

Synthesis and structure elucidation of complexes of Co(III), Mn(III), and Cu(II) from N, O donor ligand 2-[(2-hydroxyethylimino)ethyl]phenol or 2-[(2-hydroxyethylimino)methyl]phenol

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Abstract: Analogous ligands derived from salicylaldehyde, 2-[(2-hydroxyethylimino)ethyl]phenol (H_2L^1) and 2-[(2-hydroxyethylimino)methyl]phenol (H_2L^2), have been synthesized and used to prepare three complexes in which the ligands acts in different fashions. Complexes formulated as $[Co_2(L^1)_2(OCH_2CH_2NH_2)(SCN)] \cdot (CH_3CH_2OH)$ (**1**), $\{[Mn(HL^2)_2] \cdot Cl \cdot (H_2O)\}_n$ (**2**), and $\{[Cu(L^2)(NO_3)]\}_n$ (**3**) were synthesized by mixing an equimolar amount of an ethanol solution containing $Co(NO_3)_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$ or $Cu(NO_3)_2 \cdot 2H_2O$ and an ethanol solution containing the appropriate ligand H_2L^1 or H_2L^2 . In the dinuclear cobalt(III) complex **1**, each of the two metal ions is coordinated by one monodeprotonated ligand molecule through three set donors. Each of the ethanolate oxygen atom of the ligand molecules acts as bridge to connect the two metal centers yielding a dinuclear unit. Additionally, a third bridge is formed by an ethanolate oxygen atom of 2-aminoethanol which is present as co-ligand. For one of the Co(III) ion the sixth coordination site is occupied by an amino nitrogen atom while for the other one the sixth site is occupied by a nitrogen atom of a thiocyanate group. Each of the Co(III) is situated in N_2O_4 inner. For the Mn(III) complex **2**, the cation is coordinated by two ligand molecules in bidentate fashion through the phenolate oxygen atom and the azomethine nitrogen atom, the ethanolic oxygen atom of each ligand molecule being linked to a Mn(III) ion of another complex thus forming a polymeric chain in which the $Mn^{III} \cdots Mn^{III}$ distance is 5.601 (2) Å. The Mn(III) is situated in a N_2O_4 inner. The copper(II) ion of the complex **3** is coordinated by one monodeprotonated organic molecule through the phenolate oxygen atom, the azomethine nitrogen atom and the ethanolic oxygen atom and a bidentate nitrate anion. One of the oxygen atoms is coordinated to a Cu(II) ion of another complex molecule resulting in a $\eta^1:\eta^2:\mu_2-O_3N$. The complex is a polymer in which the $Cu^{II} \cdots Cu^{II}$ distance is 4.3486 (3) Å. Each copper (II) ion is situated in a severely distorted octahedral environment.

Keywords: Crystal structure; cobalt; manganese; copper; polymeric; octahedral.

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I. Introduction

Schiff bases resulting from the condensation of a derivative of salicylaldehyde and 2-aminoethanol are widely studied in coordination chemistry [1-4]. These Schiff bases can coordinate to metal ions in different fashions [5-8]. It has been shown that transition metals form stable complexes with very diverse structures depending on the metal/Schiff base ratio [6,9,10]. The multidentate ligand derived from 2-aminoethanol and salicylaldehyde or 2-hydroxy acetophenone shows various connectivity fashions and can generate mono- and polymetallic complexes [11-13].

The biological and physical properties of these compounds are strongly influenced by the nature of the metal center and its environment [13-15]. Many of these complexes have important properties both in medicine and in physics. Compounds with antimicrobial [16,17], anticancer^[18] [18] or DNA cleavage [19] properties have been reported. Complexes exhibiting magnetic [20,21] or catalysis [22,23] properties are listed.

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Our research group previously reported complexes from [2-((2-hydroxyethylimino)methyl)phenol] [6]. In this article, we report the synthesis of three new complexes of cobalt (III), manganese (III) and copper (II) obtained from the Schiff bases 2-[(2-hydroxyethylimino)ethyl]phenol or 2-[(2-hydroxyethylimino)methyl]phenol. These complexes are characterized by elementary, FTIR, UV-Vis and magnetic analyses. Single crystal X-ray diffraction studies reveal that the ligand acts differently with the metal ions. In the dinuclear complex **1** each Co(III) ion is coordinated with two H_2L^1 molecules which act in a tridentate fashion. In complex **2**, two ligand molecules act in a bidentate fashion on a single Mn(III) ion, while each of the alcoholic oxygen atom coordinate another Mn(III) ion forming a polymer. For complex **3** only one ligand molecule acts in a tridentate manner on a single Cu(II) ion.

II. Experimental section

2.1. Starting materials and instrumentations

Salicylaldehyde, 2-aminoethanol, cobalt nitrate hexahydrate, manganese chloride tetrahydrate, copper chloride dihydrate, and potassium thiocyanate were purchased from Sigma–Aldrich and used as received without further purification. All solvents used were of reagent grade. The ligand molecule were synthesized following the reported procedure [24]. 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 complexes 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 Matthey scientific magnetic susceptibility balance (Calibrant: $Hg[Co(SCN)_4]$).

2.2. Preparation of the cobalt(III) complex (1).

A solution of $Co(NO_3)_2 \cdot 6H_2O$ (1 mmol, 0.2490 g) in 5 mL of ethanol was mixed with a solution of KSCN (2 mmol, 0.1944 g) in 5 mL of ethanol before filtered. The filtrate was added to the round bottomed flask which contains a solution of the ligand (H_2L^1) (2 mmol, 0.3582 g) in 5 mL of ethanol. The resulting mixture was mixed and refluxed for two hours. On cooling, the mixture was filtered, and the filtrate was left for slow evaporation. Green crystals suitable for X-ray diffraction were collected after a week. The compound was formulated as $[Co_2(L^1)_2(OCH_2CH_2NH_2)(SCN)] \cdot (CH_3CH_2OH)$. Yield: 83%. Elemental Anal. Found (Calcd.) (%): C, 47.18 (47.11); H, 5.38 (5.40); N, 8.80 (8.77); S, 5.04 (5.01). IR (ν , cm^{-1}): $[\nu(O-H) 3209, \delta(OH) 873]; \nu(C=N) 1594; \nu(S=C=N) 2128; \nu(C=C) 1532, 1463, 1434; \nu(C-OPh) 1236$. UV-Visible (DMSO, λ_{max} (nm)): 288, 389, 545. Λ ($S \cdot cm^2 \cdot mol^{-1}$): 15. Diamagnetic.

2.3. Preparation of the manganese(III) complex (2).

A solution of $MnCl_2 \cdot 4H_2O$ (1 mmol, 0.1979 g) in 5 mL of ethanol was added to the round bottomed flask which contains a solution of the ligand (H_2L^2) (2 mmol, 0.3582 g) in 5 mL of ethanol. The resulting mixture was mixed and refluxed for two hours. On cooling, the mixture was filtered, and the filtrate was left for slow evaporation. Green crystals suitable for X-ray diffraction were collected after a week. The compound was formulated as $\{[Mn(HL^2)_2] \cdot Cl \cdot (H_2O)\}_n$. Yield: 71%. Elemental Anal. Found (Calcd.) (%): C, 49.50 (49.48); H, 5.08 (5.05); N, 6.41 (6.37); Cl, 8.12 (8.09). IR (ν , cm^{-1}): $[\nu(O-H) 3396, \delta(OH) 885]; \nu(C=N) 1605; \nu(C=C) 1545, 1446, 1434; \nu(C-OPh) 1302$. UV-Visible (DMSO, λ_{max} (nm)): 290, 329, 439. Λ ($S \cdot cm^2 \cdot mol^{-1}$): 87. μ_{eff} (μ_B): 5.31.

2.4. Preparation of the copper(II) complex (3).

A solution of $Cu(NO_3)_2 \cdot 2H_2O$ (1 mmol, 0.2236 g) in 5 mL of ethanol was mixed with a was added to the round bottomed flask which contains a solution of the ligand (H_2L^2) (2 mmol, 0.3582 g) in 5 mL of ethanol. The resulting mixture was mixed and refluxed for two hours. On cooling, the mixture was filtered, and the filtrate was left for slow evaporation. Green crystals suitable for X-ray diffraction were collected after a week. The compound was formulated as $\{[Cu(HL^2)(NO_3)]\}_n$. Yield: 69 %. Elemental Anal. Found (Calcd.) (%): C, 37.31 (37.29); H, 3.48 (3.45); N, 9.67 (9.64). IR (ν , cm^{-1}): $\nu(C=N) 1599; \nu(C=C) 1541, 1470, 1448; \nu(C-OPh) 1286$. UV-Visible (DMSO, λ_{max} (nm)): 283, 376, 637. Λ ($S \cdot cm^2 \cdot mol^{-1}$): 24. μ_{eff} (μ_B): 1.97.

2.5. X-ray crystallography

Crystals suitable for single–crystal X–ray diffraction, of the reported compounds, were grown by slow evaporation of EtOH solution of the complexes. Details of the crystal structure solution and refinement are given in Table 1. Diffraction data were collected using an ENRAF NONIUS Kappa CCD diffractometer with graphite monochromatized $MoK\alpha$ radiation ($\lambda = 0.71073$ Å). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Complex scattering factors were taken from the

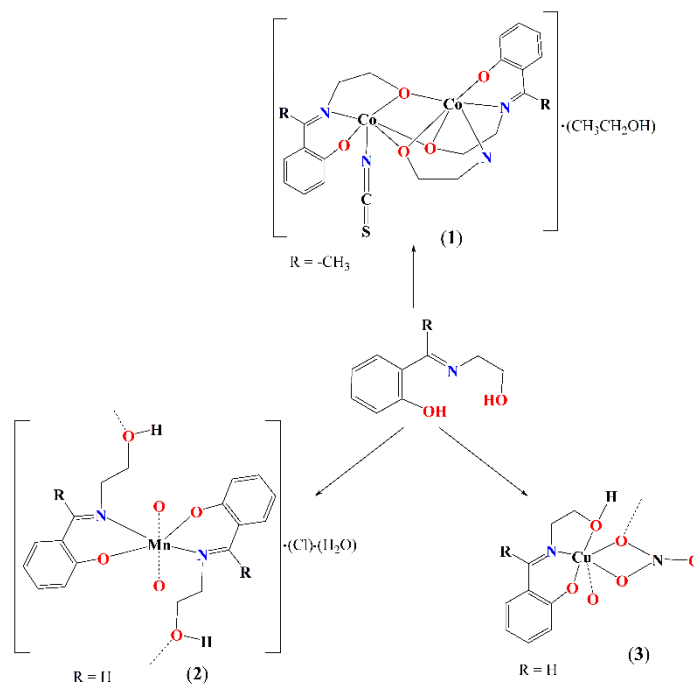
program package SHELXTL [25]. The structures were solved by direct methods, which revealed the position of all non-hydrogen atoms. All the structures were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms [26]. The hydrogen atoms of water molecules and NH groups were located in the Fourier difference maps and refined. Others H atoms (CH and CH₃ groups) were geometrically optimized and refined as riding model by AFIX instructions. Molecular graphics were generated using ORTEP-3 [27].

III. Results and discussion

3.1. General study

The reaction of 2-[(2-hydroxyethylimino)ethyl]phenol (H_2L^1) or 2-[(2-hydroxyethylimino)methyl]phenol (H_2L^2) with $Co(NO_3)_2 \cdot 6H_2O$, $MnCl_2 \cdot 4H_2O$ or $Cu(NO_3)_2 \cdot 2H_2O$ in ethanol afforded a dinuclear cobalt(III) complex formulated as $[Co_2(L^1)_2(OCH_2CH_2NH_2)(SCN)] \cdot (CH_3CH_2OH)$ and two polymeric complexes formulated as $\{[Mn(HL^2)_2] \cdot Cl \cdot (H_2O)\}_n$ and $\{[Cu(HL^2)(NO_3)]\}_n$. The reactions of those ligands with metal transition salts are depicted in scheme 1. The infrared spectra of the complexes (**1-3**) show band attributed to the C=N in the range 1600-1590 cm^{-1} . The shift to lower frequencies of this band which was pointed at *ca.* 1634 cm^{-1} in the infrared spectrum of the free ligands is indicative of the involvement of the azomethine in the coordination. The infrared spectrum of complex **1** exhibits a sharp medium intensity band at 2127 cm^{-1} which is characteristic of coordinated thiocyanate group. Additional bands pointed at 3209 cm^{-1} and 3396 cm^{-1} are observed and are attributed, respectively, to the uncoordinated ethanol molecule for complex **1** and the lattice water molecule for complex **3**. The molar conductivity values of 15 and 24 $S \cdot cm^2 \cdot mol^{-1}$ for complex **1** and complex **3** respectively, are indicative of neutral electrolyte in DMF solutions. Complex **2** exhibits a molar conductivity value of 87 $S \cdot cm^2 \cdot mol^{-1}$ in DMF which is in accordance with 1:1 electrolyte nature [28].

The electronic spectra of the complexes **1-3** show bands in the region 280-300 which are respectively attributed to the intraligand transitions $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. The peaks observed at 389 nm, in the electronic spectrum of complex **1**, at 376 nm for **2** and at 439 nm for **3** are due to the LMCT transitions due to O and N donor atoms of the ligand to the metal ion [29-31]. Cobalt (III) complex **1** shows an additional band at 534 nm which is due to a $d \rightarrow d$ transition in a Co(III) ion in octahedral environment [32]. This $d \rightarrow d$ band is due to the transition ${}^5T_{2g} \rightarrow E_g$. In the spectrum of the Manganese(III) complex **2** a much weaker band is exhibited in the lower energy region at 637 nm. This band is due to spin allowed transition for ${}^5E_g \rightarrow {}^5T_{2g}$ Mn(III) in octahedral environment [33,34]. The electronic spectrum of copper(II) complex **3** exhibited bands at 593 and 627 nm corresponding to ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transitions, respectively. Those observations are indicative of copper ion in octahedral environment [31]. The room temperature magnetic moment measurement of the complexes **1-3** were determined. As expected, complex **1** is diamagnetic low-spin Co(III)^[35] [35]. During the experiment, the Co(II) used in air atmosphere was oxidized to Co(III). Complex **2** shows room temperature magnetic moments of 5.31 μ_B which is close to the spin only value for high spin d^4 manganese(III) ion [36]. Copper complex **3** gave μ_{eff} of 1.97 μ_B close proximity to the value of 1.73 μ_B expected for one unpaired electron, which is indicative of octahedral geometry around the copper(II) ion [37].



Scheme 1. Synthesis procedure of complexes (1), (2) and (3).

Table-1. Crystallographic data and refinement parameter for the compound (1), (2) and (3).

Chemical formula	$C_{23}H_{28}Co_2N_4O_5S \cdot C_2H_6O$ (1)	$C_{18}H_{20}MnN_2O_4 \cdot Cl \cdot H_2O$ (2)	$C_9H_{10}CuN_2O_5$ (3)
<i>Mr</i>	636.48	436.76	289.73
Crystal shape/color	Prismatic/brown	Block/blue	Block/green
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1$	Monoclinic, $P2_1/n$
Crystal size (mm)	$0.25 \times 0.13 \times 0.10$	$0.27 \times 0.1 \times 0.06$	$0.24 \times 0.09 \times 0.04$
<i>a</i> , <i>b</i> , <i>c</i> (Å)	10.8445 (3)	5.59524 (17)	9.5069 (4)
<i>b</i> (Å)	12.0063 (4)	18.9792 (6)	8.0749 (3)
<i>c</i> (Å)	12.0680 (4)	9.2426 (4)	13.9843 (6)
α (°)	115.967 (3)	90	90
β (°)	96.305 (2)	93.620 (3)	101.560 (4)
γ (°)	97.568 (2)	90	90
<i>V</i> (Å ³)	1375.41 (8)	979.54 (6)	1051.76 (8)
<i>Z</i>	2	2	4
<i>D</i> _{cal} (g cm ⁻³)	1.537	1.481	1.830
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
<i>T</i> (K)	292	100	100
μ (mm ⁻¹)	1.33	0.84	2.09
Index ranges	$-13 \leq h \leq 13$; $-14 \leq k \leq 13$; $-14 \leq l \leq 14$	$-7 \leq h \leq 7$; $-25 \leq k \leq 25$; $-12 \leq l \leq 12$	$-12 \leq h \leq 12$; $-10 \leq k \leq 10$; $-18 \leq l \leq 18$
<i>F</i> (000)	600	452	588
θ range (°)	1.911-26.019	2.804-28.693	2.385-28.685
No. of measured reflections	33472	19868	25966
No. of independent	5408	5014	2712

No. of observed [$I > 2\sigma(I)$] reflections	4730	4845	2532
R_{int}	0.036	0.037	0.028
$R[F^2 > 2\sigma(F^2)]$	0.032	0.054	0.020
$wR(F^2)$	0.091	0.133	0.052
Goodness-of-fit (Gof)	1.04	1.07	1.04
No. of parameters	355	254	157
No. of restraints	1	3	0
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e \AA^{-3})	0.58, -0.50	1.78, -1.08	0.41, -0.28

3.2. Description of the crystal structure of the complex 1

The title compound crystallizes in the triclinic system in the space group $P\bar{1}$. The asymmetric unit of the title compound, $[\text{Co}_2(\text{L}^1)_2(\text{OCH}_2\text{CH}_2\text{NH}_2)(\text{SCN})]\cdot(\text{CH}_3\text{CH}_2\text{OH})$, contains two dideprotonated ligand, one deprotonated aminoethanol molecule, one thiocyanate anion and one uncoordinated ethanol molecule (Figure 1). The selected bond lengths and angles are collected in Table 2. In the dinuclear unit the two metal Co^{III} ions are hexacoordinated. Two dideprotonated Schiff bases act as bridge through the ethanolate oxygen atom of the ligand. Each Co^{III} ion is linked to the phenolic oxygen atom and the azomethine nitrogen atom of one ligand. The monodeprotonated aminoethanol molecule acts as bridge between the two Co^{III} ions through the ethanolate oxygen atom while the amino nitrogen atom is coordinated to one Co^{III} . The coordination sphere of the second Co^{III} is completed by a thiocyanate anion through its nitrogen atom. Each of the cobalt ion is hexacoordinated, exhibiting a NSO_4 environment for Co1 and N_2O_4 environment for Co2. The basal plane of Co1 is occupied by N1, O1, O2, O4 atoms while N2, O4, O5, O3 atoms occupied the basal plane of Co2. The *cisoid* angles are in the range $[80.11 (6)^\circ\text{--}96.02 (8)^\circ]$ for Co1 and $[81.22 (6)^\circ\text{--}94.37 (7)^\circ]$ for Co2 while the *transoid* angles are $\text{O1—Co1—O2} = 172.20 (7)^\circ$, $\text{N1—Co1—O4} = 168.09 (7)^\circ$, $\text{O5—Co2—N2} = 170.14 (7)^\circ$ and $\text{O3—Co2—O4} = 174.76 (6)^\circ$ (Table 2). The sum of the angles subtended by the atoms in the basal planes are 359.82° and 358.69° for Co1 and Co2 respectively. The apical positions of Co1 ions are occupied by an enolate oxygen atom of an aminoethanol molecule and one nitrogen atom of a thiocyanate group with angle value of $\text{O5—Co1—N4} = 174.26 (7)^\circ$. For Co2 the apical positions are occupied by an enolate oxygen atom of one ligand molecule and the nitrogen atom of the aminoethanol molecule with angle value of $\text{O2—Co2—N3} = 165.36 (7)^\circ$. Each ligand form with the corresponding Co ion one five-membered ring CoNCCO and one hexa-membered ring CoNCCCO , which share a vertex at the azomethine nitrogen. The N—Co—O bite angles values within the five-membered chelate rings fall in the range $[89.91 (7)^\circ\text{--}89.54 (7)^\circ]$ while the values due to the bite angle of the hexa-membered chelate are in the range $[95.47 (8)^\circ\text{--}96.02 (8)^\circ]$. These values are comparable to those reported for similar octahedral complexes [38].

In the dinuclear complex the cobalt(III) ions are displaced from their basal planes $[\text{N1}, \text{O1}, \text{O2}, \text{O4}]$ (rms deviation 0.0291 \AA) for Co1 and $[\text{N2}, \text{O4}, \text{O5}, \text{O3}]$ (rms 0.0600 \AA) for Co2 by $0.0759 (7) \text{ \AA}$ and $0.1159 (7) \text{ \AA}$ respectively. The two cobalt ions are bridged by two oxygen atoms from the ligand and one oxygen anion from an aminoethanol molecule $[\text{Co}(\mu\text{-ethanolato})\text{Co}]$. The $\text{Co—O}_{\text{bridge}}$ distances are different with values of $\text{Co1—O2} = 1.9134 (14) \text{ \AA}$ and $\text{Co2—O2} = 1.9621 (15) \text{ \AA}$; $\text{Co1—O4} = 1.9403 (14) \text{ \AA}$ and $\text{Co2—O4} = 1.9011 (14) \text{ \AA}$; $\text{Co1—O5} = 1.9103 (14) \text{ \AA}$ and $\text{Co2—O5} = 1.9131 (13) \text{ \AA}$. These values are comparable to the values reported for similar Co(III) complexes [39,40]. The angles subtended by the bridged oxygen atom to the two Co(III) ions are $\text{Co1—O2—Co2} = 83.11 (5)^\circ$, $\text{Co1—O4—Co2} = 84.02 (5)^\circ$, $\text{Co1—O5—Co2} = 84.52 (5)^\circ$. The separation between the two metal centers is about $\text{Co1—Co2} = 2.5711 (4) \text{ \AA}$. The structure is consolidated by numerous intra and intermolecular hydrogen bonds (Table 3). Intramolecular hydrogen bond $\text{C10—H10B}\cdots\text{O3}$ and intermolecular hydrogen bonds $[\text{N3—H3A}\cdots\text{S1}^i, \text{C22—H22B}\cdots\text{O1}^i, \text{C22—H22B}\cdots\text{O4}^i, \text{C18—H18C}\cdots\text{O2}^{ii}]$ ($i = -x+1, -y+1, -z$, $ii = -x+2, -y+1, -z$) link the molecules. The structure consists of chains superimposed on each other leading to the formation of a three dimensional network (Figure 2).

Table-2. Selected geometric parameters (\AA , $^\circ$) of compounds (1), (2) and (3).

Co1—O1	1.8491 (14)	Mn1—O3	1.857 (6)	Cu1—N1	1.9167 (12)
Co1—N1	1.8807 (18)	Mn1—O1	1.868 (6)	Cu1—O1	1.9021 (10)
Co1—O2	1.9134 (14)	Mn1—N1	2.030 (7)	Cu1—O2	1.9822 (10)
Co1—O4	1.9403 (14)	Mn1—N2	2.038 (7)	Cu1—O3	1.9819 (10)

Co2—O3	1.8578 (14)	Mn1—O2 ⁱ	2.226 (6)	Cu1—O4 ⁱ	2.5651 (11)
Co2—O5	1.9131 (13)	Mn1—O4 ⁱⁱ	2.235 (6)	Cu1—O4	2.6226 (11)
Co2—N3	1.9172 (19)	Mn1—Mn ⁱ	5.601 (2)	Cu1—Cu1 ⁱ	4.3486(3)
Co1—O2—Co2	83.11 (5)	O3—Mn1—O1	179.7 (3)	N1—Cu1—O2	84.31 (5)
Co2—O4—Co1	84.02 (5)	O3—Mn1—N1	90.5 (3)	N1—Cu1—O3	171.94 (5)
Co2—O5—Co1	84.52 (5)	O1—Mn1—N1	89.3 (3)	N1—Cu1—O4 ⁱ	97.08 (4)
O1—Co1—N4	90.38 (8)	O3—Mn1—N2	89.9 (3)	N1—Cu1—O4	118.36 (4)
N1—Co1—N4	91.23 (8)	O1—Mn1—N2	90.3 (3)	O1—Cu1—N1	94.92 (5)
O1—Co1—O5	93.78 (7)	N1—Mn1—N2	179.4 (3)	O1—Cu1—O2	172.18 (4)
N4—Co1—O5	174.26 (7)	O3—Mn1—O2 ⁱ	90.7 (2)	O1—Cu1—O3	90.08 (4)
O1—Co1—O2	172.20 (7)	O1—Mn1—O2 ⁱ	89.1 (2)	O1—Cu1—O4 ⁱ	86.94 (4)
O1—Co1—O4	93.75 (6)	N1—Mn1—O2 ⁱ	85.9 (2)	O1—Cu1—O4	98.91 (4)
N1—Co1—O4	168.09 (7)	N2—Mn1—O2 ⁱ	94.6 (2)	O2—Cu1—O4 ⁱ	85.44 (4)
O3—Co2—O4	174.76 (6)	O3—Mn1—O4 ⁱⁱ	89.2 (2)	O2—Cu1—O4	88.26 (4)
O3—Co2—O5	94.37 (6)	O1—Mn1—O4 ⁱⁱ	91.0 (2)	O3—Cu1—O2	91.59 (4)
N2—Co2—O5	170.14 (7)	N1—Mn1—O4 ⁱⁱ	94.2 (2)	O3—Cu1—O4	54.42 (4)
O3—Co2—O2	96.58 (7)	N2—Mn1—O4 ⁱⁱ	85.3 (2)	O3—Cu1—O4 ⁱ	89.48 (4)
O5—Co1—O4	80.29 (6)	O2 ⁱ —Mn1—O4 ⁱⁱ	179.8 (3)	O4 ⁱ —Cu1—O4	143.163 (14)
			(i) x-1, y, z; (ii) x+1, y, z.	(i) -x+1/2, y+1/2, -z+3/2.	

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

D—H...A	D—H	H...A	D...A	D—H...A
(1)				
N3—H3A...S1 ⁱ	0.89	2.74	3.493 (4)	143.0
C10—H10B...O3	0.97	2.49	3.033 (6)	115.3
C22—H22B...O1 ⁱ	0.97	2.57	3.354 (5)	138.2
C22—H22B...O4 ⁱ	0.97	2.61	3.522 (5)	155.9
C18—H18C...O2 ⁱⁱ	0.96	2.52	3.370 (6)	147.6
Symmetry codes: (i) -x+1, -y+1, -z; (ii) -x+2, -y+1, -z.				
(2)				
O4—H4...O5 ⁱ	0.82	1.90	2.713 (9)	171.5
O2—H2...Cl1 ⁱⁱ	0.82	2.20	3.017 (6)	171.1
C18—H18B...O1	0.97	2.47	3.098 (10)	121.9
C16—H16...Cl1 ⁱⁱⁱ	0.93	2.96	3.608 (8)	127.8
C9—H9A...O3	0.97	2.49	3.106 (10)	121.4
C7—H7...Cl1 ⁱⁱⁱ	0.93	2.95	3.831 (9)	159.4
C17—H17B...Cl1 ⁱⁱⁱ	0.97	2.76	3.666 (8)	156.2
Symmetry codes: (i) x-1, y, z; (ii) x+1, y, z; (iii) -x, y+1/2, -z+1.				
(3)				

C7—H7...O5 ⁱ	0.95	2.44	3.3775 (18)	169.1
C8—H8B...O3 ⁱⁱ	0.99	2.52	3.3114 (18)	136.7
O2—H2A...O1 ⁱⁱ	0.79 (2)	1.79 (2)	2.5778 (14)	171 (2)
Symmetry codes: (i) $x+1, y, z$; (ii) $-x+1/2, y-1/2, -z+3/2$.				

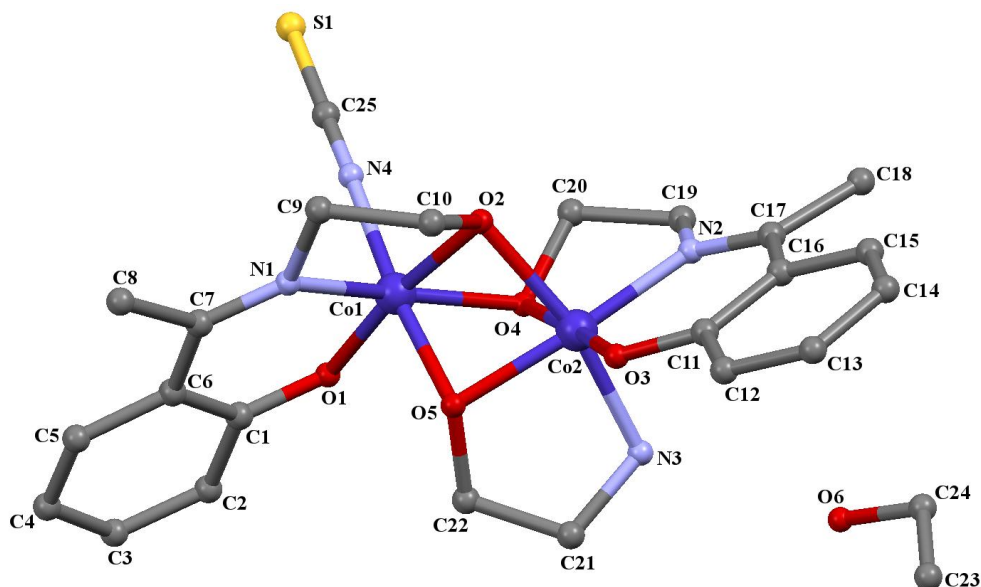


Fig. 1. Crystal structure of complex (1), showing the atom numbering scheme, H atoms are omitted for clarity.

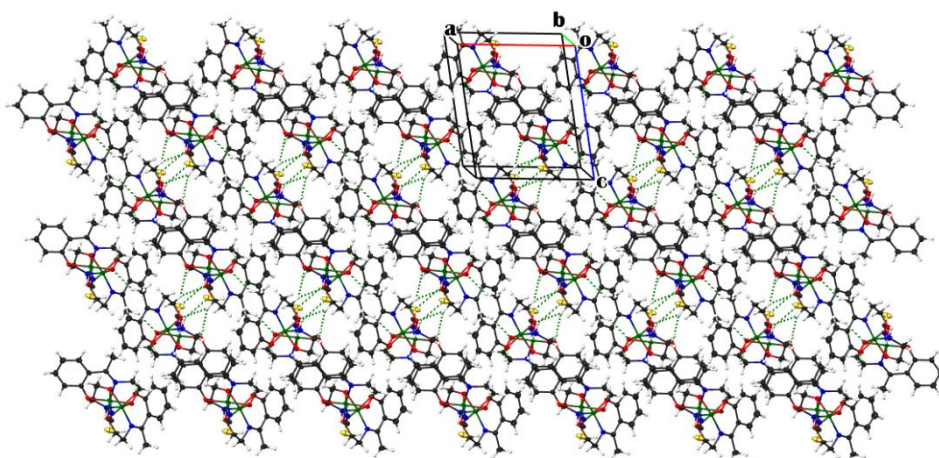


Fig. 2. Crystal packing for complex (1) showing the polymeric chain along the *a-c* direction.

3.3. Description of the crystal structure of the complex 2

The title compound crystallizes in the monoclinic system in the space group $P2_1$. The asymmetric unit of the title compound, $\{[\text{Mn}(\text{HL})_2]\cdot\text{Cl}\cdot(\text{H}_2\text{O})\}_n$, contains two monodeprotonated ligand molecule, one Mn(III) ions, one chloride ion and one uncoordinated water molecule (Figure 3a). The selected bond distances and angles are collected in Table 2. The complex is mononuclear and each of the two ligand molecules is coordinated to the Mn(III) ion through its phenolate oxygen atom and its azomethine nitrogen atom. Each of the oxygen atoms of the alcoholic functions is coordinated to Mn(III) ion of a neighboring mononuclear complex yielding a polymeric chain with Mn1...Mn1 distance of 5.601 (2) Å (Figure 3b). The environment around the Mn(III) is best described as a distorted octahedral geometry. The phenolate oxygen atoms and the two imino nitrogen atoms of the two ligand molecules, occupied the basal plane while the apical positions were occupied by the two neighboring oxygen atoms of mononuclear complex molecules with angle value of O2ⁱ—Mn1—O4ⁱⁱ = 179.8 (3)°. The *cisoid* angles values are in the range [89.3 (3)°–90.5 (3)°] and the *transoid* angles values are respectively O1—Mn1—O3 = 179.7 (3)° and N1—Mn1—N2 = 179.4 (3)°. The sum of the angles subtended by

the atoms in the basal plane is 360° . Those values are close proximity to those reported for a perfect square bipyramidal geometry [41]. Each of the ligand form with the Mn1 ion six-membered ring MnOCCCN with bite angle values of N—Mn1—O of $89.3(3)^\circ$ and $89.9(3)^\circ$. The two mean planes defined by the six-membered rings are quite co-planar with dihedral angle value of $0.776(4)^\circ$. The atoms in the basal plane are quite co-planar rms 0.0051 and the deviation of Mn1 ion from this plane is 0.0016 Å. The distances Mn—O in the basal plane [$1.857(6)$ Å and $1.868(6)$ Å] are shorter than those in the apical position [$2.226(6)$ Å and $2.235(6)$ Å]. This observation is indicative of a Jahn Teller effect [42]. Those values are comparable to the reported values for similar complexes^[36] [36]. The Mn—N bond lengths are $2.030(7)$ Å and $2.038(7)$ Å and in accordance with the values reported for analogous Mn(III) Schiff base complex [36,43]. A fragment of infinite hydrogen bonded network of **2** viewed along the *b* axis direction is showed in the Figure 4 . The polymeric chain of $\{[\text{Mn}(\text{HL})_2]\cdot\text{Cl}\cdot(\text{H}_2\text{O})\}_n$ are connected by $\text{O—H}\cdots\text{O}$ hydrogen bond within the hydrogen-bonded framework. In the crystal, intramolecular hydrogen bonds stabilized the structure of the polymeric chain along *b* axis ($\text{O4—H4}\cdots\text{O5}^i$ ($i = x-1, y, z$) and $\text{O2—H2}\cdots\text{Cl1}^{ii}$ ($ii = x+1, y, z$)) leading to the formation of dimeric $R_2^2(10)$ motif. Additional weak intramolecular $\text{C—H}\cdots\text{O}$ hydrogen bonds : $\text{C9—H9A}\cdots\text{O3}$, $\text{C18—H18B}\cdots\text{O1}$, $\text{C7—H7}\cdots\text{Cl1}^{ii}$ ($ii = x+1, y, z$), $\text{C16—H16}\cdots\text{Cl1}^{iii}$, and $\text{C17—H17B}\cdots\text{Cl1}^{iii}$ ($iii = -x, y+1/2, -z+1$) are also observed (Table 3). These sheets are stacked along the *b* axis using only van der Waals forces (Fig. 4). No intermolecular hydrogen bonds or shared chelating groups are found between the sheets in this third dimension.

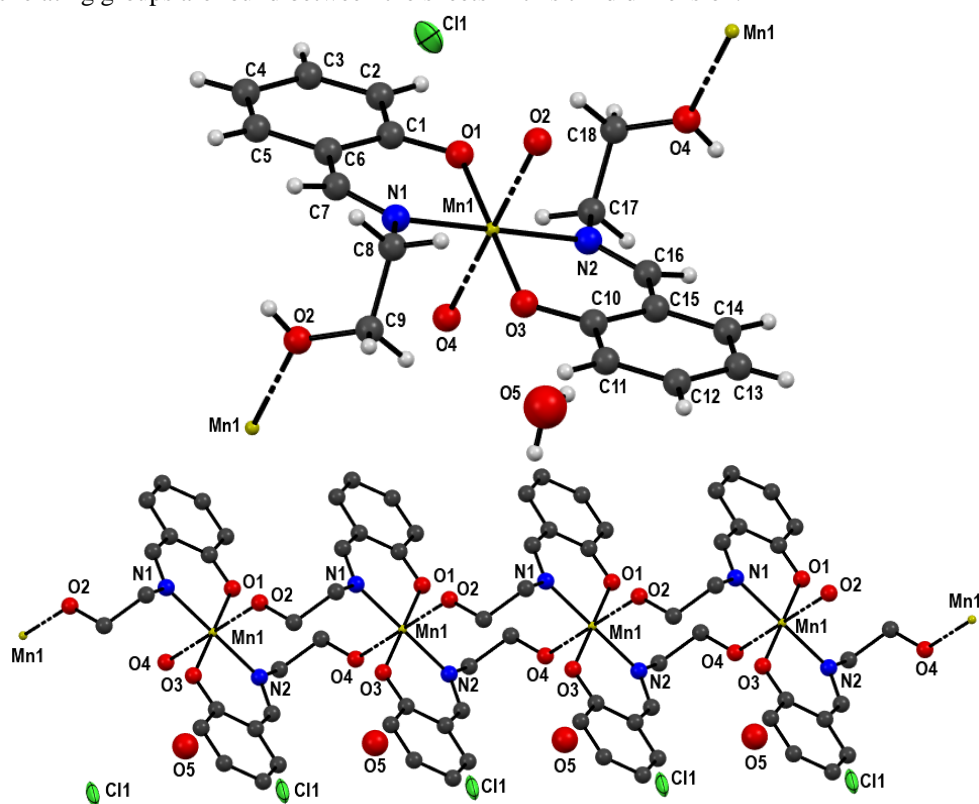


Fig. 3. (a) Crystal structure of complex (2), showing the atom numbering scheme; (b) the polymeric chain of the compound

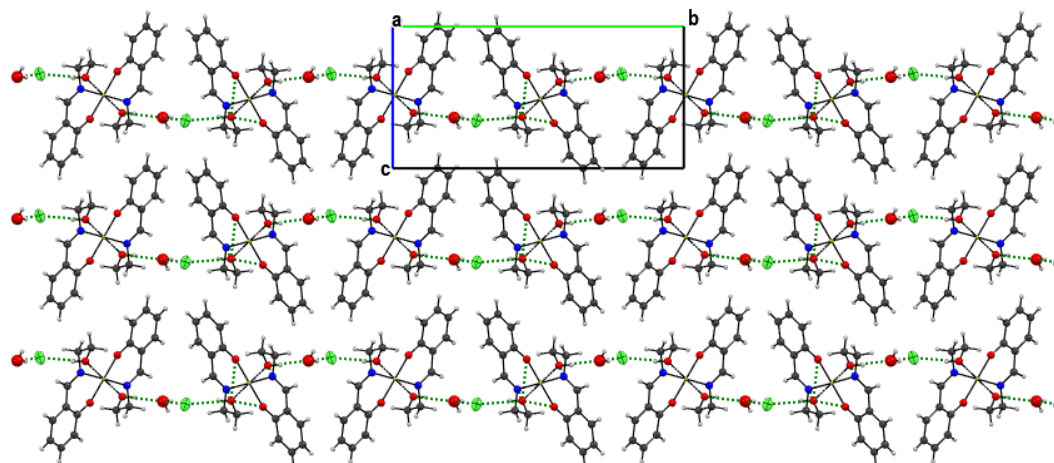


Fig. 4. Crystal packing for complex (2) showing the polymeric chain along the *b* axis.

3.4. Description of the crystal structure of the complex 3

The title compound crystallizes in the monoclinic system in the space group $P2_1/n$. The asymmetric unit of the title compound, $\{[Cu(HL^2)(NO_3)]\}_n$, contains one monodeprotonated ligand molecule, one copper(II) ion and one bidentate nitrate anion (Figure 5). The selected bond lengths and angles are collected in Table 2. The Schiff base acts in tridentate fashion through the phenolate oxygen atom, the azomethine nitrogen atom and the alcoholic oxygen atom resulting in one five-membered $[CuOCCN]$ and one six-membered $[CuOCCCN]$ rings around the Cu(II) ion. The structure is a polymeric chain in which each mononuclear unit is linked to a neighboring unit through one oxygen atom of the bidentate nitrate group. The Cu1 is in a severely distorted octahedral geometry forming by the three coordinated atoms from the ligand and one oxygen of the nitrate group defining the basal plane and two oxygen atoms from two different nitrate groups occupying the apical positions. The axial μ_2 -O-NO₂ link the Cu(II) atoms somewhat unsymmetrically. One of the bridging Cu—O bonds is significantly longer than the other as shown by the following distances values Cu1—O4 = 2.256 (1) Å and Cu2—O4ⁱ = 2.623 (1) Å (Table 2). Those bonds lengths are much longer than those found in the equatorial plane Cu1—O1 = 1.9021 (10) Å, Cu1—O2 = 1.9822 (10) Å, Cu1—O3 = 1.9819 (10) Å and Cu1—N1 = 1.9167 (12) Å. These observations are due to the Jahn Teller effect as observed in similar complex [42]. The copper (II) ion is displaced from the basal plane [O1N1O2O3, (rms deviation 0.1090 Å)] by 0.0072 Å. The dihedral angle value of 5.691 (8)° between the plane of the phenolate [O1C1C2C3C4C5C6] ring and the plane formed by the atoms in the open chain [C7N1C8C9O2], shows a distortion from planarity and is indicative of a twist in the ligand. The separation between two Cu(II) in the polymer is 4.3486 (3) Å. This value is too long to consider intermetallic interaction with a bridge angle Cu1—O4—Cu1ⁱ of 113.91(4)° [44]. The *cisoid* angles values fall in the range [84.31 (5)°–94.92 (5)°] and are in accordance with values reported for analogous complexes [45]. The sum of the angle values subtended by the atoms in equatorial positions is 360.9°. The values of 84.31 (5)° and 94.92(5)° of the N—Cu—O bite angles within five-membered and hexa-membered chelate respectively are as expected for similar complex^[45] [45]. The *transoid* angles values N1—Cu1—O3 (171.94 (5)°) and O1—Cu1—O2 (172.18 (4)°) and the angle subtended by the apical positions O4—Cu1—O4ⁱ (143.16 (3)°) deviates severely from the ideal values of 180°. The Cu1 ion is situated in a severely distorted octahedral environment.

A series of intermolecular hydrogen bonds C7—H7···O5ⁱ (*i* = *x*+1, *y*, *z*), O2—H2A···O1ⁱⁱ and C8—H8B···O3ⁱⁱⁱ (*ii* = *-x*+1/2, *y*-1/2, *-z*+3/2), connect the units forming a sheet parallel to the *b* axis. (Table 3, Figure 6). No intermolecular hydrogen bonds or shared chelating groups are found between the sheets.

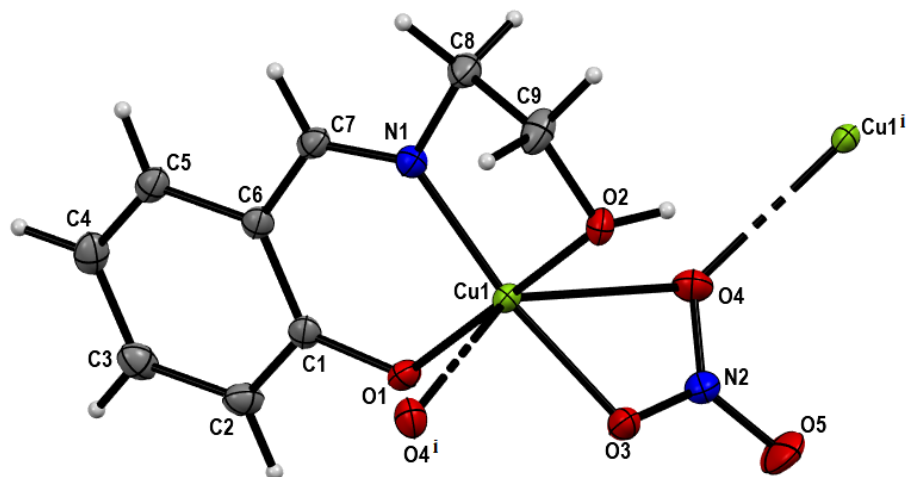


Fig. 5. Crystal structure of complex (3), showing the atom numbering scheme.

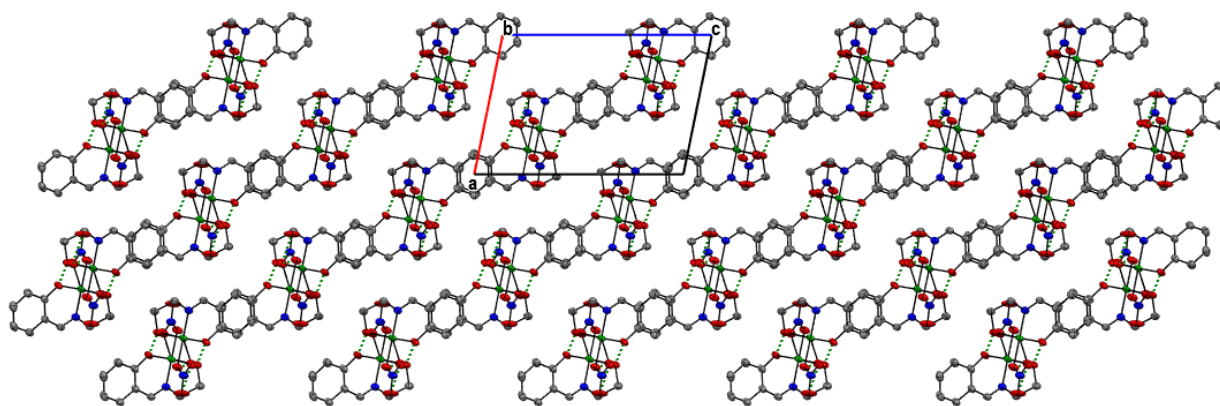


Fig. 6. Crystal packing for complex (3) showing the polymeric chain along the *b* axis.

IV. Conclusion

In the present work, we report the synthesis and characterization of a new complex of cobalt(III) (1) prepared from the 2-[(2-hydroxyethylimino)ethyl]phenol and two new complexes of manganese(III) (2) and copper (II) (3) prepared from the tridentate ligand 2-[(2-hydroxyethylimino)methyl]phenol. The structures of the complexes are completely different. The cobalt (II) complex is a mononuclear, in which the metal center is coordinated to two tridentate ligands, yielding an octahedral geometry. The cobalt(III) is situated in N_2O_4 inner. The manganese (III) complex is a polymer, in which the two phenoxo oxygen atoms and the two amino nitrogen atoms lie in the equatorial planes of a slightly distorted octahedral N_2O_4 environment. The copper complex is a polymeric complex, in which each bridging nitrate anions act in $\eta^1:\eta^2:\mu_2-O_3N$ mode. The copper (II) ions are in severely distorted octahedral environment NO_5 .

V. Supporting information

CCDC- 2118201, 2118202, 2118203 contains respectively the supplementary crystallographic data for Copper (II), Cobalt (III) and Mn(III) complexes. 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.

References

- [1]. S. Majumder, J.P. Naskar, A. Bhattacharya, R. Ganguly, P. Saha, S. Chowdhury, A new phenylimidodrhonium(V) compound containing the 2-[(2-hydroxyethylimino)methyl]phenol Schiff-base ligand: experimental and theoretical aspects, *J. Coord. Chem.* 2015, 68, 599–615.
- [2]. Y.M. Chumakov, V.L. Tsapkov, P.A. Petrenko, L.G. Popovski, Y.A. Simonov, G. Bocelli, B.Y. Antosyak, A.O. Paraschivescu, A.P. Gulea, Crystal structure of 4,4-bipyridine-containing complexes of copper(II) nitrate with 1-[(2-Hydroxyethylimino)methyl]naphthalen-2-ol and 2-[(2-hydroxyethylimino)methyl]phenol, *Russian J. Coord. Chem.*, 2009, 35, 504–511.

- [3]. L.-F. Zhang, Z.-H. Ni, Z.-M. Zong, X.-Y. Wei, C.-H. Ge, H.-Z. Kou, A novel one-dimensional complex: catena-poly-[[manganese(III)-di- μ -2-(2-hydroxy-ethyl)-imino-methyl]-phenolato- $\kappa^2 O^1, N: \kappa O^2; \kappa O^2: \kappa^2 O^1$] chloride], *Acta Crystallogr., Sect. C: Struct. Chem.*, 2015, 61, m542–m544.
- [4]. J.-L. Hou, Y. Bi, Y.-H. Xiao, H.-Y. Wu, C.-B. Sun, W. Chen, Synthesis, X-ray crystal structures, and biological activity copper(II) and nickel(II) complexes derived from 5-bromo-2-((2-hydroxyethylimino)methyl)phenol, *Inorg. Nano-Met. Chem.*, 2021, 51, 875–881.
- [5]. Z.-L. You, J.-Y. Chi, {2-[2-(Ethylamino)ethyliminomethyl]phenol} {2-[2-(ethylamino)ethyliminomethyl]phenolato} nickel(II) perchlorate, *Acta Crystallogr., Sect. E: Struct. Chem.*, 2006, 62, m1498–m1500.
- [6]. C. Ndoye, B. Diome, M.M. Sow, P.A. Gaye, P. Haba, I.E. Thiam, O. Diouf, G. Excoffier, S.J. Coles, M. Gaye, Synthesis, spectroscopic characterization, and crystal structure of Co(III), Ni(II) and Cu(II) complexes with Schiff bases derived from salicylaldehyde, *IOSR J. Appl. Chem. (IOSR-JAC)*, 2021, 14, 01–16.
- [7]. G. Cros, J.-P. Laurent, Unusual dinuclear copper(II) and nickel(II) complexes of a novel Schiff base deriving from 2-aminoethanol, *Inorg. Chim. Acta*, 1988, 142, 113–117.
- [8]. J. Szklarzewicz, M. Skaisgirski, P. Paciorek, K. Kurpiewska, P. Zabierowski, M. Radoń, Mo(IV) and W(IV) cyanido complexes with Schiff bases. Synthesis, X-ray single crystal structures, physicochemical properties and quantum chemical calculations, *Polyhedron*, 2014, 68, 112–121.
- [9]. R. Duan, B. Gao, X. Li, X. Pang, X. Wang, H. Shao, X. Chen, Zinc complexes bearing tridentate O,N,O-type half-Salen ligands for ring-opening polymerization of lactide, *Polymer*, 2015, 71, 1–7.
- [10]. N. Hoshino, T. Ito, M. Nihei, H. Oshio, Syntheses, structures and magnetic properties of multinuclear manganese complexes with Schiff base ligands, *Inorg. Chem. Commun.*, 2003, 6, 377–380.
- [11]. S. Hazra, S. Majumder, M. Fleck, S. Mohanta, Synthesis, molecular and supramolecular structure, spectroscopy and electrochemistry of a dialkoxo-bridged diuranyl(VI) compound, *Polyhedron*, 2008, 27, 1408–1414.
- [12]. P. Zabierowski, J. Szklarzewicz, K. Kurpiewska, K. Lewiński, W. Nitek, Assemblies of substituted salicylidene-2-ethanolamine copper(II) complexes: From square planar monomeric to octahedral polymeric halogen analogues, *Polyhedron*, 2013, 49, 74–83.
- [13]. H.-L. Lu, J.-J. Liang, Z.-Z. Zeng, P.-X. Xi, X.-H. Liu, F.-J. Chen, Z.-H. Xu, Three salicylaldehyde derivative Schiff base Zn^{II} complexes: synthesis, DNA binding and hydroxyl radical scavenging capacity, *Transition Met. Chem.*, 2007, 32, 564–569.
- [14]. S. Cao, R. Cheng, D. Wang, Y. Zhao, R. Tang, X. Yang, J. Chen, Dinuclear copper(II) complexes of “end-off” bicompartamental ligands: Alteration of the chelating arms on ligands to regulate the reactivity of the complexes towards DNA, *J. Inorg. Biochem.*, 2019, 192, 126–139.
- [15]. J.M. Mir, N. Jain, P.S. Jaget, R.C. Maurya, Density functionalized [Ru^{II}(NO)(Salen)(Cl)] complex: Computational photodynamics and in vitro anticancer facets, *Photodiagn. Photodyn. Ther.*, 2017, 19, 363–374.
- [16]. L.F. Cai, Copper(II) complexes of mono-condensed N,O-donor Schiff base ligands: Synthesis, crystal structures, and antibacterial activity, *Russian J. Coord. Chem.*, 2017, 43, 535–539.
- [17]. L. Shi, H.-M. Ge, S.-H. Tan, H.-Q. Li, Y.-C. Song, H.-L. Zhu, R.-X. Tan, Synthesis and antimicrobial activities of Schiff bases derived from 5-chloro-salicylaldehyde, *Eur. J. Med. Chem.*, 2007, 42, 558–564.
- [18]. H. Luo, Y. Xia, B. Sun, L. Huang, X. Wang, H. Lou, X. Zhu, W. Pan, X. Zhang, Synthesis and Evaluation of In Vitro Antibacterial and Antitumor Activities of Novel N,N-Disubstituted Schiff Bases, *Bioch. Res. Int.*, 2017, 2017, 6257240.
- [19]. M. Amjad, S.H. Sumra, M.S. Akram, Z.H. Chohan, Metal-based ethanolamine-derived compounds: a note on their synthesis, characterization and bioactivity, *J. Enzyme Inhib. Med. Chem.*, 2016, 31, 88–97.
- [20]. S.-S. Qian, Y. Zhao, M.-M. Zhen, C.-L. Zhang, Z.-L. You, H.-L. Zhu, Synthesis, crystal structures, and magnetic properties of tetranuclear nickel(II) and copper(II) complexes with tridentate Schiff bases, *Transition Met. Chem.*, 2013, 38, 63–68.
- [21]. A.V. Pestov, P.A. Slepukhin, V.N. Charushin, Copper and nickel chelate complexes with polydentate N,O-ligands: structure and magnetic properties of polynuclear complexes, *Russ. Chem. Rev.*, 2015, 84, 310–333.
- [22]. M. Ngcobo, S.O. Ojwach, Structural and ethylene oligomerization studies of chelated N⁺O (iminoamino)phenol nickel(II) complexes, *J. Organomet. Chem.*, 2017, 846, 33–39.
- [23]. I.A. Salem, Role of resin-manganese(II) complexes in hydrogen peroxide decomposition, *Int. J. Chem. Kinet.*, 1994, 26, 341–346.
- [24]. S. Yamada, Y. Kuge, K. Yamanouchi, Nickel(II) Complexes of Schiff Bases Derived from Alkanolamines and Salicylaldehyde and 3-Methoxysalicylaldehyde, *Bull. Chem. Soc. Jpn.*, 1967, 40, 1864–1867.
- [25]. G.M. Sheldrick, *SHELXT* – Integrated space-group and crystal-structure determination, *Acta Crystallograph. Sect. A: Found. Adv.*, 2015, 71, 3–8.
- [26]. G.M. Sheldrick, Crystal structure refinement with *SHELXL*, *Acta Crystallogr. Sect. C: Struct. Chem.*, 2015, 71, 3–8.
- [27]. L.J. Farrugia, *WinGX* and *ORTEP* for Windows: an update, *J. Appl. Crystallogr.*, 2012, 45, 849–854.
- [28]. W.J. Geary, The use of conductivity measurements in organic solvents for the characterisation of coordination compounds, *Coord. Chem. Rev.*, 1971, 7, 81–122.
- [29]. N. Mohan, S.S. Sreejith, R. George, P.V. Mohanan, M.R.P. Kurup, Synthesis, crystal structure and ligand based catalytic activity of octahedral salen Schiff base Co(III) compounds, *J. Mol. Struct.*, 2021, 1229, 129779.
- [30]. E. Pousaneh, S. Sadighian, R. Bikas, H. Hosseini-Monfared, A. Sousaraei, M. Siczek, T. Lis, One-pot synthesis, crystal structure and theoretical calculations of a dinuclear Mn(III) complex with in-situ generated O,N,O- and O,N-donor dichelating hydrazone ligand, *J. Mol. Struct.*, 2020, 1199, 127023.
- [31]. F.I. Abouzayed, S.M. Emam, S.A. Abouel-Enein, Synthesis, characterization and biological activity of nano-sized Co(II), Ni(II), Cu(II), Pd(II) and Ru(III) complexes of tetradentate hydrazone ligand, *J. Mol. Struct.*, 2020, 1216, 128314.
- [32]. N. Mohan, S. S. Sreejith, M. R. P. Kurup, Investigation on catecholase activity of salen Co(III) octahedral complexes, *Polyhedron*, 2019, 173, 114129.
- [33]. M. Maiti, D. Sadhukhan, S. Thakurta, E. Zangrando, G. Pilet, A. Bauzá, A. Frontera, B. Dede, S. Mitra, Synthesis, structural characterization, theoretical calculations and catecholase mimetic activity of manganese-Schiff base complexes, *Polyhedron*, 2014, 75, 40–49.
- [34]. K. Das, A. Datta, B.B. Beyene, C. Massera, E. Garribba, C. Sinha, T. Akitsu, S. Tanka, A zig-zag end-to-end azido bridged Mn^{III} 1-D coordination polymer: Spectral elucidation, magnetism, redox study and biological activity, *Polyhedron*, 2017, 127, 315–322.
- [35]. K. Ghosh, S. Roy, A. Ghosh, A. Banerjee, A. Bauzá, A. Frontera, S. Chattopadhyay, Three mononuclear octahedral cobalt(III) complexes with salicylaldehyde Schiff bases: Synthesis, characterization, phenoxazinone synthase mimicking activity and DFT study on supramolecular interactions, *Polyhedron*, 2016, 112, 6–17.
- [36]. P. Paul, K.R.N. Bhowmik, S. Roy, D. Deb, N. Das, M. Bhattacharjee, R.N.D. Purkayastha, L. Male, V. Mckee, R. Pallegu, D. Maiti, A. Bauza, A. Frontera, A.M. Kirillov, Synthesis, structural features, antibacterial behaviour and theoretical investigation of two new manganese(III) Schiff base complexes, *Polyhedron*, 2018, 151, 407–416.

- [37]. N.G. Yernale, M.B.H. Mathada, Preparation of octahedral Cu(II), Co(II), Ni(II) and Zn(II) complexes derived from 8-formyl-7-hydroxy-4-methylcoumarin: Synthesis, characterization and biological study, *J. Mol. Struct.*, 2020, 1220, 128659.
- [38]. O. Yu. Vassilyeva, K.V. Kasyanova, V.N. Kokozay, B.W. Skelton, Crystal structure of dichloridobis[μ -2-methoxy-6-[(methylimino)methyl]phenolato]-{2-methoxy-6-[(methylimino)methyl]phenolato}cadmium(II)cobalt(III) monohydrate, *Acta Crystallogr., Sect. E: Struct. Chem.*, 2018, 74, 1532–1535.
- [39]. J. Welby, L.N. Rusere, J.M. Tanski, L.A. Tyler, Syntheses and crystal structures of mono-, di- and trinuclear cobalt complexes of a salen type ligand, *Inorg. Chim. Acta*, 2009, 362, 1405–1411.
- [40]. R. Blaauw, J.L. van der Baan, S. Balt, M.W.G. de Bolster, G.W. Klumpp, H. Kooijman, A.L. Spek, Bridged (alkoxo)Co^{III}(salen) complexes: synthesis and structure, *Inorg. Chim. Acta*, 2002, 336, 29–38.
- [41]. I. Mondal, K. Ghosh, S. Chattopadhyay, Synthesis and structural characterization of three manganese(III) complexes with N₂O₂ donor tetradentate Schiff base ligands: Exploration of their catalase mimicking activity, *Inorg. Chim. Acta*, 2019, 494, 123–131.
- [42]. P.K. Mudi, N. Bandopadhyay, M. Joshi, M. Shit, S. Paul, A.R. Choudhury, B. Biswas, Schiff base triggering synthesis of copper(II) complex and its catalytic fate towards mimics of phenoxazinone synthase activity, *Inorg. Chim. Acta*, 2020, 505, 119468.
- [43]. D. Dong, N. Yu, H. Zhao, D. Liu, J. Liu, Z. Li, D. Liu, Synthesis, structure, and electrochemistry and magnetic properties of a novel 1D homochiral Mn^{III}(5-Brsalen) coordination polymer with left-handed helical character, *J. Mol. Struct.*, 2016, 1104, 58–62.
- [44]. D. Draganca, A.W. Addison, M. Zeller, M.E. Foster, M.J. Prushan, L.K. Thompson, M. D. Revenco, A.D. Hunter, A tetranuclear copper(II) complex with bis(o-aminobenzaldehyde)thiocarbohydrazone, *Inorg. Chim. Acta*, 2010, 363, 2065–2070.
- [45]. I. Buta, A. Ardelean, P. Lönnecke, G. Novitchi, E. Hey-Hawkins, M. Andruh, O. Costisor, Structural and magnetic properties of three one-dimensional nitrate-, azido- and phenoxido-bridged copper(II) coordination polymers, *Polyhedron*, 2020, 190, 114766.

Momath Kebea, et. al. “Synthesis and structure elucidation of complexes of Co(III), Mn(III), and (Cu(II) from N, O donor ligand 2-[(2-hydroxyethylimino)ethyl]phenol or 2-[(2-hydroxyethylimino)methyl]phenol. *IOSR Journal of Applied Chemistry (IOSR-JAC)*, 14(12), (2021): pp 04-15.