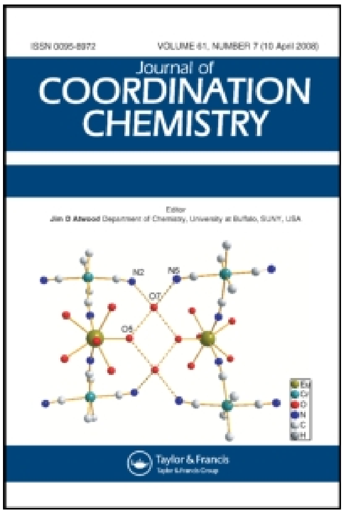

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Syntheses and crystal structures of two copper(II) complexes derived from 2-bromo-4-chloro-6-[(2-morpholin-4-ylethylimino)methyl]phenol

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Syntheses and crystal structures of two copper(II) complexes derived from 2-bromo-4-chloro-6-[(2-morpholin-4-ylethylimino)methyl]phenol

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Two new copper(II) complexes, [CuL_2] (**1**) and [$Cu_2L_2(NCS)_2$] $\cdot$ $2CH_3CN$ (**2**) (HL = 2-bromo-4-chloro-6-[(2-morpholin-4-ylethylimino)methyl]phenol), have been synthesized and characterized by elemental analyses, infrared spectroscopy, and single-crystal X-ray diffraction. Complex **1** was synthesized by reaction of HL with copper(II) acetate in methanol, while **2** was synthesized by adding ammonium thiocyanate to a methanol/acetonitrile (V : V = 2 : 1) solution of **1**. Complex **1** crystallizes in the $P2_1/n$ space group, and the thiocyanato-bridged dinuclear copper(II) complex, **2**, crystallizes in the *Pbcn* space group. The Cu in **1** is four-coordinate square-planar with two imine N and two phenolate O atoms from two Schiff-base ligands. The Cu in **2** is five-coordinate square-pyramidal with NNO donor atoms of one Schiff-base ligand and one N atom of a bridging thiocyanate ligand defining the basal plane, and with one S atom of another bridging thiocyanate ligand occupying the apical position.

Keywords: Schiff-base; Copper(II) complex; Synthesis; Crystal structure; Thiocyanate

1. Introduction

Polynuclear complexes containing bridging ligands have interesting molecular structures and may be designed with specific functionalities [1–3]. The prime strategy for designing these molecular materials is to use suitable bridging ligands. Due to the versatile coordination modes of thiocyanate, it has become one of the most extensively studied building blocks for synthesis of polynuclear complexes [4, 5].

Schiff-base compounds derived from condensation reactions of substituted salicylaldehyde with primary amines are versatile ligands, coordinating through the phenolate O, imine N, and other donor atoms [6–9]. In the present study, two new copper(II) complexes, [CuL_2] (**1**) and [$Cu_2L_2(NCS)_2$] $\cdot$ $2CH_3CN$ (**2**) (HL = 2-bromo-4-chloro-6-[(2-morpholin-4-ylethylimino)methyl]phenol (see the following scheme), have been synthesized and characterized. Complex **2** was prepared by adding ammonium thiocyanate to a methanol/acetonitrile (V : V = 2 : 1) solution of **1**. To our knowledge, the complexes derived from HL have never been reported.

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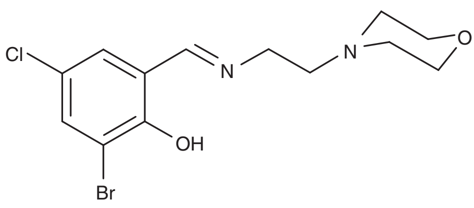

HL

2. Experimental

2.1. *Materials and methods*

All chemicals (reagent grade) were commercially available and used without further purification. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded on a Nicolet AVATAR 360 spectrometer as KBr pellets in the 4000–400 cm^{-1} region. The ^1H NMR spectrum of HL was recorded on a Bruker AVANCE 500 MHz spectrometer with tetramethylsilane as the internal reference.

2.2. *Synthesis of HL*

To a methanol solution (50 cm^3) of 3-bromo-5-chlorosalicylaldehyde (235.5 mg, 1.0 mmol) was added a methanol solution (30 cm^3) of 2-morpholin-4-ylethylamine (130.2 mg, 1.0 mmol) with stirring. The mixture was stirred for 10 min at room temperature to give a yellow precipitate. The product was filtered, washed three times with cold methanol, and dried in a vacuum desiccator containing anhydrous $CaCl_2$. Yield: 93%. Anal. Calcd for $C_{13}H_{16}BrClN_2O_2$ (%): C, 44.9; H, 4.6; N, 8.1. Found: C, 45.1; H, 4.7; N, 8.0. ^1H NMR data (CD_3CN, ppm): $\delta = 2.32$ (t, 4H), 2.68 (t, 2H), 3.62 (t, 2H), 3.71 (t, 4H), 4.51 (s, 1H), 7.27 (s, 1H), 7.36 (s, 1H), 8.23 (s, 1H).

2.3. *Synthesis of 1*

To a methanol solution (10 cm^3) of HL (34.7 mg, 0.1 mmol) was added a methanol solution (5 cm^3) of NaN_3 (6.5 mg, 0.1 mmol) and a methanol solution (5 cm^3) of $Cu(CH_3COO)_2 \cdot H_2O$ (20.0 mg, 0.1 mmol) with stirring. The mixture was stirred for 30 min at room temperature to give a clear blue solution. After keeping the solution in air for a week, blue, block-shaped crystals of **1**, suitable for X-ray crystal structural determination, formed at the bottom of the vessel on slow evaporation of the solvent. The crystals were isolated, washed three times with methanol and dried in a vacuum desiccator containing anhydrous $CaCl_2$. Yield: 63%. Anal. Calcd for $C_{26}H_{30}Br_2Cl_2CuN_4O_4$ (%): C, 41.3; H, 4.0; N, 7.4. Found: C, 41.0; H, 4.2; N, 7.6.

2.4. *Synthesis of 2*

To a methanol solution (5 cm^3) of **1** (75.7 mg, 0.1 mmol) was added a methanol solution (5 cm^3) of NH_4NCS (7.6 mg, 0.1 mmol) with stirring. The mixture was stirred for 10 min at room temperature to give deep blue precipitate. To the above mixture was added with stirring $5\,\mathrm{cm}^3$ acetonitrile, forming a clear blue solution. After keeping the solution in air for five days, blue, block-shaped crystals of **2**, suitable for X-ray crystal structural determination, formed at the bottom of the vessel on slow evaporation of the solvent. The crystals were isolated, washed three times with methanol and dried in a vacuum desiccator containing anhydrous $CaCl_2$. Yield: 51%. Anal. Calcd for $C_{32}H_{36}Br_2Cl_2Cu_2N_8O_4S_2$ (%): C, 37.7; H, 3.6; N, 11.0. Found: C, 37.4; H, 3.7; N, 11.2.

2.5. *X-ray structural determination*

Diffraction intensities for **1** and **2** were collected at 298(2) K using a Bruker SMART CCD area detector with Mo-Kα radiation ($\lambda = 0.71073$ Å). The collected data were reduced using the SAINT program [10], and empirical absorption corrections were performed using SADABS [11]. The structures were solved by direct methods and refined against F^2 by full-matrix least-squares using the SHELXTL package [12]. All non-hydrogen atoms were refined anisotropically. H atoms were placed in calculated positions and constrained to ride on their parent atoms. The crystallographic data for the two complexes are summarized in table 1. Selected bond lengths and angles are given in table 2.

Table 1. Crystallographic and experimental data for **1** and **2**.

Complex	**1**	**2**
Formula	$C_{26}H_{30}Br_2Cl_2CuN_4O_4$	$C_{32}H_{36}Br_2Cl_2Cu_2N_8O_4S_2$
Mr	756.80	1018.61
T (K)	298(2)	298(2)
Crystal shape/color	Block/blue	Block/blue
Crystal size (mm^3)	$0.20 \times 0.18 \times 0.17$	$0.30 \times 0.27 \times 0.27$
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pbcn$
Unit cell dimensions (Å, °)		
a	6.215(3)	19.019(4)
b	20.394(4)	14.169(3)
c	11.327(2)	14.871(3)
β	99.48(3)	
V (Å^3)	1416.1(5)	4007.4(14)
Z	2	4
D_{Calcd} (g cm^{-3})	1.775	1.688
μ (Mo-Kα) (mm^{-1})	3.822	3.340
$F(000)$	758	2040
Measured reflections	3195	4615
Observed reflections $I \geq 2\sigma(I)$	2494	2586
Min. and max. transmission	0.515 and 0.563	0.434 and 0.466
Parameters	178	236
Goodness-of-fit on F^2	1.037	1.007
R_1, wR_2 $[I \geq 2\sigma(I)]$[a]	0.0448, 0.1041	0.0571, 0.0983
R_1, wR_2 (all data)[a]	0.0632, 0.1137	0.1264, 0.1203
Largest diff. peak and hole (e Å^{-3})	0.556 and −0.822	0.673 and −0.512

[a] $R_1 = F_o - F_c/F_o$, $wR_2 = [\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)^2]^{1/2}$, $w_1 = [\sigma^2(F_o^2) + (0.0414(F_o^2 + 2F_c^2)/3)^2 + 1.8141(F_o^2 + 2F_c^2)/3]^{-1}$, $w_2 = [\sigma^2(F_o^2) + (0.0212(F_o^2 + 2F_c^2)/3)^2 + 5.3325(F_o^2 + 2F_c^2)/3]^{-1}$.

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

1			
Cu1–O1	1.904(2)	Cu1–N1	2.015(3)
O1–Cu1–O1$^{\text{i}}$	180	O1–Cu1–N1$^{\text{i}}$	88.6(2)
O1–Cu1–N1	91.4(2)	N1–Cu1–N1$^{\text{i}}$	180
2			
Cu1–O1	1.930(3)	Cu1–N1	1.931(4)
Cu1–N2	2.100(4)	Cu1–N3	1.940(4)
Cu1–S1$^{\text{ii}}$	2.840(4)		
O1–Cu1–N1	91.3(2)	O1–Cu1–N3	90.4(2)
N1–Cu1–N3	168.5(2)	O1–Cu1–N2	170.9(2)
N1–Cu1–N2	84.2(2)	N3–Cu1–N2	92.5(2)
O1–Cu1–S1$^{\text{ii}}$	95.8(2)	N1–Cu1–S1$^{\text{ii}}$	94.1(2)
N2–Cu1–S1$^{\text{ii}}$	92.4(2)	N3–Cu1–S1$^{\text{ii}}$	97.0(2)

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

3. Results and discussion

Complex **1** was synthesized by reaction of HL with copper(II) acetate in methanol. Considering the thiocyanate anion is a versatile bridging group in the formation of metal complexes [13–15], complex **2** was synthesized by adding ammonium thiocyanate to a methanol solution of **1**. The addition of thiocyanate leads to decrease of the solubility of the final product. The acetonitrile was added to the mixture to increase the solubility.

3.1. *IR spectra*

The IR spectra of the Schiff-base ligand HL and the two complexes provide information about the metal-ligand bonding. Assignments are based on typical group frequencies. The weak and broad absorptions at 3412 cm^{-1} arise from phenol in HL and disappear in the complexes. The strong absorption at 1645 cm^{-1} in the spectrum of HL is assigned to azomethine, ν(C=N) [16], shifted to lower wave numbers in the complexes, 1621 cm^{-1} for **1** and 1618 cm^{-1} for **2**, indicating coordination of nitrogen of the azomethine to copper(II). The strong absorption of Ar–O in HL is at 1202 cm^{-1} [17], shifting to lower frequencies for the complexes, *viz*. 1180 cm^{-1} for **1** and 1177 cm^{-1} for **2**. Strong absorption bands indicative of the bridging thiocyanate ligands in **2** are at 2067 and 2109 cm^{-1} [18], and that indicative of the lattice acetonitrile in **2** is at 2254 cm^{-1}.

3.2. *Structure of 1*

The single-crystal X-ray diffraction shows that **1** is a centrosymmetric mononuclear copper(II) compound (figure 1). The Cu atom, lying on the inversion center, is four-coordinate by two imine N and two phenolate O atoms from two Schiff-base ligands, forming square-planar coordination. The amine N atoms of the Schiff-base ligands are not coordinated to copper(II). The coordinate bond lengths are comparable to the corresponding values observed in other Schiff-base copper(II) complexes [19–21]. The plane defined by C1–C7/N1/O1/Cl1/Br1/C1$^{\text{i}}$–C7$^{\text{i}}$/N1$^{\text{i}}$/O1$^{\text{i}}$/Cl1$^{\text{i}}$/Br1$^{\text{i}}$ (symmetry code: (i) $2-x, -y, 1-z$) is approximately planar. As expected, the morpholine

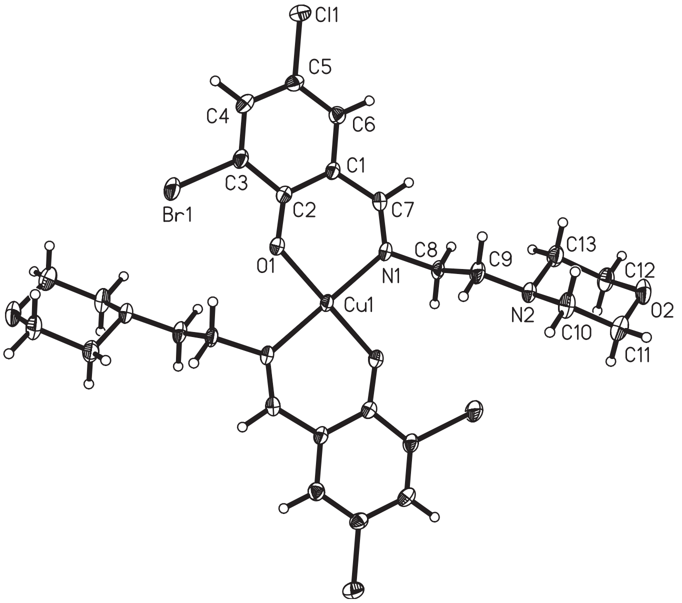

Figure 1. The structure of **1**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Unlabeled atoms are at the symmetry position $2-x, -y, 1-z$.

groups adopt chair conformations to minimize steric effects. The torsion angle of N1–C8–C9–N2 is 1.8(2)°.

3.3. *Structure of* 2

The single-crystal X-ray structural analysis shows that **2** consists of two lattice acetonitrile molecules and a double thiocyanato-bridged dinuclear copper(II) complex (figure 2). Each Cu has square-pyramidal coordination, with the NNO donor set of the Schiff-base and the terminal N atom of a bridging thiocyanate defining the basal plane, and with the terminal S^{ii} (symmetry code: (ii) $-x, -y, 1-z$) of another bridging thiocyanate ligand occupying the apical position. The Schiff-base is tridentate, and ligating to copper(II) *via* the phenolate O, imine N and amine N. The bridging thiocyanate anions are bidentate, ligating two adjacent copper(II) atoms through the end-to-end coordination.

Distortion of the square-pyramid is revealed by bond lengths and angles between apical and basal donors. The length of the apical Cu–S bond is much longer than those of the basal bonds. The basal bond lengths are within normal ranges and comparable to the corresponding values observed in other Schiff-base copper(II) complexes [15, 22–24]. The deviation of Cu1 from the least-squares plane defined by the basal donor atoms is 0.168(4) Å. The $Cu \cdots Cu^{ii}$ distance is 5.451(3) Å. The bridging thiocyanates are nearly linear and show bent coordination modes with copper(II) [N3–C14–S1 = 179.6(5)°, Cu1–N3–C14 = 169.8(4)°, $Cu1^{ii}$–S1–C14 = 92.8(5)°], as observed in other similar thiocyanato-bridged copper(II) complexes [15, 25]. As expected, the morpholine groups adopt chair conformations to minimize the steric effects, as observed in **1**. The torsion angle of N1–C8–C9–N2 is 48.6(2)°.

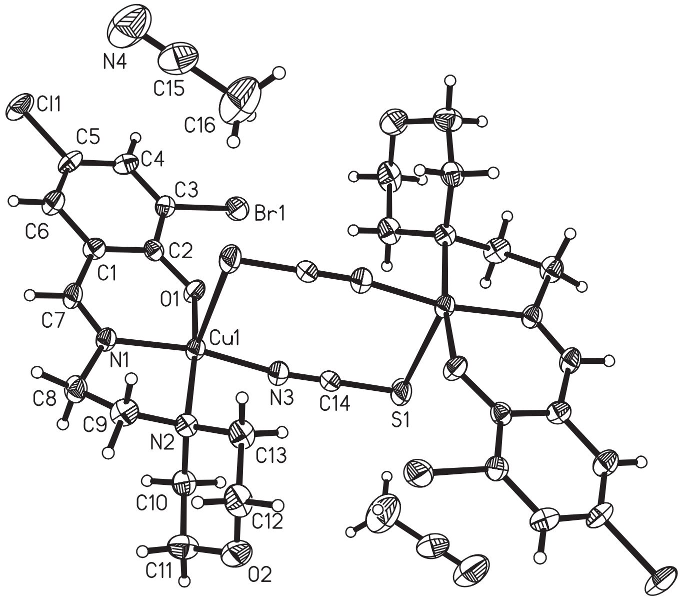

Figure 2. The structure of **2**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Unlabeled atoms are at the symmetry position $-x, -y, 1-z$.

The question arises as to whether the coordination polyhedron around five-coordinate copper ion can be described as a square-pyramid or trigonal-bipyramid. Further information can be obtained by determining the structural index τ [26] which represents the relative amount of trigonality (square pyramid, $\tau = 0$; trigonal bipyramid, $\tau = 1$; $\tau = (\beta - \alpha)/60^\circ$, α and β being the two largest angles around the central atom). The value of τ is 0.064 for each copper ion, indicating that the coordination geometry of each copper ion is square-pyramidal.

4. Conclusions

The different coordination behavior of the ligands in **1** and **2** is in accord with those observed in other Schiff-base copper(II) complexes. Schiff-base ligands similar to HL usually coordinate to copper(II) ions through the imine N and phenolate O atoms, forming square-planar coordination [27, 28], however, when thiocyanate or azide anions participate in coordination, the amine N of the Schiff-base ligands also coordinates to the copper(II) [29–32].

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