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Halide-Modulated Cu–Hg Heterodinuclear Complexes as Potential Precursors for Functional Energy and Environmental Materials

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ABSTRACT

This study reports the synthesis and comprehensive structural characterization of three novel heterodinuclear complexes, $[CuL\{HgCl_2(CH_3OH)\}]$ (1), $[CuL\{HgBr_2\}]$ (2) and $[CuL\{HgI_2\}]$ (3). These complexes were generated through the reaction of HgX_2 salts (X^- = Cl^-, Br^- and I^-) with a copper(II) Schiff base complex, (where H_2L = N,N′-bis(2-hydroxyphenylidene)-2,2′-dimethyl-1,3-propanediamine).

The resulting compounds were characterized using elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction. The structural analyses consistently revealed the formation of a heterodinuclear $[Cu^{II}Hg^{II}]$ core in all three species, with the central Cu(II) and Hg(II) ions bridged by the two phenolate oxygen atoms of the L ligand.

The coordination geometry around the Cu(II) center in all complexes is a distorted square planar (CuN_2O_2). In contrast, the coordination geometry of the Hg(II) ion is dependent on the coordinated halide: it adopts a distorted square pyramidal (HgO_3Cl_2) geometry in complex 1 (including a coordinated methanol molecule), but a tetrahedral (HgO_2Br_2 or HgO_2I_2) geometry in complexes 2 and 3, respectively. Supplementary crystallographic data for the three structures are registered with the CCDC as 1432472, 1432473, and 1432474.

The halide-dependent structural variation in the Hg(II) environment provides valuable insight for designing functional coordination materials. The robust Cu–Hg core and tunable electronic features highlight these complexes as potential precursors for optical, sensing, and environmental remediation materials within the broader field of energy and materials research.

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1. Introduction

Polynuclear heterometallic complexes play a significant role in various applications, ranging from catalysis to material science [1, 2]. These compounds exhibit a wide range of properties and structural diversity, which makes them highly versatile in various applications [3]. Unique redox properties due to the presence of different metal ions with different oxidation states [4], allows for applications in catalysis [5, 6] and electrochemistry [7]. Heterometallic complexes can serve as catalysts for a variety of chemical reactions [8], including cross-coupling reactions [9], hydrogenation [10], and oxidation reactions [5]. The presence of multiple metal ions can enhance catalytic activity and selectivity [11].

Heterometallic complexes containing paramagnetic metal ions can exhibit interesting magnetic properties [12], such as spin-crossover behavior [13] or magnetic anisotropy [14]. Certain heterometallic complexes contain metal ions with luminescent properties [15] can emit light of different wavelengths [16], which makes them useful in applications such as optoelectronics [17] and sensing. Some of them used as probes for detecting specific analytes [18] or as imaging agents in biological systems [19]. The combination of different metal ion and ligands in heterometallic complexes leads to a wide range of possible coordination geometries and structural motifs [20], which allows for the design of materials with tailored properties [21]. Overall, heterometallic complexes offer a rich area of research and have the potential to contribute to the development of new materials and technologies.

Recent advances in energy-relevant materials and environmental remediation systems have highlighted the importance of heterometallic complexes as molecular precursors for functional materials [22]. Schiff-base frameworks, particularly those featuring mixed-metal cores, have shown promise in designing photocatalytic materials, optical sensors for pollutant detection, and precursors for metal-oxide hybrid materials. The tunability of halide-coordinated heavy-metal centers such as Hg(II) and the structural rigidity of Cu(II) salen-type units provide opportunities for tailoring electronic, optical, and supramolecular properties. Therefore, understanding the structural variations induced by halide substitution in Cu–Hg complexes is relevant not only for coordination chemistry but also for the broader development of advanced materials.

Building on our previous work on heterometallic complexes, we have selected dinuclear complexes involving Cu(II) and Hg(II) cores; because among the divalent first row transition elements, Cu(II) forms stable complexes with Schiff bases [23, 24]. These Cu-chelates used frequently to form complex with another metal ions [25]. Also, we have chosen Hg(II) as hetero-metal because it may present different coordination numbers and geometries.

Herein, we report the syntheses, crystal structures and spectral properties of three new hetero-metallic complexes of Hg(II), [CuL{$HgCl_2(CH_3OH)$}] (**1**) [CuL{$HgBr_2$}] (**2**) and [CuL{HgI_2}] (**3**) with chloride, bromide and iodide as coligands [where H_2L = N,N′-bis(2-hydroxyphenylidene)-2,2′-dimethyl-1,3-propanediamine].

EXPERIMENTAL Materials

All reagents and solvents were purchased from Merck and Aldrich and used without further purification. N,N′-bis(2-hydroxyphenylidene)-2,2′-dimethyl-1,3-propanediamine ligand (H_2L) was prepared by reacting a ethanolic solution of 2-hydroxy-benzaldehyde and 2,2′-dimethyl-1,3-diaminopropane as described previously in the literature [26].

Synthesis of the complex [CuL{$HgCl_2(CH_3OH)$}] (1)

A solution of copper(II) acetate monohydrate (0.049 g, 0.25 mmol) in methanol (10 mL) was added slowly with stirring to a methanolic solution (10 mL) of the Schiff base ligand, H_2L (0.077 g, 0.25 mmol), the resulting green solution was stirred and refluxed for an hour. Then a solution of $HgCl_2$ (0.067 g, 0.25 mmol) in methanol (10 mL) was added to dropwise to the mixture. Stirring was continued for 20 min and the solution was filtered and then allowed to stand at room temperature for several days. Green crystals of **1** were isolated, washed three times with cold CH_3OH and dried under ambient conditions. Yield: 57%. Found, %: C 35.60; H 3.62; N 4.20. Calculated for $C_{20}H_{24}Cl_2CuHgN_2O_3$, %: C 35.56; H 3.58; N 4.15. Characteristic IR data (υ, cm^{-1}): 1611 υ(C=N), 3550 υ(O-H).

Synthesis of the complex [CuL{$HgBr_2$}](2)

Complex **2** was synthesized by a similar method as that described for **1**, with $HgCl_2$ being replaced by $HgBr_2$ (0.09 g, 0.25 mmol). Green crystals of **2** were isolated, washed three times with cold MeOH and dried under ambient conditions. Yield: 60%. Found, %: C 31.20; H 2.73; N 3.88. Calculated for $C_{19}H_{20}Br_2CuHgN_2O_2$, %: C 31.16; H 2.75; N 3.83. Characteristic IR data (υ, cm^{-1}): 1623 υ(C=N).

Synthesis of the complex [CuL{HgI_2}](3)

Complex **3** was synthesized by a similar method as that described for **1**, with $HgCl_2$ being replaced by HgI_2 (0.114 g, 0.25 mmol). Pink crystals of **3** were isolated, washed three times with cold MeOH and dried under ambient conditions. Yield: 68%. Found, %: C 27.58; H 2.40; N 3.40. Calculated for $C_{19}H_{20}I_2CuHgN_2O_2$, %: C

27.62; H 2.44; N 3.39. Characteristic IR data (υ, cm^{-1}): 1621 υ(C=N).

Measurements

Elemental analyses (C, H and N) were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra in KBr pellets (4000–500 cm^{-1}) were recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. The X-ray diffraction measurements were made on a STOE IPDS-II diffractometer with graphite monochromatic Mo-Kα radiation. For $[CuL\{HgCl_2(CH_3OH)\}]$ (**1**), green plate shape, for $[CuL\{HgBr_2\}]$ (**2**), green plate shape and for $[CuL\{HgI_2\}]$ (**3**) pink plate crystals were chosen using a polarizing microscope and were mounted on a glass fiber which was used for data collection. Cell constants and orientation matrices for data collection were obtained by least-squares refinement of diffraction data. Data were collected in a series of ω scans in 1° oscillations and integrated using the Stoe X-AREA [27] software package. A numerical absorption correction was applied using X-RED [28] and X-SHAPE [29] software. The data were corrected for Lorentz and Polarizing effects. The structures were solved by direct methods [30] and subsequent difference Fourier maps and then refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters [31]. The atomic factors were taken from the International Tables for X-ray Crystallography [32]. All refinements were performed using the X-STEP32 crystallographic software package [33]. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no.1432472-1432474 for **1-3**, respectively. Copy of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: (+44) 1223 336 033, or e-mail: deposit@ccdc.cam.ac.uk. A summary of crystal data, experimental details, and refinement results is given in Table 1.

Table1.Crystal data and structure refinement of complexes **1**, **2** and **3**.[a]

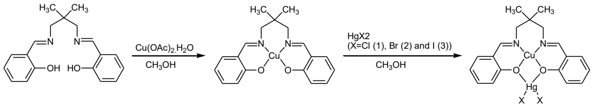
	1	**2**	**3**
Formula	$C_{20}H_{24}Cl_2CuHgN_2O_3$	$C_{19}H_{20}Br_2CuHgN_2O_2$	$C_{19}H_{20}I_2CuHgN_2O_2$
Formula weight (g mol^{-1})	675.45	732.31	826.31
Crystal system	Triclinic	Monoclinic	Monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
Temperature(K)	120(2)	120(2)	120(2)
Wavelength(Å)	0.71073	0.71073	0.71073
Crystal size (mm)	0.45 × 0.35 × 0.20	0.20 × 0.20 × 0.20	0.21 × 0.15 × 0.09
a (Å)	9.7278 (19)	11.822(2)	12.037(2)
b (Å)	10.844 (2)	13.948(3)	14.104(3)
c (Å)	11.247 (2)	12.999(3)	13.292(3)
α (˚)	76.41(3)	90	90
β (˚)	73.13(3)	160.42(3)	106.78(3)
γ (˚)	76.42(3)	90	90
Volume ($Å^3$)	1085.7(4)	2056.0(8)	2160.4(7)
Z	2	4	4
D_{calc} (g cm^{-3})	2.066	2.366	2.540
F (000)	650	1372	1516
μ (mm^{-1})	8.311	12.396	10.956
θ Range (°)	2.49 to 29.15	2.52 to 25.00	2.48 to 29.17
Index range	$-13 \le h \le 13$, $-14 \le k \le 11$, $-15 \le l \le 15$	$-13 \le h \le 14$, $-16 \le k \le 16$, $-15 \le l \le 15$	$-16 \le h \le 16$, $-19 \le k \le 19$, $-17 \le l \le 18$
Maximum and minimum transmission	0.2872 and 0.1177	0.1906 and 0.1906	0.4388 and 0.2069
Unique data (R_{int})	5803 (0.0733)	3590(0.1438)	5820(0.0823)
Data/restraints/ parameters	5801 / 1/269	3590/0 / 186	5820 / 0 / 246
Final *R* indices [I>2σ(I)]	$R_1 = 0.0499$, $wR2 = 0.1229$	$R_1 = 0.0639$, $wR_2 = 0.1409$	$R_1 = 0.0435$, $wR_2 = 0.0777$
R indices (all data)	$R_1 = 0.0551$, $wR2 = 0.1261$	$R_1 = 0.1047$, $wR_2 = 0.1638$	$R_1 = 0.0631$, $wR_2 = 0.0827$
Goodness-of-fit on F^2 (*GOF*)	1.046	1.001	1.061
Largest diff. peak and hole, (e. $Å^{-3}$)	5.377 and -4.128	4.578 and -2.777	1.437 and -1.578

$^aR_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2-F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$

RESULTS AND DISCUSSION

Synthesis

Complexes **1**, **2** and **3** were obtained as crystalline solids by reacting copper acetate, HgX_2 (X^-= Cl^-, Br^- and I^-) and the H_2L tetradentate Schiff base ligand in a 1:1:1 molar ratio in methanol medium (Scheme 1). Three complexes have been characterized by elemental analysis, IR spectroscopy and single crystal X-ray structural analysis.



Scheme 1. Synthetic route of complexes 1-3.

Infrared and UV-Vis absorption Spectra

Besides elemental analysis, three complexes were initially characterized by IR spectra. A strong and sharp band due to the azomethine υ(C=N) group of the Schiff base appears at 1611, 1623 and 1621 cm^{-1} for complexes **1-3**, respectively. In addition, a broad absorption band centered at about 3550 cm^{-1} in the spectrum of **1** is assigned to the stretching vibration of the O-H group in the coordinated CH_3OH molecule.

The electronic spectra of three complexes have been measured in acetonitrile solution. The electronic spectra of complexes **1**, **2** and **3** containing H_2L ligand are very similar, showing a broad absorption band centered at 377, 383 and 385 nm respectively, attributed to ligand-to-metal charge transfer transitions. The gradual red-shift of LMCT transitions from Cl → Br → I reflects the increasing polarizability of halide donors, indicating tunable optical properties relevant to the design of functional coordination materials.

Besides this band, a broad absorption band is observed in the visible region at 593, 600 and 601 nm for **1**, **2** and **3**, respectively (compared to 604 nm in the non-coordinated metalloligand [CuL]). This band is typical of d–d transitions of Cu(II) ions with a square planar environment [25].

Description of the molecular structures of 1, 2 and 3

The structure of **1** is shown in Fig.1 together with the atomic numbering scheme. Dimensions in the metal coordination sphere are given in Table 2.

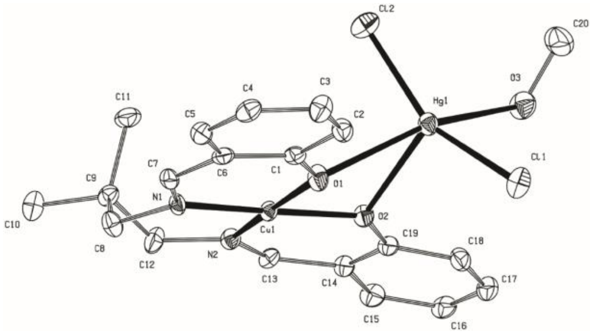


Fig.1. *ORTEP* diagram for the complex [CuL{$HgCl_2(CH_3OH)$}] showing the atom labeling scheme. Ellipsoids drawn at 50% probability level and hydrogen atoms removed for clarity.

The asymmetric unit of complex **1** consists of one [CuL] unit, one Hg(II) ion, One CH_3OH and two chloride ions (Figure 1). The copper(II) ion 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). Bond distances and angles around the coordination chromophore are almost the same as those reported in the literature [34-37]. The Hg(II) atom is penta-coordinated, being bonded to two terminal chloride ions (Cl1 and Cl2), one O atom from a CH_3OH (O3) 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-square pyramidal geometry. In five coordinated compounds, the observed structures can be distorted square-pyramidal or distorted trigonal bipyramidal. A parameter, τ, has been defined to characterize the coordination geometry, with $\tau = (\alpha - \beta)/60$, ($\alpha > \beta$, α and ß are the two largest angles around the metal ion). The coordination is then assumed to be an ideal square pyramid when τ is 0 and an ideal trigonal bipyramid when τ is 1 [38]. The distortion of the regular pyramids is revealed by the bond angles [Cl(2)−Hg(1)−Cl(1) and O(1)−Hg(1)−O(3) are 154.80(7)° and 153.09(14)°, respectively] between the donor atoms. The τ value for Hg^{2+} is 0.0285. This value is very close to that of a square pyramid. The coordination around the terminal Hg^{2+} ion is irregular square pyramidal, with two O atoms of the Schiff base ligand and two chloride ions in the basal plane and one O atom from a methanol molecule in the apical position.

Table 2. Selected bond lengths (Å) and angles (º) for complexes of **1-3**

1		2		3	
Hg(1)-Cl(2)	2.3383(17)	Hg(1)-Br(2)	2.4316(19)	Hg(1)-I(1)	2.6066(7)
Hg(1)-Cl(1)	2.3460(17)	Hg(1)-Br(1)	2.436(2)	Hg(1)-I(2)	2.6120(10)
Hg(1)-O(2)	2.438(4)	Hg(1)-O(2)	2.444(11)	Hg(1)-O(2)	2.488(4)
Hg(1)-O(1)	2.556(4)	Hg(1)-O(1)	2.542(11)	Hg(1)-O(1)	2.568(4)
Hg(1)-O(3)	2.744(5)	Cu(1)-O(1)	1.893(11)	Cu(1)-O(1)	1.914(4)
Cu(1)-O(1)	1.922(4)	Cu(1)-O(2)	1.905(11)	Cu(1)-O(2)	1.899(4)
Cu(1)-O(2)	1.930(4)	Cu(1)-N(1)	1.926(13)	Cu(1)-N(1)	1.929(5)
Cu(1)-N(1)	1.986(5)	Cu(1)-N(2)	1.957(13)	Cu(1)-N(2)	1.944(5)
Cu(1)-N(2)	1.977(5)	Br(2)-Hg(1)-Br(1)	153.99(7)	I(1)-Hg(1)-I(2)	151.88(2)
Cl(2)-Hg(1)-Cl(1)	154.80(7)	Br(2)-Hg(1)-O(1)	107.2(3)	O(2)-Hg(1)-I(2)	94.55(11)
Cl(2)-Hg(1)-O(2)	99.88(11)	Br(1)-Hg(1)-O(1)	96.3(3)	O(1)-Hg(1)-I(1)	108.72(10)
Cl(1)-Hg(1)-O(2)	105.29(11)	O(2)-Hg(1)-O(1)	62.9(3)	O(2)-Hg(1)-O(1)	62.89(14)
Cl(2)-Hg(1)-O(1)	90.98(12)	Br(2)-Hg(1)-O(2)	106.1(3)	O(2)-Hg(1)-I(1)	106.87(11)
Cl(1)-Hg(1)-O(1)	102.69(12)	Br(1)-Hg(1)-O(2)	94.4(3)	O(1)-Hg(1)-I(2)	97.09(10)
O(2)-Hg(1)-O(1)	59.55(14)	O(1)-Cu(1)-O(2)	86.5(4)	O(1)-Cu(1)-O(2)	87.55(18)
Cl(2)-Hg(1)-O(3)	90.77(12)	O(1)-Cu(1)-N(1)	94.9(5)	O(1)-Cu(1)-N(1)	94.7(2)

Cl(1)-Hg(1)-O(3)	86.47(12)	O(2)-Cu(1)-N(1)	156.4(6)	O(2)-Cu(1)-N(1)	155.2(2)
O(2)-Hg(1)-O(3)	93.72(15)	O(1)-Cu(1)-N(2)	157.8(6)	O(1)-Cu(1)-N(2)	158.1(2)
O(1)-Hg(1)-O(3)	153.09(14)	O(2)-Cu(1)-N(2)	94.4(5)	O(2)-Cu(1)-N(2)	94.3(2)
O(1)-Cu(1)-O(2)	80.24(17)	N(1)-Cu(1)-N(2)	93.0(5)	N(1)-Cu(1)-N(2)	92.7(2)
O(1)-Cu(1)-N(2)	170.90(19)	Cu(1)-O(1)-Hg(1)	100.1(4)	Cu(1)-O(1)-Hg(1)	99.00(17)
O(2)-Cu(1)-N(2)	91.75(19)	Cu(1)-O(2)-Hg(1)	103.2(4)	Cu(1)-O(2)-Hg(1)	102.20(18)
O(1)-Cu(1)-N(1)	91.45(19)				
O(2)-Cu(1)-N(1)	171.47(19)				
N(2)-Cu(1)-N(1)	96.7(2)				
Cu(1)-O(1)-Hg(1)	102.00(18)				
Cu(1)-O(2)-Hg(1)	106.06(17)				

Single-crystal X-ray diffraction shows that the complexes **2** and **3** are structurally similar dinuclear copper(II)–mercury(II) compounds (Figs. 2, 3). Also selected bond lengths and angles are listed in Table 2. Each Cu atom in the complexes is four-coordinated by two imino N and two phenolic O atoms of the corresponding Schiff base ligand, forming a slightly distorted square-planar coordination. The bond angles within the coordination plane around the Cu^{II} ion range from 86.5(4) (O1–Cu–O2) to 157.8(6) ° (O1–Cu–N2) for **2** and 87.55(18) to 158.1(2) ° for **3**. In the bridging plane, the two Cu–O distances [1.905(11) and 1.893(11) Å for **2**; 1.914(4) and 1.899(4) for **3**] are equal within experimental error and compare well with values reported previously [35, 36, 38], but the Hg–O bond lengths [2.542(11) (Hg–O1) and 2.444(11) Å (Hg–O2) for **2** and 2.488(4) (Hg–O2) and 2.568(4) Å (Hg–O1) for **3**] are slightly different. The Cu---Hg distances are 3.425 Å for **2** and 3.435 Å for **3**. The Hg atom in each complex is four-coordinated by two phenolic O atoms of the corresponding Schiff base ligand, and by two X atoms (X = Br for **2**; X = I for **3**) forming a slightly distorted tetrahedral coordination. The smallest bond angle of the distorted tetrahedron around the Hg^{II} ion is 62.9(3)° (O1–Hg–O2) for **2** or 62.89(14)° for **3** and the largest bond angle is 153.99(7)° (Br2–Hg–Br1) for **2** or 151.88(2)° (I2–Hg–I1) for **3**.

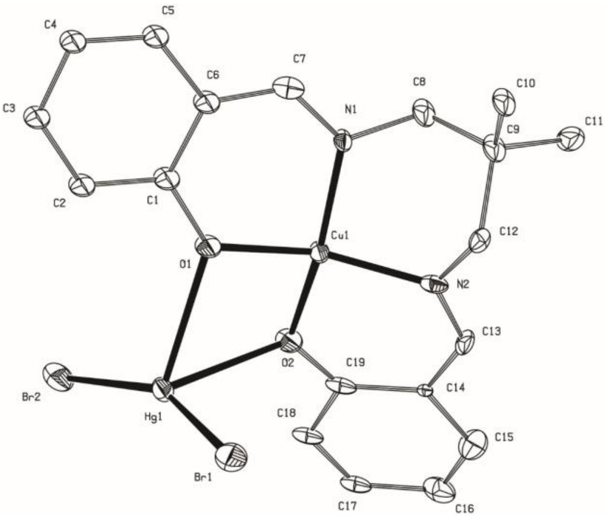


Fig.2. *ORTEP* diagram for the complex [CuL{$HgBr_2$}] showing the atom labeling scheme. Ellipsoids drawn at 50% probability level and hydrogen atoms removed for clarity.

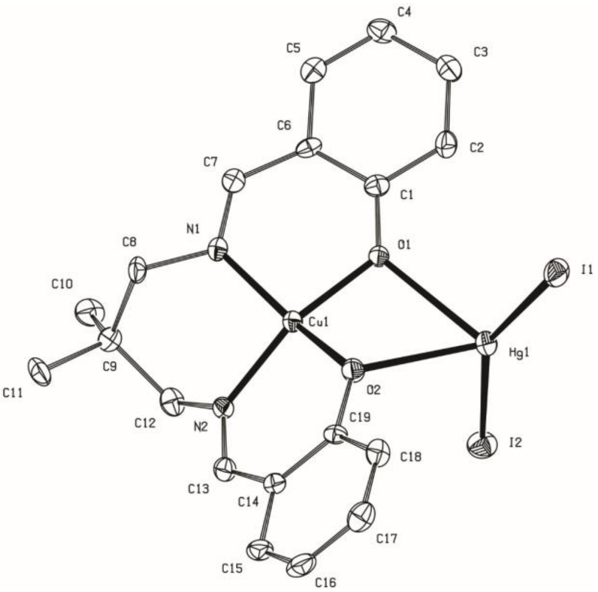


Fig.3. *ORTEP* diagram for the complex [CuL{HgI_2}] showing the atom labeling scheme. Ellipsoids drawn at 50% probability level and hydrogen atoms removed for clarity.

The Hg–O bond lengths are comparable across complexes, while Hg–I bonds in 3 are significantly longer than Hg–Cl or Hg–Br bonds in 1 and 2. All the coordinate bond lengths in the complexes related to the Hg atoms are comparable to the corresponding values observed in similar Hg(II) complexes with Schiff bases [25, 34, 39].

Although the present study focuses on synthesis and structural determination, the observed halide-dependent coordination geometries have practical implications. The LMCT bands in the UV–Vis spectra and the strong Cu–O(Hg) phenoxido bridges suggest potential optical and electronic tunability. Such features are desirable in functional materials including heavy-metal sensing platforms, photoactive complexes, and molecular precursors for engineered metal-oxide materials. The inherent affinity of the ligand framework for Hg(II) also indicates possible applications in environmental purification and mercury immobilization systems. These structure–property considerations provide a foundation for future studies aimed at integrating these complexes into emerging materials-based technologies.

CONCLUSIONS

In summary, we have presented here the syntheses of three new heterometallic Schiff base complexes, *i.e.*. dinuclear $[CuL\{HgCl_2(CH_3OH)\}]$ (**1**), $[CuL\{HgBr_2\}]$ (**2**) and $[CuL\{HgI_2\}]$ (**3**), (where L^{2-} = N,N'-bis(salicylidene)-2,2-dimethylpropylenediaminato).

The complexes have been characterized by microanalytical, spectroscopic and single crystal X-ray diffraction studies. In each of the complexes, the Cu(II) ion adopts a distorted square planar (CuN_2O_2) geometry while the Hg(II) ions in **1** adopts distorted square pyramidal (HgO_3Cl_2) but in **2** and **3** adopt tetrahedral (HgO_2Br_2 or HgO_2I_2) geometries.

Beyond structural interest, the halide-dependent modulation of the Hg(II) coordination sphere and the robust Cu–Hg core render these complexes potential candidates for future materials development. Their LMCT features, structural rigidity, and bridging phenoxido motifs are consistent with properties sought in optical, sensing, and environmental remediation materials. Thus, the present findings not only expand structural chemistry knowledge but also position these complexes as promising molecular precursors for advanced energy and environmental materials.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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Authors' Contributions

All aspects of this study were performed collaboratively by both authors. Both authors contributed equally and approved the final manuscript.

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