

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 act 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 prepared from salicylaldehyde are widely used in coordination chemistry for the synthesis of complexes with physical and biological properties [1–4]. Schiff bases obtained by condensation reaction between salicylaldehyde, and functionalized or non-functionalized amines are compounds having donor sites of the N, O, S, P... type [5–8]. When these compounds are reacted with salts of transition metals or lanthanides, compounds with various structures and properties were obtained [9–12]. The versatility of these compounds is observed with their different modes of coordination to metal ions. Several of these Schiff bases exhibit antimicrobial [13,14], antifungal [15,16], antitumor properties [17,18]. These properties can be improved or reduced after complexation with various metal ions [19–22]. Thus, the synthesis of new basic Schiff complexes and the study of the structure-activity relationship have become a major issue in coordination chemistry. Controlling the size of the ligand cavities and the type of donor sites makes it possible to make them specific.

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Salicylaldehyde and its derivatives lead with the same amine, Schiff bases having different biological activities. Indeed, the type of substituent used and the position of the substitution on the aromatic nucleus have particularly important effects on the properties of the molecule [13,23–25]. On the other hand, 2-aminoethanol has received great interest from coordination chemists because of the properties of the complexes formed with it. Certain complexes based on ethanolamine are used as buffer [26], catalysts [27], anti-cancer [28], antimicrobial [29], cytotoxic agent [23]. It is in this context that we report the synthesis, the spectroscopic characterization, and the crystal structure of three complexes (**1-3**) with the same tridentate Schiff base 2-((2-hydroxyethylimino)methyl)phenol (H_2L), identical to that used by several authors [23,30–33]. Single crystal X-ray diffraction studies reveal that the ligand acts differently with the metal ions. In complex **1** a single Co(III) ion is coordinated with two H_2L molecules which act in a tridentate fashion. In complex **2**, two ligand molecules act in a tridentate fashion, forming a bridge between two Ni(II) ions. For complex **3** the ligand acts in a tridentate manner on a single Cu(II) ion while the two copper(II) ions are bridged by two chloride ions.

II. Experimental section

2.1. Material and procedures

Salicylaldehyde, 2-aminoethanol, 2-acetylpyridine, cobalt chloride hexahydrate, nickel chloride hexahydrate and copper chloride dihydrate were commercial products (from Aldrich) and were used without further purifications. The solvents were reagent grade and were purified by usual methods. Elemental analyses were carried out using a VxRio EL Instrument. The IR spectra were recorded on a FTIR Spectrum Two of Perkin Elmer ($4000\text{--}400\text{ cm}^{-1}$). The UV–Vis spectra were run on a Perkin-Elmer UV/Visible spectrophotometer Lambda 365 ($1000\text{--}200\text{ nm}$). The 1H and ^{13}C NMR spectra of the Schiff bases were recorded in DMSO- d_6 on a BRUKER 500 MHz spectrometer at room temperature using TMS as an internal reference. The molar conductance of 10^{-3} M solutions of the metal complexes in DMF was measured at 25 °C using a WTW LF-330 conductivity meter with a WTW conductivity cell. Magnetic measurements for complexes were performed at room temperature by using a Johnson Matthey scientific magnetic susceptibility balance (Calibrant: $Hg[Co(SCN)_4]$).

2.1.1. Synthesis of 2-((2-hydroxyethylimino)methyl)phenol (H_2L)

Method from literature [23] was used with slight modification. In a 250 mL flask containing 30 mL of methanol, 2.5 g (20.471 mmol) of salicylaldehyde, 1.25 g (20.471 mmol) of 2-aminoethanol in 10 mL of methanol was added. The resulting mixture was refluxed for two hours. The methanol was removed, and a viscous red oil was recovered. Yield 75.2 %. M.p. 92 °C. Anal. Calc for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.46; H, 6.68; N, 8.45. (300 MHz, DMSO- d_6) (δ , ppm): 13.56 (s, OH, 1H); 8.51 (s, HC=N, 1H); 4.77 (s, $-CH_2-OH$, 1H); 6.87–7.44 (m, H-Ar, 4 H); 3.54 (t, $-CH_2-N$, 2H); 3.74 (t, $-CH_2-OH$, 2H). NMR ^{13}C [DMSO, 300 MHz, (δ , ppm)]: 118.61 (C_{Ar-C}); 161.06 (C_{Ar-OH}); 118.05 (C_{Ar}); 132.12 (C_{Ar}); 118.24 (C_{Ar}); 131.99 (C_{Ar}); 166.60 (C=N); 60.24 ($-CH_2-$); 60.90 (C–OH).

2.1.2. Synthesis of the complexes $\{[Co(L)_2][Co(HL)_2]\cdot 4H_2O\}$ (**1**)

To a methanolic solution (10 mL) of the ligand H_2L 0.1 g (1 mmol) a solution of the $CoCl_2\cdot 6H_2O$ salt 0.2379 g (1 mmol) in methanol (10 mL) was added. The solution was stirred at room temperature for one hour and then filtered. The filtrate was left to slow evaporation and yellow crystals suitable for X-ray analyze were formed after 3 days. Yield 55 %. Anal. Calc for $C_{36}H_{48}N_4O_{12}Co_2$: C, 51.07; H, 5.71; N, 6.62. Found: C, 51.03; H, 5.68; N, 6.59. IR (cm^{-1}): 3722, 1644, 1597, 1572, 1492, 1467, 1299, 1197, 1106, 942, 836, 781. Magnetic moment: diamagnetic. Conductance Λ ($S\cdot cm^2\cdot mol^{-1}$): 9.

2.1.3. Synthesis of the complexes $[Ni_2(HL)_2(Cl)_2(H_2O)_2]$ (**2**)

The procedure used for the synthesis of (**1**) was used: $NiCl_2\cdot 6H_2O$ 0.2369 g (1 mmol) instead $CoCl_2\cdot 6H_2O$. Yield 61 %. Anal. Calc for $C_{18}H_{24}N_2O_6Cl_2Ni_2$: C, 40.61; H, 3.61; N, 21.92; S, 7.17. Found: C, 40.59; H, 3.59; N, 21.89; S, 7.15. IR (cm^{-1}): 3737, 1646, 1585, 1545, 1466, 1305, 1197, 1077, 925, 858, 776. $\mu_{eff} = 3.7\ \mu_B$ per nickel ion. Conductance Λ ($S\cdot cm^2\cdot mol^{-1}$): 8.

2.1.4. Synthesis of the complexes $\{[Cu_2(HL)_2(Cl)_2][Cu_2(HL)_2(Cl)_2]\cdot (H_2O)\}$ (**3**) and $[Cu_2(HL)_2(Cl)_2]$ (**4**)

The procedure used for the synthesis of (**1**) was used: $CuCl_2\cdot 2H_2O$ 0.1705 g (1 mmol) instead $CoCl_2\cdot 6H_2O$. The black filtrate was left to slow evaporation and green crystals suitable for X-ray analyze were formed after 5 days. (**3**): Yield 58 %. Anal. Calc for $C_{36}H_{42}N_4O_9Cl_4Cu_4$: C, 40.38; H, 3.95; N, 5.28; Cl, 13.24. Found: C, 40.35; H, 3.93; N, 5.26; Cl, 13.21. IR (cm^{-1}): 3784, 1635, 1579, 1568, 1465, 1332, 1194, 1071, 928, 892, 751. $\mu_{eff} = 2.49\ \mu_B$ per dimer. Conductance Λ ($S\cdot cm^2\cdot mol^{-1}$): 12. On continuing the slow evaporation blue

crystals suitable for X-ray analyze were formed after three weeks. **(4)** : Yield 25 %. Anal. Calc for $C_{18}H_{20}Cl_2N_2O_4Cu_2$: C, 41.07; H, 3.83; N, 5.32. Found: C, 41.01; H, 3.80; N, 5.33. IR (cm^{-1}): 3501, 1650, 1597, 1540, 1470, 1195, 1150, 1064, 964, 8976, 751. $\mu_{eff} = 1.75 \mu_B$ per copper ion. Conductance Λ ($S.cm^2.mol^{-1}$): 5. When methanol solvent was used instead ethanol, compounds **(3)** and **(4)** were isolated again.

2.2. Crystal structure determination of complexes 1, 2, 3 and 4

The details of the crystal structure solution and refinement are given in Table 1. Measurements were made on a Rigaku Oxford Diffraction Dual source diffractometer at the $CuK\alpha$ radiation (1.54184 Å). All data were corrected for Lorentz and polarization effects. Empirical absorption correction was applied. Complex scattering factors were taken from the program package *SHELXTL* [34]. The structures were solved by intrinsic phasing, 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]. All hydrogen atoms were located in their calculated positions and refined using a riding model. Molecular graphics were generated using *ORTEP-3* [36].

Table-1. Crystal data and details of the structure determination of **1, 2, 3 and 4.**

Complex	1	2	3	4
Empirical formula	$C_{36}H_{48}Co_2N_4O_{12}$	$C_{18}H_{24}Ni_2Cl_2N_2O_6$	$C_{36}H_{42}Cu_4Cl_4N_4O_9$	$C_{18}H_{20}Cl_2Cu_2N_2O_4$
Formula weight	846.65	552.69	1070.74	526.37
Temperature (K)	293	295	295	293
Radiation type (Å)	1.54184	1.54184	1.54184	0.71073
Crystal system	Trigonal	Monoclinic	Triclinic	Monoclinic
space group	<i>R</i> 3	<i>P</i> c	<i>P</i> - $\bar{1}$	<i>P</i> ₂ / <i>c</i>
<i>a</i> (Å)	29.9090(4)	9.8449(1)	12.4033(4)	17.1076(3)
<i>b</i> (Å)	29.9090(4)	9.0046(1)	12.4521(4)	8.94199(19)
<i>c</i> (Å)	10.9643(2)	11.9809(1)	15.3409(4)	13.0010(3)
α (°)	90	90	77.979(3)	90
β (°)	90	93.139(1)	86.543(2)	97.1106(18)
γ (°)	120	90	66.209(3)	90
<i>V</i> (Å ³)	8494.1(3)	1060.51(2)	2119.73(12)	1973.55(7)
<i>Z</i>	32	4	2	4
<i>D</i> _{cal} (g·cm ⁻³)	1.486	1.731	1.618	1.5999
μ (mm ⁻¹)	7.46	4.87	5.05	0.88
Crystal size (mm)	0.12 × 0.08 × 0.06	0.40 × 0.30 × 0.08	0.06 × 0.06 × 0.02	0.10 × 0.08 × 0.05
θ range (°)	2.955-73.018	4.498-70.735	2.946-72.960	2.399-31.792
Absorption correction	Multi scan	Multi scan	Multi scan	
Index ranges	-28 ≤ <i>h</i> ≤ 37, -37 ≤ <i>k</i> ≤ 20, -13 ≤ <i>l</i> ≤ 13	-12 ≤ <i>h</i> ≤ 11, -9 ≤ <i>k</i> ≤ 10, -14 ≤ <i>l</i> ≤ 14	-15 ≤ <i>h</i> ≤ 15, -15 ≤ <i>k</i> ≤ 15, -18 ≤ <i>l</i> ≤ 19	-25 ≤ <i>h</i> ≤ 24 -12 ≤ <i>k</i> ≤ 11 -18 ≤ <i>l</i> ≤ 18
No. of measured Reflections collected	16700	17769	38168	40018
Independent Reflections	7137	3484	8284	5905
Observed reflections [<i>I</i> > 2σ(<i>I</i>)]	5606	3468	6828	5089
<i>R</i> _{int}	0.046	0.035	0.055	0.050
Final <i>R</i> ₁ , <i>wR</i> ₂ indices [<i>I</i> > 2σ(<i>I</i>)]	0.0409, 0.1033	0.0357, 0.0902	0.0379, 0.0967	0.0266, 0.0607

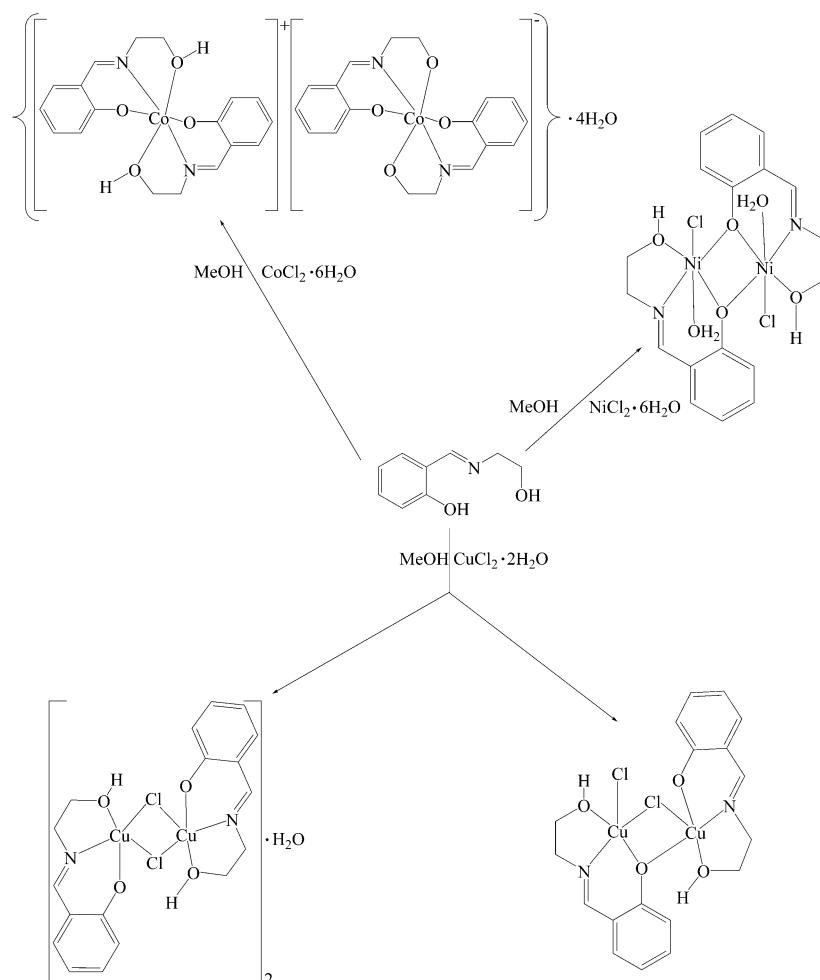
Final R_1 , wR_2 (all data)	0.0565, 0.1384	0.0357, 0.0902	0.0483, 0.1051	0.0352, 0.0627
Data/restraints/parameters	5606/4/499	3468/8/279	6828/12/529	5089/0/256
GOF	1.11	1.06	1.03	1.05
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ ($e \text{ \AA}^{-3}$)	0.46, -0.47	0.26, -0.56	1.33, -0.46	0.54, -0.48

III. Result and discussion

3.1. Synthesis and spectroscopic studies

The acyclic Schiff base ligand H_2L was prepared following a method in the literature [23]. The synthesis of H_2L was achieved in one step procedure by the condensation reaction between salicylaldehyde and 2-aminoethanol in quantitative yield. The infrared spectrum of the ligand reveals a broad band between 3200 and 3500 cm^{-1} which is attributable to the ν_{OH} vibrations of the phenol and the alcohol groups. The band pointed at 1632 cm^{-1} is assigned to the $\nu_{C=N}$ vibration of the imine group. The band pointed at 1276 cm^{-1} is attributed to the ν_{C-O} vibration. The bands observed between 2876 and 2971 cm^{-1} are attributed to the methylene groups. Bands characteristic of phenyl ring are pointed in the region 1490-1580 cm^{-1} . The 1H NMR spectrum of the ligand recorded in DMSO- d_6 reveals singlet spotted at 13.56 ppm which is attributed to the phenolic proton Ar-OH. Signals at 8.51 and 4.77 ppm are respectively assigned to the protons of the imine function (HC=N) and the primary alcohol -CH₂-OH. Signals observed in the range [6.87-7.44] ppm as a multiplet are assigned to the aromatic protons. Two signals appearing as triplet are pointed at 3.54 and 3.74 ppm and assigned to the methylene protons (-N-CH₂-CH₂-OH) and to the protons of the carbon atom supporting the alcoholic function (-CH₂-CH₂-OH). The ^{13}C NMR shows a signal at 166.60 ppm attributed to the azomethine carbon atom (C=N). The signal at 161.06 ppm is assigned to the C_{ipso} -OH of the phenol ring. The signals of the methylene carbon atoms are pointed at 60.24 (-N-CH₂-CH₂-OH) and 60.90 ppm (-N-CH₂-CH₂-OH). The signals in the range [118 ppm - 132 ppm] are attributed to the aromatic carbon atoms.

The reactions of H_2L with chloride metal transitions salts in 1:1 ratio, were screened. The complexation was achieved in methanol or ethanol solutions by mixing both ligand and salts. The air-stable complexes were isolated as mononuclear or dinuclear. Crystals suitable for X-ray analyses were isolated by slow evaporation of the solution of $\{[Co(L)_2][Co(HL)_2] \cdot 4H_2O\}$ (1), $[Ni_2(HL)_2(Cl)_2(H_2O)_2]_2$ (2), $\{[Cu_2(HL)_2(Cl)_2] \cdot [Cu_2(HL)_2(Cl)_2] \cdot (H_2O)\}$ (3), $[Cu_2(HL)_2(Cl)_2]$ (4). All the complexes are characterized by elemental analysis, IR and UV spectroscopies, molar conductivity measurements, room temperature magnetic moments measurements and X-ray diffraction.



Scheme 1. The process of preparation of the complexes.

Upon coordination to metal ion, a shift was observed for the azomethine infrared band comparatively to the free ligand. For complexes **1–4**, the C=N band appears respectively at 1644 cm^{-1} , 1646 cm^{-1} , 1635 cm^{-1} and 1650 cm^{-1} . Those displacements are indicative of the involvement of the azomethine in the coordination. The electronic spectrum of the free ligand shows two main bands at 38610 cm^{-1} and 31348 cm^{-1} attributable to the aromatic ring and the azomethine C=N. The electronic spectrum of the complex of Co(III) (**1**) exhibits distinct absorption bands at 19048 cm^{-1} , 24876 cm^{-1} , 31153 cm^{-1} and 38314 cm^{-1} . The band at 38314 cm^{-1} is attributed to $\pi \rightarrow \pi^*$ while the band at 31153 cm^{-1} is due to $n \rightarrow \pi^*$ transition. These transitions are due to the benzene ring and azomethine moiety. Comparatively to the band on the spectrum of the free ligand, reduction in intensity is observed. The band at 24876 cm^{-1} is assigned to the ligand to metal charge transfer (LMCT) $\text{PhO}^- \rightarrow \text{Co}^{3+}$ and $\text{C}=\text{N} \rightarrow \text{Co}^{3+}$ [37]. In spin paired cobalt(III) octahedral complex, two spin allowed $d \rightarrow d$ transitions at relatively low energy are expected. In the spectrum of complex **1**, bands at 19048 cm^{-1} and 13423 cm^{-1} assigned to $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$ [38,39]. Room temperature magnetic susceptibility measurements show that the complex **1** is diamagnetic as expected for low-spin cobalt(III) complexes [40]. The electronic spectrum of complex **2** shows high intensity bands at 38462 cm^{-1} and 27027 cm^{-1} which are assigned to $\pi \rightarrow \pi^*$ transitions of the aromatic ring and to LMCT $\text{PhO}^- \rightarrow \text{Ni}^{2+}$ and $\text{C}=\text{N} \rightarrow \text{Ni}^{2+}$, respectively [41]. The band at 16949 cm^{-1} is assigned to $d \rightarrow d$ transition. Additional band with low intensity is pointed at 13369 cm^{-1} . This band is assigned to a spin-forbidden transition [42]. Room temperature magnetic susceptibility measurements shows that the complex **2** is diamagnetic with a magnetic moment value of $3.7 \mu_B$ per Ni(II) ion. This value is indicative of the presence of two unpaired electrons in an octahedral environment around each of the two uncoupled nickel atoms [43–45]. The electronic spectrum of complex **3** shows band at 38461 and 32894 cm^{-1} which are due to the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition for the aromatic ring and the azomethine moiety. The band at 27247 cm^{-1} is typical to LMCT [41]. The band of low intensity appearing at 15360 cm^{-1} is attributable to the $d \rightarrow d$ transition of copper ion in square-pyramidal environment [46]. Complex **3** is diamagnetic with an effective room temperature magnetic moment of $2.49 \mu_B$ per dimer which is comparable to the spin only value of $2.45 \mu_B$, expected for two non-interaction copper (II) ions. The magnetic moment value of complex **3** is close proximity to those reported

for similar copper (II) complexes [47,48]. Complex **4** shows three main bands. The bands at 25710 cm⁻¹ and 21413 cm⁻¹ are due to the intra-ligand transitions, while the band at 14556 cm⁻¹ is attributable to the d→d transition in copper(II) ion in square pyramidal geometry [49]. The magnetic moment value of 1.75 μ_B per copper ion in complex **4**, is closer to the expected value of 1.73 μ_B for a well-separated copper (II) ion [50]. The molar conductance Λ measured in 10⁻³ M DMF solutions of complexes **1-4** are respectively 9, 8, 12 and 5 S cm² mol⁻¹. These values are indicative of neutral electrolytes in DMF [51].

Table-2. Selected bond lengths [Å] and bond angles [°] of complexes **1, 2, 3** and **4**.

1		2		3		4	
Co1-O1	1.874 (5)	Ni2-N2	2.004 (3)	Cu2-N2	1.947 (3)	Cu2-N2	1.9410 (12)
Co1-O3	1.895 (5)	Ni2-O3	2.007 (3)	Cu2-Cl2	2.2649 (8)	Cu2-O3	1.9434 (11)
Co1-N1	1.897 (7)	Ni2-O1	2.056 (3)	Cu2-Cl1	2.7688 (9)	Cu2-O4	1.9812 (11)
Co1-N2	1.912 (6)	Ni2-O6	2.090 (3)	Cu4-O5	1.889 (2)	Cu1-O3	1.9888 (10)
Co1-O4	1.919 (5)	Ni2-O4	2.195 (3)	Cu4-N4	1.943 (2)	Cu1-N1	1.9305 (12)
Co1-O2	1.929 (5)	Ni2-Cl2	2.4711 (10)	Cu4-Cl4	2.2815 (8)	Cu2-Cl1	2.2629 (4)
Co2-O6	1.880 (5)	Ni1-O1	2.001 (3)	Cu3-O8	2.018 (3)	Cu2-Cl2	2.6194 (4)
Co2-N4	1.895 (7)	Ni1-N1	2.012 (3)	Cu3-Cl3	2.2607 (8)	Cu1-O1	1.8769 (12)
Co2-N3	1.901 (6)	Ni1-O3	2.061 (3)	Cu3-Cl4	2.7664 (9)	Cu1-O2	2.0200 (11)
Co2-O8	1.911 (5)	Ni1-O5	2.076 (3)	Cu1-O1	1.902 (3)	Cu1-Cl1	2.6735 (4)
Co2-O9	1.916 (5)	Ni1-Cl1	2.3915 (11)	Cu1-O2	1.987 (2)		
Co2-O7	1.927 (5)	Ni1-O2	2.395 (3)	Cu1-Cl1	2.2418 (9)		
N1-Co1-N2	174.1 (3)	N2-Ni2-O1	170.43 (12)	O3-Cu2-O4	174.04 (9)	O3-Cu2-O4	168.47 (5)
O3-Co1-O4	177.7 (3)	N1-Ni1-O3	169.71 (12)	N2-Cu2-Cl2	168.98 (9)	N2-Cu2-Cl1	163.07 (4)
N4-Co2-N3	174.7 (3)	O3-Ni2-O4	170.85 (11)	O5-Cu4-O6	170.30 (10)	N1-Cu1-O3	169.60 (5)
O8-Co2-O9	178.4 (2)	O5-Ni1-Cl1	169.49 (9)	N4-Cu4-Cl4	152.82 (8)	O1-Cu1-O2	168.15 (5)
O6-Co2-O7	178.2 (3)	O1-Ni1-O2	168.81 (11)	O7-Cu3-O8	175.42 (9)	O3-Cu2-Cl1	89.36 (3)
O1-Co1-O2	179.1 (2)	O6-Ni2-Cl2	168.82 (9)	N3-Cu3-Cl3	166.31 (10)	O4-Cu2-Cl1	93.68 (3)
O6-Co2-N3	95.0 (2)	N2-Ni2-Cl2	95.35 (9)	O1-Cu1-O2	174.78 (10)	O3-Cu1-O2	90.90 (4)
O3-Co1-N1	90.2 (3)	O3-Ni2-O6	91.29 (12)	N1-Cu1-Cl1	166.03 (8)	O1-Cu1-Cl1	105.90 (4)
O1-Co1-N2	89.2 (2)	O1-Ni1-O5	93.69 (11)	Cu4-Cl4-Cu3	85.62 (3)	N2-Cu2-O3	92.30 (5)
N3-Co2-O9	91.8 (2)	N1-Ni1-O5	92.50 (12)	Cu1-Cl1-Cu2	87.87 (3)	O1-Cu1-O3	90.90 (5)

3.2. Description of the crystal structure of the complex 1

The title compound crystallizes in the trigonal system in the space group *R3*. The asymmetric unit of the title compound, {[Co(L)₂].[Co(HL)₂].4(H₂O)}, contains two mononuclear ionic units, anionic [Co(L)₂]⁻ and cationic [Co(HL)₂]⁺ and two uncoordinated water molecules (Figure 1a). The selected bond lengths and angles are collected in Table 2. In one of the two unit, the Co^{III} ion is coordinated by two monodeprotonated ligand through one phenolate oxygen atom, one alcoholic oxygen atom and one nitrogen atom. In the second unit the Co^{III} ion is coordinated to two dideprotonated ligand molecule through one phenolate oxygen atom, one alcoholate oxygen atom and one nitrogen atom. The environment of the Co^{III} ion in both molecules is a N₂O₄. For both Co^{III} the two ligands are in *mer* configuration. Each Co atom is in a distorted octahedral geometry. The basal planes are occupied by N1, O3, N2, O4 for Co1 and N3, O6, N4, O7 for Co2. The *cisoid* angles are in the range [84.4 (3)-94.4 (3)] for Co1 and [85.2 (2)-95.0 (2)] for Co2 while the *transoid* angles are O3-Co1-O4 = 177.7 (3)°, N1-Co1-N2 = 174.1 (3)°, O6-Co2-O7 = 178.2 (3)° and N3-Co2-N4 = 174.7 (3)° (Table 2). The sum of the angles subtended by the atoms in the basal planes are 360.1° and 359.9° for Co1 and Co2 respectively. The apical positions are occupied by one phenolate oxygen atom and one alcoholic oxygen atom for each Co^{III} ion with angle values of O1-Co1-O2 = 179.1 (2)° and O8-Co2-O9 = 178.4 (2)°. Each ligand form with the corresponding Co ion five-membered ring CoOCCN and hexa-membered ring CoOCCCN, 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 [84.4 (3)°–86.0 (3)°] and the values in the range [94.4 (3)–95.0 (2)°] are attributed to the N–Co–O bite angles within hexa-membered chelate. These angle values are in accordance with the expected values for similar octahedral cobalt complex [52]. The deviation of the Co1 and Co2 ions from their corresponding basal plane are 0.0127 Å and 0.0269 Å, respectively. The mean planes defined by the atoms of the ligand coordinated to Co1 are quite perpendicular with dihedral angle of 89.614 (8)°. The dihedral angle between the means planes of the ligand coordinated to Co2 is 84.479 (5)°. The distances Co–O and Co–N are comparable and fall in the range [1.874 (5) Å–1.929 (5) Å] and are compatible with the expected values for those type of bond [53]. In the crystal, intramolecular and intermolecular hydrogen bonds are simultaneously present. The crystal packing of compound **1** is stabilized by intramolecular O9–H9···O2 and O5–H5A···O3 and intermolecular O7–H7···O4ⁱ (*i* = –*y*+1, *x*–*y*, *z*) hydrogen bonds. Additional C–H···O hydrogen bonds C25–H25···O12ⁱⁱ and C8–H8···O7ⁱⁱ (*ii* = –*x*+*y*+1, –*x*+1, *z*) connect the unit forming a planar two dimensional structure in the *ab* plane (Figure 1b, Table 3).

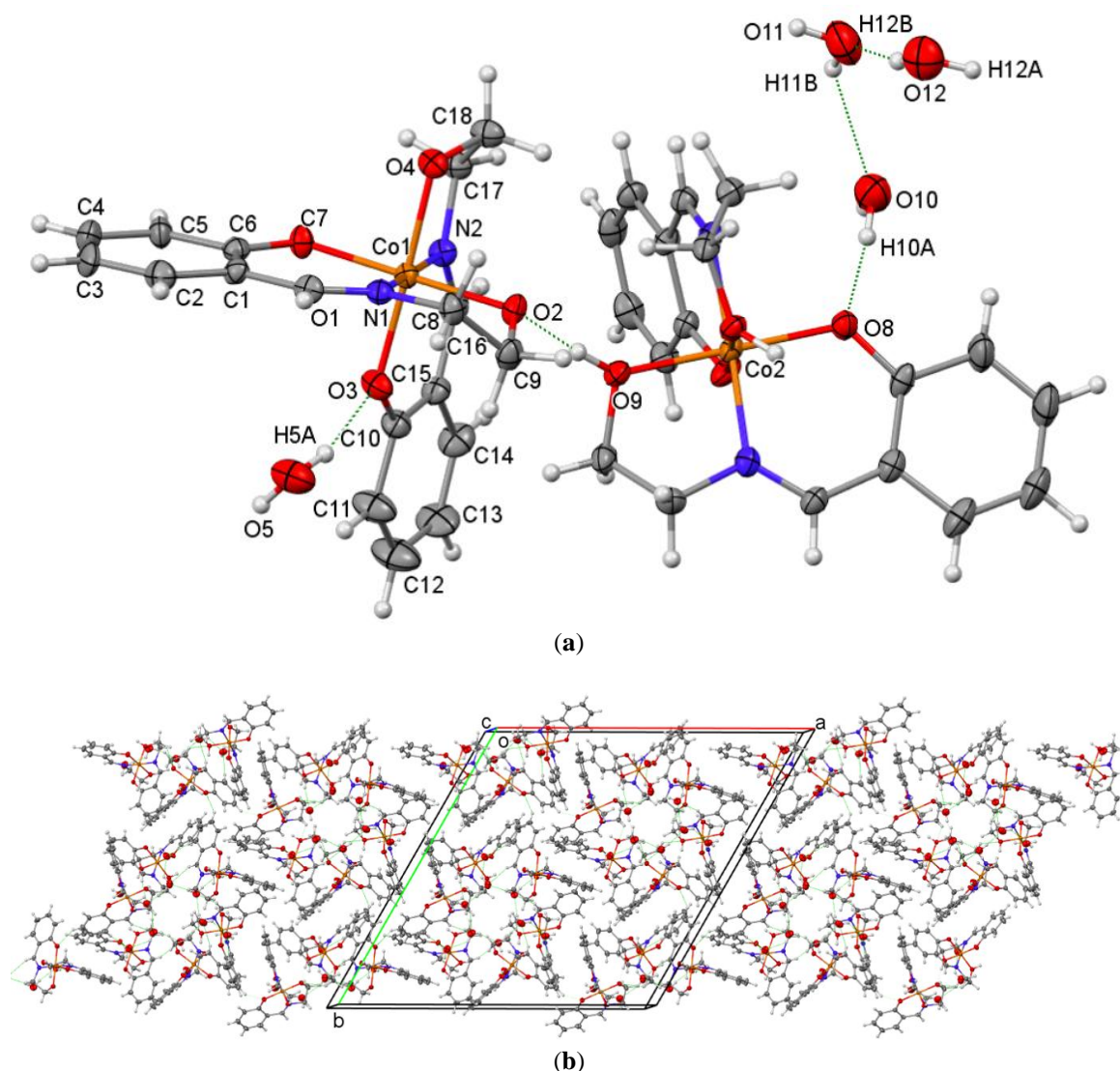


Fig 1. (a) Crystal structure of the dinuclear complex $\{[\text{Co}(\text{L})_2][\text{Co}(\text{HL})_2]\cdot 4\text{H}_2\text{O}\}$ (**1**), (b) packing diagram of (**1**) viewed along the *ab* plane.

Table-3. Hydrogen-bond geometry (Å, °) of complex **1**.

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
O9–H9···O2	0.862 (14)	1.550 (19)	2.407 (7)	172 (6)
O7–H7···O4 ^{<i>i</i>}	0.86	1.64	2.425 (7)	150.5

O5—H5A...O3	0.85	1.99	2.827 (10)	166.6
C25—H25...O12 ⁱⁱ	0.93	2.61	3.498 (12)	160.8
C8—H8B...O7 ⁱⁱ	0.97	2.65	3.427 (10)	137.4
C27—H27B...O2	0.97	2.55	3.388 (9)	144.9

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

3.3. Description of the crystal structure of the complex 2

The title compound crystallizes in the monoclinic system in the space group Pc . The asymmetric unit consists of a dinuclear neutral unit, $[\text{Ni}_2(\text{HL})_2(\text{Cl})_2]$ (Figure 2a). The selected bond lengths and angles are collected in Table 2. In the dinuclear unit, both nickel ions are in an NO_4Cl environment, which can be described as a square bipyramidal geometry. The basal planes around each of these two nickel ions are occupied by one phenolate, one alcoholic oxygen atoms and one nitrogen atom from one ligand molecule and one phenolate oxygen atom from a second ligand. The two phenolate oxygen atoms acts as bridge between the two nickel ions. The apical positions are occupied by one oxygen from a coordinated water molecule and one chloride anion. The apical bond lengths Cl1-Ni1 and Cl2-Ni2 are 2.394 (3) and 2.471 (1) Å, respectively, and are the longest distances around these two nickel ions. These values are close proximity to the values reported for the complex $\text{Ni}(\text{2aepy})_2\text{Cl}(\text{H}_2\text{O})[\text{Cl}\cdot\text{H}_2\text{O}]$ (2aepy is 2-aminoethylpyridine) in which the chlorido ion is in terminal position as in the studied complex [54]. The two other apical bonds $\text{O}_{\text{water}}\text{-Ni}$ distances are respectively 2.076 (3) Å and 2.090 (3) Å for O5-Ni1 and O6-Ni2 ad agree with the bond length values of $\text{O}_{\text{water}}\text{-Ni}$ in reported complex Bis[μ -2-{bis(2-pyridylethyl)amino}phenolato]-bis[aquanickel(II)] dinitrate tetrahydrate [55]. The the $\text{Ni-N}_{\text{imino}}$ distance of are quite identical with value of 2.012 (3) Å [Ni1-N1] and 2.004 (3) Å [Ni2-N2]. The $\text{Ni-O}_{\text{phenoxo}}$ bridge is asymmetric as revealed by $\text{Ni1-O1} = 2.000$ (3) Å, $\text{Ni2-O1} = 2.056$ (2) Å, $\text{Ni1-O3} = 2.061$ (2) Å and $\text{Ni2-O3} = 2.007$ (3) Å. The Ni-N , Ni-O and Ni-Ni distances are in the range reported for Ni complexes having Ni_2O_2 moiety in which the oxygen atoms are issued from phenolic units [56,57]. The separation between the two metal centers is about 3.1437(8) Å. This distance is too long to consider an intermetallic interaction with a bridge angle of $\text{Ni1-O1-Ni2} = 101.59$ (11)° and $\text{Ni1-O3-Ni2} = 101.21$ (11)°. These observations are in accordance with those found for similar dinuclear nickel complex [58]. The *transoid* angles at the Ni1 ion are equal to 169.71 (12) and 168.81 (11)°, the *cisoid* angles vary from 76.52 (12) to 112.01 (11)°. Around Ni2 ion, the *transoid* angles are equal to 170.43 (12) and 170.85 (11)°, the *cisoid* angles vary from 78.59 (10)° to 110.14 (11)° (Table 2). These angle values which deviate severely from the ideal values of 180° for *transoid* angles and 90° for *cisoid* angles are indicative of the deformation of the octahedrons around Ni ions. The deviation of the Ni1 and Ni2 ions from their corresponding basal plane are 0.0623 Å and 0.0367 Å, respectively. The sum of the angles subtended by the atoms in the basal planes are 359.70° and 359.88° for Ni1 and Ni2, respectively. For each Ni, the ligand forms one five-membered ring and one hexa-membered ring which share one vertex at nitrogen imino atom. The values of 76.52(12)° and 79.02(12)° of the N-Ni-O bite angles within five-membered chelate rings and the values of 92.58(12)° and 92.13(12)° of the N-Ni-O bite angles within hexa-membered chelate are as expected [29]. The dihedral angle between the phenolato-rings (O1-C6) and (O3-C15) is 3.82° and these planes form dihedral angles with the Ni_2O_2 plane of 2.11° and 4.83°, respectively. A series of intramolecular $\text{O5-H5B}\cdots\text{Cl2}$, $\text{O6-H6A}\cdots\text{Cl1}$ and $\text{C11-H11}\cdots\text{O2}$ hydrogen bonds stabilize the structure. The intermolecular hydrogen bond $\text{O4-H4}\cdots\text{O2}^{\text{i}}$ ($i = x, y+1, z$), $\text{O5-H5A}\cdots\text{Cl1}^{\text{ii}}$ ($\text{ii} = x, -y+1, z-1/2$), $\text{O6-H6B}\cdots\text{Cl2}^{\text{iii}}$ ($\text{iii} = x, -y+2, z+1/2$) and $\text{O2-H2}\cdots\text{Cl2}^{\text{iv}}$ ($i = x, -y+1, z+1/2$) connect the units forming a planar two dimensional structure in the ab plane (Figure 2b, Table 4).

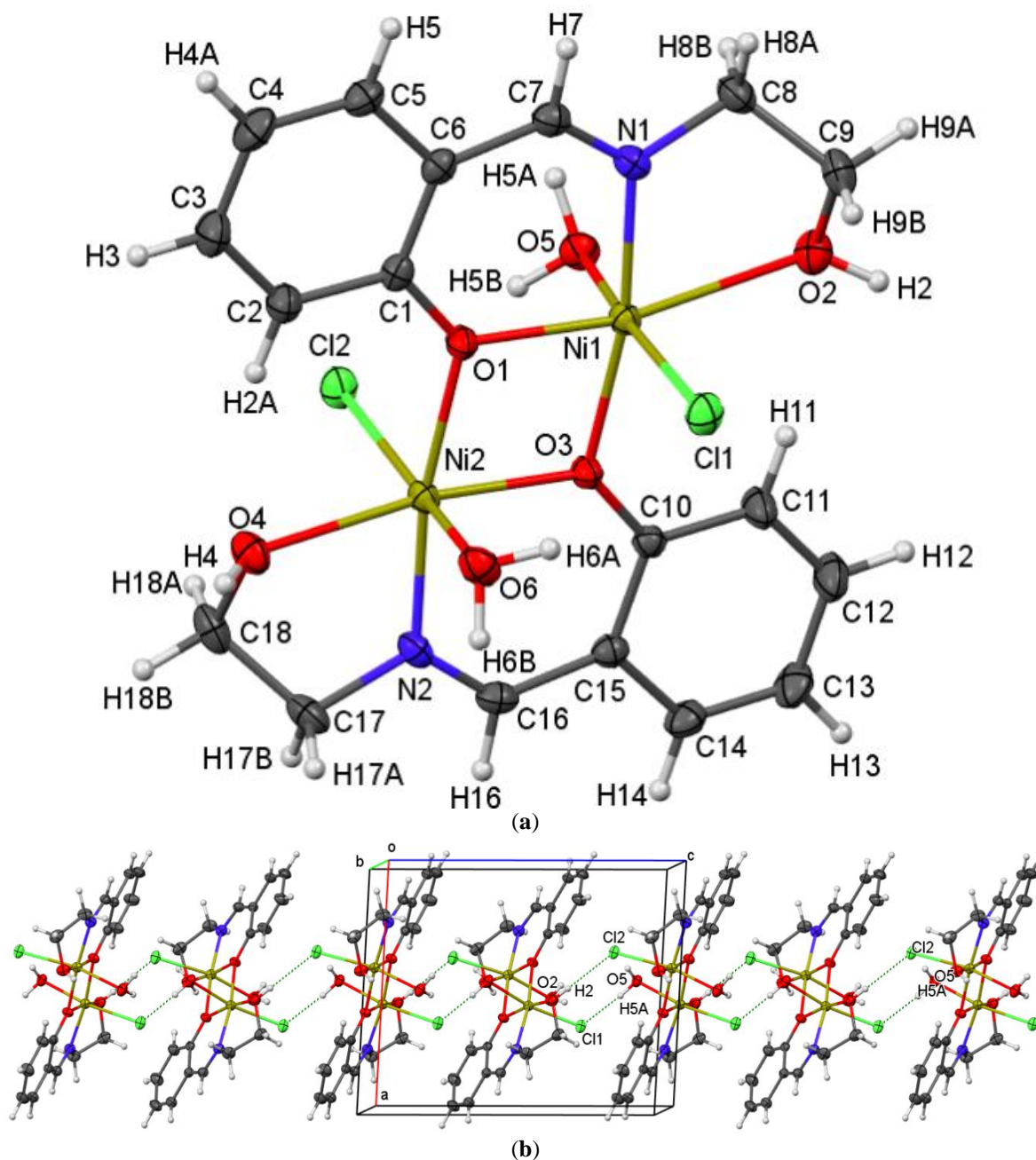


Fig. 2. (a) Crystal structure of the dinuclear complex $[\text{Ni}_2(\text{HL})_2(\text{Cl})_2(\text{H}_2\text{O})_2]_2$ (**2**), (b) packing diagram of (**2**) viewed along the ab plane.

Table-4. Hydrogen-bond geometry (\AA , $^\circ$) of complex **2**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O4}-\text{H4}\cdots\text{O2}^{\text{i}}$	0.870 (13)	2.19 (3)	2.985 (4)	152 (4)
$\text{O5}-\text{H5A}\cdots\text{Cl1}^{\text{ii}}$	0.90	2.24	3.118 (3)	164.4
$\text{O5}-\text{H5B}\cdots\text{Cl2}$	0.90	2.39	3.241 (3)	156.9
$\text{O6}-\text{H6A}\cdots\text{Cl1}$	0.85	2.41	3.188 (3)	153.1
$\text{O6}-\text{H6B}\cdots\text{Cl2}^{\text{iii}}$	0.85	2.34	3.173 (3)	165.7
$\text{O2}-\text{H2}\cdots\text{Cl2}^{\text{iv}}$	0.862 (13)	2.457 (16)	3.309 (3)	170 (4)
$\text{C11}-\text{H11}\cdots\text{O2}$	0.93	2.48	3.387 (5)	163.6

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

3.4. Description of the crystal structure of the complex 3

The title compound **3** crystallizes in the triclinic system in the space group *P-1*. The asymmetric unit consists of two binuclear neutral copper(II) complexes [Cu₂(HL)₂(Cl₂), and one guest water molecule (Figure 3a). The selected bond lengths and angles are collected in Table 2. Each Cu^{II} is pentacoordinated in a NO₂Cl₂ environment. The ligand acts in tridentate fashion through one azomethine nitrogen atom, one phenoxo oxygen atom and one alcoholic oxygen atom. The Cu ion is in a distorted square pyramidal environment formed by the three coordinated atoms of the ligand and one bridged chloro atom defining the basal plane, while the second bridged chloro ion occupying the apical position. According to the Addison index [59] ($\tau = (\beta - \alpha)/60$ where β and α are the largest values of the bond angles around the central ion) the coordination geometry around a pentacoordinated metal center can be discussed: $\tau = 0$ describes a perfect square pyramidal, while $\tau = 1$ describes a perfect trigonal bipyramidal geometry. The τ values of 0.146 (Cu1), 0.084 (Cu2), 0.151 (Cu3) and 0.291 (Cu4) are indicative of a distorted square pyramidal geometry around each metal center. In the dinuclear unit Cu1/Cu2, Cu2 is more less distorted from a square-pyramidal geometry than Cu1, while in the dinuclear unit Cu3/Cu4, Cu4 is more distorted from a square-pyramidal geometry than Cu3. The modified index suggested by Konno et al. [60] $\chi = (\beta + \gamma + \delta - 2\alpha)/180$ (which considers the other angles, β and α are the largest angles, γ and δ are the other angles around the metal centers without the donor atoms defining β) which is more efficient confirms the geometries around the copper ions. The χ values of 0.1919 (Cu1), 0.1311 (Cu2), 0.1913 (Cu3) and 0.3901 (Cu4) are indicative of distorted square pyramid for each Cu center.

The two μ_2 -chlorido ligands link the Cu(II) ions somewhat unsymmetrically. One of the bridging Cu–Cl bonds is significantly longer than the other as shown by the following values for the two units *ie.* Cu1–Cl1 = 2.2418 (9) Å and Cu2–Cl1 = 2.7688 (9) Å (Table 2). The axial longest Cu–Cl distances [Cu1–Cl2 = 2.957 (1) Å, Cu2–Cl1 = 2.7688 (9) Å, Cu4–Cl3 = 2.8183 (8) Å and Cu3–Cl4 = 2.7664 (9) Å] fall in the range [2.66 Å - 3.36 Å] reported for similar complexes [61–63]. The Cu–O [1.889 (2) Å - 2.018 (2) Å] and Cu–N [1.931 (3) Å - 1.947 (3) Å] distances are in the range expected for similar square pyramidal complexes [63–65]. The separation between the two metal centers in the two units are 3.4973 (6) Å [Cu1–Cu2] and 3.4973 (6) Å [Cu3–Cu4]. For each of the coordinated ligand, the dihedral angle value between the plane of the phenolate ring and the plane formed by the atoms in the open chain, shows a distortion from planarity. For example, for the ligand molecule coordinated to Cu1, the plane of the phenolate ring (O1C1C2C3C4C5C6) and the plane formed by (O2N1C8C9) forms a dihedral angle of 7.130 (12)° which is indicative of a twist in the ligand. For Cu2, Cu3 and Cu4 the dihedral angles formed by the two parts of the coordinated ligand molecule are respectively 18.269 (25)°, 21.004(3)° and 19.319 (6)°. In all cases the ligand is twisted. For the dinuclear unit Cu1/Cu2 the copper ions are displaced from their basal planes N1, O2, O1, Cl1 (rms deviation 0.1294 Å) for Cu1 and N2, O3, O4, Cl2 (rms 0.0843 Å) for Cu2 by 0.0616 (10) Å and 0.0010 (1) Å respectively. The dihedral angle between these two planes is 13.799 (5)°. For the dinuclear unit Cu3/Cu4 the copper ions are displaced from their basal planes O8, N3, O7, Cl3 (rms deviation 0.1002 Å) for Cu3 and O5, N4, O6, Cl4 (rms 0.2752 Å) for Cu4 by 0.0986 (1) Å and 0.1349 (9) Å respectively. The dihedral angle between these two planes is 13.717 (9)°. Numerous intramolecular bonds are observed in the structure. In each of the two molecules in the asymmetric unit, intramolecular O(alcohol)–H···O(phenolate) which close in *S*(6) stabilized the structure. The guest water molecule connect the two molecules complex in the asymmetric unit by intramolecular bonds of type O(alcohol)–H···O(water), O(water)–H···O(phenolate). Additional intermolecular hydrogen bonds C25–H25···O3ⁱ(phenolate) (*i* = $-x+1, -y+1, -z+2$) connect the units forming a planar two dimensional structure in the *bc* plane (Figure 3b, Table 5).

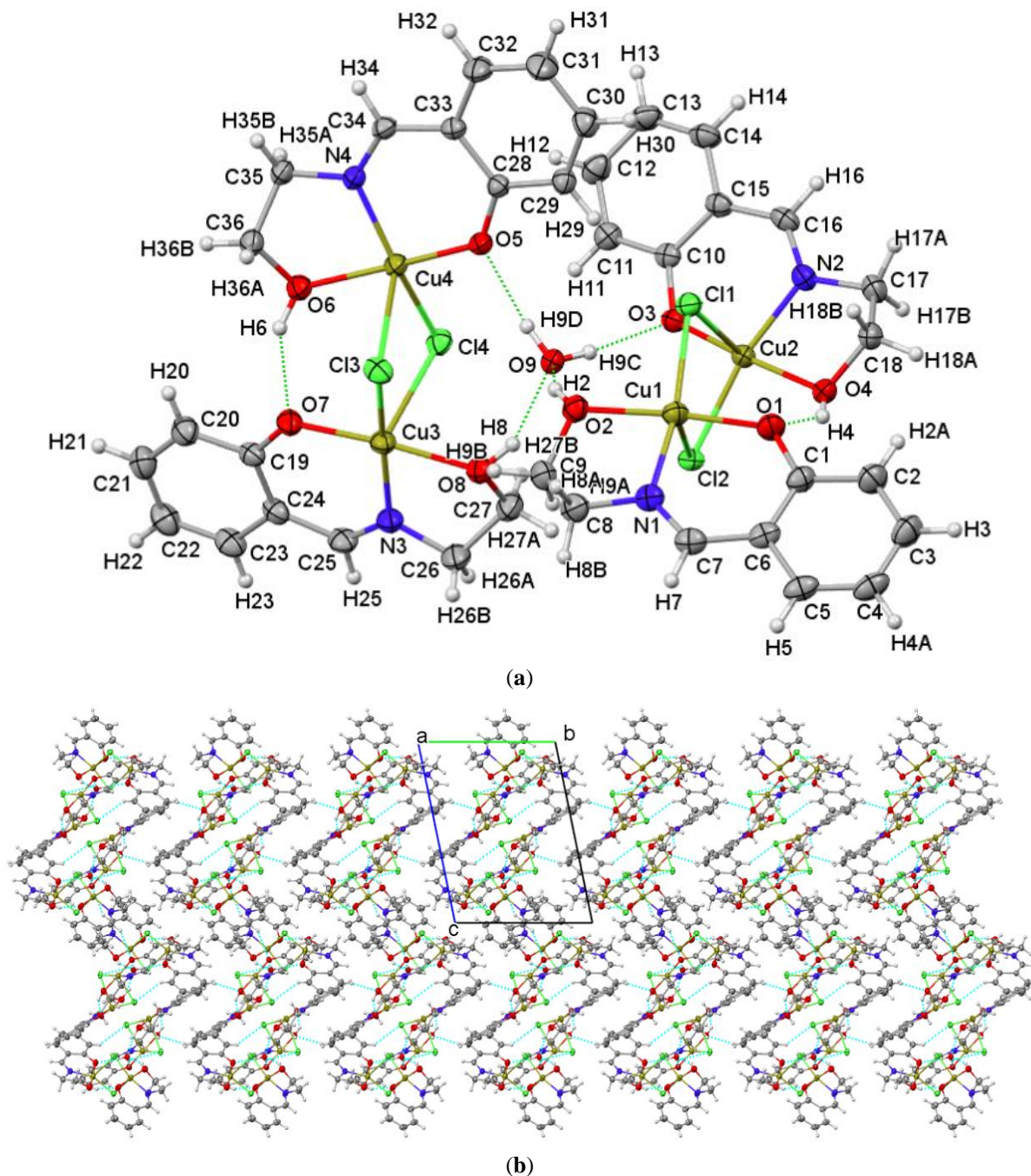


Fig. 3. (a) Crystal structure of the dinuclear complex $\{[\text{Cu}_2(\text{HL})_2(\text{Cl})_2] \cdot [\text{Cu}_2(\text{HL})_2(\text{Cl})_2] \cdot (\text{H}_2\text{O})\}$ (**3**), (b) packing diagram of (**3**) viewed along the *bc* plane

Table-5. Hydrogen-bond geometry (Å, °) of complex **3**.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O4—H4...O1	0.868 (9)	1.86 (2)	2.602 (3)	142 (3)
O6—H6...O7	0.868 (9)	1.856 (16)	2.630 (3)	148 (2)
O2—H2...O9	0.869 (9)	1.86 (2)	2.658 (3)	153 (3)
O8—H8...O9	0.869 (9)	1.811 (19)	2.616 (3)	153 (3)
O9—H9C...O3	0.85	1.98	2.822 (3)	174.1
O9—H9D...O5	0.85	1.86	2.709 (3)	173.3

C29—H29...C11	0.93	2.88	3.679 (3)	145.1
C25—H25...O3 ⁱ	0.93	2.61	3.434 (4)	147.8

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

3.5. Description of the crystal structure of the complex 4

The complex crystallizes in the monoclinic system in the space group $P2_1/c$. The crystallographic data and the lattice parameters of the complex are recorded in the table 1. A perspective view of the structure and numbering of the atoms of this complex is shown in the Figure 4. The selected bond lengths and angles are collected in Table 2. The asymmetric unit consists of two copper (II) ions, two NO_2 -donor tridentate ligands and two chloride ions. In the unsymmetrical complex, the pentacoordinated copper ion Cu1 is situated in the NO_3Cl inner, while the copper ion Cu2 is located in the NO_2Cl_2 cage. The two copper ions are bridged by one chloro ion $[\text{Cu}(\mu\text{-Cl})\text{Cu}]$ and one phenolate oxygen ion $[\text{Cu}(\mu\text{-phenolato})\text{Cu}]$. The geometries around the Cu (II) ions can be elucidated using the Addison parameter (τ). The τ values of 0.024 (Cu1) and 0.09 (Cu2) are indicative of a slightly distorted square pyramidal environment for the two copper (II) ions.

The basal planes for Cu1 and Cu2 ions are defined respectively by N1, O2, O3, O1 (rms 0.0600) and O3, N2, O4, Cl1 (rms 0.0299) with the Cu ions 0.1328 Å (Cu1) and 0.1934 Å (Cu2) out of their corresponding plane. The apical position for Cu1 is occupied by the bridged chloro ion Cl1, while the apical position for Cu2 is occupied by the terminal Cl2. In the basal planes, the *transoid* angles values are 168.15 (5)° and 169.60 (5)° for Cu1 and 163.07 (4)° and 168.47 (5)° for Cu2 and the *cisoid* angles are in the ranges [94.90 (5)°–81.69 (5)°] for the Cu1, and [92.30 (5)°–81.60 (5)°] for Cu2. The angle formed between the two basal planes is 76.584 (6)°.

The μ_2 -chlorido ligand and the μ_2 -phenolato oxygen ions link the Cu(II) ions somewhat unsymmetrically. The lengths of the bridging Cu1–Cl1 [2.6735 (4) Å] and Cu2–Cl1 [2.2629 (4) Å] bonds are significantly different. The lengths of the bridging Cu1–O3 [1.9888 (10) Å] and Cu2–O3 [1.9434 (11) (4) Å] bonds are also different. The axial bonds distances Cu1–Cl1 [2.6735 (4) Å] and Cu2–Cl2 [2.6194 (4) Å] are similar to the distances reported for similar complexes [66]. The Cu–O [1.8769 (12) Å–2.020 (11) Å] and Cu–N [1.9305 (12) Å–1.9410 (12) Å] distances are in the range expected for similar square pyramidal complexes [67].

The crystal packing of compound 4 is stabilized by intramolecular O(alcohol)–H...Cl(terminal) and C9–H9A...Cl(bridged) and intermolecular O(alcohol)–H...Cl(terminal) hydrogen bonds which form layers parallel to *b* axis. Additional C–H...Cl hydrogen bonds consolidate the structure. In the crystal, intramolecular and intermolecular hydrogen bonds are simultaneously present. The intramolecular hydrogen bond O2_(alcohol)–H2...Cl2_(terminal) forms a six-membered ring. Intermolecular hydrogen bonds, O4_(alcohol)–H4...Cl2_(terminal)ⁱ (i: $-x+1, -y, -z+1$), C18–H18B...Cl1ⁱⁱ (ii: $x, -y+1/2, z-1/2$), C8–H8A...Cl2ⁱⁱⁱ (iii: $x, -y-1/2, z+1/2$) and C8–H8B...Cl1^{iv} (iv: $x, -y+1/2, z+1/2$) lead to the formation of layers. Additional C–H...O1ⁱ_(carbonyl) (i: $1-x, 2-y, 1-z$) and C–H...O2_(phenol) connect the layers and consolidate the structure into a two-dimensional network in the *ac* plane (Figure 4b, Table 6).

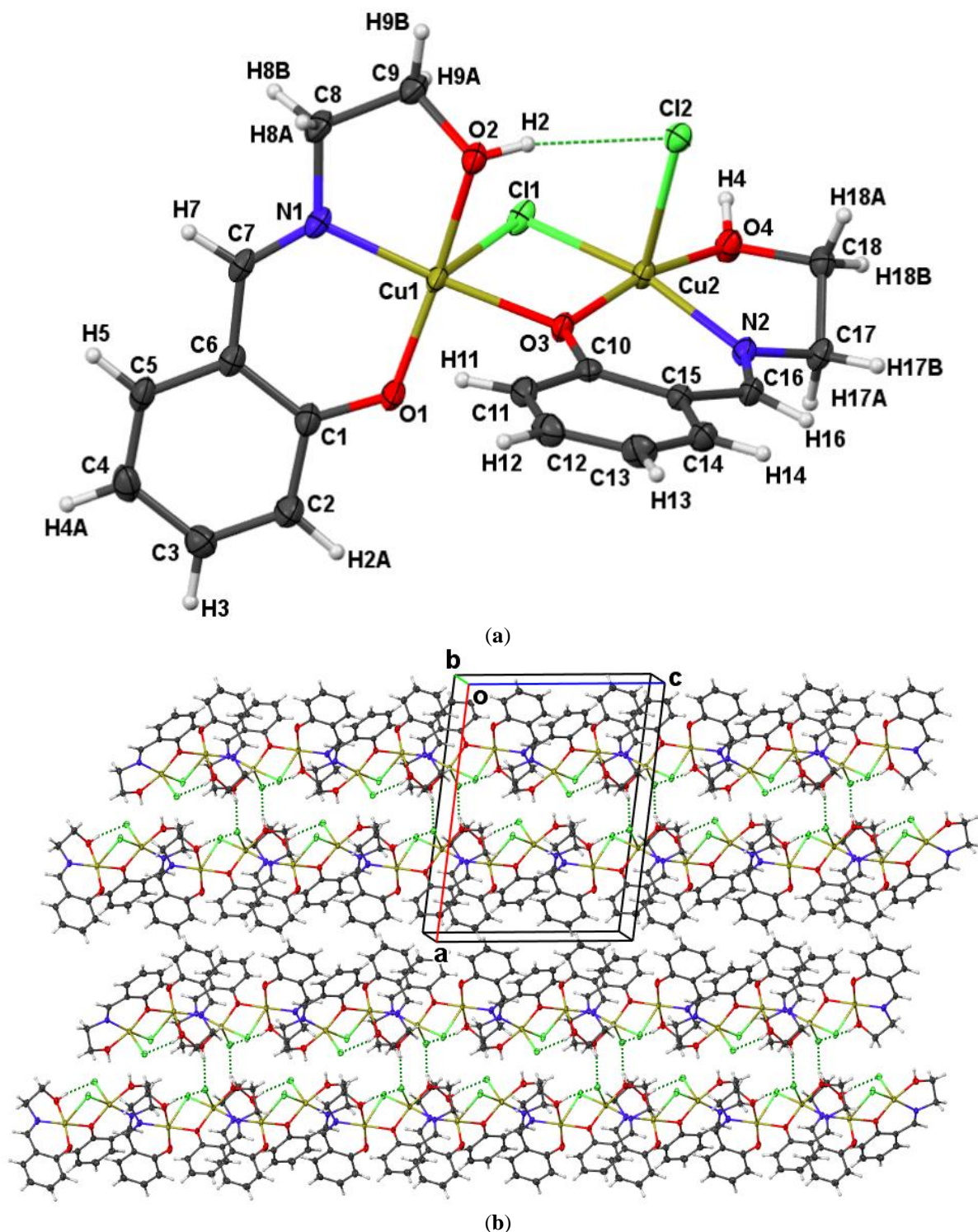


Fig. 4. (a) Crystal structure of the dinuclear complex $[\text{Cu}_2(\text{HL})_2(\text{Cl})_2]$ (**4**), (b) packing diagram of (**4**) viewed along the ac -plane.

Table-6. Hydrogen-bond geometry (\AA , $^\circ$) of complex **4**.

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
$\text{O2---H2}\cdots\text{Cl2}$	0.82	2.23	3.0260 (11)	165.5
$\text{O4---H4}\cdots\text{Cl2}^{\text{i}}$	0.82	2.15	2.9598 (11)	169.1
$\text{C18---H18B}\cdots\text{Cl1}^{\text{ii}}$	0.97	2.87	3.5833 (16)	130.8

C9—H9A...C11	0.97	2.94	3.5234 (16)	119.7
C8—H8A...C12 ⁱⁱⁱ	0.97	2.87	3.5207 (16)	125.5
C8—H8B...C11 ^{iv}	0.97	2.80	3.6917 (16)	152.9

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

IV. Conclusion

In the work presented in this article, we report the synthesis and characterization of three new complexes of cobalt, nickel and copper prepared from the tridentate ligand 2-((2-hydroxyethylimino) methyl) phenol. The structures of these three complexes $\{[Co(L)_2] \cdot [Co(HL)_2] \cdot 4H_2O\}$ (**1**), $[Ni_2(HL)_2(Cl)_2(H_2O)_2]_2$ (**2**), $\{[Cu_2(HL)_2(Cl)_2] \cdot [Cu_2(HL)_2(Cl)_2] \cdot (H_2O)\}$ (**3**), $[Cu_2(HL)_2(Cl)_2]$ (**4**) are completely different. The cobalt (II) complex (**1**) is a mononuclear, in which the metal center is coordinated to two tridentate ligands, yielding an octahedral geometry N_2O_4 . The nickel (II) complex (**2**) is a di-phenoxo-bridged dinuclear complex, in which the two phenoxo oxygen ions lie in the equatorial planes of the octahedral $NClO_4$ environment around the two nickel (II) ions. The structures of the complexes **3** and **4** show isomeric forms which differs in the set of bridging donor atoms and the presence of a guest water molecule in complex **3**. The copper complex (**3**) is a di-chlorido-bridged dinuclear complex, in which each bridging chloride occupies simultaneously an in-plane coordination site on one copper (II) ion and an apical site on the other copper(II) ion. The copper (II) ions are in pentagonal environment NO_2Cl_2 . The two unit in the asymmetric unit are connected by the guest water molecule through hydrogen bond. The copper complex (**4**) is a dissymmetric bridged complex in which the two copper are in two different pentagonal environment NO_3Cl and NO_2Cl_2 . The two copper ions are bridged by one chloride ion and one phenolate oxygen ion.

Supplementary data

CCDC–2062391, 2062390, 2062389 and 2063454 contains the supplementary crystallographic data for the complexes **1**, **2** and **3**, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Telephone: +44–01223–762910; Fax: +44–1223–336033; or E-mail: deposit@ccdc.cam.ac.uk).

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