CH}_3\text{-O-}$ and Ar-OH groups, respectively. The signal appearing as doublet at 1.4 ppm is attributed to

the $\text{CH}_3\text{-CH}$. The multiplet in the range 3.79-3.85 ppm represents the $-\text{CH}_2-$ and the CH-CH_3 . The signal at 8.3 ppm is attributed to the H-C=N . The signals of the aromatic protons appear in the range 6.92-6.75 ppm. The ^{13}C NMR spectrum of H_2L shows a signal at 166.5 ppm which represent the azomethine carbon atom. The signals at 151.4 and 64.49 ppm represent respectively the aromatic C_{ipso} of the OH of the phenol and the $\text{CH}_3\text{-O-}$.

The preparation of the manganese(III) complex is achieved by reaction of H_2L and $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and NaNO_3 in 1:1:1 ratio in methanol solution. The complex is isolated as dinuclear crystals suitable for X-ray analyses and formulated as $\{[\text{Mn}(\text{L})(\text{H}_2\text{O})](\mu\text{-NO}_2)[\text{Mn}(\text{L})(\text{H}_2\text{O})]\} \cdot (\text{ClO}_4)$. The complex is characterized by elemental analysis, IR, molar conductivity measurements, room temperature magnetic moments measurements and X-ray diffraction. Since no nitrite source was added in the reaction medium, nitrite anions must be formed from reduction of nitrate anions by dimethylformamide as reported in the literature [23, 24].

Upon coordination to the Mn(II) metal, the band due to C=N shifts to low frequency and appears at 1600 cm^{-1} , indicating the involvement of the azomethine nitrogen atom to the coordination to the Mn(II) ion[25]. Additionally, the bands due to the phenolic O-H disappears and the band due to the C-O shifts to low frequency. These facts are indicative of the deprotonation of the phenolic function and the involvement of the phenolic oxygen atom in the coordination to the Mn(II) ion. The bands pointed at 1100 cm^{-1} (ν_{as}) and 618 cm^{-1} (δ_{as}) are indicative of the presence of free tetrahedral perchlorate anions [26].

The values of the conductance of the complex in DMF is $83.1\ \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$ for the Mn(II) complex which is 1:1 electrolyte in nature [27]. The magnetic susceptibility measurement of the complex was performed at room temperature. The value of the room-temperature magnetic susceptibility of $5.22\ \mu\text{B}$ for the manganese complex is in accordance with the value expected for mononuclear Mn(II) complex [27,28]. This observation is indicative of a d^5 hexacoordinated manganese(II) complex.

Table 1. Crystal data, X-ray data collection, data reduction and structure refinement for the complex.

Chemical formula	$C_{38}H_{44}ClMn_2N_5O_{16}$
<i>Mr</i>	972.11
Crystal system	Triclinic
space group	$P\bar{1}$
Temperature (K)	293
<i>a</i> (Å)	12.4175 (3)
<i>b</i> (Å)	13.6360 (4)
<i>c</i> (Å)	14.5266 (4)
α (°)	62.243 (3)
β (°)	83.036 (2)
γ (°)	88.469 (2)
<i>V</i> (Å ³)	2159.39 (11)
<i>Z</i>	9
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.72
Crystal size (mm)	0.30 × 0.20 × 0.20
No. of measured reflections	40527
independent reflections	10270
Observed [<i>I</i> > 2σ(<i>I</i>)] reflections	7441
<i>R</i> _{int}	0.050
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)]	0.075
<i>wR</i> (<i>F</i> ²)	0.280
<i>GOF</i>	1.11
No. of reflections	10270
No. of parameters	577
No. of restraints	8
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	1.31, -1.22

3.2. Single crystal structure of the complex

Suitable single crystals for X-ray diffraction of the dinuclear manganese (III) complex was 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 triclinic system with the space group *P*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 dideprotonated ligand molecules, two Mn(III) ions, one bridge nitrite moiety, two coordinated water molecules and one free perchlorate anion. Each of the two Mn(III) cations is coordinated to one ligand in tetradentate fashion, through two phenolate oxygen atoms and two imino nitrogen atoms. Thus, the two units yielded are bridged by one nitrite anion through its oxygen atoms. Each Mn(III) cation is coordinated to one water molecule. For each ligand molecule, the oxygen atom of the methoxy group remains. Thus, the Mn(III) ion is coordinated to two phenolate oxygen atom, two alcoholic oxygen atoms and two imino nitrogen cation are six-coordinated and are situated in N₂O₄ inners. The environment around each Mn(III) cation is best described as a distorted octahedron. The best equatorial plane around Mn1 is occupied by the two phenolate oxygen atoms and the two azomethine nitrogen atoms which are quite coplanar (rms 0.0229), with the metal ion 0.0311(2) Å out of the plane. The axial positions are occupied by the oxygen atoms of the water molecule and the nitrite moiety, O1W—Mn1—O5A, 179.1 (1)°. The ranges of equatorial *cisoid* angles [82.1(2)°—93.4(1)°] and the values of the *transoid* angles [173.4(2)° and 174.1(1)°] reflect the slightly distortion of the N₂O₄ environment from the ideal octahedral geometry. For Mn2 cation, the best equatorial plane is occupied by the two phenolate oxygen atoms and the two azomethine nitrogen atoms which are quite coplanar (rms 0.0261), with the metal ion 0.0153(2) Å out of the plane. As observed for Mn1, the axial positions are occupied by the oxygen atoms of the water molecule and the nitrite moiety, O2W—Mn2—O5B, 177.1 (1)°. The ranges of equatorial *cisoid* angles [82.2(2)°—94.0(1)°] and the *transoid* angle values [173.6(1)° and 174.0(1)°] reflect the slightly distortion of the N₂O₄ environment from the ideal octahedral geometry. The sum of the of the angles subtended by the atoms in equatorial around is 359.93(°) for Mn1 and 360.03° for Mn2. The coordination of the ligand molecules to the Mn(III) cation results in the formation of two six membered rings of type MnOCCCN [i.e. Mn1/O1A/C1A/C2A/C8A/N1A and Mn1/O3A/C13A/C12A/C11A/N2A with bite angle values of 91.4(1)° and 93.0(2)°] and

one five membered ring of type MnNCCN [i.e. Mn1/N1A/C9A/C10A/N2A with bite angle value of 82.1(2)°]. The bite angle values observed for Mn2 are quite equal to those of Mn1 [O3B—Mn2—N2B = 92.0(1); O1B—Mn2—N1B = 91.8(1) and N2B—Mn2—N1B = 82.2(2)°]. The three mean planes formed by the two six-membered rings and the five-membered ring share a vertex occupied by the metal atom. They are twisted relative to each other with dihedral angles of 5.246(2)°, 9.115(3)° and 13.184(2)° for Mn1 and 6.678(1)°, 8.750(1)° and 15.196(1)° for Mn2. The bond distances Mn—O [1.880(3) Å – 1.892(2) Å] and Mn—N [1.969(4) Å – 1.988(4) Å] in the basal planes are different as observed in similar complexes reported in the literature [30–32]. The distances Mn—O [2.182(4) Å – 2.311(3) Å] in the axial positions are longer than those in the equatorial plane and are comparable to those reported for the complex [Mn(L)(CH₃OH)₂]ClO₄ (H₂L = *N,N'*-bis(1-(1'-hydroxy-2-naphthyl)ethylidene)propane-1,3-diamine) [33]. This is indicative of Jahn Teller distortion as expected for high spin manganese(III) complex [33,34]. The uncoordinated perchlorate anion is tetrahedral as shown by O—Cl—O angle values which fall in the range 94.7(5)—117.5(8)°. Numerous hydrogen bonds form layers propagating in bc plane and ensure the cohesion of crystalline structure in three-dimensional network.

Table 2. Selected geometric parameters (Å, °) for the complex.

Mn1—O1A	1.879 (3)	Mn1—O3A	1.884 (3)
Mn1—N1A	1.981 (3)	Mn1—O5A	2.181 (3)
Mn1—N2A	1.970 (4)	Mn1—O1W	2.299 (3)
O1A—Mn1—N1A	91.39 (14)	N1B—Mn2—O2W	89.00 (13)
O1A—Mn1—N2A	173.48 (14)	O1B—Mn2—N1B	91.77 (15)
O1A—Mn1—O5A	89.69 (14)	O1B—Mn2—N2B	173.96 (14)
O1A—Mn1—O1W	90.28 (11)	O1B—Mn2—O3B	94.05 (12)
N1A—Mn1—O5A	92.88 (14)	O1B—Mn2—O5B	91.73 (14)
N1A—Mn1—O1W	86.26 (13)	O1B—Mn2—O2W	88.68 (12)

N2A—Mn1—N1A	82.17 (16)	N2B—Mn2—O5B	87.94 (15)
N2A—Mn1—O5A	91.68 (17)	N2B—Mn2—O2W	91.88 (13)
N2A—Mn1—O1W	88.26 (15)	O3B—Mn2—N1B	173.56 (14)
O3A—Mn1—N1A	174.08 (13)	O3B—Mn2—N2B	91.98 (15)
O3A—Mn1—N2A	92.93 (14)	O3B—Mn2—O5B	89.49 (13)
O3A—Mn1—O5A	90.57 (13)	O3B—Mn2—O2W	88.39 (11)
O3A—Mn1—O1W	90.29 (12)	O5B—Mn2—O2W	177.86 (12)
O5A—Mn1—O1W	179.14 (12)	N1B—Mn2—O5B	93.08 (14)

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C8A—H8A...O5B ⁱ	0.93	2.40	3.100(5)	132.5
C11A—H11A...O1 ⁱⁱ	0.93	2.42	3.318(7)	163.4
C9B—H9B...O4A	0.98	2.56	3.459(6)	151.7
C11B—H11B...O3	0.93	2.50	3.317(12)	146.3
C19B—H19A...O2W	0.96	2.66	3.408(9)	134.7
O1W—H1WA...O1A ⁱⁱⁱ	0.84(2)	2.16(4)	2.893(4)	146(5)
O1W—H1WA...O2A ⁱⁱⁱ	0.84(2)	2.25(3)	2.970(4)	143(5)
O1W—H1WB...O3A ⁱⁱⁱ	0.85(2)	2.17(4)	2.914(4)	146(5)
O1W—H1WB...O4A ⁱⁱⁱ	0.85(2)	2.24(3)	2.955(4)	142(5)
O2W—H2WA...O1B ^{iv}	0.84(2)	2.29(5)	2.907(4)	130(5)

$O2W-H2WA \cdots O2B^{iv}$	0.84(2)	2.21(3)	3.005(4)	159(5)
$O2W-H2WB \cdots O3B^{iv}$	0.83(2)	2.28(4)	2.954(4)	139(5)
$O2W-H2WB \cdots O4B^{iv}$	0.83(2)	2.28(3)	3.019(4)	148(5)

Symmetry codes : (i) $-x+1, -y+1, -z+1$; (ii) $x, y-1, z+1$; (iii) $-x, -y+1, -z+1$; (iv) $-x+1, -y+2, -z+1$.

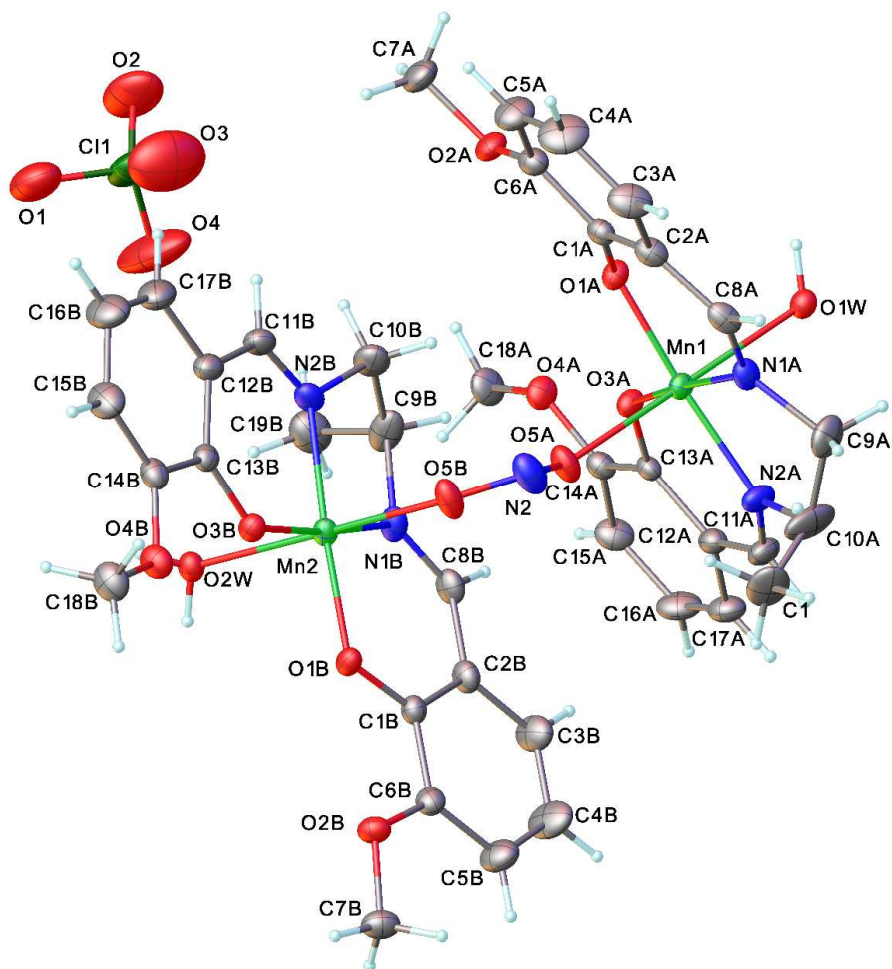


Figure 1. Crystal structure of the Mn(III) complex. Displacement ellipsoids are drawn at the 30% probability level.

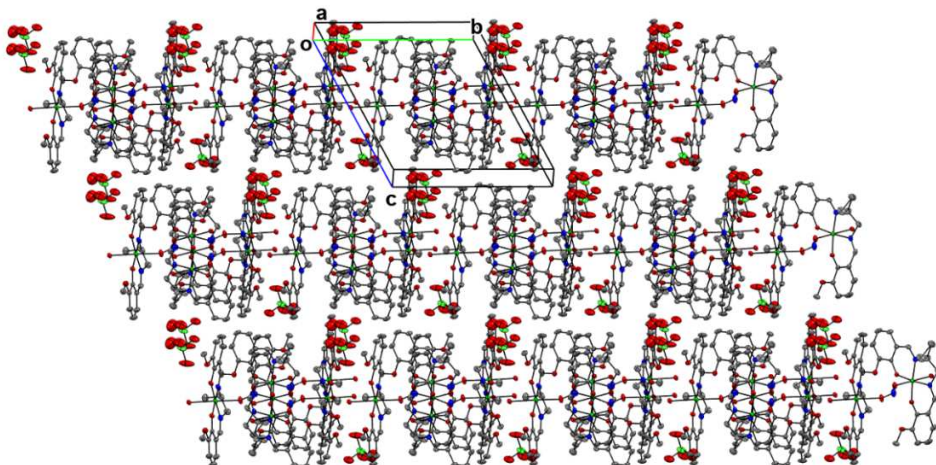


Figure 2. The packing of the compound in the crystal structure.

4. Conclusion

The dinuclear complex $\{[\text{Mn}(\text{L})(\text{H}_2\text{O})](\mu\text{-NO}_2)[\text{Mn}(\text{L})(\text{H}_2\text{O})]\} \cdot (\text{ClO}_4)$ synthesized from the ligand 2-((2-hydroxyethylimino)methyl)-6-methoxyphenol and the manganese (II) di perchloride tetrahydrate have been characterized by the infrared spectroscopy, conductivity and room-temperature measurement, elemental analysis, and X-ray diffraction technique. Despite the presence of nitrite source, the two mononuclear are bridged by a NO_2^- moiety which is formed in situ by the reduction of nitrate group by DMF. In the resulting complex the ligand is dideprotonated yielding two phenolate oxygen atoms. Each of the two ligand molecules acts in tetradentate fashion in the coordination to Mn(III) through the phenolate oxygen atoms and the azomethine nitrogen atoms. Each Mn(III) is coordinated to a water molecule and two Mn(III) are bridged by NO_2 in $\mu(\text{O}, \text{O}')$ -mode. Each manganese (III) ion occupied N_2O_4 inner site, resulting in an octahedral geometry around Mn (III). Numerous hydrogen bonds connect the dinuclear into layer propagation along bc plane.

Supporting information

CCDC-2232745 contains the supplementary crystallographic data for the compound. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

In Memorium

Mouhamadou Moustapha SOW 1982–2022.

While preparing this work, we were shocked to hear of the death of Dr Mouhamadou Moustapha SOW. Dr Mouhamadou Moustapha SOW was a very talented young chemist working in inorganic chemistry. SOW has helped many PhD students over the years and his informed advice and support will be greatly missed by our team, both personally and professionally. This article is dedicated to his memory.

Conflicts of Interest

The authors declare that they have no conflict of interest.

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