

Synthesis, Crystal Structures and Spectroscopic Properties of a Trinuclear $[\text{Cu}_3(\text{HL})_2(\text{NO}_3)_2](\text{H}_2\text{O})(\text{CH}_2\text{CH}_2\text{OH})$ Complex and a $[\text{Mn}(\text{HL})(\text{CH}_3\text{COO})]_n$ Polymer With $\text{H}_3\text{L} = \text{N},\text{N}'\text{-(2-hydroxypropane-1,3-diyl)-bis-(salicylaldimine)}$

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Abstract

A new trinuclear copper(II) complex $[\text{Cu}_3(\text{HL})_2(\text{NO}_3)_2](\text{H}_2\text{O})(\text{CH}_2\text{CH}_2\text{OH})$ (**1**) and a new polymer complex of manganese (III) $[\text{Mn}(\text{HL})(\text{CH}_3\text{COO})]_n$ (**2**) where H_3L is $\text{N},\text{N}'\text{-(2-hydroxypropane-1,3-diyl)-bis-(salicylaldimine)}$ have been prepared and characterized by molar conductance, magnetic measurements, infrared spectral studies and the single crystal structure of the complexes. The crystal structure features the presence of two independent molecules in the asymmetric unit of **1**. The polymeric unit of **2** is formed by a Mn–O bridge of one molecule with its centrosymmetric homologue. The Schiff base acts as tridentate in its dianionic form in the two complexes. In the case of the copper complex **1** the nitrate groups are found to be bidentate bridging and the terminal copper(II) ions assume a square pyramidal geometry while the central copper(II) has distorted square bipyramidal geometry. In complex **2** the acetate group acts as bidentate bridging and the manganese (III) ion has distorted octahedral geometry.

Keywords: copper(II), manganese(III), crystal structure, nitrate, acetate.

1. Introduction

Transition metal complexes of Schiff bases are being investigated more frequently now than ever before because of their potential properties. They have a pharmacological application such as in *Gram positive* bacteria in vitro.¹ In the last decade, a large number of copper(II) complexes have been prepared and structurally studied in attempt to mimic the potent inhibitor properties of DNA synthesis.^{2,3} Salicylaldehyde and benzoylhydrazone were found to possess bacterial activity.⁴ Using copper (II), complex of salicylaldehyde or benzoylhydrazone was shown to be more potent than the free ligand, suggesting that the metal center is the biologically active site. Analogous compounds have been investigated as drugs for genetic disorders such as thalassemia.⁵⁻⁷

This paper is devoted to the trinuclear species derived from $\text{N},\text{N}'\text{-(2-hydroxypropane-1,3-diyl)-bis-(salicylaldimine)}$ (H_3L). This Schiff base is an acyclic ligand bearing both nitrogen and oxygen donors, which exhibit both hard and soft base character. This ligand contains two adjacent coordination inners, which can encapsulate ions such as transition metals. In order to

understand the coordination chemistry, we synthesized a series of complexes and investigated their spectroscopic properties. Molecular structures of $[\text{Cu}_3(\text{HL})_2(\text{NO}_3)_2](\text{H}_2\text{O})(\text{CH}_2\text{CH}_2\text{OH})$ and $[\text{Mn}(\text{HL})(\text{CH}_3\text{COO})]_n$ have been elucidated by X-ray diffraction.

2. Experimental

2.1. General

NMR spectrum was recorded on a Bruker 400 spectrometer, infrared spectra were recorded on a Nicolet 5SXC FT-IR spectrophotometer using KBr pellets or nujol mulls. Elemental analysis of C, H, N and Cl was performed by the analytical laboratory of the Department of Inorganic Chemistry (University of Padua, Italy). Molar conductance measurement was made using a WTW LF-330 conductivity meter with a WTW conductivity cell on about 1 mmol dm^{-3} dimethylformamide solution at room temperature. Room temperature magnetic susceptibility measurements were made on solid complexes using a Johnson Matthey balance with $\text{Hg}[\text{Co}(\text{SCN})_4]$ as the calibrator.

All chemicals and solvents used were of reagent grade. All metal(II) salts were used as nitrate or acetate.

2.2. Synthesis of the Schiff base ligand

The Schiff base N,N' -(2-hydroxypropane-1,3-diyl)-bis-(salicylalimine) (H_3L) was prepared with slight modification of literature procedures.⁸ 1,3-diaminopropan-2-ol (22 mmol) dissolved in ethanol was refluxed with an ethanolic solution of salicylaldehyde (44 mmol), in the presence of few drops of glacial acetic acid. A yellow solution was obtained. The reflux was maintained for 3 hours. On cooling the reactant media, no precipitate was separated. The solvent was eliminated by a rotary evaporator. Yellow oil was obtained. On adding diethyl ether a yellow precipitate was separated. The compound was thoroughly washed with ether and dried over P_4O_{10} . The yield is 93%. The compound was characterized by elemental analysis and different spectral methods (see Figure 1). Elemental *Anal. Calc.* for $C_{17}H_{18}N_2O_3$ (298.13): C 68.44; H 6.08; N 9.39. Found: C 68.39; H 6.02; N 9.25%. IR (nujol mulls) $\nu = 3440$ (s), 3135 (s), 1633 (s), 1579 (m), 1523 (m), 1463 (m), 1278 (m), 1078 (s), 1027 (m), 983 (s), 894 (s), 758 (s) cm^{-1} . NMR 1H ($CDCl_3$); δ (ppm) 3.6 (d, 4H, CH_2), 3.8 (m, 1H, $CH(OH)$), 6.9–7.4 (m, 8H, H_{Ar}), 8.5 (s, 1H, $HC=N$), 10.1 (s, 1H, $(OH)CH$), 12.2 (s, 2H, $OH-Ar$). NMR ^{13}C ($CDCl_3$); δ (ppm) 62.7 (CH_2), 69.3 ($CH(OH)$), 116.49 (CAr), 118.3 (CAr), 118.6 (CAr), 131.6 (CAr), 132.3 (CAr), 160.9 ($C(OH)Ar$), 167 ($C=N$).

2.3. Synthesis of $[Cu_3(HL)_2(NO_3)_2](H_2O)(CH_2CH_2OH)$ (1)

An ethanol solution (10 ml) of the ligand H_3L (3 mmol) was added to copper nitrate trihydrate (2 mmol) in ethanol (10 ml). The resulting mixture was heated for one hour and filtered while hot. Slow evaporation of the filtrate led to the formation of brown crystals suitable for X-ray analyses, after one week. The yield is 58.9%. Elemental *Anal. Calc.* for $C_{36}H_{40}N_6O_{14}Cu_3$ (971.36): C 44.51; H 4.15; N 8.65. Found: C 44.48; H 4.19; N 8.62%. IR (cm^{-1} , nujol mulls): $\nu(O-H)$ 3404, $\nu(C=N)$ 1599, $\nu_1(NO_3)$ 1425, $\nu_5(NO_3)$ 1314, $\nu_2(NO_3)$ 1042; $\mu_{eff} = 1.99 \mu_B$; $\Lambda_M = 16.1 S cm^2 mol^{-1}$.

2.4. Synthesis of $\{Mn(HL)(CH_3COO)\}_n$ (2)

An ethanol solution (10 ml) of the ligand H_3L (3 mmol) was added to manganese acetate dihydrate (2 mmol) in ethanol (10 ml). The resulting mixture was heated for two hours. After cooling the solution was filtered and left to stand for two weeks. Small green crystals suitable for X-ray analyses were collected. The yield is 26.7%. Elemental *Anal. Calc.* for $[C_{19}H_{19}N_2O_5Mn]_n$ (410.07) C 55.62; H 4.67; N 6.83. Found: C 55.59; H 4.68; N 6.80%. IR (cm^{-1} , nujol mulls): $\nu(O-H)$ 3407, $\nu(C=N)$ 1601, $\nu_{as}(C=O)$ 1578, $\nu_s(C=O)$ 1435. $\mu_{eff} = 5.07 \mu_B$; $\Lambda_M = 5.6 S cm^2 mol^{-1}$.

2.5. X-ray structure analysis

Crystal with dimension 0.13 mm x 0.10 mm x 0.08 mm for compound **1** and 0.10 mm x 0.10 mm x 0.10 mm for **2** were carefully selected and mounted on a Kappa CCD area detector with graphite monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods using SHELXS-97, which revealed the position of all non-hydrogen atoms, and refined by least-squares procedure on F_o^2 with SHEXL-97. All H-atoms in the ligand were located in the Fourier difference maps and refined using riding model by AFIX instructions. Only one hydrogen atom of the solvent water molecule was found in the Fourier difference. The other one was placed at calculated position. These water H-atoms were not refined. In the solvent ethanol molecule, an abnormal longer $C \cdots OH$ distance was observed. This bond distance was then refined using DFIX instructions. Further details of the crystals structure investigation are available in Table 1 and from the Cambridge Crystallographic Center with quotation numbers ⁹ CCDC 279329 for complex **1** and CCDC 279330 for complex **2**.

3. Results and Discussion

3.1. Synthesis and characterization

The 1H NMR spectrum of H_3L (Figure 1) shows three singlets, one doublet and two multiplets in the region 6.9–7.4 ppm. The singlet at $\delta = 8.5$ ppm is assigned to $HC=N$. The singlets at $\delta = 10.1$ and $\delta = 12.2$ ppm represent $OHCH$ and $-OHAr$ respectively. These two signals are obtained downfield due to the possibility of the formation of intramolecular hydrogen bonding with the azomethine nitrogen or the oxygen atom. The intensity of these signals decrease significantly upon addition of D_2O . This fact supports the assignment. The doublet at $\delta = 3.6$ ppm represents the CH_2 . The multiplet at $\delta = 3.8$ ppm is assigned to the $-OHCH$. The aromatic protons appear as multiplets in the region 6.9–7.4 ppm. The ^{13}C NMR spectra show a signal at $\delta = 167$ ppm which represent the carbon atom of the imine $C=N$. The peaks at $\delta = 161$ and $\delta = 62.7$ ppm represent respectively the aromatic Cipso of the OH of the phenol and the $CH-OH$.

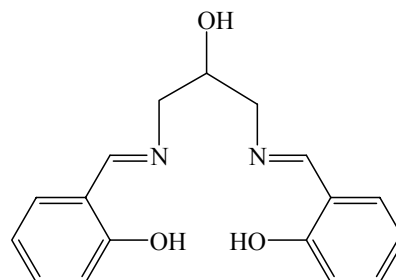


Figure 1. Structural formula of H_3L .

The polynuclear transition metal complexes **1** and **2** were prepared by mixing two fold of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ or $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and three fold of H_3L in ethanol at reflux. The immediate colour change indicated instant occurrence of the formation of the complex. The yields are 58.9 and 26.7% for **1** and **2**, respectively. Crystals suitable for X-ray analysis were isolated. The complexes are characterized by elemental analysis, molar conductance, magnetic measurements, and X-ray crystallography studies. The colors, elemental analyses, molar conductance and magnetic moment are presented in the experimental section. The elemental analyses data are consistent with the proposed formulae.

The molecular structures of the trinuclear complex of cooper(II) and the polymer of manganese (III) are obtained from single crystal X-ray crystallographic investigations. Selected bonds distances and angle are listed in Table 2 and a *PLUTON* views are given in Figure 2 and Figure 3.

3.2. Spectroscopic studies of the compounds

The ligand is expected to be pentadentate, the possible coordination sites being phenol-oxygen (two) azomethine nitrogen (two) and the alcohol oxygen (one). Comparison of the infrared spectra of the ligand and the complexes suggests that the ligand is tetradentate with ligand coordinating to the metal through the two phenolic oxygen atoms, which act as bridge between two copper atoms in the complex **1**, and as monodentate in the complex **2** and the two azomethine sites. The alcohol oxygen atom remains uncoordinated in the two complexes.

A strong band at 1633 cm^{-1} is assigned to the $\nu(\text{C}=\text{N})$ vibration. The broad band of medium intensity that appear in the range $3500\text{--}3400\text{ cm}^{-1}$ is due to the O–H stretching vibration of the phenolic and alcohol OH groups. A considerable lowering of the $\nu(\text{C}=\text{N})$ frequency is observed in the spectra of the two complexes, indicating a decrease in the stretching force constant of the C=N bond as a consequence of the coordination of the nitrogen atom to the metal ion. This band appears at 1580 cm^{-1} . The phenolic C–O stretching is present at 1277 and 1285 cm^{-1} . In the spectrum of **1** the broad band of medium intensity occurring in $3300\text{--}3400\text{ cm}^{-1}$ region is due to the symmetric and the antisymmetric O–H stretching vibrations of the lattice water.¹⁰ From the infrared spectra of this nitrate complex, information regarding the possible bonding modes of the nitrate group was obtained. The bands at 1425 cm^{-1} and 1314 cm^{-1} are due respectively to $\nu(\text{N}=\text{O})$ (ν_1) and $\nu_{\text{as}}(\text{NO}_2)$ (ν_5) of the coordinated nitrate. The $\nu_{\text{s}}(\text{NO}_2)$ (ν_2) is detected at 1042 cm^{-1} . These facts are characteristic of bidentate bridging nitrate.^{10, 11} The separation $\Delta\nu = \nu_1 - \nu_5$ has been used as criterion of differentiation between mono and bidentate chelating nitrates, with

$\Delta\nu$ increasing as the coordination changes from mono to bidentate and/or bridging modes. The magnitude of this separation for the complex **1** (111 cm^{-1}) is indicative of a bidentate bridging nitrate.¹² In summary, this nitrate complex contains only coordinated nitrate groups. In the spectrum of the complex **2** we note also intense absorption bands in the regions $1600\text{--}1620\text{ cm}^{-1}$ and $1380\text{--}1450\text{ cm}^{-1}$, which are associated with the asymmetric and the symmetric stretching modes in carboxylates. The $\Delta\nu$ value ($\nu_{\text{as}} - \nu_{\text{s}}$) of the carboxylate is 153 cm^{-1} and provides good evidence that the carboxylate group acts as bidentate bridging units to the manganese(III) ions.^{13, 14}

The electronic spectra of the complexes were recorded in freshly prepared dmf solutions. The spectra are virtually identical for all the complexes. A 'fairly' symmetrical new band is observed for each complex at 405 nm . This band disappears when the complexes are treated with NaBH_4 in order to reduce the C=N group in saturated moiety. Therefore, the absorption at 405 nm must be associated with the C=N chromophore coordinated to the metal ion through the nitrogen atom. The UV spectra of the complex **1** provided also further information. The absorption at maximum 640 nm attributable to the d-d transition is typical for pentacoordinated Cu(II) complex with square pyramidal geometry.^{15, 16} An intense band was also observed at 335 nm , in the complex **1**. It was absent both for the free ligand and the nitrate salt. This band is assigned to charge transfer between the coordinated ligand and the metal ion. Electronic spectra for manganese complexes with multidentate Schiff base ligands are not good support for geometry determination. The complex **2** displays also, two absorption bands at 348 and 417 nm which can be assigned to the LMCT from the phenoxo oxygen atom to the Mn(III).¹⁷ A low-intensity absorption bands appears in the region $485\text{--}505\text{ nm}$ and are attributed to the d-d transitions for Mn(III).

The magnetic moments in solid state measured at room temperature were found to be $1.99\ \mu_{\text{B}}$ for complex **1** and $5.07\ \mu_{\text{B}}$ for complex **2**.

The complexes are insoluble in most common polar and non-polar organic solvent. They are soluble in dmf. The molar conductivities of the complexes were measured in dimethylformamide (dmf) for freshly prepared solutions and after standing for two weeks. The conductivities increased very slightly with time in dmf for all the complexes. The present coordination moieties cannot be replaced by the solvent molecules. The values of these conductances are in the range $5\text{--}17\ \text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ in dmf and are in accordance with those reported for non-electrolytes in this solvent.¹⁸ This is indicative that these complexes dissociate very slightly in this solvent. As observed in the infrared spectra, where the compounds were formulated as non-electrolytes the

molar conductivities show that all the anions are present in the coordination sphere in solution.

3.3. Structure of $[\text{Cu}_3(\text{HL})_2(\text{NO}_3)_2](\text{H}_2\text{O})(\text{CH}_3\text{CH}_2\text{OH})$ (1)

The structure of the trinuclear copper compound in Figure 2 shows a trinuclear centrosymmetric complex with three Cu^{2+} ions in linear array. The two terminals Cu are pentacoordinated with two nitrogen atoms donors and three oxygen atoms donors. Two nitrogen atoms (N1 and N5) and two oxygen atoms (O4 and O5) from the ligand form the base of the distorted square pyramidal [O5–Cu2–N3, 170.31; O4–Cu2–N1, 170.88; O5–Cu2–N1, 91.69; O4–Cu2–O5, 81.25; O4–Cu2–N3, 91.49; N3–Cu2–N1, 94.83°]. The Cu–N distances of 1.947 Å (Cu2–N1) and 1.953 Å (Cu2–N3) as well as the Cu–O distances of 1.949 Å (Cu2–O4) and 1.955 Å (Cu2–O5) can be regarded as normal. The average Cu2–N distance (1.950 Å) is comparable to those in square pyramidal $[\text{Cu}_2\text{L}(\text{O}_2\text{CC}_6\text{H}_4\text{-p-NH}_2)]$ (1.934 Å).¹⁹

The axial position is occupied by an oxygen atom O11 from the bidentate nitrate with a distance of 2.354 Å. This Cu–O–Nitrate is appreciably longer, compared to those in square pyramidal $[\text{Cu}_2\text{L}(\text{N}_3)(\text{NO}_3)_2]$ (2.172 Å).²⁰ The N_2O_3 ligand is tetradentate; the phenolate moieties of the two molecules of ligand bridges to the central Cu3 atom resulting in a CuO_4 moiety while the oxygen atoms of the alcohol function remain uncoordinated. The central Cu3 atom has distorted square bipyramidal geometry. Four oxygen atoms from the phenolate moieties (O4 and O5 and their related symmetry) form the base of the octahedron with two oxygen atoms (O10 and his related symmetry) from the nitrate groups occupying the apical positions. The Cu···Cu distances are 2.974 Å and 2.948 Å. The average Cu3–O distances 1.984 Å for O–Ligand and 2.396 Å for O–nitrate are clearly distinguishable. The Cu3–O_{Ligand} bond length can be comparable with $[\text{Cu}(\text{HL})(\text{py})(\text{NO}_3)_2]$ having CuN_2O_4 coordination sphere.²¹

Table 1. Crystal data and structures refinement for complexes (1) and (2).

Empirical formula	$\text{C}_{36}\text{H}_{40}\text{N}_6\text{O}_{14}\text{Cu}_3$ (1)	$\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}_5\text{Mn}$ (2)
Color; Habit	Green, prism	Colorless, prism
Formula weight / g	971.36	410.30
Temperature / K	293(2)	293(2)
Crystal system	Triclinic	Orthorhombic
Space group	<i>P1</i>	<i>Pnma</i>
Unit cell dimensions		
<i>a</i> / Å	12.6618(2)	6.5052(1)
<i>b</i> / Å	13.9201(2)	16.6686(4)
<i>c</i> / Å	14.1277(3)	16.7207(5)
α / °	61.5819(9)	90.0 (0)
β / °	65.3031(9)	90.0 (0)
γ / °	88.9260(1)	90.0 (0)
Volume / Å ³	1938.49(6)	1813.07(7)
Z	2	8
Density / Mg/m ³	1.50	1.503
Absorption coefficient / mm ⁻¹	1.708	0.762
<i>F</i> (000)	988	848
Crystal size / mm ³	0.20 x 0.20 x 0.15	0.10 x 0.10 x 0.10
Theta range for data collection / °	0.998 - 30.03	0.998 - 30.03
Index ranges	-17 ≤ <i>h</i> ≤ 17, -19 ≤ <i>k</i> ≤ 19, -19 ≤ <i>l</i> ≤ 19	-8 ≤ <i>h</i> ≤ 9, -23 ≤ <i>k</i> ≤ 22, -22 ≤ <i>l</i> ≤ 23
Reflections collected	22108	14561
Independent reflections	11298 [R(int) (0.054)]	2736 [R(int) (0.0536)]
Completeness to theta 30.03°	99.7%	100%
Refinement method	Full-matrix least-square on <i>F</i> ²	Full-matrix least-square on <i>F</i> ²
Data/restraints/parameters	11298/0/515	2736/0/134
Goodness-of-fit on <i>F</i> ²	1.041	1.059
Final <i>R</i> Indices (<i>I</i> > 2σ (<i>I</i>))	<i>R</i> ₁ 0.062, <i>wR</i> ₂ 0.0745	<i>R</i> ₁ 0.0457, <i>wR</i> ₂ 0.1277
<i>R</i> Indices (all data)	<i>R</i> ₁ 0.107, <i>wR</i> ₂ 0.191	<i>R</i> ₁ 0.0740, <i>wR</i> ₂ 0.1410
Largest difference peak/hole (e Å ⁻³)	1.52 -1.10	0.528 -0.463

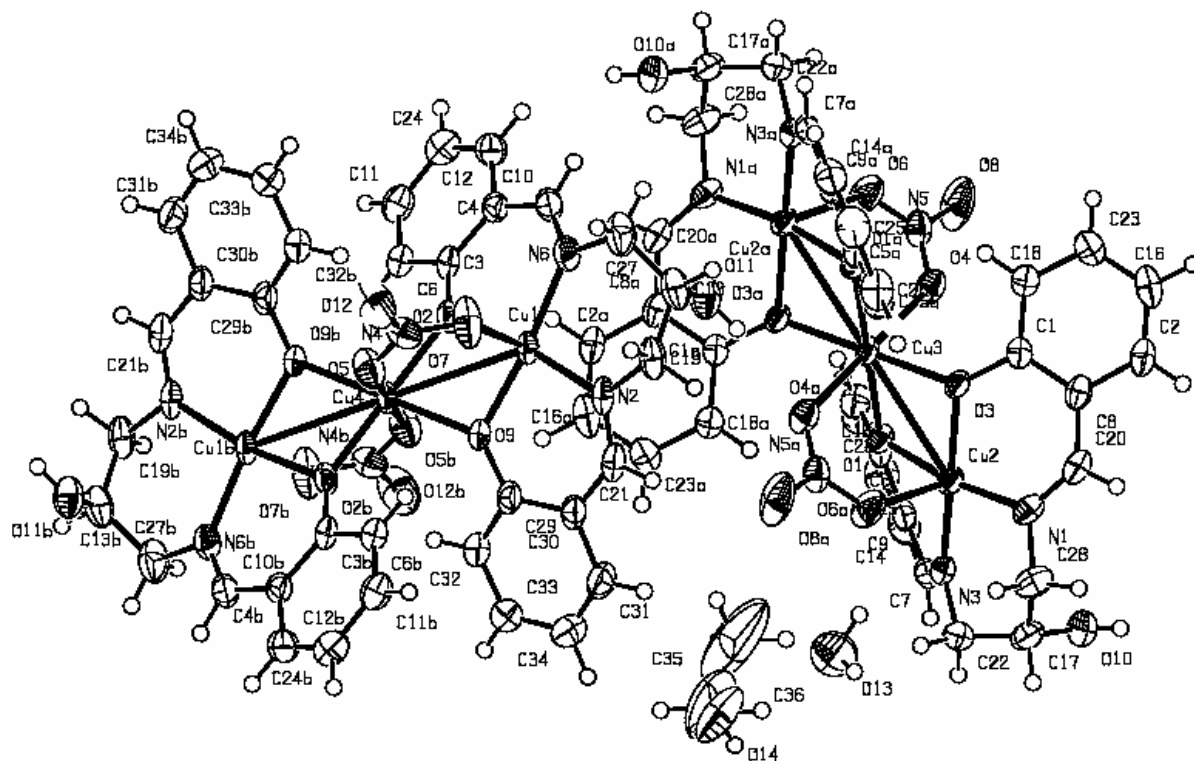


Figure 2. Asymmetric unit of $[\text{Cu}_3(\text{HL})_2(\text{NO}_3)_2](\text{H}_2\text{O})(\text{CH}_3\text{CH}_2\text{OH})$ (**1**) with an atom numbering scheme. Thermal ellipsoids are drawn at 30% level.

3.4. Structure of $[\text{Mn}(\text{HL})(\text{O}_2\text{CCH}_3)]_n$

The polynuclear crystal structure of the complex **2** was determined and the molecular structure is given in Figure 3. The compound crystallises in a centrosymmetric space group. The asymmetric unit consists

of one manganese atom, one molecule of ligand and one acetate group. Each Mn center is coordinated to two carboxylate oxygen atoms from the free acetate groups, two oxygen atoms and two nitrogen atoms from the dideprotonated ligand molecule. The Mn(III)

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

$[\text{Cu}_3(\text{HL})_2(\text{NO}_3)_2](\text{H}_2\text{O})(\text{CH}_2\text{CH}_2\text{OH})$				$\{\text{Mn}(\text{HL})(\text{CH}_3\text{COO})\}_n$			
Cu1–O9	1.940(3)	O9–Cu1–N2	92.26(14)	Mn1–N1	2.0516(18)	O3–Mn1–O3 ⁱ	84.95(10)
Cu1–N2	1.948(3)	N2–Cu1–O2	169.45(14)	Mn1–O1	2.161(2)	O3–Mn1–N1 ⁱ	174.39(8)
Cu1–O2	1.951(3)	N2–Cu1–N6	97.80(15)	Mn1–O2	2.232(2)	O3 ⁱ –Mn1–N1 ⁱ	90.05(8)
Cu1–N6	1.955(4)	O2–Cu1–N6	91.87(13)	Mn1–O3	1.8788(15)	O3–Mn1–N1	90.05(8)
Cu1–O7	2.387(3)	N6–Cu1–O7	88.49(16)			O3 ⁱ –Mn1–N1	174.39(8)
Cu2–N1	1.948(3)	N1–Cu2–O1	170.90(14)			N1 ⁱ –Mn1–N1	94.81(11)
Cu2–O1	1.949(3)	N1–Cu2–N3	94.82(14)			O3–Mn1–O1	98.66(7)
Cu2–N3	1.953(4)	N1–Cu2–O3	91.70(13)			O3 ⁱ –Mn1–O1	98.66(7)
Cu2–O3	1.955(3)	N3–Cu2–O3	170.30(13)			N1 ⁱ –Mn1–O1	84.59(6)
Cu2–O6	2.354(3)	N1–Cu2–O6	92.52(13)			N1–Mn1–O1	84.59(6)
Cu3–O1	1.983(3)	O1–Cu2–O6	93.45(11)			O3–Mn1–O2 ⁱⁱ	97.07(6)
Cu3–O3	1.986(2)	N3–Cu2–O6	95.08(14)			O3 ⁱ –Mn1–O2 ⁱⁱ	97.07(6)
Cu3–O4	2.396(3)	O3–Cu2–O6	91.80(12)			N1 ⁱ –Mn1–O2 ⁱⁱ	80.98(6)
Cu4–O9	1.959(2)	O1–Cu3–O3	79.66(10)			N1–Mn1–O2 ⁱⁱ	80.98(6)
Cu4–O2	1.966(3)	O9–Cu4–O2	76.95(11)			O1–Mn1–O2 ⁱⁱ	158.61(9)
Cu4–O5	2.403(3)	O9–Cu4–O5	89.91(11)				

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

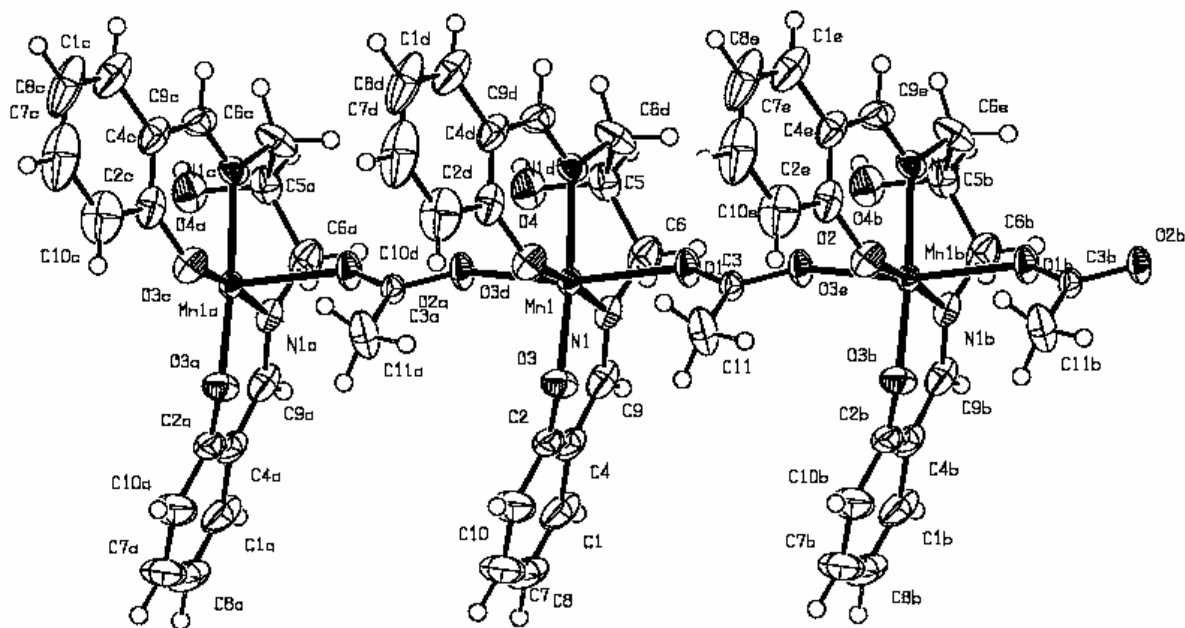


Figure 3. Molecular structure of $[\text{Mn}(\text{HL})(\text{O}_2\text{CCH}_3)]_n$ (**2**) with an atom numbering scheme. Thermal ellipsoids are drawn at 30% level.

ion adopt a geometry, in which the equatorial plane is formed by the coordination of the Schiff base. Two imino-nitrogen atoms (N1 and his related symmetry) and two phenoxo-oxygen atoms (O3 and his related symmetry) form the equatorial plane. The sum of the angles N–Mn–N, O–Mn–O and N–Mn–O is 359.86° . The coordination environment around the Mn(III) center is Jahn-Teller elongation as expected for a distorted octahedral d^4 ion.²² The equatorial plane contains the shortest coordination bond, which is to the phenoxo-oxygen atoms (Mn1–O3 = $1.8788(15)$ Å) and the imino-nitrogen atoms (M1–N1 = $2.0516(18)$ Å). The O atoms [O1 and O2 from acetate groups] are occupying the remaining apical positions (Mn1–O1 = $2.1610(2)$ Å and Mn–O2 = $2.232(2)$ Å and the angle O1–Mn–O2 = 158.61°). This fact indicates a market compression type of Jahn-Teller distortion. Each acetate group is acting as bidentate ligand by using one O atom acting as monodentate fashion to one Mn atom with the second O atom binding also as monodentate with another Mn atom. The $[\text{Mn}(\text{HL})(\text{O}_2\text{CCH}_3)]_n$ forms polymer, in which $[\text{Mn}(\text{HL})(\text{O}_2\text{CCH}_3)]$ units are linked via axial coordination of the acetate group of one unit to the Mn center of another unit. The O atoms of the alcohol functions remain uncoordinated.

4. Conclusions

This paper describes a trinuclear copper(II) complex and a polynuclear complex of manganese(III) synthesized from N,N' -(2-hydroxypropane-1,3-diyl)-bis(salicylaldimine). The structure of $[\text{Cu}_3(\text{HL})_2(\text{NO}_3)_2](\text{H}$

$_2\text{O})(\text{CH}_2\text{CH}_2\text{OH})$ **1** reveals tetradentate coordination of the ligand via two nitrogen atoms and two deprotonated phenolic oxygen atoms, which acts as a bridge between two copper atoms. In this complex, the two terminal metal centers are pentacoordinated, while the central metal center is hexacoordinated. In the structure of $[\text{Mn}(\text{HL})(\text{O}_2\text{CCH}_3)]_n$ **2** the ligand is also tetradentate but the two oxygen atoms act monodentate to the manganese atom. This structure consists in a polymeric chain where the $[\text{Mn}(\text{HL})(\text{O}_2\text{CCH}_3)]$ units are linked via axial coordination of the acetate group of one unit to the Mn center of another unit. In this second complex, the metal central atom is hexacoordinated.

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6. References

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Povzetek

Pripravili smo bakrov(II) kompleks $[\text{Cu}_3(\text{HL})_2(\text{NO}_3)_2](\text{H}_2\text{O})(\text{CH}_2\text{CH}_2\text{OH})$ (**1**) in polimerni manganov(III) kompleks $[\text{Mn}(\text{HL})(\text{CH}_3\text{COO})]_n$ (**2**), H_3L je Schiffova baza $\text{N,N}'$ -(2-hidroksipropan-1,3-diil)-bis-(salicilaldimin). Kompleksa smo karakterizirali z meritvami prevodnosti, infrardečo spektroskopijo, magnetnimi meritvami in določitvijo struktur z rentgensko difrakcijo. Ligand je tridentaten v dianionski obliki. Geometrija bakrovih atomov v kompleksu **1** je kvadratno planarna in trigonalno-bipiramidalna, geometrija manganovega atoma v **2** pa je popačen oktaeder.