

## Diamminebis(2,4,6-tribromophenolato-O)copper(II)

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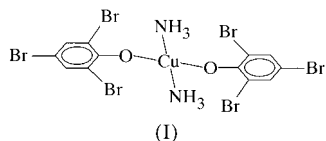
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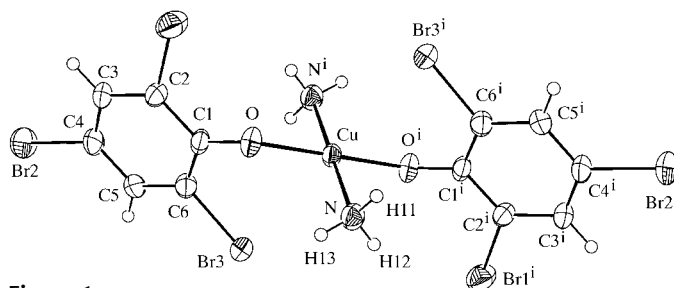
The title compound,  $[\text{Cu}(\text{C}_6\text{H}_2\text{Br}_3\text{O})_2(\text{NH}_3)_2]$ , a monomeric centrosymmetric  $\text{Cu}^{\text{II}}$  complex, crystallizes in the monoclinic system. The  $\text{CuO}_2\text{N}_2$  coordination sphere is *trans* planar, [ $\text{Cu}-\text{O}$  1.943 (5) Å and  $\text{Cu}-\text{N}$  1.977 (6) Å], with the fifth and sixth coordination sites occupied by Br atoms from the phenoxide ions [ $\text{Cu}-\text{Br}$  3.129 (1) Å], resulting in an elongated distorted octahedral structure for the  $\text{CuO}_2\text{N}_2\text{Br}_2$  coordination. Each of the  $\text{NH}_3$  groups forms two hydrogen bonds with the Br and O atoms of the  $\text{CuO}_2\text{N}_2\text{Br}_2$  moiety of a neighbouring molecule. This arrangement constitutes a one-dimensional chain along the *x* axis of the unit cell.

### Comment

Several complexes of  $\text{CuL}_2(\text{THP})_2$  have been utilized to synthesize poly(dihalophenylene oxide) using either thermal polymerization or electro-initiation in solution as well as in the solid state ( $L$  = pyridine or ethylenediamine, THP = 2,4,6-trichlorophenolato, 2,4,6-tribromophenolato, 4-chloro-2,6-dibromophenolato or 4-fluoro-2,6-dibromophenolato; Baştürkmen *et al.*, 1993; Kısakürek *et al.*, 1998; Şanlı *et al.*, 1995; Toppare *et al.*, 1990). Halogenated poly(phenylene oxides) exhibit interesting mechanical, electrical and thermal properties, such as fire resistivity. Investigations have showed that  $L$ , the halogens and their positions in the complex affect the mechanism of polymerization (Pulat *et al.*, 1994). The title complex, (I), has been prepared and its crystal structure studied in order to obtain a better understanding of the polymerization process.

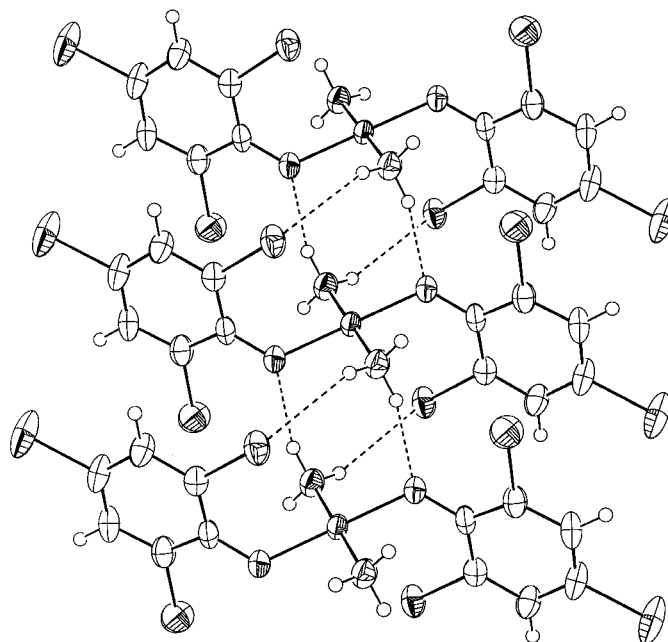


We have previously reported the structures of other complexes of this type, namely  $[\text{Co}(\text{C}_6\text{H}_2\text{Br}_3\text{O})_2(\text{C}_5\text{H}_5\text{N})_2]$  (Ülkü *et al.*, 1997) and  $[\text{Cu}(\text{C}_6\text{H}_2\text{Cl}_3\text{O})_2(\text{NH}_3)_2]$  (Göktaş *et al.*, 1999). The latter complex is isostructural with (I) but not with the former. Using a different nitrogen-donor ligand


**Figure 1**

ORTEP-3 for Windows (Farrugia, 1997) drawing of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii. Symmetry code as in Table 1.

affects the coordination sphere around the transition metal. In the isostructural complexes, the Cu atom is located in the inversion centre at the origin. The coordination around the Cu atom is a tetragonally elongated octahedron, involving centrosymmetrically related O and N atoms from two THP molecules in the equatorial plane and with Br atoms as a secondary interaction in the axial positions. In (I), the bond lengths  $\text{Cu}-\text{N}$ ,  $\text{Cu}-\text{O}$  and  $\text{Cu}-\text{Br}$  are 1.977 (6), 1.943 (5) and 3.129 (1) Å, respectively. The bond angles  $\text{N}-\text{Cu}-\text{O}$  [ $89.1 (2)^\circ$ ],  $\text{N}-\text{Cu}-\text{O}^i$  [ $90.9 (2)^\circ$ ; symmetry code: (i)  $-x, -y, -z$ ],  $\text{Br}-\text{Cu}-\text{N}$  [ $87.1 (2)^\circ$ ] and  $\text{Br}-\text{Cu}-\text{O}$  [ $70.9 (2)^\circ$ ] indicate that the tetragonally elongated octahedron is distorted. The  $\text{Br}-\text{Br}^i$  axis has a more noticeable tilt towards the  $\text{Cu}-\text{O}$  bond than towards the  $\text{Cu}-\text{N}$  bond. These bond lengths and angles are very similar to the corresponding values observed in the isostructural complex where Br atoms are replaced by Cl atoms. On the other hand, in the Co complex mentioned


**Figure 2**

PLATON99 (Spek, 1990) drawing illustrating the hydrogen bonding in (I).

above, the coordination around the Co atom is a distorted tetrahedron.

The dihedral angle between the equatorial plane (N/O/N<sup>i</sup>/O<sup>j</sup>) around the Cu atom and the six-membered bromophenol ring (C1–C6) is 82.6 (2)°. This is similar to the corresponding value of 81.7 (1)° observed in the Cu–tribromophenol complex. The C–C bond lengths in the tribromophenol ligand have values between 1.37 (1) and 1.40 (1) Å, which indicates delocalization of the double bonds (Csp<sup>2</sup>–Csp<sup>2</sup>) within the tribromophenol ring.

Intermolecular hydrogen bonds exist between the H atoms of the NH<sub>3</sub> group and one of the Br atoms of one 2,4,6-tribromophenol ligand, as well as the O atom of the second 2,4,6-tribromophenol ligand. The two ligands are *trans* to each other. This constitutes a one-dimensional chain along the [100] direction, where neighbouring centrosymmetric molecules are linked through four intermolecular hydrogen bonds, keeping the structure together. Hydrogen bonds were calculated with PLATON99 (Spek, 1990). Details of the hydrogen-bonding geometry are given in Table 2. The closest contacts between the chains are between Cu–H11(1 + x, y, z) [3.1217 (2) Å] and Br1–H5(½ – x, –½ + y, ½ – z) [3.1357 Å]. High residual electron-density regions were observed within 0.9 Å of the Br atoms.

## Experimental

An aqueous solution (25 ml) of sodium 2,4,6-tribromophenolate was prepared by mixing excess NaOH (0.21500 g, 0.00537 mol) dissolved in water (10 ml) with 2,4,6-tribromophenolate (0.87384 g, 0.00264 mol) in water (15 ml). This solution was added dropwise to a concentrated aqueous solution (5 ml) of CuSO<sub>4</sub> (0.21073 g, 0.00132 mol) with stirring. Initially, the formation of a light-brown precipitate was observed. The precipitate colour then turned to light blue after addition of all of the 2,4,6-tribromophenolate solution. Concentrated ammonia (5.2 ml, 0.06947 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 on the bench for several days, dark-brown precipitates were formed. These crystals were collected, washed with a small amount of cold water, dried in a vacuum overnight and used for X-ray data collection. Elemental analysis found for C<sub>12</sub>H<sub>10</sub>Br<sub>6</sub>CuN<sub>2</sub>O<sub>2</sub>: C 19.27, H 1.36, N 3.55%; calculated: C 19.03, H 1.33, N 3.70%.

**Table 1**

Selected geometric parameters (Å, °).

Cu–O	1.943 (5)	Br2–C4	1.903 (8)
Cu–N	1.977 (6)	Br3–C6	1.909 (7)
Cu–Br3	3.129 (1)	O–C1	1.322 (8)
Br1–C2	1.888 (8)		
N–Cu–O	89.1 (2)	Br1–C2–C1	118.5 (5)
N–Cu–O <sup>i</sup>	90.9 (2)	Br1–C2–C3	117.9 (6)
Br3–Cu–N	87.1 (2)	Br2–C4–C3	118.9 (6)
Br3–Cu–O	70.9 (2)	Br2–C4–C5	119.5 (7)
Cu–O–C1	123.7 (4)	Br3–C6–C1	118.4 (5)
O–C1–C2	122.1 (7)	Br3–C6–C5	117.5 (6)
O–C1–C6	123.8 (6)		

Symmetry code: (i) –x, –y, –z.

**Table 2**

Hydrogen-bonding geometry (Å, °).

D–H...A	D–H	H...A	D...A	D–H...A
N–H11...O <sup>i</sup>	0.96	2.06	2.976 (7)	159
N–H13...Br3 <sup>ii</sup>	0.86	2.85	3.648 (6)	157

Symmetry codes: (i) –1 – x, –y, –z; (ii) x – 1, y, z.

## Crystal data

[Cu(C <sub>6</sub> H <sub>3</sub> Br <sub>3</sub> O) <sub>2</sub> (NH <sub>3</sub> ) <sub>2</sub> ]	<i>D</i> <sub>x</sub> = 2.573 Mg m <sup>–3</sup>
<i>M</i> <sub>r</sub> = 757.2	Cu Kα radiation
Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>	Cell parameters from 25 reflections
<i>a</i> = 4.8249 (5) Å	<i>θ</i> = 12.89–42.94°
<i>b</i> = 13.0267 (16) Å	<i>μ</i> = 16.02 mm <sup>–1</sup>
<i>c</i> = 15.5518 (11) Å	<i>T</i> = 295 K
<i>β</i> = 90.766 (7)°	Prismatic, dark brown
<i>V</i> = 977.4 (1) Å <sup>3</sup>	0.10 × 0.10 × 0.08 mm
<i>Z</i> = 2	

## Data collection

Enraf–Nonius CAD-4 diffractometer	<i>R</i> <sub>int</sub> = 0.030
<i>ω</i> / <i>θ</i> scans	<i>θ</i> <sub>max</sub> = 74.3°
Absorption correction: empirical via <i>ψ</i> scans (Fair, 1990)	<i>h</i> = 0 → 6
<i>T</i> <sub>min</sub> = 0.239, <i>T</i> <sub>max</sub> = 0.301	<i>k</i> = –16 → 0
2330 measured reflections	<i>l</i> = –19 → 19
1979 independent reflections	3 standard reflections
1662 reflections with <i>I</i> > 2σ( <i>I</i> )	frequency: 120 min
	intensity decay: 0.05%

## Refinement

Refinement on <i>F</i>	H-atom parameters constrained
<i>R</i> = 0.045	<i>w</i> = 1/[σ <sup>2</sup> ( <i>F</i> ) + (0.02 <i>F</i> ) <sup>2</sup> + 0.64]
<i>wR</i> = 0.057	(Δ/σ) <sub>max</sub> < 0.001
<i>S</i> = 1.00	Δρ <sub>max</sub> = 0.57 e Å <sup>–3</sup>
1662 reflections	Δρ <sub>min</sub> = –1.25 e Å <sup>–3</sup>
106 parameters	

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1993); cell refinement: CAD-4 EXPRESS; data reduction: MolEN (Fair, 1990); program(s) used to solve structure: MolEN; program(s) used to refine structure: MolEN; molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: MolEN and PLATON99 (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1366). Services for accessing these data are described at the back of the journal.

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