

Spectroscopic, Magnetic and Crystal Structure Analysis of Diammine-bis(2,6-dibromo-4-chlorophenolato-O)copper(II)

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The $[\text{Cu}(\text{C}_6\text{H}_2\text{Br}_2\text{ClO})_2(\text{NH}_3)_2]$ complex was synthesized and characterized by XRD, UV/vis, FTIR, DSC, elemental analysis and magnetic susceptibility measurements. The structural analysis of the title complex indicated that it is a monomeric centrosymmetric compound which crystallizes in the monoclinic system, $P2_1/c$, and has a *trans*-planar CuO_2N_2 coordination [Cu-O 1.940(5) and Cu-N 1.978(7) Å]. In the coordination sphere of the Cu atom, there are long range interactions with Br2 and the centrosymmetrically related Br2i (i: $-x, -y, -z$) atoms [Cu-Br2: 3.079(2) Å], resulting in a tetragonally elongated octahedral structure for the $\text{CuO}_2\text{N}_2\text{Br}_2$ coordination. The molecules form one-dimensional chains along the *x*-axis of the unit cell held together by intermolecular hydrogen bonds.

Key words: UV/vis, FTIR, DSC, Crystal Structure, Cu(II) Complex, Magnetic Susceptibility

Introduction

Preparation of polymers from inorganic complexes is a very interesting subject in inorganic and polymer chemistry. For instance, flame-retarding polymers, poly(dihalophenolates), can be prepared with $\text{CuL}_2(\text{THP})_2$ complexes, where L is pyridine, ethylenediamine, 2,2'-dipyridyl, or ammonia, and THP is 2,4,6-trichloro-phenolato, 2,4,6-tribromo-phenolato, 4-chloro-2,6-dibromo-phenolato or 4-fluoro-2,6-dibromo-phenolato. There are several criteria which affect the molecular weight and the structure of the polymers. These are the structure of the complexes and the kind of the ligands [1 – 5]. Therefore, in this study, the Cu(II) complex $[\text{Cu}(\text{C}_6\text{H}_2\text{ClBr}_2\text{O})_2(\text{NH}_3)_2]$ has been prepared and characterized by structural, spectroscopic, thermal, and elemental analysis, and magnetic susceptibility measurements. The polymerization study with the title complex is currently under investigation.

Experimental Section

Preparation of potassium 2,6-dibromo-4-chloro-phenolate

4-Chlorophenol was brominated by adding a solution containing 0.1 M bromine and 0.15 M KBr in 150 ml of distilled water to another solution containing stoichiometric amounts of the phenol in the minimum amount of ethanol very slowly.

The solution with a white precipitate was cooled in an ice bath for 20 minutes, filtered and then dried in a vacuum oven. The structure and the purity of the product were established by the ^1H NMR spectrum [6].

Preparation of the diammine-bis(2,6-dibromo-4-chloro-phenolato-O)copper(II) complex

An aqueous solution (15 ml) of potassium 2,6-dibromo-4-chloro-phenolate was prepared by adding an excess of KOH (0.12 g, 3 mmol) dissolved in water (10 ml) to 2,6-dibromo-4-chloro-phenol (0.43 g, 1.5 mmol) solution dissolved in water (5 ml). This solution was added dropwise to a concentrated aqueous solution (5 ml) of CuSO_4 (0.12 g, 0.75 mmol) with stirring. Initially, the formation of a dark brown precipitate was observed. Upon addition of all 2,6-dibromo-4-chloro-phenolate solution, the dark brown precipitate turned to a light blue color. Concentrated ammonia (13 ml, 0.695 mol) and water (60 ml) were added to this mixture until the light blue precipitate dissolved to give a clear dark blue solution. Upon leaving this solution in a dark place for several days, dark brown crystals were formed. These crystals were collected, washed with cold water and dried in a vacuum overnight [2, 3].

Structure determination

To determine the crystal structure of the title compound X-ray diffraction data were collected at room temperature with graphite-monochromated $\text{Mo-K}\alpha$ radiation on an Enraf-

Table 1. Summary of crystallographic data.

Formula	[Cu(C ₆ H ₂ Br ₂ ClO) ₂ (NH ₃) ₂]
Fw	668.27
Wavelength [Å]	0.71073
Temperature [°C]	25
Crystal shape	needle
Crystal color	dark-brown
Crystal size [mm ³]	0.40 × 0.20 × 0.15
Crystal system	monoclinic
Space group	P2 ₁ /n (no. 14)
a [Å]	4.887(3)
b [Å]	12.760(8)
c [Å]	15.243(4)
β	92.77(3)
V [Å ³]	949.4(9)
Z	2
D _{calc} [g/cm ³]	2.338
Absorption coefficient [mm ⁻¹]	9.856
F(000)	630
Scan method	ω/2θ
2θ _{max} [°]	52.6
Index range	0 ≤ h ≤ 6, 0 ≤ k ≤ 15, -18 ≤ l ≤ 18
No. of reflections collected	2135
No. of reflections unique	1909
No. of variables	106
Max shift/esd	0.992
Phasing method	direct methods
R/Rw(%)	0.0543/0.1305

Nonius CAD4 diffractometer [7]. The cell parameters were determined from a least-squares refinement of 25 centred reflections in the range of $8.45 \leq \theta \leq 18.84^\circ$. Cell refinement was carried out using CAD-4 EXPRESS. During data collection, three standard reflections were periodically measured every 120 minutes, showing no significant intensity variation. Data reduction was carried out using SHELXL97 [8].

The structure was solved by direct methods using the program SHELXS97 [8] in the WinGX package [9]. ψ -Scan absorption correction was applied ($T_{\min} = 0.108$, $T_{\max} = 0.228$). A full-matrix least-squares refinement on F^2 was done. For all non-hydrogen atoms anisotropic displacement parameters were refined. All hydrogen atoms were placed geometrically and a riding model was used with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$ and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{N})$. Electron density synthesis with coefficients $F_o - F_c$: A positive residual electron density of $1.21 \text{ e}/\text{\AA}^3$ was observed at a distance of 0.95 \AA from the Cu atom and negative residual electron density of $-1.29 \text{ e}/\text{\AA}^3$ at a distance of 1.01 \AA from the Br1 atom. The data collection details, crystal data and refinement parameters are summarised in Table 1. The atomic coordinates and isotropic displacement parameters are listed in Table 2, selected bond lengths and angles are given in Table 3 and the ORTEP drawing is given in Fig. 1. Displacements ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles with arbitrary radii.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for non-hydrogen atoms.

Atom	x	y	z	U_{eq} [Å ²]
Cu	0	0	0	0.0294(4)
O	0.1796(11)	-0.0134(5)	-0.1102(3)	0.0364(15)
N	0.2881(14)	-0.0902(6)	0.0558(5)	0.0395(18)
Br1	0.3415(2)	0.12859(9)	-0.25975(7)	0.0563(4)
Br2	-0.2272(2)	-0.19807(7)	-0.09304(6)	0.0448(3)
Cl	-0.3637(8)	-0.1304(3)	-0.44875(18)	0.0850(11)
C1	0.0509(17)	-0.0378(7)	-0.1852(5)	0.033(2)
C2	0.0994(18)	0.0119(7)	-0.2643(5)	0.037(2)
C3	-0.021(2)	-0.0134(8)	-0.3440(6)	0.048(3)
C4	-0.207(2)	-0.0939(8)	-0.3472(6)	0.052(3)
C5	-0.2723(19)	-0.1471(8)	-0.2731(6)	0.044(2)
C6	-0.1431(18)	-0.1203(7)	-0.1952(5)	0.034(2)
H1A	0.2562	-0.0988	0.1123	0.059
H1B	0.4509	-0.06	0.0509	0.059
H1C	0.2868	-0.1523	0.0292	0.059
H3	0.022	0.0227	-0.3945	0.057
H5	-0.402	-0.2005	-0.276	0.053

Table 3. Selected bond lengths (Å) and bond angles (°).

Cu–O	1.940(5)	Cu–N	1.978(7)
Cu–Br2	3.079(2)	Br1–C2	1.901(9)
Br2–C6	1.908(8)	Cl–C4	1.757(9)
O–C1	1.315(9)		
O–Cu–N	88.8(3)	O–Cu–N	91.2(3)
Br2–Cu–O	72.4(2)	Br2–Cu–N	87.4(2)
C1–O–Cu	123.8(5)	C3–C2–Br1	117.3(7)
C1–C2–Br1	117.2(7)	C5–C6–Br2	118.2(7)
C1–C6–Br2	117.9(6)	C5–C4–Cl	119.1(8)
C3–C4–Cl	119.4(8)		

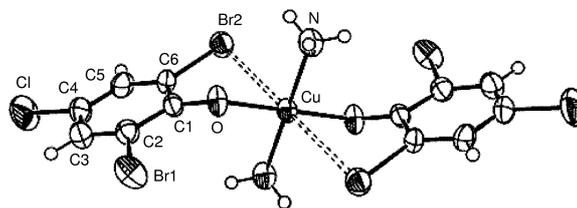


Fig. 1. ORTEP [10] drawing of the title molecule with the atom numbering scheme.

A differential scanning calorimeter, DSC, was used in order to investigate the thermal behaviour of the complex. The thermogram was taken with a heating of $1 \text{ }^\circ\text{C}/\text{min}$ under atmospheric conditions by a Dupont thermal analyst 2000 DSC 910S model differential scanning calorimeter. At $170.02 \text{ }^\circ\text{C}$, a sharp exothermic peak was observed.

Results and Discussion

Crystal structure

We previously reported the structures of the isostructural complexes $[\text{Cu}(\text{C}_6\text{H}_2\text{Br}_3\text{O})_2(\text{NH}_3)_2]$ [3] and $[\text{Cu}(\text{C}_6\text{H}_2\text{Cl}_3\text{O})_2(\text{NH}_3)_2]$ [2]. In these complexes, the

Table 4. Coordination bond lengths (Å) and angles (°) for three isostructural copper complexes.

	[Cu(C ₆ H ₂ -Cl ₃ O) ₂ (NH ₃) ₂]	[Cu(C ₆ H ₂ -Br ₃ O) ₂ (NH ₃) ₂]	[Cu(C ₆ H ₂ -Br ₂ ClO) ₂ (NH ₃) ₂]
Cu–Br	–	3.129(1)	3.079(2)
Cu–Cl	2.982(1)	–	–
Cu–O	1.946(2)	1.943(5)	1.940(5)
Cu–N	1.984(2)	1.977(6)	1.978(7)
O–Cu–N	90.66(9)	89.1(2)	88.8(3)
Br–Cu–O	–	70.9(2)	72.4(2)
Br–Cu–N	–	87.1(2)	87.4(2)
Cl–Cu–O	71.20(7)	–	–
Cl–Cu–N	86.99(8)	–	–

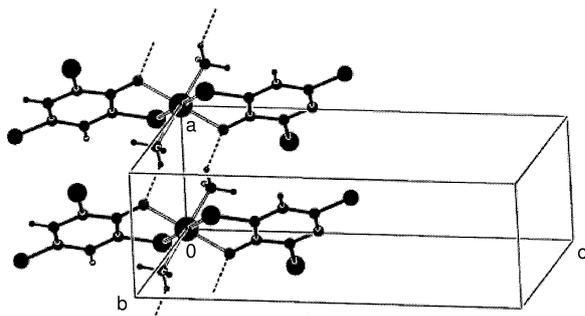


Fig. 2. Hydrogen bonding geometry and the molecular packing.

copper atom is located at the inversion centre. The coordination around the Cu atom is a tetragonally elongated octahedron involving centrocymetrically related O and N atoms from THP molecules in the equatorial plane, and Br and Cl atoms with secondary interaction in the axial positions, respectively. In the present study, [Cu(C₆H₂Br₂ClO)₂(NH₃)₂] is reported. The coordination sphere of the Cu atom is similar to that of the isostructural complexes (Table 3). A comparison of the bond lengths and angles is given in Table 4 for the three isostructural complexes. The remarkable similarity of the three structures is obvious.

The dihedral angle between the O/Cu/N plane and the least-squares plane defined by the six-membered ring (C1...C6) is 80.8(2)° (Fig. 1). This is slightly smaller than the corresponding values of 81.7(1)° and 82.6(2)° observed in the Cu-tribromophenolate [3] and Cu-trichlorophenolate [2] complexes, respectively. The O/Cu/Br₂ and N/Cu/Br₂ planes are almost perpendicular to each other. The dihedral angle between these two planes is 89.5(2)°. The Br₂/Cu/O/Cl/C6 ring has an envelope conformation.

The hydrogen bonding and molecular packing geometry of the title molecule was calculated

with PLATON [11]. There is an intermolecular N–H1B...Oⁱⁱ hydrogen bond with D...A and H...A distances of 2.999(9) and 2.19 Å, respectively and a D–H...A angle of 150.8(5)° [symmetry code ii: 1 – x, –y, –x]. As shown in Fig. 2, the complexes form hydrogen bonded polymeric bands of [Cu(C₆H₂Br₂ClO)₂(NH₃)₂] molecules which are lined up along the [100] direction like as the isostructural complexes [2, 3]. There is a difference in the hydrogen bonding geometry between the title molecule and the isostructural molecules reported previously [Cu(C₆H₂Br₃O)₂(NH₃)₂] [3] and [Cu(C₆H₂Cl₃O)₂(NH₃)₂] [2]. These molecules have two intermolecular hydrogen bonds, but [Cu(C₆H₂Br₂ClO)₂(NH₃)₂] has only one. However, all these molecules show a similar molecular packing geometry. The shortest intermolecular contact less than the sum of the van der Waals Radii was observed between Cu and H1Bⁱⁱ [2.9311 Å << 3.52 Å].

UV/vis

The UV/vis electronic spectra of the title complex and of the ligand, 2,6-dibromo-4-chlorophenolate, and detailed data are given in Figs 3, 4 and Table 5, respectively. The complex has intense peaks at 208, 290 and 296 nm, shoulders at 222 and 318 nm, and a broad peak at 410 nm. The ligand has intense peaks at 208, 290, 296 nm and a shoulder at 222 nm. It is well known that π electrons of a phenol give characteristic ultraviolet absorption bands between 200 and 300 nm [12]. The ligand displays four absorption bands which might originate from $\pi \rightarrow \pi^*$ transitions. Their peak intensities are about half as large as the corresponding peaks of the complex. The shoulder at 318 nm and a broad peak at 410 nm for the title complex might be due to

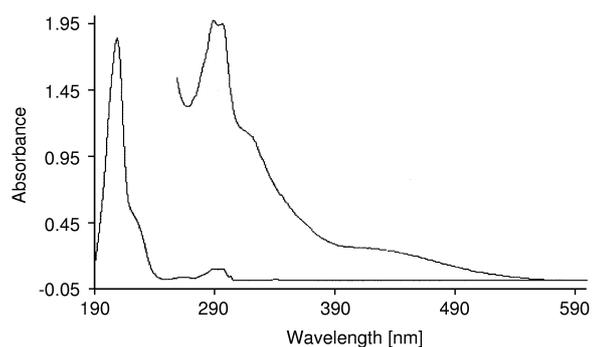
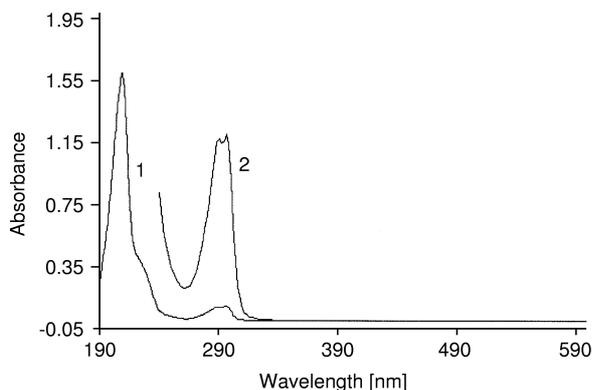
Fig. 3. UV/vis spectrum of the complex in an acetonitrile solvent. Curve 1: 3.5×10^{-4} M; curve 2: 2.02×10^{-5} M in [Cu(C₆H₂ClBr₂O)₂(NH₃)₂].

Table 5. UV/vis data λ_{\max} [nm] (ϵ [l/mol⁻¹cm⁻¹]) of the title complex and the ligand.

[Cu(C ₆ H ₂ ClBr ₂ O) ₂ (NH ₃) ₂]	[C ₆ H ₂ ClBr ₂ O] ⁻ K ⁺
208 (89100)	208 (44500)
222 (25150) (sh)	222 (12500) (sh)
290 (5810)	290 (2900)
296 (6050)	296 (3000)
318 (2990) (sh)	
410 (980) (broad)	

Fig. 4. UV/vis spectrum of the ligand in an acetonitrile solvent. Curve 1: 3.6×10^{-5} M K[C₆H₂ClBr₂O]; curve 2: 4.14×10^{-4} M in K[C₆H₂ClBr₂O].

d-d transitions and/or ligand to metal charge transfer transitions in the complex. The color of the complex in an acetonitrile solution is yellow and one of the d-d transitions is observed in the violet region of the spectrum as it is expected.

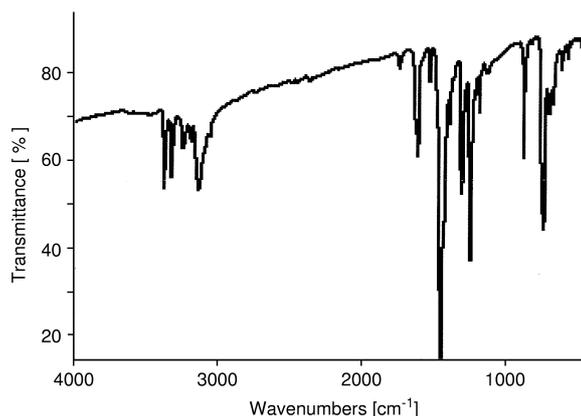
IR data

The FTIR spectrum of the Cu(II) complex is given in Fig. 5 and the characteristic bands are:

$\gamma_{(\text{N-H})}$ and $\gamma_{(\text{C-H aromatic})} = 3500 - 3000 \text{ cm}^{-1}$,
 $\gamma_{(\text{aromatic rings})} = 1602 \text{ cm}^{-1}$, $\gamma_{(\text{C=C ring stretchings})} = 1460 - 1260 \text{ cm}^{-1}$, $\gamma_{(\text{C-O})} = 1225 \text{ cm}^{-1}$,
 $\gamma_{(\text{C-H bending})} = 855 \text{ cm}^{-1}$, $\gamma_{(\text{C-Cl})} = 800 - 650 \text{ cm}^{-1}$,
 $\gamma_{(\text{C-Br})} = 750 - 600 \text{ cm}^{-1}$ and $\gamma_{(\text{C=C bending})} = 438 \text{ cm}^{-1}$ [13, 14].

Magnetic susceptibility

Magnetic susceptibility measurement was performed at room temperature using a Sherwood magnetic susceptibility balance. The magnetic moment of

Fig. 5. FTIR spectrum of [Cu(C₆H₂ClBr₂O)₂(NH₃)₂].

the title complex was found to be $1.85 \mu\text{B}$. The calculated spin-only magnetic moment ($\mu/\mu\text{B}$) for a single unpaired electron complexes is $1.73 \mu\text{B}$. The difference might be due to spin-orbit coupling [15] which was also observed for the [Cu(C₆H₂I₃O)₂(NH₃)₂] complex [13].

Conclusions

The crystal structure of [Cu(C₆H₂Br₂ClO)₂(NH₃)₂] has been determined by X-ray diffraction. It crystallizes in the monoclinic system and shows a *trans*-planar CuO₂N₂ coordination sphere, with the fifth and sixth coordination sites occupied by Br atoms of the phenoxide ions to form a tetragonally elongated octahedral structure. Intermolecular hydrogen bonds hold the complex molecules together in a one-dimensional chain.

The complex [Cu(C₆H₂Br₂ClO)₂(NH₃)₂] has intense UV/vis absorption peaks at 208, 290 and 296 nm, and a shoulder at 222 nm tentatively assigned to $\pi \rightarrow \pi^*$ transitions of the 2,6-dibromo-4-chloro-phenolate ligand, and a shoulder at 318 nm and a broad peak at 410 nm probably due to d-d transitions and/or ligand to metal charge transfer transitions. The magnetic susceptibility data indicate that the title complex has a d⁹ electron configuration with one unpaired electron as expected.

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