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Synthesis, crystal structure and infrared spectra of Cu(II) and Co(II) complexes with 4,4′-dichloro-2,2′-[ethylene dioxybis(nitrilomethylidyne)]diphenol

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Novel 4,4′-dichloro-2,2′-[ethylenedioxybis(nitrilomethylidyne)]diphenol (H_2L) and its complexes [CuL] and {[CoL(THF)]$_2$(OAc)$_2$Co} have been synthesized and characterized by elemental analyses, IR, ^{1}H-NMR and X-ray crystallography. [CuL] forms a mononuclear structure which may be stabilized by the intermolecular contacts between copper atom (Cu) and oxygen atom (O3) to form a head-to-tail dimer. In {[CoL(THF)]$_2$(OAc)$_2$Co}, two acetates coordinate to three cobalt ions through Co–O–C–O–Co bridges and four μ-phenoxo oxygen atoms from two [CoL(THF)] units also coordinate to cobalt ions.

Keywords: 4,4′-dichloro-2,2′-[ethylenedioxybis(nitrilomethylidyne)]diphenol; Cu(II) complex; Co(II) complex; synthesis; crystal structure

Introduction

Salen [*N*,*N*′-bis(salicylaldehydo)ethylenediamine] and its derivatives are well-known chelating ligands in coordination chemistry.[1–3] During the past few decades, metallosalen complexes have been of considerable current interest due to their ubiquitous use in a variety of catalytic chemical transformations. Examples where salen complexes offer both high reactivity and selectivity include epoxidation of olefins, asymmetric ring-opening of epoxides, olefin aziridination, olefin cyclopropanation and formation of cyclic and linear polycarbonates.[4] Salen can be used to obtain non-linear optical materials,[5] biological systems,[6] interesting magnetic properties[7] and building blocks for cyclic supramolecular structures.[8] Thus, new materials can be produced by using these compounds. These compounds, containing Salen, seem to be suitable candidates for further chemical modifications.[9]

The reported copper(II)–salen and cobalt(II)–salen complexes show structures of [Cu(salen)]$_2$, [Cu(5-MeOsalen)]$_2$, [Cu(5-Clsalen)][10] and [Co(salen)]$_2$.[11] Recently, a preferable class of salen-type bisoxime ligands was reported, using an O-alkyloxime unit [–CH=N–O–(CH)$_2$–O–N=CH–] instead of the [–CH=N–(CH)$_2$–N=CH–] group; the large electronegativity of oxygen atoms is expected to affect strongly the electronic properties of the N_2O_2 coordination sphere, which can lead to different and novel properties and structures of the resulting complexes.[12–15]

Here, in continuation of our previous studies on synthesis and structural characterization of transition metal complexes,[15,16] a novel salen-type bisoxime chelating ligand H_2L {4,4′-dichloro-2,2′-[ethylenedioxybis(nitrilomethylidyne)]diphenol} and its mononuclear Cu(II) complex **1**, [CuL], and trinuclear Co(II) complex **2**, {[CoL(THF)]$_2$(OAc)$_2$Co}, have been synthesized and structurally characterized by X-ray crystallography.

Experimental

Reagents and physical measurements

5-Chloro-2-hydroxybenzaldehyde from Alfa Aesar was used without further purification. 1,2-Dibromoethane was dried and redistilled before use. 1,2-Bis(aminooxy)ethane was synthesized according to an analogous method reported earlier.[13,14] The other reagents and solvents were analytical-grade reagents from Tianjin Chemical Reagent Factory.

Elemental analyses for Cu and Co were detected by an IRIS ER/S·WP-1 ICP atomic emission spectrometer. C, H and N analyses were carried out with a GmbH VariuoEL V3.00 automatic elemental analyzer. IR spectra were recorded on a Vertex70 FT-IR spectrophotometer, with samples prepared as KBr (500–4000 cm^{-1}) and CsI (100–500 cm^{-1}) pellets. The ^{1}H NMR spectra were recorded on a Mercury-400BB spectrometer at room temperature using $CDCl_3$ as solvent. X-ray single crystal structure was determined on a Bruker Smart APEX CCD area detector. Melting points were measured by the use of a ×10 microscopic melting point apparatus made in Beijing Taike Instrument Limited Company, and the thermometer was uncorrected.

Synthesis of H_2L

The synthetic route of H_2L is shown in Scheme 1. 1,2-Bis(phthalimidooxy)ethane and 1,2-bis(aminooxy)ethane were prepared by an analogous method.[13,15]

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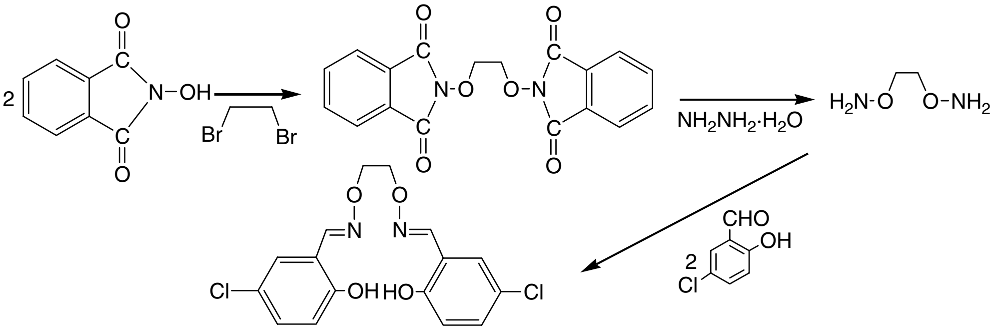

Scheme 1. Synthetic route to H_2L.

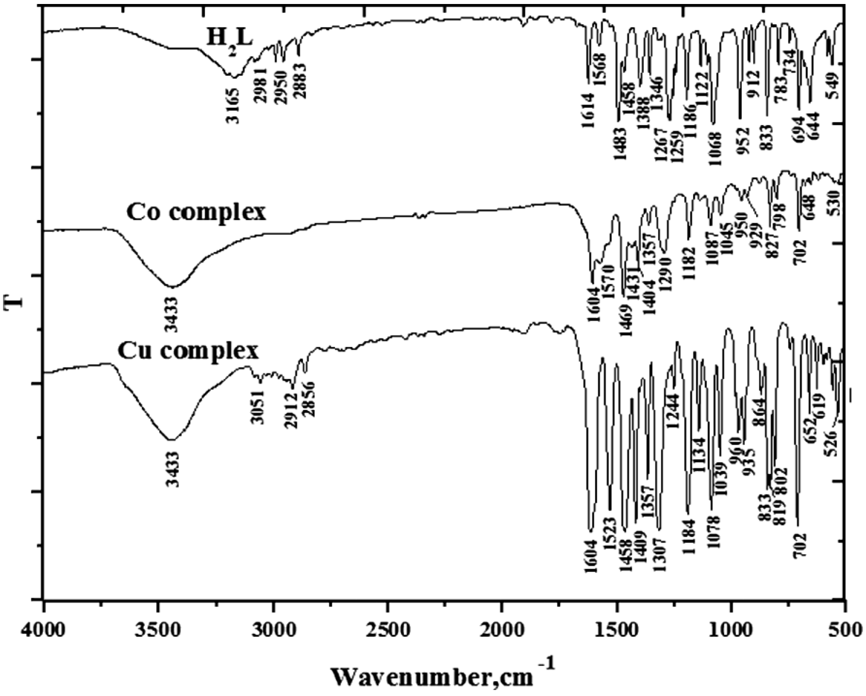

Figure 1. Infrared absorption spectra of H_2L, complex **1** and complex **2**.

4,4′-Dichloro-2,2′-[ethylenedioxybis(nitrilomethylidyne)]diphenol (H_2L) was synthesized according to a slightly modified literature method.[15–17] To an ethanol solution (5 ml) of 5-chloro-2-hydroxybenzaldehyde (0.1679 g, 0.001 mol) was added an ethanol solution (5 ml) of 1,2-bis(aminooxy)ethane (0.0491 g, 0.0005 mol). After the solution had been stirred at 55 °C for 4 h, the mixture was filtered, then washed successively with ethanol and hexane, respectively. The product was dried under reduced pressure and purified with recrystallization from ethanol to yield 0.1279 g of colorless block-shaped crystalline solid. Yield, 65.0%, m.p. 138–140 °C. ^1H NMR (400 MHz, $CDCl_3$) 4.49 (s, 4H), 6.92 (d, $J = 9.2$ Hz, 2H), 7.13 (d, $J = 2.4$ Hz, 2H), 7.23 (dd, $J = 2.6$ Hz 2H), 8.15 (s, 2H), 9.73 (s, 2H). Anal. calcd for $C_{16}H_{14}C_{l2}N_2O_4$ (%): C 52.05, H 3.82, N 7.59. Found: C 51.98, H 3.86, N 7.63.

The crystals of H_2L suitable for X-ray crystal analysis were grown from the acetone solution by slow evaporation of the solvent at room temperature.

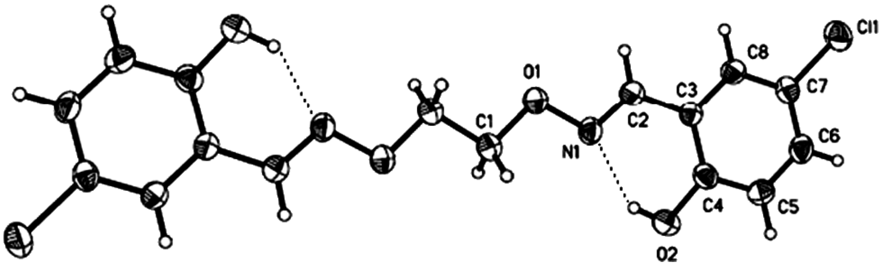

Figure 2. The molecule structure of H_2L with the atom numbering. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level.

Synthesis of complex 1

A solution of Cu(II) acetate monohydrate (0.021 g, 0.0001 mol) in methanol (10 ml) was added dropwise to a solution of H_2L (0.039 g, 0.0001 mol) in acetone (30 ml). The color of the mixing solution turned green immediately, and then stirring was continued for 2 h at room temperature. The solution was filtered and the filtrate was allowed to stand at room temperature for about one week; the solvent was partially evaporated and dark-green rhombohedral single crystals were obtained that were suitable for X-ray crystallographic analysis. Anal. calcd for $C_{32}H_{24}Cl_4Cu_2N_4O_8$ (%): C 44.62, H 2.81, N 6.50, Cu, 14.75. Found: C 44.58, H 2.85, N 6.52, Cu 14.73.

Table 1. Crystal data and structure refinement for H_2L, complexes **1** and **2**

Compound code	H_2L	Cu complex	Co complex
Empirical formula	$C_{16}H_{14}Cl_2N_2O_4$	$C_{16}H_{12}Cl_2CuN_2O_4$	$C_{44}H_{46}Cl_4Co_3N_4O_{14}$
Formula weight	369.19	430.72	1173.44
Temperature (K)	293(2)	298(2)	298(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P2(1)/n	P2(1)/n	P - 1
a (Å)	4.0771(11)	9.9868(15)	10.7360(15)
b (Å)	11.7135(15)	8.7833(14)	10.9270(16)
c (Å)	17.502 (2)	18.681(2)	11.4950(18)
α (deg)	90	90	100.938(3)
β (deg)	96.18(2)	115.691(2)	114.124(3)
γ (deg)	90	90	90.704(2)
Volume ($Å^3$)	830.3(3)	2568.4(12)	1202.3(3)
Z	2	4	1
D_c (Mg/m^3)	1.477	1.805	1.621
μ (mm^{-1})	0.414	1.741	1.315
$F(000)$	380	868	599
Crystal size (mm)	0.58 × 0.45 × 0.16	0.47 × 0.42 × 0.34	0.35 × 0.32 × 0.10
θ range (deg)	2.10–25.00	2.12–25.01	1.91–25.01
Index ranges	$-4 \le h \le 4$, $-13 \le k \le 13$, $-19 \le l \le 20$	$-11 \le h \le 9$, $-9 \le k \le 10$, $-21 \le l \le 22$	$-12 \le h \le 9$, $-12 \le k \le 12$, $-13 \le l \le 13$
Independent reflections	4191	7170	5797
R(int)	0.0432	0.1459	0.0635
Completeness to $\theta = 25.00$ (%)	99.9	97.3	96.6
Max. and min. transmission	0.9367 and 0.7953	0.5891 and 0.4950	0.8797 and 0.6561
Data/restraints/parameters	1448/0/109	2721/0/226	4090/0/307
GOF	1.033	1.043	0.995
R_1	0.0408	0.0688	0.0735
wR_2 [$I > 2\sigma(I)$]	0.0837	0.1519	0.1589
$\Delta\rho_{max,min}$ (e $Å^{-3}$)	0.173 and -0.169	1.074 and -0.691	0.819 and -1.288

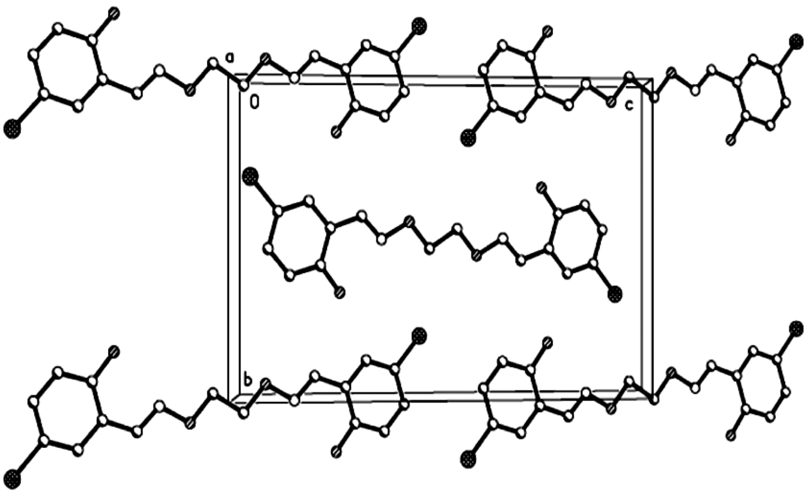

Figure 3. Packing diagram of H_2L viewed along the b-axis. H atoms are omitted for clarity.

Synthesis of complex 2

A solution of cobalt(II) acetate tetrahydrate (0.0124 g, 0.00005 mol) in ethanol (18 ml) was added dropwise to a solution of H_2L (0.0184 g, 0.00005 mmol) in tetrahydrofuran–acetonitrile (3 : 2; 20 ml). The color of the mixing solution turned yellow immediately, and stirring was continued for 3 h at room temperature. The solution was filtered and the filtrate was allowed to stand at room temperature; after about three weeks, the solvent had partially evaporated and several reddish-brown block-shaped single crystals were obtained that were suitable for X-ray crystallographic analysis. Anal. calcd for $C_{44}H_{46}Cl_4Co_3N_4O_{14}$ (%): C 45.04, H 3.95, N 4.77, Co 15.07. Found: C 45.10, H 3.88, N 4.85, Co 15.01.

X-ray crystallography

The single crystals of H_2L, complex **1** and complex **2** with approximate dimensions of $0.58 \times 0.45 \times 0.16$, $0.47 \times 0.42 \times 0.34$, $0.35 \times 0.32 \times 0.10$ mm were placed on a Bruker Smart diffractmeter equipped with Apex CCD area detector. The diffraction data were collected using a graphite monochromated Mo K_α radition ($\lambda = 0.71073$ Å) at 293(2), 298(2) and 298(2) K, respectively. The structure were solved by direct methods (SHELXS 97)[18] and Fourier difference techniques, refined by full-matrix least-squares on F^2 using the program (SHELXL 97).[19] Details of the data collection and refinements are given in Table 1. The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added theoretically.

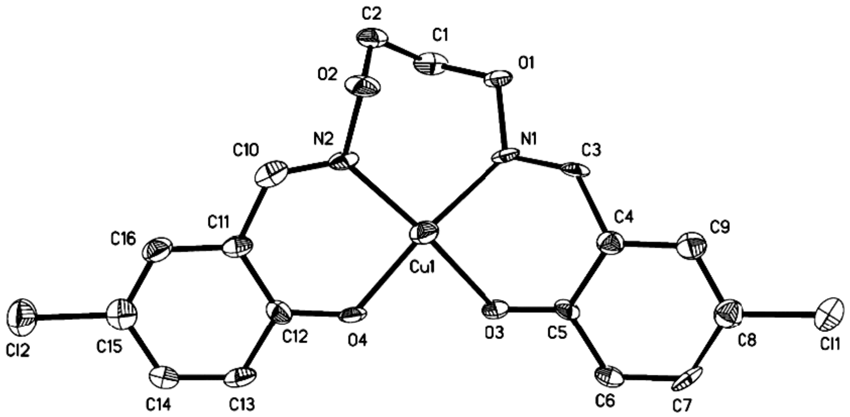

Figure 4. The molecule structure of complex **1** with the atom numbering. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level.

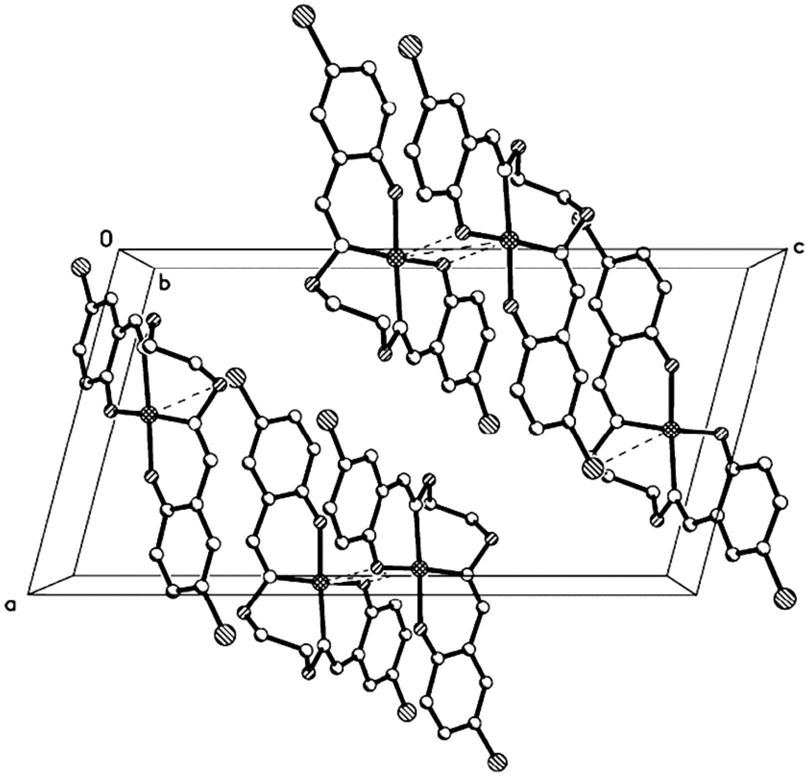

Figure 5. Crystal packing of complex **1** viewed along the *b*-axis. H atoms are omitted for clarity.

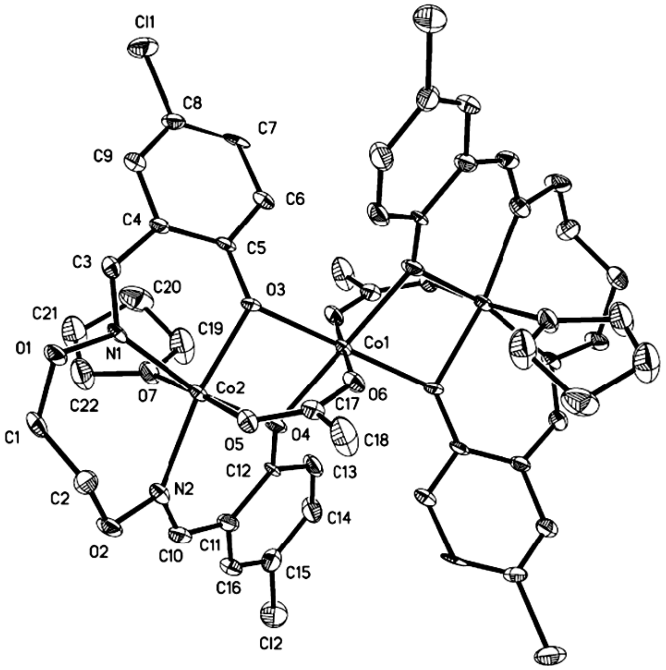

Figure 6. The molecule structure of complex **2** with the atom numbering. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level. Each of the cobalt atoms sits in an octahedral geometry.

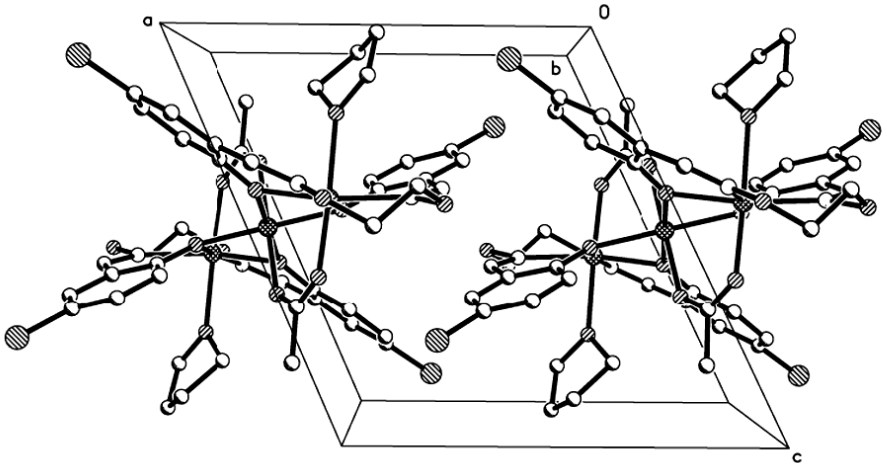

Figure 7. Crystal packing of complex **2** viewed along *b*-axis. H atoms are omitted for clarity.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary data (no. CCDC-644 787 for H_2L, CCDC-644 789 for complex **1** and CCDC-644 790 for complex **2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ,UK (Fax: +44 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

IR spectra

IR spectra of H_2L and its copper(II) and cobalt (II) complexes are given in Fig. 1. The free ligand H_2L exhibits Ar–O and C═N stretching bands at 1259 and 1614 cm^{-1}, which are shifted to lower frequencies by ca. 75 and 10 cm^{-1} upon complexation. This lowering of energy results from the M–O and M–N interaction upon complexation and is similar to that reported for copper(II) and cobalt (II) complexes.[14,16] In addition, the infrared spectra of complex **2** show the expected absorption band due to the stretching mode of THF at ca. 1087 cm^{-1}, which is evidence for the existence of the THF molecule.

The far-infrared spectra of complexes **1** and **2** were also obtained in the region 500–100 cm^{-1} in order to identify frequencies due to the M–O and M–N bonds. The IR spectrum of the complex **1** shows ν (Cu–O) and ν (Cu–N) vibrational absorption frequencies at 411 and 453 cm^{-1}, respectively, and complex **2** shows ν (Co–O) and ν (Co–N) vibrational absorption frequencies at 413 and 478 cm^{-1}, respectively. These assignments are consistent with the literature frequency values.[20]

Table 2. Selected bond distances (Å) and bond angles (deg) for H_2L

Bond distances (Å)			
Cl(1)–C(7)	1.742(3)	C(3)–C(8)	1.391(3)
N(1)–C(2)	1.270(3)	C(3)–C(4)	1.394(3)
N(1)–O(1)	1.406(3)	C(4)–C(5)	1.380(4)
O(1)–C(1)	1.424(3)	C(5)–C(6)	1.371(4)
O(2)–C(4)	1.357(3)	C(6)–C(7)	1.375(4)
C(1)–C(1)#1	1.492(5)	C(7)–C(8)	1.369(3)
C(2)–C(3)	1.456(3)		
Bond angles (deg)			
C(2)–N(1)–O(1)	111.8(2)	O(2)–C(4)–C(3)	122.5(2)
N(1)–O(1)–C(1)	108.66(18)	C(5)–C(4)–C(3)	119.6(3)
O(1)–C(1)–C(1)#1	106.2(3)	C(6)–C(5)–C(4)	121.2(3)
N(1)–C(2)–C(3)	121.1(2)	C(5)–C(6)–C(7)	119.2(3)
C(8)–C(3)–C(4)	118.8(2)	C(8)–C(7)–C(6)	120.8(3)
C(8)–C(3)–C(2)	118.7(2)	C(8)–C(7)–Cl(1)	119.7(2)
C(4)–C(3)–C(2)	122.5(2)	C(6)–C(7)–Cl(1)	119.5(2)
O(2)–C(4)–C(5)	117.9(2)	C(7)–C(8)–C(3)	120.5(2)

Symmetry transformations used to generate equivalent atoms: #1 $-x+2, -y+2, -z$.

Crystal structural of H_2L

The crystal structure of H_2L was determined by X-ray crystallography (Figs 2 and 3 and Table 2).

All of the non-hydrogen atoms are nearly planar. The molecule adopts an extended conformation where the two 5-chlorosalicylaldoxime moieties are apart from each other; the dihedral angle of the two benzene rings is 0.22(3)°. The oxime groups and phenolic alcohols have the anti-conformation, and there is an intramolecular hydrogen bond, O2–H2···N1 (d(O2–H2) = 0.820 Å, d(H2···N1) = 1.924 Å, d(O2···N1) = 2.640 Å, <O2–H2···N1 = 145.42°).

Crystal structural of complex 1

The structure of complex **1**, [CuL], was determined by X-ray crystallography, revealing that the copper atom lies in the N_2O_2 coordination sphere (Fig. 4), the dihedral angle between the coordination plane of O3–Cu–N1 and that of O4–Cu–N2 is 6.32°, indicating slight distortion toward tetrahedral geometry from the square planar structure.

On the other hand, the complex [CuL] was found to have a slightly pyramidalized square planar geometry around the copper atom. The complex has a 'stepped' conformation, as observed in the dimers of [Cu(salen)][1,10] and [Cu(salamo)].[12] This structure may be stabilized by the intermolecular contacts between copper atom (Cu) and oxygen atom (O3) to form a head-to-tail dimer (Fig. 5). The ethylenedioxime carbons C1 and C2 are also buckled asymmetrically from the Cu–N1–N2 plane, with the displacement for C1 being 1.454 Å toward the plane and for C2 being only 0.835 Å in the same direction.

It is noteworthy that the Cu–N bond lengths, 1.999(6) and 1.960(6) Å, are considerably longer than the Cu–O bond lengths, 1.916(5) and 1.919(5) Å, respectively. The distance of copper–oxygen [d(Cu–O3) = 2.660(2) Å] (Table 3) in the [CuL] dimer is longer than those of unsubstituted Cu(salen) (2.415 Å) and Cu(salamo) [2.4269(18) Å]. The lengthening of Cu–O3 should be attributed to the involvement of O3 in a dimer bridge formation, similar elongations of M–O bonds having also been observed in dimers $[Co(salen)]_2$[11] and $[CuL]_2$.[16]

Table 3. Selected bond distances (Å) and bond angles (deg) for complex **1**

Bond distances (Å)			
Cu(1)–O(4)	1.916(5)	C(3)–C(4)	1.43(1)
Cu(1)–O(3)	1.919(5)	C(4)–C(9)	1.41(1)
Cu(1)–N(2)	1.960(6)	C(4)–C(5)	1.42(1)
Cu(1)–N(1)	1.999(6)	C(5)–C(6)	1.42(1)
Cl(1)–C(8)	1.739(8)	C(6)–C(7)	1.38(1)
Cl(2)–C(15)	1.727(9)	C(7)–C(8)	1.38(1)
N(1)–C(3)	1.28(1)	C(8)–C(9)	1.36(1)
N(1)–O(1)	1.419(7)	C(10)–C(11)	1.43(1)
N(2)–C(10)	1.28(1)	C(11)–C(16)	1.40(1)
N(2)–O(2)	1.428(7)	C(11)–C(12)	1.41(1)
O(1)–C(1)	1.428(9)	C(12)–C(13)	1.41(1)
O(2)–C(2)	1.42(1)	C(13)–C(14)	1.36(1)
O(3)–C(5)	1.305(9)	C(14)–C(15)	1.39(1)
O(4)–C(12)	1.308(9)	C(15)–C(16)	1.37(1)
C(1)–C(2)	1.46(1)		
Bond angles (deg)			
O(4)–Cu(1)–O(3)	84.8(2)	O(3)–C(5)–C(4)	123.7(7)
	90.2(2)		120.0(6)
O(4)–Cu(1)–N(2)	172.1(2)	O(3)–C(5)–C(6)	116.3(7)
	174.1(2)		121.9(7
O(3)–Cu(1)–N(2)	89.4(2)	C(4)–C(5)–C(6)	119.8(7)
	95.4(2)		121.1(8)
O(4)–Cu(1)–N(1)	108.0(6)	C(7)–C(6)–C(5)	118.1(6)
	124.1(5)		120.7(6)
O(3)–Cu(1)–N(1)	127.6(5)	C(6)–C(7)–C(8)	119.9(8)
	111.2(6)		124.8(7)
N(2)–Cu(1)–N(1)	127.6(5)	C(9)–C(8)–C(7)	119.3(7)
	120.7(4)		117.5(7)
C(3)–N(1)–O(1)	111.1(6)	C(9)–C(8)–Cl(1)	123.2(7)
	109.3(6)		122.8(7)
C(3)–N(1)–Cu(1)	127.4(4)	C(7)–C(8)–Cl(1)	118.8(7)
	129.2(5)		118.4(7)
O(1)–N(1)–Cu(1)	110.1(7)	C(8)–C(9)–C(4)	121.0(7)
	113.4(7)		120.4(8)
C(10)–N(2)–O(2)	126.0(7)	N(2)–C(10)–C(11)	120.0(8)
	121.0(7)		120.1(7)
C(10)–N(2)–Cu(1)	116.5(7)	C(16)–C(11)–C(12)	119.9(6)
	122.0(7)		120.8(8)
O(2)–N(2)–Cu(1)		C(16)–C(11)–C(10)	
N(1)–O(1)–C(1)		C(12)–C(11)–C(10)	
C(2)–O(2)–N(2)		O(4)–C(12)–C(11)	
C(5)–O(3)–Cu(1)		O(4)–C(12)–C(13)	
C(12)–O(4)–Cu(1)		C(11)–C(12)–C(13)	
O(1)–C(1)–C(2)		C(14)–C(13)–C(12)	
O(2)–C(2)–C(1)		C(13)–C(14)–C(15)	
N(1)–C(3)–C(4)		C(16)–C(15)–C(14)	
C(9)–C(4)–C(5)		C(16)–C(15)–Cl(2)	
C(9)–C(4)–C(3)		C(14)–C(15)–Cl(2)	
C(5)–C(4)–C(3)		C(15)–C(16)–C(11)	

Crystal structural of complex 2

X-ray crystallographic analysis of complex **2** reveals the formation of symmetric trinuclear structure (Fig. 6), which consists of three

Table 4. Selected bond distances (Å) and bond angles (deg) for complex **2**

Bond distances (Å)					
Co(1)–O(6)	2.060(5)	N(1)–O(1)	1.440(7)	C(5)–C(6)	1.40(1)
Co(1)–O(6)#1	2.060(5)	N(2)–C(10)	1.28(1)	C(6)–C(7)	1.38(1)
Co(1)–O(3)	2.120(5)	N(2)–O(2)	1.425(8)	C(7)–C(8)	1.38(1)
Co(1)–O(3)#1	2.120(5)	O(1)–C(1)	1.431(9)	C(8)–C(9)	1.37(1)
Co(1)–O(4)	2.134(5)	O(2)–C(2)	1.417(9)	C(10)–C(11)	1.44(1)
Co(1)–O(4)#1	2.134(5)	O(3)–C(5)	1.335(8)	C(11)–C(16)	1.40(1)
Co(2)–O(4)	2.034(5)	O(4)–C(12)	1.317(9)	C(11)–C(12)	1.43(1)
Co(2)–O(3)	2.053(5)	O(5)–C(17)	1.265(9)	C(12)–C(13)	1.42(1)
Co(2)–O(5)	2.058(5)	O(6)–C(17)	1.260(9)	C(13)–C(14)	1.38(1)
Co(2)–N(2)	2.128(7)	O(7)–C(22)	1.43(1)	C(14)–C(15)	1.41(1)
Co(2)–N(1)	2.129(6)	O(7)–C(19)	1.45(1)	C(15)–C(16)	1.38(1)
Co(2)–O(7)	2.254(5)	C(1)–C(2)	1.53(1)	C(17)–C(18)	1.51(1)
Cl(1)–C(8)	1.739(8)	C(3)–C(4)	1.47(1)	C(19)–C(20)	1.51(1)
Cl(2)–C(15)	1.731(8)	C(4)–C(9)	1.41(1)	C(20)–C(21)	1.52(1)
N(1)–C(3)	1.283(9)	C(4)–C(5)	1.42(1)	C(21)–C(22)	1.46(1)
Bond angles (deg)					
O(6)–Co(1)–O(6)#1	180.0(1)	N(2)–Co(2)–O(7)	88.2(2)	O(3)–C(5)–C(4)	120.2(6)
	86.7(2)		84.6(2)		118.8(7)
O(6)–Co(1)–O(3)	93.3(2)	N(1)–Co(2)–O(7)	105.7(6)	C(6)–C(5)–C(4)	119.9(7)
	93.3(2)		125.4(5)		121.9(7)
O(6)#1–Co(1)–O(3)	86.7(2)	C(3)–N(1)–O(1)	128.9(4)	C(7)–C(6)–C(5)	119.4(8)
	180.0(3)		109.9(6)		120.5(7)
O(6)–Co(1)–O(3)#1	88.6(2)	C(3)–N(1)–Co(2)	123.7(5)	C(6)–C(7)–C(8)	120.1(6)
	91.4(2)		126.3(5)		120.9(7)
O(6)#1–Co(1)–O(3)#1	77.4(2)	O(1)–N(1)–Co(2)	110.0(5)	C(9)–C(8)–C(7)	127.2(8)
	102.6(2)		111.8(6)		118.8(7)
O(3)–Co(1)–O(3)#1	91.4(2)	C(10)–N(2)–O(2)	127.5(4)	C(9)–C(8)–Cl(1)	116.6(7)
	88.6(2)		129.7(4)		124.6(7)
O(6)–Co(1)–O(4)	102.6(2)	C(10)–N(2)–Co(2)	97.2(2)	C(7)–C(8)–Cl(1)	120.7(6)
	77.4(2)		126.7(4)		121.6(7)
O(6)#1–Co(1)–O(4)	180.00(1)	O(2)–N(2)–Co(2)	134.2(4)	C(8)–C(9)–C(4)	117.6(7)
	81.1(2)		97.4(2)		122.0(8)
O(3)–Co(1)–O(4)	92.7(2)	C(1)–O(1)–N(1)	125.2(5)	N(2)–C(10)–C(11)	120.0(8)
	93.4(2)		133.7(5)		118.6(8)
O(3)#1–Co(1)–O(4)	87.3(2)	C(2)–O(2)–N(2)	106.4(6)	C(16)–C(11)–C(12)	121.5(7)
	168.4(2)		129.3(5)		119.8(7)
O(6)–Co(1)–O(4)#1	88.0(2)	C(5)–O(3)–Co(2)	123.6(5)	C(16)–C(11)–C(10)	122.8(8)
	163.8(2)		113.5(7)		125.8(8)
O(6)#1–Co(1)–O(4)#1	85.9(2)	C(5)–O(3)–Co(1)	111.7(7)	C(12)–C(11)–C(10)	116.4(7)
	97.7(2)		125.3(7)		117.7(7)
O(3)–Co(1)–O(4)#1	105.3(2)	Co(2)–O(3)–Co(1)	119.0(7)	O(4)–C(12)–C(13)	102.9(8)
	85.7(2)		115.5(7)		101.1(8)
O(3)#1–Co(1)–O(4)#1	90.0(2)	C(12)–O(4)–Co(2)	125.4(7)	O(4)–C(12)–C(11)	104.5(8)
	176.0(2)		121.0(7)		108.9(8)
O(4)–Co(1)–O(4)#1		C(12)–O(4)–Co(1)		C(13)–C(12)–C(11)	
O(4)–Co(2)–O(3)		Co(2)–O(4)–Co(1)		C(14)–C(13)–C(12)	
O(4)–Co(2)–O(5)		C(17)–O(5)–Co(2)		C(13)–C(14)–C(15)	
O(3)–Co(2)–O(5)		C(17)–O(6)–Co(1)		C(16)–C(15)–C(14)	
O(4)–Co(2)–N(2)		C(22)–O(7)–C(19)		C(16)–C(15)–Cl(2)	
O(3)–Co(2)–N(2)		C(22)–O(7)–Co(2)		C(14)–C(15)–Cl(2)	
O(5)–Co(2)–N(2)		C(19)–O(7)–Co(2)		C(15)–C(16)–C(11)	
O(4)–Co(2)–N(1)		O(1)–C(1)–C(2)		O(6)–C(17)–O(5)	
O(3)–Co(2)–N(1)		O(2)–C(2)–C(1)		O(6)–C(17)–C(18)	
O(5)–Co(2)–N(1)		N(1)–C(3)–C(4)		O(5)–C(17)–C(18)	
N(2)–Co(2)–N(1)		C(9)–C(4)–C(5)		O(7)–C(19)–C(20)	
O(4)–Co(2)–O(7)		C(9)–C(4)–C(3)		C(19)–C(20)–C(21)	
O(3)–Co(2)–O(7)		C(5)–C(4)–C(3)		C(22)–C(21)–C(20)	
O(5)–Co(2)–O(7)		O(3)–C(5)–C(6)		O(7)–C(22)–C(21)	

cobalt (II) ions, two L^{2-} units, two acetate ions and two coordinated tetrahydrofuran molecules. The cobalt ion (Co2 or Co2#) is six-coordinated by two nitrogen (N1, N2) atoms and two oxygen atoms (O3, O4) in the N_2O_2 moieties of the ligand, one oxygen atom (O5) from the bridging acetate ion and one oxygen atom (O7) from the coordinated tetrahydrofuran molecule. Consequently, around the Co2 atom is a slightly distorted octahedral geometry.

In addition, the central cobalt's (Co1) coordination sphere is completed by quadruple μ-phenoxo oxygen atoms (O3, O4, O3#, O4#) from two [CoL] chelates, and both oxygen atoms (O6, O6#) from the ligating acetate ions which adopt a familiar μ–O–C–O fashion, and constitute another octahedral geometry. Therefore, all of the cobalt atoms are six-coordinated. Furthermore, the trinuclear structure is probably stabilized by the two μ-acetato ligand, which neutralize the whole charge of the complex (Fig. 7).

The selected bond distances (Å) and bond angles (°) for complex **2** is shown in Table 4. Complex **2** shows that the Co–O distances range from 2.034(5) to 2.254(5) Å, and those for Co–N are 2.128(4) and 2.129(4) Å, respectively, which are close to those of the reported cobalt complexes previously.[21,22] The equatorial plane of Co2 is defined by N1, N2, O4, O3 atoms with the largest deviation of Co2 at 0.107(2) Å. The apical positions are occupied by O5 atom from the μ-acetato and O7 atoms from the coordinated tetrahydrofuran molecule. The distorted octahedral coordination sphere around the Co2 has equatorial angles in the range 81.1(2)–97.7(2)°, and an axial angle O5–Co2–O7 of 176.0(2)°. This is not similar to what was observed in our previously reported complex $[L_4Co_8(H_2O)_2X]$ ($X = H_2O$ or EtOH).[14]

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