

Synthesis, spectroscopic studies and X-ray structure determination of metal transition complexes derived from the Schiff base ligand *N,N'*-bis[(4-methyl-3*H*-imidazol-5-yl)methylidene]-1,3-diaminopropan-2-ol

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Abstract: Metal transition [Mn(HL)(H₂O)₂].2(SCN) (**1**), [Co(HL)].2(SCN) (**2**), [Ni(HL)].2(SCN) (**3**), [Cu(HL)(NO₃)(H₂O)].(NO₃). (H₂O) (**4I**) and [Zn(HL)].2(SCN) (**5**) with tetradentate ligand *N,N'*-bis[(4-methyl-3*H*-imidazol-5-yl)methylidene]-1,3-diaminopropan-2-ol were prepared and characterized by FT-IR, UV-Vis spectroscopies, conductivity measurements and room temperature magnetic moment measurement. The structure of complex **5** is determined by X-ray diffraction. The complex crystallizes in the monoclinic system with the space group P2₁/c with unit cell dimensions *a* = 8.5459 (3) Å, *b* = 10.9177 (3) Å, *c* = 22.4562 (6) Å, β = 96.954 (3)°, *V* = 2079.79 (11) Å³, *Z* = 4, *R*₁ = 0.050 and *wR*₂ = 0.134. The complex displays octahedral geometry around the copper (II) ion which is coordinated by four nitrogen atoms from the ligand HL and two oxygen atoms from water molecule and nitrate anion. In the structure numerous intermolecular hydrogen bonds which consolidate the structure into three dimensional network were observed.

Keywords: Schiff base, metal transition, crystal, complex, magnetism, X-ray diffraction.

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I. Introduction

Polydentate ligands are of great interest in coordination chemistry due to their ability to form transition metal complexes with applications in various fields of technology [1–5]. These ligands allow the controlled design of molecular architectures with original structures and various functions [6–9]. Depending on the metal/ligand ratio, nature and size of the metal cation, compounds with unusual stereochemistry may be generated [10–12]. These compounds are very attractive due to potential applications in the fields of molecular magnetism [13, 14], electroluminescent [15, 16], catalysis [17, 18] or medicine [19, 20]. These compounds are also used in biomimetic chemistry to study the behavior of certain biological molecules [21–23]. Indeed, the use of copper coordination compounds in the development of new materials in biomimetic chemistry has led to increased interest in the synthesis of complexes with original architectures from polydentate ligands [24–27].

Following our continuous study of complexes of Schiff bases synthesized from 1,3-diaminopropan-2-ol [28, 29], we explored the possibility of preparing complexes with several metal cations from a polydentate Schiff base obtained by condensation of 1,3-diaminopropan-2-ol and 5-methyl-1*H*-imidazole-4-carbaldehyde. The resulting ligand *N,N'*-bis[(4-methyl-3*H*-imidazol-5-yl)methylidene]-1,3-diaminopropan-2-ol (HL) has two symmetrical pendant arms which carry nitrogen atoms. The presence of a hydroxyl group on the center of the molecule allows the possible formation of cavities capable of accommodating one or more cations depending on the conformation of the ligand [30–33]. In this work we report the synthesis of the ligand HL and its complexes with some transition metals of the first series.

II. Experimental

2.1. Starting materials and Instrumentations

All chemicals and solvents were of analytical reagent grade and were used directly without further purification. The ligand *N,N'*-bis[(4-methyl-3*H*-imidazol-5-yl)methylidene]-1,3-diaminopropan-2-ol (HL) was synthesized according to the literature [34]. 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-

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400 cm⁻¹ region. The UV-Visible spectra were recorded on a Perkin Elmer Lambda UV-Vis spectrophotometer. The molar conductance of 1×10⁻³ M in DMF 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. Synthesis of the ligand of *N,N'*-bis[(4-methyl-3*H*-imidazol-5-yl)methylidene]-1,3-diaminopropan-2-ol (HL)

In a 10 mL flask containing 5 mL of methanol and 1,3-diaminopropan-2-ol (0.711 g; 7.9 mmol), 5-methyl-1*H*-imidazole-4-carbaldehyde (1.739 g; 15.8 mmol) previously dissolved in a minimum of methanol was added. The resulting yellow solution was refluxed for 4 hours. After cooling to room temperature, the yellow precipitate formed was recovered by filtration and washed with 2x10 mL of ether before being dried in a desiccator under P₂O₅.

2.3. General procedure for the synthesis of the complexes from the ligand HL

In a 100 mL flask containing 5 mL of methanol, HL (0.3 g; 1 mmol) is added. In a beaker, M(NO₃)₂·nH₂O (M = Mn, Co, Ni, Cu or Zn; n = 3, 4 or 6) (1 mmol) and KSCN (2 mmol) were dissolved in 10 mL of methanol. The resulting mixture was stirred for 10 minutes and filtered into the flask containing the HL ligand. The mixture was refluxed for 2 hours then the clear solution obtained was filtered and left to slow evaporation. After three weeks, the copper complex gives crystals suitable for X-ray diffraction analysis while the other complexes were isolated as powders.

Table 1. Physical characteristics, yield and analytical data of the ligand and its complexes.

Compound	Colour	M.p. (°C)	Yield (%)	Found (Calc) %			
				C	H	N	S
HL	Yellow	189	83	56.90 (56.92)	6.59 (6.61)	30.61 (30.64)	-
C ₁₅ H ₂₂ MnN ₈ O ₃ S ₂ (1)	Brown	250	32	37.43 (37.42)	4.63 (4.61)	23.24 (23.27)	13.30 (13.32)
C ₁₅ H ₁₈ CoN ₈ OS ₂ (2)	Green	260	31	40.06 (40.09)	4.03 (4.04)	24.90 (24.93)	14.29 (14.27)
C ₁₅ H ₁₈ NiN ₈ OS ₂ (3)	Brown	240	43	40.09 (40.11)	4.01 (4.04)	24.92 (24.95)	14.25 (14.28)
C ₁₃ H ₂₂ CuN ₈ O ₉ (4)	Blue	236	67	31.34 (31.36)	4.51 (4.45)	22.53 (22.50)	-
C ₁₅ H ₁₈ ZnN ₈ OS ₂ (5)	Yellow	248	63	39.52 (39.48)	3.98 (4.01)	24.58 (24.55)	14.07 (14.04)

2.4. Crystal structure determination

Crystals suitable for single-crystal X-ray diffraction, of the reported compound (**4**), were grown by slow evaporation of EtOH solution of the complexes. Details of the crystal structure solution and refinement are given in Table 2. Diffraction data were collected using an ENRAF NONIUS Kappa CCD diffractometer with graphite monochromatized MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Complex scattering factors were taken from the program package SHELXTL [34]. 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 [35]. 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 [36].

Table 2. Crystallographic data and refinement parameters for the complex [Cu(HL)(NO₃)(H₂O)]·(NO₃)·(H₂O) (**4**).

Chemical formula	C ₁₃ H ₂₂ CuN ₈ O ₉
Formula weight	497.92
Crystal system	Monoclinic
Space group	<i>P2₁/c</i>

<i>T</i> (K)	293
<i>a</i> (Å)	8.5459 (3)
<i>b</i> (Å)	10.9177 (3)
<i>c</i> (Å)	22.4562 (6)
α (°)	90
β (°)	96.954 (3)
γ (°)	90
<i>V</i> (Å ³)	2079.79 (11)
<i>Z</i>	4
ρ_{cal} (g cm ⁻³)	1.590
Radiation type	Mo K α
μ (mm ⁻¹)	1.11
Crystal size (mm ³)	0.10 × 0.10 × 0.05
<i>hkl</i> range	-11 ≤ <i>h</i> ≤ 11 ; -14 ≤ <i>k</i> ≤ 13 ; -30 ≤ <i>l</i> ≤ 27
No. Measured reflections	22594
No. independent reflections	4980
Reflections with [<i>I</i> > 2 σ (<i>I</i>)]	4044
<i>R</i> _{int}	0.043
R[F ² > 2 σ (F ²)]	0.050
wR(F ²)	0.134
Goodness-of-fit	1.09
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	1.08, - 0.45

III. Results and discussion

3.1. General studies

The aim of the reported work was to study the coordination chemistry of ligand N,N'-bis[(4-methyl-3H-imidazol-5-yl)methylidene]-1,3-diaminopropan-2-ol(HL) isolated from condensation of 1,3-diaminopropan-2-ol and 5-methyl-1H-imidazole-4-carbaldehyde. HL present numerous coordination sites and can act as strong chelating ligand with transition metal ions (Scheme 1). Accordingly, the methanolic solution of HL was treated with transition metal salts in 1:1 molar ratio to yield compounds as powders or as crystals suitable for X-ray diffraction. The elemental analysis results are in good agreement with the calculated values for the five synthesized mononuclear complexes which are non-hygroscopic and stable in air (Table 1). The ¹H NMR spectrum of the HL ligand, recorded in CDCl₃, shows a signal at 8.10 ppm as a singlet characteristic of the protons of the azomethine functions. It exhibits also signals at 7.18 and 6.43 ppm in singlet form attributed to the –NH and –CH protons of imidazole, respectively. The proton signal from the alcohol function is at 6.19 ppm. The signals observed at 3.55 and 4.15 ppm are attributed, respectively, to the methylene protons –CH₂– and to the methynic proton –CH(OH)–. The signal at 2.62 ppm in the form of a singlet is due to the protons of the –CH₃ groups. The J-modulated proton spectrum of the HL ligand is recorder to easily assign ¹³C signals. The signals at 129.60 and 124.43 ppm are attributed, respectively, to the quaternary carbon atoms of the imidazole group carrying the methyl or the azomethine function. The signal of the carbon atom of the azomethine group is pointed at 159.56 ppm while the signal of the unsubstituted *sp*² carbon atom of the imidazole group is pointed at 140.58 ppm. The signals pointed at 71.11; 69.96 and 15.07 ppm are respectively attributed to the carbon atoms of the methynic –CH(OH)–, the methylenic –CH₂– and the methyl –CH₃ groups.

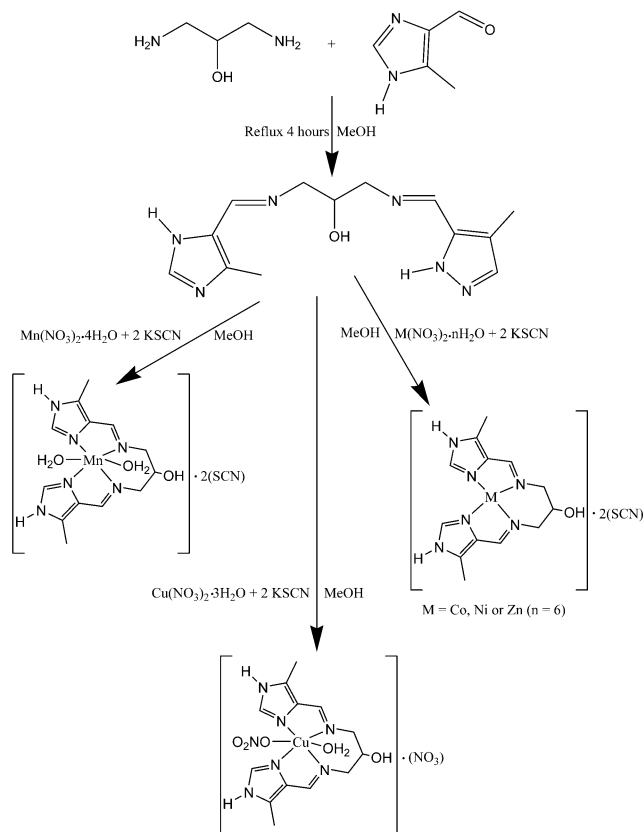

Scheme 1. Synthetic scheme for ligand and complexes preparation

Table 3. Main FT-IR spectral data of the ligand and its complexes.

Compound	$\nu(\text{O-H})$	$\nu(\text{N-H})$	$\delta(\text{H}_2\text{O})$	$\nu(\text{C=N})$	$\nu(\text{imidazol})$	$\nu(\text{SCN})$	$\nu(\text{NO}_3)_{\text{coord}}$	$\nu(\text{NO}_3)_{\text{uncoord}}$
HL	3300	3114	-	1641	1601	-	-	-
1	3221	3221	830	1635	1547	2067	-	-
2	3300	3224	-	1607	1487	2062	-	-
3	3226	3226		1634	1539	2095	-	-
4	3419	3109	835	1642	1604	-	1323 ; 1258 ; 1180	1366
5	3326	3326	-	1621	1489	2073	-	-

The FT-IR spectral data of the ligand and its complexes are summarized in Table 3. The FT-IR spectrum of the ligand shows two bands at 3300 and 3114 cm^{-1} attributed respectively to the valence vibration $\nu_{\text{O-H}}$ [13] of the alcohol function and $\nu_{\text{N-H}}$ [14] of the imidazole. The band pointed at 1641 cm^{-1} is due to the azomethine absorption band $\nu_{\text{C=N}}$ and the band at 1601 cm^{-1} is attributed the $\nu_{\text{C=N}}$ of the imidazole ring [1]. The bands observed at 1580 and 1437 cm^{-1} are due to the $\nu_{\text{C=C}}$ vibrations of the imidazole ring [14]. After coordination, in all the FTIR spectra of the complexes the bands due to $\nu_{\text{O-H}}$ and $\nu_{\text{N-H}}$ remain present and are, respectively, in the ranges [3221-3419 cm^{-1}] and [3109-3226 cm^{-1}]. The ligand acts in its neutral form [15]. A deformation vibration band $\delta(\text{O-H})$, pointed at *ca.* 830 cm^{-1} on the FTIR spectra of manganese and copper complexes is indicative of the presence of uncoordinated water molecule [16]. The bands due to the elongation vibrations of azomethine and imidazole undergo a displacement after the coordination, thus indicating the participation of the nitrogen atoms of the azomethine and the imidazole in the coordination [17]. These bands are pointed, respectively, in the regions [1601-1635 cm^{-1}] and [1487-1550 cm^{-1}] on the spectra of the complexes (Table 3). On the spectra of complexes **1**, **2**, **3** and **5**, a new strong and broad band is pointed respectively at 2067; 2062; 2095 and 2073 cm^{-1} and is attributed to the ν_{NCS} vibration bands of free thiocyanate moiety [18]. For the spectrum of copper complex **4**, a

strong and sharp band is observed at 1366 cm^{-1} attributed to the free nitrate group [16]. Three bands are also observed at 1323 cm^{-1} (ν_1); 1258 cm^{-1} (ν_2) and 1180 cm^{-1} (ν_5). The separation $\Delta\nu = \nu_1 - \nu_5$, has been used as a criterion to distinguish the nitrate group coordination mode. The $\Delta\nu$ value increases from monodentate mode to bidentate mode. In the case of this copper complex, the value $\Delta\nu = 143 \text{ cm}^{-1}$ indicates the presence of unidentate nitrate group in complex **4** [37]. Electronic spectral data, molar conductivity and magnetic data for all complexes derived from the ligand (HL) are reported in Table 4. The conductometric measurements are carried out in millimolar DMF solutions of the complexes at two week intervals. Molar conductivity values of complexes **1**, **2**, **3** and **5** in the range [134 – 140 $\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$] which characterizes 1:2 type electrolytes [38]. All these values are almost identical to the values measured two weeks later, indicating a high stability of these complexes in DMF. For complex **4**, the molar conductivity of 70 $\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$, which remains practically constant after two weeks, indicates that it is a 1:1 type electrolyte which is stable in DMF [38]. The UV-Vis spectrum of the ligand HL and all the UV-Vis spectra of the complexes show bands attributable to $\pi \rightarrow \pi^*$ transition of imidazole ring the range 270 – 293 nm. Additional band attributed to the $n \rightarrow \pi^*$ transitions of the C=N chromophore is observed in the range 310-322 nm. The value of the magnetic moment at room temperature is indicative of a mononuclear complex. The value of 5.6 MB recorded for the manganese complex (**1**) is in agreement with the value of 5.92 MB predicted for a high spin d^5 configuration. It is comparable to the values reported for similar octahedral manganese (II) complexes [39]. The magnetic moment value of 4.5 MB exhibited by the cobalt(II) complex (**2**) is attributed to spin orbit coupling which allows mixing in of higher levels tetrahedral cobalt(II) complex. This value is in the range [4.2-4.8 MB] expected for cobalt(II) ion in tetrahedral geometry. The electronic spectrum of cobalt(II) complex shows additional weak intensity band at 620 nm, which is due to ${}^4A_2(F) \rightarrow {}^4T_1(P)$ transition for the tetrahedral cobalt(II) complexes [40]. The nickel(II) complex (**3**) which is a 1:2 electrolyte and formulated as $[\text{Ni}(\text{HL})] \cdot 2(\text{SCN})$ is diamagnetic. This indicates that the complex has square-planar geometry. Two bands in the UV-Vis spectrum of the complex **3** pointed at 430 and 672 nm confirms the square planar geometry around the nickel [41]. For complex **4** high intensity band due to the LMCT appeared at 408 nm. The electronic spectrum of the copper complex **4** exhibits also a shoulder at 620 nm which is attributed to the $d \rightarrow d$ transition of the copper (II) unit. This fact is typical for distorted octahedral copper complexes [40, 42]. The value of the magnetic moment value of 1.85 MB of the copper (II) complex (**4**) is in agreement with that of a mononuclear copper complex with one unpaired electron [43]. As the zinc(II) ion present completely filled d-orbital the complex **5** is diamagnetic and does not exhibit $d \rightarrow d$ electronic transition. As reported in literature, tetraordinated zinc(II) complexes, in general, would have tetrahedral geometry [44].

Table 4. Electronic spectral data and magnetic data of the complexes.

Complexes	$\lambda(\text{nm})$	μ_{eff} (MB)	Mol. Cond. ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$)	
1	272 ; 289 ; 322	5.6	140	139
2	289 ; 315 ; 620	4.5	142	140
3	293 ; 318 ; 430 ; 672		138	140
4	242 ; 271 ; 295 ; 320 ; 408 ; 620	1.85	70	72
5	270 ; 287 ; 320	diamagnetic	142	139

3.2. Crystal structure description

Suitable single crystals for X-ray diffraction of the complex **4** were obtained by slow evaporation of the solvent at room temperature. Crystal data, collection and refinement parameters are listed in Table 2. Selected bond lengths and angles are summarized in Table 5. Hydrogen bond data for complex are gathered in Table 6. Figure 1 displays the asymmetric unit of compound **4** with atom numbering while Figure 2 displays the packing diagram of the structure. Compound **4** crystallizes in the monoclinic system with the space group $P2_1/c$. The asymmetric unit contains a single molecule of complex formed by a copper (II) ion which is bound to one neutral organic ligand molecule HL, one coordinated water molecule, one coordinated nitrate anion, one uncoordinated water molecule and one uncoordinated nitrate anion. The ligand HL acts in tetradentate fashion through two azomethine nitrogen atoms and two imidazole nitrogen atoms. Thus, the copper(II) ions situated in a N_2O_4 core is hexacoordinated. The geometry around the copper (II) is best described as an octahedral polyhedron. The imidazole nitrogen atoms, N2 and N5, and the azomethine nitrogen atoms, N3 and N4 from the ligand molecule form the equatorial plane (rms 0.0346) with the Cu ion 0.0074(9) Å out of it. The apical positions being occupied by the oxygen atom of the coordinated water molecule [O2] and one oxygen atom of the coordinated nitrate group [O3]. The *cisoid* angles in the basal plane N—Cu—N are in the range [82.40 (9) – 101.74 (9)°] and deviates

severely from the ideal value of 90°. The sum of the angles subtended by the atoms in the basal planes is 359.69°. The *transoid* angles values are N2—Cu1—N4 = 173.10 (9)° and N3—Cu1—N5 = 174.46 (9)°. The angle subtended by the atoms in apical positions [O2—Cu1—O3 = 176.61 (11)°]. Those angle value which deviate from the ideal value of 180° are indicative of a distorted octahedral polyhedron around the copper (II) metal center. The coordination of the ligand to the metal ion results in the formation of two five-membered rings of type NCCNCu and one six-membered ring of type NCCCNCu. The mean planes of the two five-membered rings are not coplanar and form a dihedral angle of 4.86°. They are inclined from the mean plane of the six-membered ring with, respectively, dihedral angle values of 7.00° and 9.71°. The Cu—N distances are in the range [1.993 (2) – 2.002 (2) Å] and are shorter than those reported for analogous complexes [Cu(L1)Cl]Cl and [Cu(L2)Cl]Cl in which L1 is *N,N'*-Bis[(1-methylimidazol-2-yl)methyl]-1,3- diaminopropan-2-ol (L1) and L2 is *N,N'*-Bis[(1-methylimidazol-2-yl)methyl]-1,3- diaminopropane [45]. In the elongated axial direction, one site is occupied by an O atom from a nitrate anion [Cu1—O3 = 2.424 (4) Å] and the other site by an O atom from a water molecule [Cu1—O2 = 2.813 (3) Å]. Both bond distances are longer than those corresponding to usual coordination bonds indicating a weak interaction with the metal ion. Those are the longest distances in the complex as expected due to the Jahn Teller effect [46]. Each of the three oxygen atoms of the coordinated nitrate group are disordered with two sites having occupancies of 0.8 and 0.2 for the coordinated atom O3, 0.5 and 0.5 for non-coordinated O5 and 0.6 and 0.4 for non-coordinated O4. The alcoholic oxygen atom (O1) of the ligand is also disordered with two sites having occupancies of 0.6 and 0.4.

Table 5. Selected bond distances [Å] and angles [deg] for complex **4**.

Cu1—N2	1.996 (2)	Cu1—N3	1.995 (2)
Cu1—N5	1.993 (2)	Cu1—O2	2.813 (3)
Cu1—N4	2.002 (2)	Cu1—O3	2.424 (4)
N2—Cu1—N4	173.10 (9)	N4—Cu1—O2	86.60 (8)
N2—Cu1—O2	87.81 (8)	N4—Cu1—O3	96.78 (12)
N2—Cu1—O3	88.80 (12)	N3—Cu1—N2	82.67 (9)
N5—Cu1—N2	101.74 (9)	N3—Cu1—N4	92.88 (9)
N5—Cu1—N4	82.40 (9)	N3—Cu1—O2	85.74 (9)
N5—Cu1—N3	174.46 (9)	N3—Cu1—O3	93.72 (14)
N5—Cu1—O2	91.06 (9)	O3—Cu1—O2	176.61 (11)
N5—Cu1—O3	89.74 (14)		

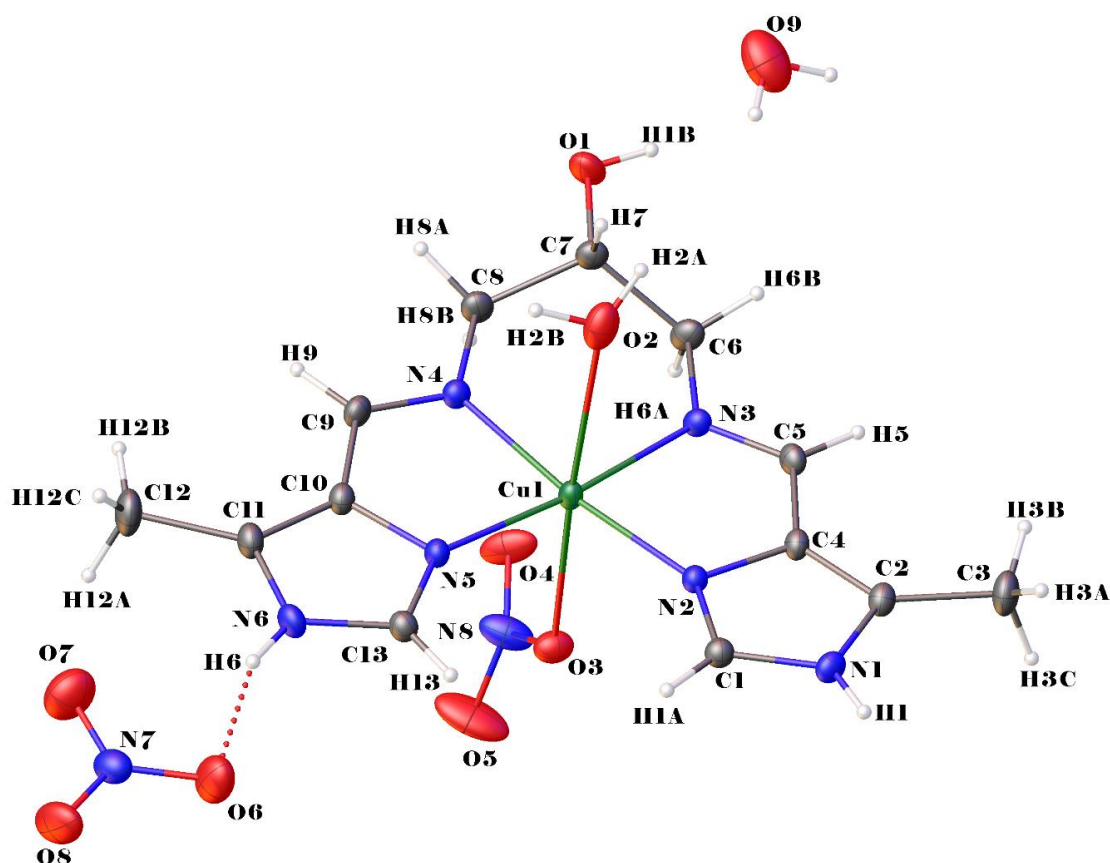


Figure 1. ORTEP plot (30% probability ellipsoids) showing the molecule structure of the copper (II) complex of HL.

Intramolecular hydrogen bonds involving the NH of the imidazole group as donors and oxygen atoms of free nitrate anions as acceptor are observed (N6—H6···O67 and N6—H6···O7). Intermolecular hydrogen bonds involving the uncoordinated alcoholic OH moiety as donors and oxygen atoms of free nitrate anions as acceptor are observed (O1—H1B···O8^v; $v = x-1, -y+1/2, z-1/2$). Numerous C—H···O hydrogen bonds with alcoholic and nitrate nitrogen atoms as acceptors consolidate the three dimensional network (Table 6, Figure 2).

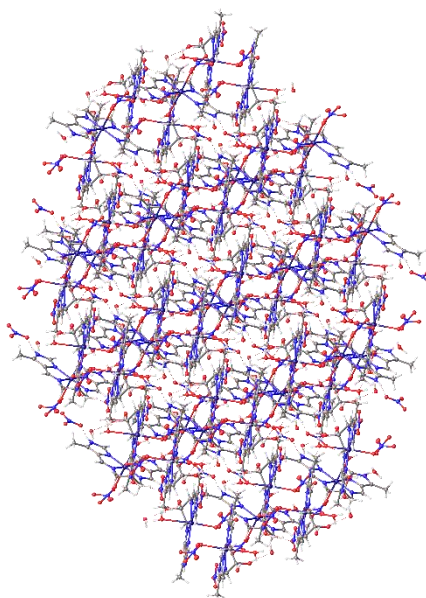


Figure 2. Plot showing the inter and intramolecular hydrogens bonds in the crystal.

Table 6. Hydrogen-bond geometry (Å, °) in compound **4**.

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...O2 ⁱ	0.86	1.99	2.801 (3)	156.1
N6—H6...O6	0.86	2.09	2.908 (4)	159.7
N6—H6...O7	0.86	2.40	3.149 (5)	145.3
C1—H1A...O3 ⁱⁱ	0.93	2.46	3.346 (6)	160.0
C13—H13...O3 ⁱⁱ	0.93	2.40	3.299 (5)	163.5
C9—H9...O4 ⁱⁱⁱ	0.93	2.52	3.390 (7)	155.7
C5—H5...O1 ^{iv}	0.93	2.63	3.480 (15)	151.5
C6—H6B...O8 ^v	0.97	2.62	3.335 (4)	130.3
C8—H8A...O5 ⁱⁱⁱ	0.97	2.58	3.501 (10)	158.0
C8—H8B...O4	0.97	2.60	3.268 (8)	126.1
C3—H3B...O5 ^{vi}	0.96	2.61	3.294 (12)	128.8
C3—H3B...O1 ^{iv}	0.96	2.61	3.403 (12)	139.8
O1—H1B...O8 ^v	0.82	1.89	2.700 (12)	168.7

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

IV. Conclusion

The organic ligand *HL* incorporating two imidazole moieties showed a similar mode of coordination in the complexes prepared and characterized by magnetic moment, molar conductivity, IR, UV-Vis and XRD. In all structures, the Schiff base *HL* acts as a tetradentate ligand through the two nitrogen atoms of the azomethine function and two nitrogen atoms of imidazole moieties. In Complex **1** the polyhedron around the manganese (II) atom is best described as an octahedral geometry. The polyhedron around the metal centers in complex **2** and **5** are described as tetrahedral geometry while the nickel (II) atom, in complex **3**, is situated in square planar environment. The structure of the copper complex **4** determined by single crystal X-ray diffraction exhibits a slightly distorted octahedral geometry.

V. Supporting information

CCDC-2285926 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/>, or by emailing 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]. Nishal, V., Singh, D., Kumar, A., Tanwar, V., Singh, I., Srivastava, R., & Kadyan, P. S. (2014). A new zinc–Schiff base complex as an electroluminescent material. *Journal of Organic Semiconductors*, 2(1), 15–20. <https://doi.org/10.1080/21606099.2014.942767>
- [2]. Karakas, A., Elmali, A., Yahsi, Y., & Kara, H. (2007). Third-order nonlinear optic and optical limiting properties of a Mn (III) transition metal complex. *Journal of Nonlinear Optical Physics & Materials*, 16(04), 505–518. <https://doi.org/10.1142/S0218863507003858>
- [3]. Köse, A., Güngör, Ö., Ballı, J. N., & Erkan, S. (2022). Synthesis, characterization, non-linear optical and DNA binding properties of a Schiff base ligand and its Cu(II) and Zn(II) complexes. *Journal of Molecular Structure*, 1268, 133750. <https://doi.org/10.1016/j.molstruc.2022.133750>
- [4]. Omar (Al-Ahdal), Z. T., Jadhav, S., Pathrikar, R., Shejul, S., & Rai, M. (2023). Synthesis, Magnetic Susceptibility, Thermodynamic Study and Bio-Evaluation of Transition Metal Complexes of New Schiff Base Incorporating INH Pharmacophore. *Polycyclic Aromatic Compounds*, 43(1), 523–537. <https://doi.org/10.1080/10406638.2021.2015397>
- [5]. Sonawane, H. R., Vibhute, B. T., Aghav, B. D., Deore, J. V., & Patil, S. K. (2023). Versatile applications of transition metal incorporating quinoline Schiff base metal complexes: An overview. *European Journal of Medicinal Chemistry*, 258, 115549. <https://doi.org/10.1016/j.ejmech.2023.115549>
- [6]. Popov, L. D., Levchenkov, S. I., Shcherbakov, I. N., Lukov, V. V., Suponitsky, K. Y., & Kogan, V. A. (2012). Binuclear copper(II) complexes of Schiff base ligand derived from 1-phenyl-3-methyl-4-formylpyrazol-5-one and 1,3-diaminopropan-2-ol: Synthesis, structure and magnetic properties. *Inorganic Chemistry Communications*, 17, 1–4. <https://doi.org/10.1016/j.inoche.2011.11.020>
- [7]. Popov, L. D., Tupolova, Yu. P., Lukov, V. V., Shcherbakov, I. N., Kogan, V. A., & Mishchenko, A. V. (2008). Physicochemical study on bis-hydrazone derived from 1,3-diaminoguanidine and salicylaldehyde and its complexes with transition metals. *Russian Journal of General Chemistry*, 78(11), 2094–2099. <https://doi.org/10.1134/S1070363208110182>

- [8]. Popov, L. D., Levchenkov, S. I., Shcherbakov, I. N., Lukov, V. V., Suponitsky, K. Y., & Kogan, V. A. (2012). Binuclear copper(II) complexes of Schiff base ligand derived from 1-phenyl-3-methyl-4-formylpyrazol-5-one and 1,3-diaminopropan-2-ol: Synthesis, structure and magnetic properties. *Inorganic Chemistry Communications*, 17, 1–4. <https://doi.org/10.1016/j.inoche.2011.11.020>
- [9]. Biswas, S., Mitra, K., Schwalbe, C. H., Lucas, C. R., Chattopadhyay, S. K., & Adhikary, B. (2005). Synthesis and characterization of some Mn(II) and Mn(III) complexes of *N,N'*-o-phenylenebis(salicylideneimine)(LH₂) and *N,N'*-o-phenylenebis(5-bromosalicylideneimine)(L'H₂). Crystal structures of [Mn(L)(H₂O)(ClO₄)], [Mn(L)(NCS)] and an infinite linear chain of [Mn(L)(OAc)]. *Inorganica Chimica Acta*, 358(8), 2473–2481. <https://doi.org/10.1016/j.ica.2005.01.026>
- [10]. Dasgupta, S., Karim, S., Banerjee, S., Saha, M., Das Saha, K., & Das, D. (2020). Designing of novel zinc(II) Schiff base complexes having acyl hydrazone linkage: study of phosphatase and anti-cancer activities. *Dalton Trans.*, 49(4), 1232–1240. <https://doi.org/10.1039/C9DT04636D>
- [11]. Banerjee, A., & Chattopadhyay, S. (2019). Synthesis and characterization of mixed valence cobalt(III)/cobalt(II) complexes with *N,O*-donor Schiff base ligands. *Polyhedron*, 159, 1–11. <https://doi.org/10.1016/j.poly.2018.10.059>
- [12]. Banerjee, A., & Chattopadhyay, S. (2020). A benzoate bridged dinuclear mixed valence cobalt(III/II) complex with CoIII₂O₄CoII core: Synthesis, structure and investigation of its phenoxazinone synthase mimicking activity. *Polyhedron*, 177, 114290. <https://doi.org/10.1016/j.poly.2019.114290>
- [13]. Middy, P., Roy, D., & Chattopadhyay, S. (2023). Synthesis, structures and magnetic properties of end-on pseudo-halide bridged dinuclear copper(II) complexes with *N,O*-donor salicylaldimine Schiff base blocking ligands: A review. *Inorganica Chimica Acta*, 548, 121377. <https://doi.org/10.1016/j.ica.2023.121377>
- [14]. Khalil, E. A. M., & Mohamed, G. G. (2023). Synthesis and characterization of some transition and inner transition mixed ligand complexes derived from Schiff base ligand and o-aminophenol. *Inorganic Chemistry Communications*, 153, 110825. <https://doi.org/10.1016/j.inoche.2023.110825>
- [15]. Nayak, P. H. A., Naik, H. S. B., Viswanath, R., & Kirthan, B. R. (2021). Green light emitting fluorescent [Zn(II)(Schiff base)] complexes as electroluminescent material in organic light emitting diodes. *Journal of Physics and Chemistry of Solids*, 159, 110288. <https://doi.org/10.1016/j.jpics.2021.110288>
- [16]. Solanki, J. D., Siddiqui, I., Gautam, P., Gupta, V. K., Jou, J.-H., & Surati, K. R. (2022). Blue fluorescent Zinc(II) complexes bearing schiff base ligand for solution-processed organic light-emitting diodes with CIEy ≤ 0.09. *Optical Materials*, 134, 113222. <https://doi.org/10.1016/j.optmat.2022.113222>
- [17]. Ghorbani, S., Habibi, D., Heydari, S., & Asl, H. E. (2023). A novel Schiff-based palladium-complex as a capable nanocatalyst for the green synthesis of hexahydroquinolines and benzochromenes. *Catalysis Communications*, 181, 106721. <https://doi.org/10.1016/j.catcom.2023.106721>
- [18]. Zhu, H., Wang, J., Lu, Y., Soloshonok, V. A., Lan, L., Xu, J., & Liu, H. (2022). Cu(II) Complexes with Proline-Derived Schiff Base Ligand: Chemical Resolution of *N,C*-Unprotected α -Amino Acids and Their Antibacterial Activity. *The Journal of Organic Chemistry*, 87(19), 12900–12908. <https://doi.org/10.1021/acs.joc.2c01481>
- [19]. Mahadevi, P., & Sumathi, S. (2023). Schiff base metal complexes: Synthesis, optoelectronic, biological studies, fabrication of zinc oxide nanoparticles and its photocatalytic activity. *Results in Chemistry*, 6, 101026. <https://doi.org/10.1016/j.rechem.2023.101026>
- [20]. Reddy, G. N., Losetty, V., & Yadav, C. H. (2023). Synthesis of novel Schiff base metal complexes and their spectroscopic characterization, biological activity and molecular docking investigation. *Journal of Molecular Structure*, 1282, 135161. <https://doi.org/10.1016/j.molstruc.2023.135161>
- [21]. Ramadan, A. E.-M. M., Ibrahim, M. M., & Shaban, S. Y. (2011). Synthesis, characterization, and tyrosinase biomimetic catalytic activity of copper(II) complexes with schiff base ligands derived from α -diketones with 2-methyl-3-amino-(3H)-quinazolin-4-one. *Journal of Molecular Structure*, 1006(1), 348–355. <https://doi.org/10.1016/j.molstruc.2011.09.031>
- [22]. Jana, N. C., Patra, M., Brandão, P., & Panja, A. (2019). Synthesis, structure and diverse coordination chemistry of cobalt(III) complexes derived from a Schiff base ligand and their biomimetic catalytic oxidation of o-aminophenols. *Polyhedron*, 164, 23–34. <https://doi.org/10.1016/j.poly.2019.02.024>
- [23]. Jana, N. C., Patra, M., Brandão, P., & Panja, A. (2019). Biomimetic catalytic activity and structural diversity of cobalt complexes with N3O-donor Schiff base ligand. *Inorganica Chimica Acta*, 490, 163–172. <https://doi.org/10.1016/j.ica.2019.03.017>
- [24]. Muthusami, R., Kesavan, A., Ramachandran, V., Vasudevan, V., Irena, K., & Rangappan, R. (2020). Synthesis of mesoporous silica nanoparticles with a lychee-like morphology and dual pore arrangement and its application towards biomimetic activity via functionalization with copper(II) complex. *Microporous and Mesoporous Materials*, 294, 109910. <https://doi.org/10.1016/j.micromeso.2019.109910>
- [25]. Ayad, M. I. (2016). Synthesis, characterization and catechol oxidase biomimetic catalytic activity of cobalt(II) and copper(II) complexes containing N₂O₂ donor sets of imine ligands. *Arabian Journal of Chemistry*, 9, S1297–S1306. <https://doi.org/10.1016/j.arabjc.2012.02.007>
- [26]. Chirinos, J., Ibarra, D., Morillo, A., Llovera, L., González, T., Zárraga, J., ... Guerra, M. (2021). Synthesis, characterization and catecholase biomimetic activity of novel cobalt(II), copper(II), and iron(II) complexes bearing phenylene-bis-benzimidazole ligand. *Polyhedron*, 203, 115232. <https://doi.org/10.1016/j.poly.2021.115232>
- [27]. Arca, M., Azimi, G., Demartin, F., Devillanova, F. A., Escriche, L., Garau, A., Isaia, F., Kivekas, R., Lippolis, V., Muns, V., Perra, A., Shamsipur, M., Sportelli, L., & Yari, A. (2005). Complexes of CuII with mixed-donor phenanthroline-containing macrocycles: analysis of their structural, redox and spectral properties in the context of Type-I blue copper proteins biomimetic models. *Inorganica Chimica Acta*, 358(7), 2403–2412. <https://doi.org/10.1016/j.ica.2005.01.014>
- [28]. Diallo, A. S., Thiam, I. E., Gueye-Ndiaye, M., Dieng, M., Orton, J., Simon, C., & Gaye, M. (2022). Tetranuclear copper(II) complex of 2-hydroxy-*N,N'*-bis[1-(2-hydroxyphenyl)ethylidene]propane-1,3-diamine. *Acta Crystallographica Section E*, 78(4), 349–353. <https://doi.org/10.1107/S2056989022002225>
- [29]. Kébé, M., Thiam, I. E., Sow, M. M., Diouf, O., Barry, A. H., Sall, A. S., P. Retailleau, Gaye, M. (2021). Hexanuclear copper(II) complex of 2-hydroxy-*N,N'*-bis[1-(2-hydroxyphenyl)ethylidene]propane-1,3-diamine incorporating an open-cubane core. *Acta Crystallographica Section E*, 77(7), 708–713. <https://doi.org/10.1107/S2056989021005570>
- [30]. Musie, G. T., Li, X., & Powell, D. R. (2003). Synthesis, crystal structure and redox properties of bis-imidazolyl-containing copper(II) complexes. *Inorganica Chimica Acta*, 348, 69–74. [https://doi.org/10.1016/S0020-1693\(02\)01469-X](https://doi.org/10.1016/S0020-1693(02)01469-X)
- [31]. Mitra, M., Maji, A. K., Ghosh, B. K., Raghavaiah, P., Ribas, J., & Ghosh, R. (2014). Catecholase activity of a structurally characterized dinuclear iron(III) complex [FeIII₂(L)₂] [H₃L=N,N'-bis(3-methoxysalicylaldimine)-1,3-diaminopropan-2-ol]. *Polyhedron*, 67, 19–26. <https://doi.org/10.1016/j.poly.2013.08.064>
- [32]. Sarkar, C., Sk, S., Majumder, A., Haldar, S., Vijaykumar, G., & Bera, M. (2023). Synthesis, structure, thermal and magnetic properties of new tetranuclear copper(II) complex supported by multidentate ligand and glutarate functionality. *Journal of Molecular Structure*, 1277, 134855. <https://doi.org/10.1016/j.molstruc.2022.134855>

- [33]. Sk, S., Majumder, A., Sow, P., Samadder, A., & Bera, M. (2023). Exploring a new family of designer copper(II) complexes of anthracene-appended polyfunctional organic assembly displaying potential anticancer activity via cytochrome c mediated mitochondrial apoptotic pathway. *Journal of Inorganic Biochemistry*, 243, 112182. <https://doi.org/10.1016/j.jinorgbio.2023.112182>
- [34]. Sheldrick, G. M. (2015). SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallographica Section A*, 71(1), 3–8. <https://doi.org/10.1107/S2053273314026370>
- [35]. Sheldrick, G. M. (2015). Crystal structure refinement with SHELXL. *Acta Crystallographica Section C*, 71(1), 3–8. <https://doi.org/10.1107/S2053229614024218>
- [36]. Farrugia, L. J. (2012). WinGX and ORTEP for Windows: an update. *Journal of Applied Crystallography*, 45(4), 849–854. <https://doi.org/10.1107/S0021889812029111>
- [37]. Ferraro, J. R. (1959). The nature of the nitrate in the TBP solvates $M(NO_3)_3 \cdot 3TBP$, $M(NO_3)_4 \cdot 2TBP$ and $MO_2(NO_3)_2 \cdot 2TBP$. *Journal of Inorganic and Nuclear Chemistry*, 10(3), 319–322. [https://doi.org/10.1016/0022-1902\(59\)80124-X](https://doi.org/10.1016/0022-1902(59)80124-X)
- [38]. Geary, W. J. (1971). The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. *Coordination Chemistry Reviews*, 7(1), 81–122. [https://doi.org/10.1016/S0010-8545\(00\)80009-0](https://doi.org/10.1016/S0010-8545(00)80009-0)
- [39]. Diop, A., Sarr, M., Diop, M., Thiam, I. E., Barry, A. H., Coles, S., Orton, J., Gaye, M. (2019). Metal transition complexes of tridentate Schiff base ligands derived from 2-hydrazinopyridine: synthesis, spectroscopic characterization and X-ray structures. *Transition Metal Chemistry*, 44(5), 415–423. <https://doi.org/10.1007/s11243-019-00317-3>
- [40]. Lever, A. B. P. (1984). Inorganic electronic spectroscopy. 2nd Edition, Elsevier Science, New York.
- [41]. Chandra, S., & Sharma, S. D. (2002). Chromium(III), manganese(II), cobalt(II), nickel(II), copper(II) and palladium(II) complexes of a 12-membered tetraaza [N4] macrocyclic ligand. *Transition Metal Chemistry*, 27(7), 732–735. <https://doi.org/10.1023/A:1020309322470>
- [42]. Roy Choudhury, C., Dey, S. K., Mitra, S., & Gramlich, V. (2003). Isolation and characterisation of a novel thermally stable octahedral bicarbonato complex of bis(2-picolyamine)copper(II): identification of rare monodentate coordination. *Dalton Trans.*, (6), 1059–1060. <https://doi.org/10.1039/B300548H>
- [43]. Puchoňová, M., Matejová, S., Jorík, V., Šalitraš, I., Švorc, L., Mazúr, M., ... Valigura, D. (2018). Two versatile salicylatocopper(II) complexes: Structure, spectral, magnetic, electrochemical properties and SOD mimetic activity. *Polyhedron*, 151, 152–159. <https://doi.org/10.1016/j.poly.2018.05.036>
- [44]. Dhanaraj, C. J., & Nair, M. S. (2014). Synthesis and characterization of cobalt(II) and zinc(II) complexes of poly(3-nitrobenzylidene-1-naphthylamine-co-succinic anhydride). *Journal of Saudi Chemical Society*, 18(5), 479–485. <https://doi.org/10.1016/j.jscs.2011.10.006>
- [45]. Musie, G. T., Li, X., & Powell, D. R. (2003). Synthesis, crystal structure and redox properties of bis-imidazolyl-containing copper(II) complexes. *Inorganica Chimica Acta*, 348, 69–74. [https://doi.org/10.1016/S0020-1693\(02\)01469-X](https://doi.org/10.1016/S0020-1693(02)01469-X)
- [46]. Patel, A. K., Jadeja, R. N., Roy, H., Patel, R. N., Patel, S. K., Butcher, R. J., ... Herrero, S. (2020). Copper(II) hydrazone complexes with different nuclearities and geometries: Synthesis, structural characterization, antioxidant SOD activity and antiproliferative properties. *Polyhedron*, 186, 114624. <https://doi.org/10.1016/j.poly.2020.114624>