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ORIGINAL PAPER

Synthesis and Crystal Structures of Two Novel Complexes with *N*-[2-(5-Bromo-2-Hydroxybenzylideneamino)Ethyl]-4-Methylbenzenesulfonamide as Ligand

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Abstract Two novel complexes constructed from the sulfonamide Schiff base ligand **H_2L**, *N*-[2-(5-bromo-2-hydroxybenzylideneamino)ethyl]-4-methylbenzene-sulfonamide, [Cu(**HL**)$_2$] (**1**) and [Cu**L**(H_2O)] (**2**) are synthesized and characterized via X-ray single-crystal diffraction, elemental analysis, FT-IR and UV–Vis. **1** and **2** both form 1-D supramolecular architectures by π–π stacking interactions. **1** and **2** both crystallize in monoclinic, with space group *C2/c* and *P2/c* for **1** and **2**, with unit cell parameters $a = 27.640(18)$ Å, $b = 7.907(5)$ Å, $c = 17.945(14)$ Å, $\beta = 118.27(2)°$, $V = 3454(4)$ Å^3, $Z = 4$ for **1**, and $a = 16.758(5)$ Å, $b = 7.272(2)$ Å, $c = 15.080(4)$ Å, $\beta = 106.334(5)°$, $V = 1763.6(9)$ Å^3, $Z = 4$ for **2**.

Keywords *N*-Tosylethylenediamine · Sulfonamide Schiff base · Crystal structure · Supramolecular architecture

Introduction

Schiff base complexes attract many researchers' interest due to their importance in the development of coordination chemistry and the application in biological and catalytic fields [1–3]. Recent progresses made in Salen like Schiff base complexes have been summarized [4–6]. Despite advancement made in the salen like ligands and complexes, little attention has been paid to asymmetric sulfonamide Schiff base [7, 8], as research has focused mainly on two types: those derived from the condensation of 2-tosylaminobenzaldehyde and diamines [9–13], and those from condensation of *N*-tosyl-diamine and aldehydes [14–16].

As a part of our ongoing research of sulfonamide Schiff base [17, 18], we select a sulfonamide Schiff base ligand, *N*-[2-(5-bromo-2-hydroxybenzylideneamino)ethyl]-4-methylbenzenesulfonamide (**H_2L**) (Scheme 1), to construct new complexes. In this work, two novel complexes, [Cu(**HL**)$_2$] (**1**) and [Cu**L**(H_2O)] (**2**) have been prepared and characterized by elemental analysis, X-ray single-crystal diffraction, FT-IR, and UV–Vis measurements. π–π stacking interactions lead **1** and **2** to present a 1-D supramolecular structure.

Experimental Section

Ethylenediamine and $Cu(NO_3)_2{\cdot}3H_2O$ were commercial products and used without further purification. 5-Bromosalicylaldehyde was prepared by salicylaldehyde and liquid bromine. *N*-Tosyl-ethylenediamine was synthesized according to the literature method [19]. $Cu(ClO_4)_2{\cdot}6H_2O$ was obtained by the reaction of $Cu_2(OH)_2CO_3$ and dilute $HClO_4$.

C, H, and N elemental analysis was performed on a Vario EL–III analyzer. Infrared spectra were recorded as KBr pellet on a Nicolet Avatar 360 spectrophotometer in the range 4000–400 cm^{-1}. UV–Vis absorptions were recorded on a SHIMADZU UV-1700 spectrophotometer.

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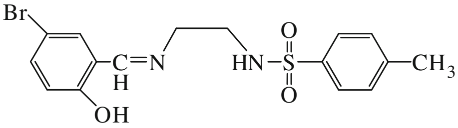

Scheme 1 *N*-[2-(5-Bromo-2-hydroxybenzylideneamino)ethyl]-4-methylbenzenesulfonamide (**H_2L**)

Synthesis of *N*-[2-(5-Bromo-2-Hydroxybenzylideneamino)Ethyl]-4-Methylbenzenesulfonamide (H_2L)

An ethanol solution (60 mL) of *N*-tosyl-ethylenediamine (2.14 g, 0.01 mol) and 5-bromo-salicylaldehyde (2.01 g, 0.01 mol) was refluxed for 1 h with constant stirring. Yellow precipitate was collected by filtration. m.p. 157.2–158.1 °C. Calculated for $C_{16}H_{17}BrN_2O_3S$: C 48.33%, H 4.279%, N 7.048%. Obtained: C 48.65%, H 4.323%, N 6.894%.

Synthesis of $[Cu(HL)_2]$ (**1**)

To a hot ethanol solution (25 mL) of H_2L (0.532 g, 1 mmol), the ethanol solution of $Cu(NO_3)_2{\cdot}6H_2O$ 0.242 g (1 mmol) was added. The solution was reacted under microwave condition for 15 min. The filtrate was set aside. Brown needle crystals were collected after 2 days. Calculated for $C_{32}H_{32}N_4O_6S_2Br_2Cu$: C 44.89%, H 3.770%, N 6.540%. Obtained: C 44.37%, H 3.724%, N 6.528%.

Synthesis of $[CuL(H_2O)]$ (**2**)

To an ethanol solution (20 mL) of H_2L (0.532 g, 1 mmol), four drops of 0.01 mol L^{-1} NaOH aqueous solution were added. Then the ethanol solution (10 mL) of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.37 g, 1 mmol) was added dropwise to the above solution while it was stirred. The mixture was brought to react under microwave for 12 min. The filtrate was set still and dark green block shaped crystals suitable for X-ray diffraction were obtained after 2 days. It was collected by filtration and air-dried. Calculated for $C_{16}H_{17}N_2O_4SBrCu$: C 40.29%, H 3.568%, N 5.876%. Obtained: C 40.35%, H 3.510%, N 5.543%.

X-Ray Crystallographic Analysis

The crystal determination was performed at room temperature on a Brucker-Smart APEX CCD diffractometer, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were made using the SADABS program [20]. The structures were solved by direct methods and refined by full-matrix least squares based on F^2, using SHELX-97 software [21]. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were included at geometrically calculated positions and refined using a riding model except those bonded to the water molecule. The H atoms of water molecular were located in a difference map and refined with $U_{iso}(H) = 1.5U_{eq}(O)$. The O–H and H···H distances were restrained to be 0.82(2) and 1.32(2) Å, respectively. The crystal data, experimental details, refinement results and details of structure determinations are shown in Table 1. Selected bond lengths and bond angles are listed in Table 2.

Table 1 Crystal data and structure refinements for complexes **1** and **2**

Identification code	**1**	**2**
Empirical formula	$C_{32}H_{32}Br_2CuN_4O_6S_2$	$C_{16}H_{17}BrCuN_2O_4S$
Formula weight	856.10	476.83
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*C2/c*	*P2/c*
a (Å)	27.640(18)	16.758(5)
b (Å)	7.907(5)	7.272(2)
c (Å)	17.945(14)	15.080(4)
β (°)	118.27(2)	106.334(5)
Volume ($Å^3$)	3454(4)	1763.6(9)
Z	4	4
$D_{calc.}$ (Mg/m^3)	1.646	1.796
Absorption coefficient (mm^{-1})	3.116	3.646
F(000)	1724	956
Crystal size (mm)	0.26 × 0.11 × 0.09	0.35 × 0.23 × 0.11
θ range for data collection (°)	2.31–24.15	2.53–25.09
Limiting indices	$-31 \le h \le 31$ $-9 \le k \le 8$ $-18 \le l \le 20$	$-16 \le h \le 20$ $-8 \le k \le 8$ $-17 \le l \le 17$
Reflections collected	7735	8256
Independent reflections	2760 (R_{int} = 0.1260)	3096 (R_{int} = 0.0650)
Max. and min. transmission	0.7668 and 0.4957	0.7007 and 0.3626
Data/restraints/parameters	2760/0/185	3096/3/198
Goodness-of-fit on F^2	0.936	1.001
Final *R* indices $I > 2\sigma(I)$	$R_1 = 0.0538$, $wR_2 = 0.0731$	$R_1 = 0.0585$, $wR_2 = 0.1435$
R indices (all data)	$R_1 = 0.1619$, $wR_2 = 0.0829$	$R_1 = 0.0981$, $wR_2 = 0.1743$
Largest diff. peak and hole (e $Å^{-3}$)	0.481 and −0.418	0.722 and −0.772

Table 2 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

	Bond length (Å)		Bond angles (°)	
Complex **1**	Cu1–O1	1.917(4)	O1–Cu1–N1	91.1(2)
	Cu1–N1	2.010(6)	O1–Cu1–N1#1	88.9(2)
Complex **2**	Cu1–O1	1.925(5)	O1–Cu1–N1	92.6(2)
	Cu1–N1	1.926(6)	O1–Cu1–O4	88.4(2)
	Cu1–O4	1.949(5)	N1–Cu1–N2	84.8(3)
	Cu1–N2	1.985(7)	N1–Cu1–O4	172.5(2)
			O1–Cu1–N2	175.3(2)
			O4–Cu1–N2	94.7(2)

Symmetry transformations used to generate equivalent atoms: #1 $-x + 3/2$, $-y + 1/2$, $-z$

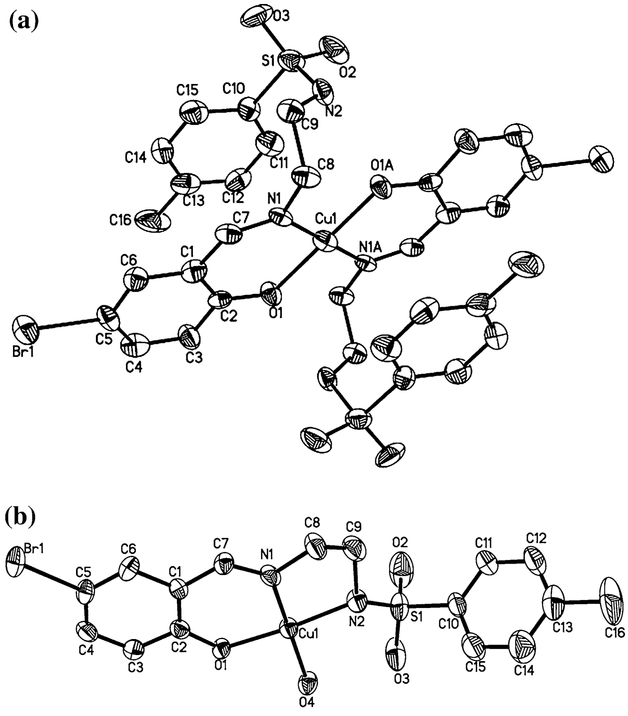

Fig. 1 Molecular structure of complexes **1** (**a**) and **2** (**b**). Ellipsoids are drawn at 40% probability. H atoms are omitted for clarity

Results and Discussion

Crystal Structure of [Cu(HL)$_2$] (**1**)

The molecular structure of complex **1** is presented in Fig. 1a. The Cu(II) ion is tetra-coordinated by the imine nitrogen atoms and phenolate oxygen atoms of two bidentate anionic Schiff base ligands. The Cu–N$_{imine}$ (2.010(6) Å) is longer than Cu–O$_{phenolate}$ (1.917(4) Å) distance. And the Cu–N$_{imine}$ and Cu–O$_{phenolate}$ are both longer than those in [Cu(HL′)$_2$] (1.927(3) and 1.833(3) Å, H$_2$L′ = *N*-[2-(2-hydroxybenzylideneamino)ethyl]-4-methylbenzenesulfonamide) [17] due to the electron withdrawing of Br in the ligand. The coordination geometry around Cu(II) ion is a slightly distorted square planar with the *cis* angles of 91.1(2) and 88.9(2)°. The ligand forms one Cu1–O1–C2–C1–C7–N1 six-membered chelate ring (deviation 0.06 Å), and Cu^{2+} lies deviating from this calculated plane with −0.09 Å. Complex **1** is extended into the final 1-D chain supramolecular structure as shown in Fig. 2a, through weak aromatic π–π stacking interactions between phenyl rings from adjacent organic ligands, with a center-to-center distance of about 3.9 Å. Moreover, the chelate ring–aromatic ring interactions (center-to-center distance of about 3.6 Å) help to stabilize the structure. This packing mode is much different from that in [Cu(HL′)$_2$] [17] because of the steric effect of Br group in the ligand.

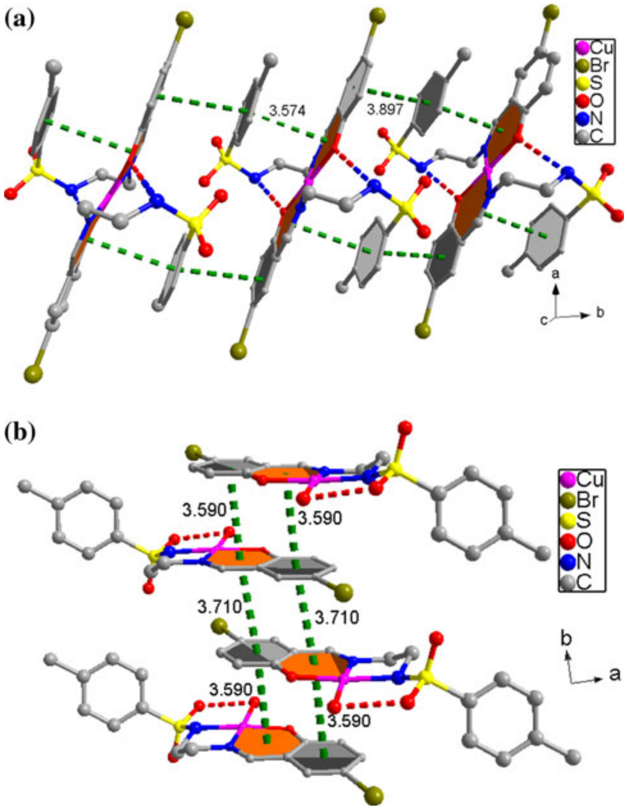

Fig. 2 1D chain structure of complexes **1** (**a**) and **2** (**b**)

Crystal Structure of [CuL(H$_2$O)] (**2**)

The molecular structure of complex **2** is shown in Fig. 1b. In the complex, the Cu(II) atom is coordinated to one dianionic tridentate Schiff base ligand and one water molecule. The Schiff base ligands coordinate to metal through the imine and sulfonamide nitrogens and phenol oxygen. The coordination geometry around Cu(II) ion is in a slightly distorted square planar with N$_2$O$_2$ in a *cis* arrangement. The *cis* angles are from 84.8(3) to 94.7(2)°

and the *trans* angles are 172.5(2) and 175.3(2)°. The bond lengths increase in the sequential as Cu–$O_{phenolate}$, Cu–N_{imine}, Cu–O_{water} and Cu–N_{amide}. And in complex **2**, one-six-membered chelate ring Cu1–O1–C2–C1–C7–N1 and one-five-membered chelate ring Cu1–N1–C8–C9–N2 (deviation 0.01 and 0.15 Å, and Cu^{2+} lies deviating from the calculated plane with −0.02 and −0.04 Å for six-membered ring and five-membered ring, respectively) are formed.

As shown in Fig. 2b, two molecules of complex **2** are linked to form a centrosymmetric head-to-tail subunits by the double weak $\pi \cdots \pi$ interactions between six-membered chelate ring and aromatic ring (center-to-center distance of about 3.6 Å). Then the subunits are further connected to a 1D chain by the double weak $\pi \cdots \pi$ interactions of about 3.7 Å.

FT-IR spectra and UV–Vis absorption

In the IR spectrum of free ligand H_2L, the v(O–H) and v(N–H) are at 3444 and 3244 cm^{-1}). Complex **1** shows the absence of the v(O–H) and the presence of the v(N–H) at about 3047 cm^{-1}. And in the complex **2**, the band at about 3424 cm^{-1} can be attributed to the O–H vibration. Moreover, the bands at about 1618 cm^{-1} for **1** and 1642 cm^{-1} for **2** are attributed to v(C=N), showing the frequency shift of −15 and 9 cm^{-1} compared with the free ligand at 1633 cm^{-1}. This suggests the coordination of the ligand to the metal through the imine nitrogen atoms.

The UV–Vis absorption spectra of the ligand, complex **1** and **2** in ethanol were given in Fig. 3. The absorption band at 372 nm for free ligand shift to 375 and 378 nm in complexes **1** and **2**. The red shift indicates the coordination of C=N to the metal. It can be assigned to the intraligand $\pi \rightarrow \pi^*$ transition of C=N group. Moreover, there exist weak d–d transition at about 616 and 614 nm for complex **1** and **2**.

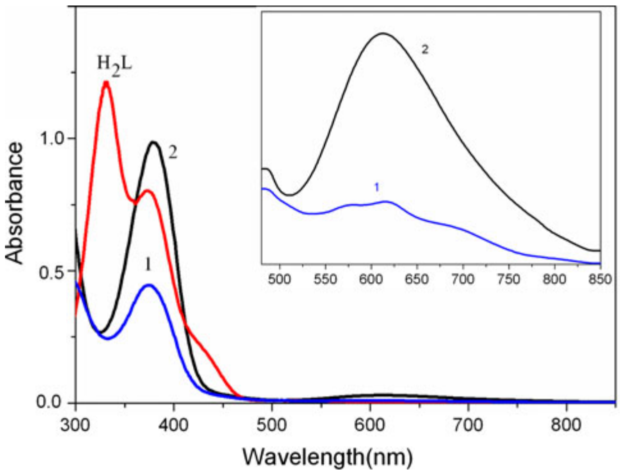

Fig. 3 UV–Vis spectra of the ligand and complexes

Supplementary Materials

CCDC 748158 and 748159 contain the supplementary crystallographic data of **1** and **2** for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

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