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Copper(II)−Mercury(II) Heterometallic Complexes Derived from a Salen-Type Ligand: A New Coordination Mode of the Old Schiff Base Ligand

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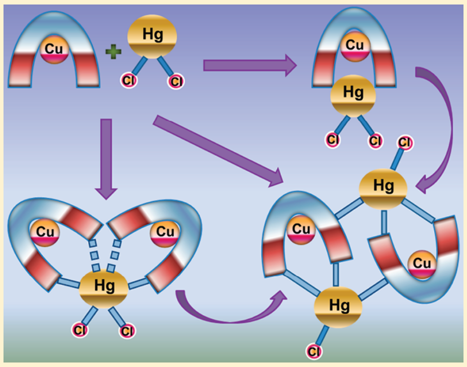
S *Supporting Information*



ABSTRACT: Three heterometallic copper(II)−mercury(II) complexes, [(CuL-CH_3)$HgCl_2$] (**1**), [(CuL-CH_3)$_2HgCl_2$] (**2**), and [(CuL-CH_2-HgCl)$_2$] (**3**), have been synthesized by reacting the "complex as ligand" [CuL-CH_3] with $HgCl_2$ by varying the reaction conditions and stoichiometry of the reactants, where H_2L-CH_3 = the di-Schiff base of 1,3-propanediamine and 2-hydroxyacetophenone. All three complexes have been characterized by X-ray single-crystal structure, elemental, and spectroscopic analyses. In complex **1**, the Hg(II) ion is bonded by two phenoxido oxygen atoms of a [CuL-CH_3] moiety and two terminal chloride ions to form a dinuclear species. In the trinuclear complex **2**, the central Hg(II) ion is coordinated by two terminal [CuL-CH_3] units through one phenoxido oxygen from each unit and two chloride ions. On the other hand, in the tetranuclear complex **3**, the Hg(II) ion has a distorted-tetrahedral geometry, being bonded to one chloride, two phenoxido oxygen atoms of one [CuL−CH_2]$^-$ unit, and a methyl carbon atom of another [CuL−CH_2]$^-$ unit. The structure of complex **3** reveals an unprecedented heptadentate coordination mode (1-κ^4NN′OO′:2-κ^2OO′:3-κC) of the Schiff base ligand that resulted in a unique organomercury metallamacrocycle.

■ INTRODUCTION

Since Hugo Schiff first synthesized the "Schiff bases",[1] by the condensation of an amine with an aldehyde, their complexes with transition-metal ions have been one of the most exhaustively studied topics in coordination chemistry because of the ease with which they can be synthesized, their wide range of complexing ability, and their uses in various fields of chemistry: e.g. inorganic biochemistry, catalysis, and magnetism.[2] Among the Schiff bases, "salen-types", which are formed by the condensation of various diamines and salicylaldehyde derivatives, are arguably the most popular ones. In general, the dinegative anionic form of this type of Schiff base acts as a tetradentate chelating ligand with two nitrogen and two oxygen atoms as donor sites to produce a mononuclear complex.[3] However, in several cases it has been found[4] that the oxygen atoms of such metal complexes can coordinate to a second metal ion and generate multinuclear complexes.[5] As a result, the mononuclear complexes of such ligands with dipositive first-row transition elements can conveniently be used as a "complex as ligand" for the synthesis of heterometallic complexes in which the coordinating modes of these di-Schiff bases are penta- or hexadentate with the nitrogen and oxygen atoms as donor centers. Recently, we have incorporated Na(I), Cd(II), Pb(II), and Mn(II) ions with the help of such Cu(II) chelates, to result in tri- and tetranuclear heterometallic complexes.[6] Mercury is well known to form an adduct with several metal chelates. A CSD (updated May 2011) search reveals that to date 14 heteronuclear complexes of Hg(II) have been reported with various "complex as ligand" species; among them 10 are copper(II) chelates. Out of these 10 complexes, 4 are dinuclear, 2 are trinuclear, 2 are tetranuclear, and 2 are polynuclear.

Herein, we report the synthesis and crystal structure of the dinuclear complex [(CuL-CH_3)$HgCl_2$] (**1**), the trinuclear complex [(CuL-CH_3)$_2HgCl_2$] (**2**), and the tetranuclear cyclic organomercurial complex [(CuL-CH_2-HgCl)$_2$] (**3**), where the di-Schiff base H_2L-CH_3 = *N*,*N*′-bis(*α*-methylsalicylidene)-1,3-propanediamine (Scheme 1). We show here that upon changing the molar ratios of [CuL-CH_3] to the Hg(II) salt, dinuclear and trinuclear complexes can conveniently be prepared. Both of the complexes convert slowly into the tetranuclear complex **3**, in which the methyl group of [CuL-CH_3] undergoes direct mercuration. To our knowledge, complex **3** is the first report of an organomercurial species where a methyl carbon at the α position of a imine nitrogen of a metal-bound Schiff base undergoes direct mercuration by C−H bond activation.

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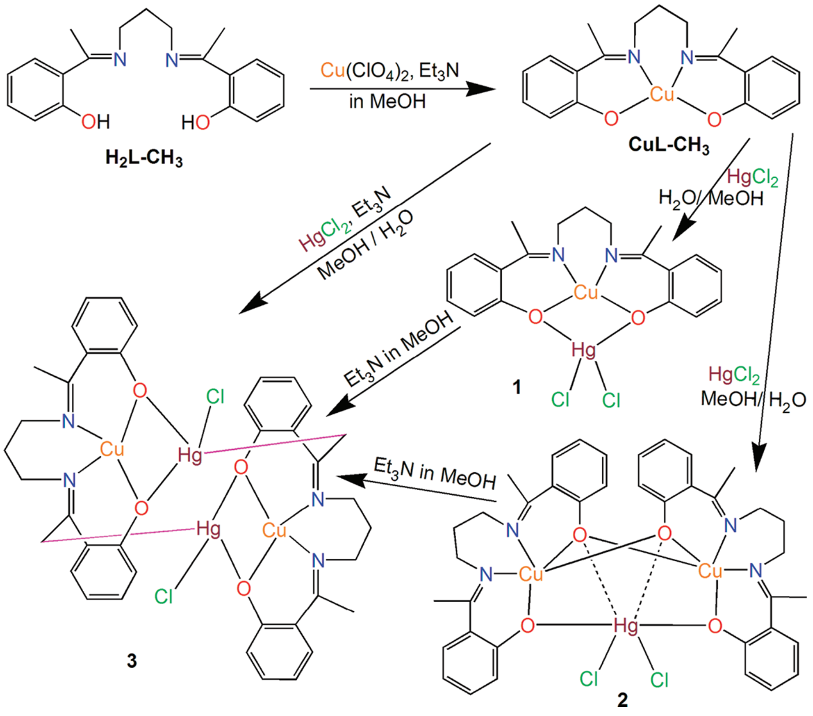
Scheme 1. Synthetic Route to Complexes 1−3



■ EXPERIMENTAL SECTION

Starting Materials. 2-Hydroxyacetophenone and 1,3-propanediamine were purchased from Lancaster and were of reagent grade. They were used without further purification.

Caution! Organomercurials are extremely toxic, and appropriate handling conditions should be used for their generation and disposal. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared, and it should be handled with care.

Synthesis of the Schiff Base Ligand H$_2$L-CH$_3$ and Its Copper Complex [CuL-CH$_3$]. The di-Schiff base ligand H$_2$L-CH$_3$ was prepared by the reported method.[7] Briefly, 5 mmol of 1,3-propanediamine (0.42 mL) was mixed with 10 mmol of the required 2-hydroxyacetophenone (1.20 mL) in methanol (20 mL). The resulting solution was refluxed for ca. 2 h and cooled. The yellow methanolic solution was used directly for complex formation.

A methanolic solution (10 mL) of Cu(ClO$_4$)$_2$·6H$_2$O (5 mmol, 1.855 g), was added to a methanolic solution of H$_2$L-CH$_3$ (5 mmol, 20 mL) in the presence of Et$_3$N (1.40 mL, 10 mmol) to prepare the complex [CuL-CH$_3$] as reported earlier.[7]

Synthesis of the Complex [CuL-CH$_3$-HgCl$_2$] (1). An aqueous solution (5 mL) of HgCl$_2$ (1 mmol, 0.271 g) was added to a methanolic solution (20 mL) of [CuL-CH$_3$] (1 mmol, 0.372 g). Microcrystalline greenish brown solid started to separate immediately on stirring the mixture. The stirring was continued for 30 min, and the solid product was isolated by filtration, washed with Et$_2$O, and dried in a vacuum desiccator containing anhydrous CaCl$_2$. X-ray-quality single crystals were obtained by layering a methanolic solution of this compound with diethyl ether. Yield: 0.519 g (81%). Anal. Calcd for C$_{19}$H$_{20}$HgCuN$_2$O$_2$Cl$_2$ (643.41): C, 35.47; H, 3.13; N, 4.35. Found: C, 35.18; H, 3.16; N, 4.52. HRMS (*m*/*z*, ESI$^+$): found for HgCl$_2$ + H + CH$_3$CN 311.9379 (calcd 311.9404), [CuL-CH$_3$] + H 372.1117 (calcd 372.0999), [CuL-CH$_3$] + Na 394.1055 (calcd 394.0818), [CuL-CH$_3$]$_2$ + H 743.1989 (calcd 743.1920), [CuL-CH$_3$]$_2$ + Na 765.1672 (calcd 765.1739).

Synthesis of the Complex [(CuL-CH$_3$)$_2$HgCl$_2$] (2). A methanolic solution (20 mL) of [CuL-CH$_3$] (2 mmol, 0.744 g) was mixed with 5 mL of an aqueous solution of HgCl$_2$ (1 mmol, 0.271 g). The solution was warmed in a water bath for 10 min to redissolve most of the precipitate that appeared on mixing. A small amount of precipitate that did not get dissolved was removed by filtration, and the filtrate was allowed to stand at room temperature. Overnight, deep green X-ray-quality single crystals appeared at the bottom of the vessel. The crystals were isolated, washed with Et$_2$O, and dried in a vacuum desiccator containing anhydrous CaCl$_2$. Yield: 0.652 g (64%). Anal. Calcd for C$_{38}$H$_{40}$Cu$_2$Hg$_1$N$_4$O$_4$Cl$_2$ (1015.31): C, 44.95; H, 3.97; N, 5.52. Found: C, 45.18; H, 3.96; N, 5.42. HRMS (*m*/*z*, ESI$^+$): found for HgCl$_2$ + H + CH$_3$CN 311.9276 (calcd 311.9404), [CuL-CH$_3$] + H 372.1049 (calcd 372.0999), [CuL-CH$_3$] + Na 394.0813 (calcd 394.0818), [CuL-CH$_3$]$_2$ + H 743.1896 (calcd 743.1920), [CuL-CH$_3$]$_2$ + Na = 765.1735 (calcd 765.1739).

Synthesis of the Complex [(CuL-CH$_2$-HgCl)$_2$] (3). An aqueous solution (10 mL) of HgCl$_2$ (0.5 mmol, 0.136 g) was added to a methanolic solution (40 mL) of [CuL-CH$_3$] (0.5 mmol, 0.186 g) followed by the addition of triethylamine (0.5 mmol, 0.07 mL), and the mixed solution was stirred well for about 15 min. There was no immediate precipitation. The solution was allowed to stand at room temperature for slow evaporation of solvent. Deep brown X-ray-quality single crystals started to appear as the volume was reduced. The crystals were isolated when the volume of the solution was reduced to about 5 mL, washed with Et$_2$O, and dried in a desiccator containing anhydrous CaCl$_2$. Yield: 0.185 g (61%). Anal. Calcd for C$_{38}$H$_{38}$Hg$_2$Cu$_2$N$_4$O$_4$Cl$_2$ (1213.88): C, 37.60; H, 3.16; N, 4.62. Found: C, 37.45; H, 3.28; N, 4.29. HRMS (*m*/*z*, ESI$^+$): found for HgCl 236.93 (calcd 236.94), HgCl + 2MeOH 301.01 (calcd 300.99), [CuL-CH$_3$] + H 372.09 (calcd 372.10), [CuL-CH$_3$] + Na 394.09 (calcd. 394.08), [CuL-CH$_2$-HgCl] + H 608.02 (calcd 608.03), [CuL-CH$_2$-HgCl] + Na 630.00 (calcd 630.01), [CuL-CH$_2$-HgCl] + H + MeOH 672.09 (calcd 672.09), [CuL-CH$_3$]$_2$ + H 743.14 (calcd 743.19), [CuL-CH$_3$]$_2$ + Na 767.16 (calcd 767.16), [(CuL-CH$_2$-HgCl)(CuL-CH$_3$)] + H 979.12 (calcd 979.12), [(CuL-CH$_2$-HgCl)-(CuL-CH$_3$)] + Na 1001.11 (calcd 1001.11), [(CuL-CH$_2$-HgCl)$_2$] + H 1213.13 (calcd 1213.05).

Alternative Method for the Synthesis of Complex 3. Complex **3** has also been synthesized by dissolving complex **1** (0.25 mmol, 0.161 g) in 50 mL of methanol in the presence of triethylamine (0.25 mmol, 0.035 mL). The solvent was allowed to evaporate slowly at ambient temperature. When the volume of the solution was reduced to ca. 10 mL (after about 4 days), the crystalline product of **3** started to appear, which was collected by filtration. Yield: 0.090 g, 59%.

Table 1. Crystal Structure and Refinement Data for Complexes 1−3

	1	2	3
formula	$C_{19}H_{20}CuHgN_2O_2Cl_2$	$C_{38}H_{40}Cu_2HgN_4O_4Cl_2$	$C_{38}H_{38}Cu_2Hg_2N_4O_4Cl_2$
formula wt	643.41	1015.31	1213.88
space group	*Pbca*	*P*2/*c*	*P*2$_1$/*c*
cryst syst	orthorhombic	monoclinic	monoclinic
a (Å)	15.976(2)	20.640(1)	9.378(5)
b (Å)	13.598(2)	10.304(1)	9.902(5)
c (Å)	18.897(2)	17.955(1)	20.420(5)
$\alpha = \gamma$ (deg)	90	90	90
β (deg)	90	91.095(2)	91.009(5)
V (Å^3)	4105.2(8)	3818.1(3)	1895.9(2)
Z	8	4	2
d_{calcd} (g cm^{-3})	2.082	1.766	2.126
μ (mm^{-1})	8.783	5.300	9.366
R_{int}	0.0612	0.1229	0.0277
no. of unique data	4291	7388	3866
no. of data with $I > 2\sigma(I)$	3058	4002	3540
R1 on $I > 2\sigma(I)$	0.0469	0.0861	0.1074
wR2 on $I > 2\sigma(I)$	0.0942	0.2271	0.2985
GOF	1.025	1.024	1.178

Physical Measurements. Elemental analyses (C, H, and N) were performed using a Perkin-Elmer 2400 Series II CHN analyzer. IR spectra in KBr pellets (4500−500 cm^{-1}) were recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. Electronic spectra in methanolic solutions (800−220 nm) were recorded with a Hitachi U-3501 spectrophotometer. High-resolution mass spectra (HRMS) electrospray ionization (ESI) was recorded on a Qtof Micro YA263 high-resolution mass spectrometer. For HRMS (ESI), compounds **1** and **2** were taken up in CH_3CN and compound **3** was taken up in MeOH. Powder X-ray diffraction patterns were recorded on a Bruker D-8 Advance diffractometer operated at 40 kV voltage and 40 mA current and calibrated with a standard silicon sample, using Ni-filtered Cu Kα (α = 0.154 06 nm) radiation. Experimental and simulated powder XRD plots are given in Figure S4 (Supporting Information).

Crystallographic Data Collection and Refinement. Suitable single crystals of the three complexes were mounted on a Bruker-AXS SMART APEX II diffractometer equipped with a graphite monochromator and Mo Kα (λ = 0.710 73 Å) radiation. The crystal was positioned at 60 mm from the CCD. A total of 360 frames were measured with a counting time of 10 s. The structure was solved using Patterson methods by using SHELXS-97. Subsequent difference Fourier synthesis and least-squares refinement revealed the positions of the remaining non-hydrogen atoms. Non-hydrogen atoms were refined with independent anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions, and their displacement parameters were fixed to be 1.2 times larger than those of the attached non-hydrogen atom. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle of the least-squares refinement. Absorption corrections were carried out using the SADABS program.[8] All calculations were carried out using SHELXS-97,[9] SHELXL-97,[10] PLATON 99,[11] ORTEP-32,[12] and WinGX system version 1.64.[13] Data collection and structure refinement parameters and crystallographic data for the complexes are given in Table 1. The relatively high *R* value of complex **3** is due to the poor quality of the crystal. Three different crystals were diffracted to get a better result. However, we were unable to get a lower *R* value.

RESULTS AND DISCUSSION

Syntheses and IR, UV−Vis, and Mass Spectra of the Complexes. The Schiff base ligand H_2L-CH_3 and its Cu(II) complex [CuL-CH_3] were synthesized using the reported procedure.[7] The neutral complex [CuL−CH_3] on reaction with $HgCl_2$ in a 1/1 molar ratio in MeOH/H_2O medium (4/1, v/v) resulted in an immediate precipitation of the greenish crystalline complex [CuL-CH_3-$HgCl_2$] (**1**). When the proportion of [CuL-CH_3] was increased to make it the double the molar concentration of $HgCl_2$, the deep green complex [(CuL-CH_3)$_2$$HgCl_2$] (**2**) was obtained from the MeOH/H_2O medium. Formation of mono-, bis-, and tris-complex species of metal ions with increased proportions of the bidentate chelating ligand is a usual phenomenon in coordination chemistry. However, isolation of di- and trinuclear heterometallic complexes simply by varying the proportion of [CuL-CH_3] seems to be a very rare phenomenon. On the other hand, when $HgCl_2$ and [CuL-CH_3] were allowed to react in the same medium (MeOH/H_2O) but in low concentration and in the presence of Et_3N, the brown tetranuclear complex [(CuL-CH_2-HgCl)$_2$] (**3**) resulted after 4−5 days. The concentration was kept low in order to avoid immediate precipitation of complex **1**. Complexes **1** and **2** both slowly transformed into compound **3** when triethylamine was added to their methanol solutions and the resulting solution was kept for several days. For **2** transformation takes a longer time and the yield is lower compared to that for **1**; moreover, the product contains both **3** and crystals of [CuL-CH_3]. The conversion of the dinuclear compound [CuL-CH_3-$HgCl_2$] (**1**) into the tetranuclear [(CuL-CH_2-HgCl)$_2$] (**3**) clearly shows that in the presence of triethylamine the methyl group of **1** slowly undergoes mercuration and consequently two dinuclear units join together through the C−Hg bond to form the cyclic tetranuclear organomercurial compound **3**. The added triethylamine helps to remove the liberated HCl molecule and thus facilitate the formation of **3**.

In addition to elemental analysis, the complexes were initially characterized by IR spectra. A strong and sharp band due to the azomethine ν(C═N) group of the Schiff base appears at 1598, 1601, and 1596 cm^{-1} for complexes **1**−**3**, respectively. The electronic spectra of the complexes (measured in methanol solution) display a single absorption band for **1** and **3** at 534 nm. In complex **2**, this band appears at 545 nm. These absorption bands may be attributed to the d−d transitions in copper(II) ions with a square-based geometry. The intense broad band at about 350, 344, and 354 nm for complexes **1**−**3**, respectively, is due to a ligand-to-metal charge transfer transition. A higher energy band at about 269, 269, and 270 nm for complexes **1**−**3**, respectively, is due to the $\pi-\pi^*$ transition of aromatic rings (Figure S5 and Table S1, Supporting Information).

The HRMS-ESI of **1** and **2** were recorded in acetonitrile solution while that of complex **3** was measured in methanolic solution (Figures S1−S3, Supporting Information). The spectra of complexes **1** and **2** show a similar pattern. It seems that both complexes dissociate into [CuL-CH_3] and $HgCl_2$ in solution and the dimeric species [CuL-CH_3]$_2$ is formed. On the other hand, the spectra of complex **3** are quite different. The existence of tetranuclear species is confirmed by the presence of a peak at m/z $[M + H]^+$ 1213.13. Several fragments were observed in the mass spectra of complex **3**. The fragments [CuL-CH_2-HgCl + H]$^+$, [CuL-CH_2-HgCl + Na]$^+$, [CuL-CH_2-HgCl + H + 2MeOH]$^+$, [(CuL-CH_2-HgCl)(CuL-CH_3) + H]$^+$ and [(CuL-CH_2−HgCl)(CuL-CH_3) + Na]$^+$ from the tetranuclear species show distinct peaks at m/z 608.02, 630.00, 672.09, 979.12, and 1001.11, respectively. The peaks due to [HgCl]$^+$ and [HgCl + 2MeOH]$^+$ are also observed at m/z 236.93 and 301.01, respectively, which are absent in the spectra of **1** and **2**. The appearance of peaks at m/z 372.09 and 743.14 may be attributed to the presence of [CuL-CH_3] and [CuL-CH_3]$_2$, respectively, as in **1** and **2**.

Structure Description of the Complexes. ***[(CuL-CH_3)-$HgCl_2$] (1).*** The asymmetric unit of complex **1** consists of one [CuL-CH_3] unit, one Hg(II) ion, and two chloride ions (Figure 1). The copper atom shows a distorted-square-planar geometry, being coordinated by the two phenoxido oxygen atoms O(1) and O(2) and the two imine nitrogen atoms N(1) and N(2) (Table 2). The rms deviation of the four coordinating atoms from the mean plane passing through them is 0.338 Å. The metal atom is 0.028(1) Å from this plane.

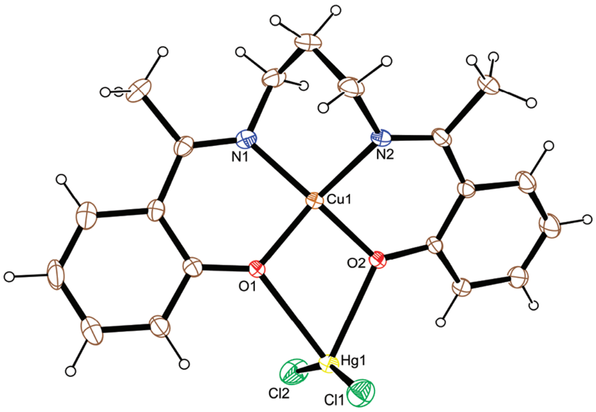


Figure 1. ORTEP diagram of complex **1**. Ellipsoids are drawn at the 20% probability level.

The Hg(II) atom is tetracoordinated, being bonded to two terminal chloride ions (Cl1 and Cl2) and two bridging phenoxido oxygens (O1 and O2) of the copper chelate (Figure 1). The environment around Hg(II) may be viewed as a distorted-tetrahedral geometry with ∠Cl(1)−Hg(1)−Cl(2) = 160.8(1)° and ∠O(1)−Hg(1)−O(2) = 62.9(1)°.

Table 2. Bond Angles and Distances of Complexes 1 and 3[a]

	distance (Å)			angle (deg)	
atoms	**1**	**3**		**1**	**3**
Hg1−Cl1	2.322(2)	2.322(8)	Cl1−Hg1−O1	98.0(1)	94.2(4)
Hg1−O1	2.536(4)	2.610(14)	Cl1−Hg1−O2	97.5(1)	95.1(4)
Hg1−O2	2.439(4)	2.624(13)	Cl1−Hg1−Cl2/Cl2*	160.8(1)	162.9(6)
Hg1−Cl2/Cl2*	2.316(2)	2.05(2)	O1−Hg1−O2	62.9(1)	61.1(4)
Cu1−O1	1.879(4)	1.873(13)	O1−Hg1−Cl2/Cl2*	94.8(1)	101.6(6)
Cu1−O2	1.883(3)	1.887(12)	O2−Hg1−Cl2/Cl2*	101.0(1)	98.2(6)
Cu1−N1	1.938(4)	1.978(15)	O1−Cu1−O2	87.3(2)	90.1(6)
Cu1−N2	1.959(5)	1.938(14)	O1−Cu1−N1	93.2(2)	92.6(6)
			O1−Cu1−N2	157.4(2)	157.1(6)
			O2−Cu1−N1	161.0(2)	154.6(6)
			O2−Cu1−N2	91.6(2)	93.2(6)
			N1−Cu1−N2	95.1(2)	94.0(6)

[a] Symmetry code: (*) $1 - x, -y, 1 - z$ for complex **3**.

[(CuL-CH_3)$_2$$HgCl_2$] (2). The structure of complex **2** contains two trinuclear units (A and B) with an Cu_2Hg core, both of which contain a crystallographic 2-fold axis passing through the Hg atom. Both units consist of two [CuL-CH_3] groups, one mercury(II) ion, and two chloride ions and have the formula [(CuL-CH_3)$_2$$HgCl_2$]. The two units are equivalent, with only some minor differences in bond angles and distances. The ORTEP view of unit A is shown in Figure 2, and the bond distances and angles of both units are given in Table 3. The two terminal Cu(II) ions possess a pentacoordinate, square-pyramidal coordination sphere. The basal plane in the copper ion is constituted by the four coordinating atoms (two oxygen and two nitrogen) from the di-Schiff base. Two [CuL-CH_3] units in the molecule are also joined together through the coordination of one of the phenoxido oxygens, O(2A)^a or O(2B)^b, to the axial position of the other unit to complete the square-pyramidal geometry (symmetry code: (a) $1 - x, y, {}^3/_2 - z$; (b) $-x, y, {}^5/_2 - z$). The rms deviations of the four

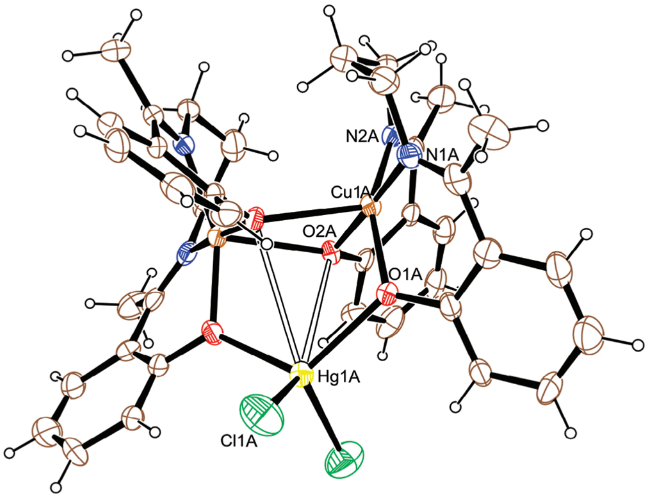


Figure 2. ORTEP diagram of unit A of complex **2**. Ellipsoids are drawn at the 20% probability level. The open bonds show the weak Hg(1)···O(2) interactions.

Table 3. Bond Angles and Distances of Complex 2[a]

A unit		B unit	
atoms	distance (Å)	atoms	distance (Å)
Hg1A–O1A	2.307(8)	Hg1B–O1B	2.341(8)
Hg1A–Cl1A	2.466(6)	Hg1B–Cl1B	2.451(13)
Hg1A–O2A	3.117(8)	Hg1B–O2B	3.007(8)
Cu1A–O1A	1.954(8)	Cu1B–O2B	1.893(8)
Cu1A–N1A	1.967(12)	Cu1B–N1B	1.967(12)
Cu1A–N2A	1.976(9)	Cu1B–N2B	1.974(12)
Cu1A–O2A	1.915(8)	Cu1B–O1B	1.926(7)
Cu1A–O2A^a	2.321(7)	Cu1B–O2B^b	2.483(9)
A unit		B unit	
atoms	angle (deg)	atoms	angle (deg)
O1A–Cu1A–N2A	154.5(3)	O1B–Cu1B–N2B	152.5(4)
O1A–Cu1A–N1A	88.6(4)	O1B–Cu1B–O2B^b	84.4(3)
O1A–Cu1A–O2A	90.9(4)	O2B–Cu1B–N1B	166.7(4)
O2A^a–Cu1A–N1A	101.8(3)	O2B–Cu1B–N2B	88.5(4)
O1A–Cu1A–O2A^a	85.9(3)	O1B–Cu1B–O2B	88.7(4)
Cl1A–Hg1A–O1A	100.0(2)	Cl1B–Hg1B–O1B	103.7(4)
Cl1A–Hg1A–O1A^a	112.0(2)	Cl1B–Hg1B–Cl2^b	115.4(3)
O2A–Cu1A–N1A	177.2(3)	Cl1B–Hg1B–O1B^b	108.4(4)
O2A–Cu1A–N2A	86.7(4)	O1B–Hg1B–O1B^b	117.8(3)
O2A–Cu1A–O2A^a	75.3(3)	O2B–Cu1B–O2B^b	75.6(3)
O2A^a–Cu1A–N2A	117.8(3)	N1B–Cu1B–N2B	98.0(5)
N1A–Cu1A–N2A	95.0(4)	O2B^b–Cu1B–N1B	91.1(4)
Cl1A–Hg1A–Cl1A^a	118.0(2)	O2B^b–Cu1B–N2B	121.2(4)
O1A–Hg1A–O1A^a	115.6(3)	O1B–Cu1B–N1B	90.8(4)

[a] Symmetry code: (a) $1 - x, y, {}^3/_2 - z$; (b) $-x, y, {}^5/_2 - z$.

equatorially coordinating atoms from the mean plane passing through them are 0.242 and 0.330 Å for the A and B units, respectively. The metal atoms Cu(1A) and Cu(1B) are 0.067(1) and 0.115(2) Å from this plane, respectively.

The mercury atom, which sits on a 2-fold axis, is bonded with two oxygen atoms from two different [CuL-CH$_3$] units and two chloride ions. In addition to these four short bonds, there are two additional long bonds formed by the other oxygen atoms, O(2), of the two terminal [CuL-CH$_3$] units (Table 3). Note that this O(2) atom is the one that is semicoordinated to the axial position of the other copper atom in the trinuclear unit.

Each discrete unit is connected by C(8B)–H(8B3)···Cl(1A) hydrogen-bonding interactions to form 1D supramolecular chains along the crystallographic *a* axis, as shown in Figure 3A. The hydrogen-bonding interactions are summarized in Table 4.

Table 4. Hydrogen-Bonding Interaction of Complex 2

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠D–H···A (deg)	symmetry
C8B–H8B3···Cl1A	0.9600	2.6900	3.613(15)	161.00	$x, 1 - y, {}^1/_2 + z$

These 1D supramolecular chains are further connected by C–H···*π* interactions to form 2D supramolecular sheets in the *ab* plane (Figure 3B). The hydrogen atom H(4B) interacts with one of the phenyl rings of the CuL-CH$_3$ unit. All these dimensions are given in Table 5.

Table 5. C–H···*π* Interaction of Complex 2

C–H···R1	H···R1 (Å)[a]	C···R1 (Å)	∠C–H···R1 (deg)	symmetry
C4B–H4B···R1	2.910	3.746	151	$1 - x, 2 - y, 2 - z$

[a] R1 = C14A–C15A–C16A–C17A–C18A–C19A.

*[(CuL-CH$_2$-HgCl)$_2$] (**3**).* Complex **3** is a tetranuclear metal cluster. The asymmetric unit contains one [CuL-CH$_2$]$^-$ ion, one Hg(II) ion, and one chloride ion (Figure 4). The Cu(II) atom has a distorted-square-planar geometry, being coordinated by the two phenoxido oxygen atoms O(1) and O(2) and the two imine nitrogen atoms N(1) and N(2). The rms deviations of the four coordinating atoms from the mean plane passing through them is 0.399 Å, indicating significant distortion

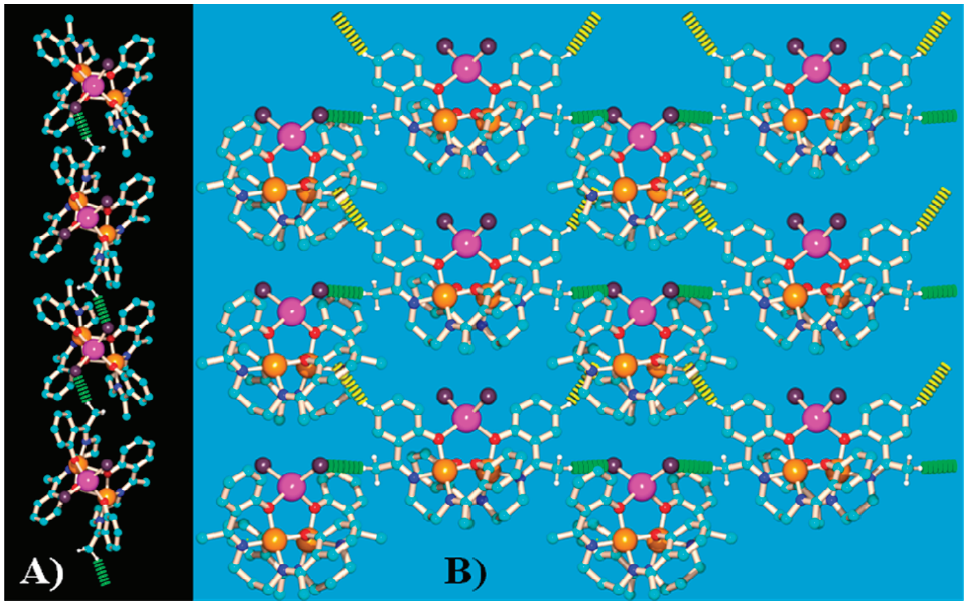


Figure 3. (A) Supramolecular chain formed by C(8B)–H(8B3)···Cl(1A) hydrogen-bonding interactions along the crystallographic *a* axis. (B) 2D supramolecular sheets formed by both hydrogen-bonding and C–H···*π* interactions within the crystallographic *ab* plane of complex **2**.

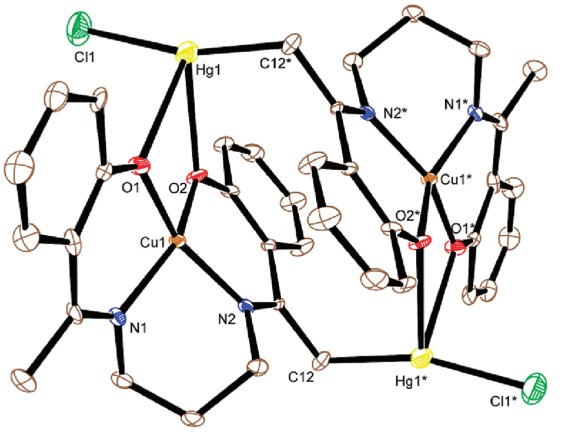


Figure 4. ORTEP diagram of complex **3**. Ellipsoids are drawn at the 20% probability level. Hydrogen atoms are omitted for simplicity.

toward tetrahedral geometry. The metal atom is 0.022(2) Å from this plane.

The Hg(II) atom has a distorted-tetrahedral coordination geometry. The chloride ion (Cl1) and the carbon atom (C12*) (symmetry code: (*) $1 - x, -y, 1 - z$) of the methylene group from another [CuL-CH$_2$]$^-$ coordinate to Hg(II) in nearly linear positions, and the two oxygen atoms O(1) and O(2) of the Schiff base bridge the Cu(II) and Hg(II) at angular positions (Figure 4). The organomercury bond (C12*−Hg1) distance is 2.05(2) Å and is in the range of other C−Hg bonds.[14−16] The Cu(1)···Hg(1) and Cu(1)···Hg(1)* bond distances are 3.545 and 5.519 Å and Cu(1)···Cu(1)* and Hg(1)···Hg(1)* bond distances are 5.343 and 7.583 Å, respectively.

A CSD search reveals that only 10 heterometallic complexes have been reported to incorporate Hg(II) ion with the help of a "complex as ligand", [CuL] (H$_2$L = any salen type Schiff base). Among them, four[16,17] resemble complex **1** in the present paper, where one [CuL] unit on chelation with a mercuric halide (chloride/bromide) results in a dinuclear compound. However, the geometry around Hg is distorted tetrahedral as in **1** in only two complexes.[17a,b] The Hg atom is pentacoordinated in one,[17c] having a close contact with the solvent molecule, and is hexacoordinated[16] in the other one. Of the remaining six compounds, one pair each of trinuclear,[18] tetranuclear,[19] and polymeric[16,20] compounds have been reported. However, unlike compound **2**, both of the reported trinuclear compounds are linear, whereas the reported tetranuclear complexes are formed by the dimerization of dinuclear units; one through μ_2-chloro bridges[19a] and other by μ_3-phenoxido bridges.[19b] Compound **3** is also formed by dimerization of the dinuclear complex **1**. However, here the dimerization takes place, very unexpectedly, through the mercuration of the methyl group of the Schiff base ligand. Hence, the structure of **3** is very different from that of the two reported tetranuclear complexes.

The flexidentate behavior of the di-Schiff base ligand H$_2$L-CH$_3$ is well known, generally through the donor centers N and O. However, the most important aspect of complex **3** is the coordination of the Schiff base to the metal centers through carbon atoms that makes it heptadentate with the $1\text{-}\kappa^4NN'OO'{:}2\text{-}\kappa^2OO'{:}3\text{-}\kappa C$ coordination mode. To our knowledge, this is the first example of such a coordination mode of salen-type Schiff base ligands. The methyl group of the coordinated Schiff base undergoes direct mercuration in the presence of HgCl$_2$ to form complex **3**. Metal-mediated C−H bond activation is of considerable importance, because it can lead to the formation of unexpected products through reactive organometallic intermediates.[21] In the rich and diverse chemistry of Hg(II), the formation of various new organometallic materials by the interaction of mercury(II) with alkynyl compounds deserves special mention.[22] Usually organolithium or Grignard reagents are used for the formation of Hg−C bonds.[14] Direct mercuration is reported to occur in some compounds that contain acidic hydrogen atoms.[15] In the metal-bound substrate, however, such examples are found in very few systems: e.g., in a Ni(II)-bound tetraaza macrocycle,[15b] a platinum(II)-bound [acac],[23] and a Cu(II)-bound 8-hydroxyquinoline complex.[15c,d] Very recently, a Cu(II)-bound Schiff base ligand has been reported to undergo C-mercuration at the phenyl ring.[16] Complex **3** is thus the first example of methyl carbon mercuration in a metal-bound Schiff base complex.

■ CONCLUSIONS

In summary, we have presented here an unique example for the synthesis of heterometallic dinuclear Cu^{II}-Hg^{II}, bent trinuclear Cu$^{II}_2$Hg^{II}, and cyclic tetranuclear Cu$^{II}_2$Hg$^{II}_2$ complexes by reacting the same "complex as ligand" [CuL-CH$_3$] with HgCl$_2$ simply by controlling the molar ratios and reaction conditions (i.e., concentration of reactants and addition of triethylamine). The nuclearity of similar heterometallic complexes is known to be modulated by anionic coligands.[6d] The uniqueness of the present examples lies in the fact that the same reactants, [CuL−CH$_3$] and HgCl$_2$, have been used to synthesize three different complexes. Moreover, we have shown here for the first time that the methyl group of a Cu(II)-bound Schiff base complex can undergo direct mercuration under ambient conditions to make the coordination mode of the salen-type di-Schiff base heptadentate. Such a coordination mode enabled us to produce the novel tetranuclear organomercuiral Cu(II)−Hg(II) metallamacrocycle.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

HRMS (ESI) spectra of complexes **1**−**3** (Figures S1−S3), powder X-ray spectrum of complex **3** (Figure S4), UV−vis spectra (Figure S5) and data (Table S1), and CIF files giving crystallographic data for complexes **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 835847 contains the supplementary crystallographic data for **3**. These data can be also obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223-336-033; e-mail, deposit@ccdc.cam.ac.uk).

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Notes

The authors declare no competing financial interest.

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