

Crystal data[Ag(C₁₉H₁₅N₅)(C₁₈H₁₅P)₂]-
ClO₄ $M_r = 1045.22$

Monoclinic

 $P2_1/c$ $a = 16.7610(2) \text{ \AA}$ $b = 14.2287(2) \text{ \AA}$ $c = 21.1305(2) \text{ \AA}$ $\beta = 97.691(1)^\circ$ $V = 4994.02(10) \text{ \AA}^3$ $Z = 4$ $D_x = 1.390 \text{ Mg m}^{-3}$ D_m not measuredMo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$ Cell parameters from 8192
reflections $\theta = 1.23\text{--}28.36^\circ$ $\mu = 0.572 \text{ mm}^{-1}$ $T = 293(2) \text{ K}$

Slab

 $0.38 \times 0.36 \times 0.18 \text{ mm}$

Colourless

*Data collection*Siemens SMART CCD area-
detector diffractometer ω scans

Absorption correction:

empirical (SADABS;

Sheldrick, 1996)

 $T_{\min} = 0.812, T_{\max} = 0.904$

33 642 measured reflections

12 270 independent
reflections8462 reflections with
 $I > 2\sigma(I)$ $R_{\text{int}} = 0.045$ $\theta_{\max} = 28.26^\circ$ $h = -22 \rightarrow 19$ $k = -15 \rightarrow 18$ $l = -28 \rightarrow 23$ *Refinement*Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.040$ $wR(F^2) = 0.111$ $S = 1.047$

12 270 reflections

641 parameters

H atoms constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0503P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} = 0.002$ $\Delta\rho_{\max} = 0.330 \text{ e \AA}^{-3}$ $\Delta\rho_{\min} = -0.357 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

*International Tables for
Crystallography* (Vol. C)Table 1. Selected geometric parameters ($\text{\AA}, ^\circ$)

P1—C19	1.818 (3)	P2—C7	1.826 (3)
P1—C31	1.826 (3)	P2—C1	1.826 (3)
P1—C25	1.829 (3)	P2—C13	1.834 (3)
N1—Ag1—P1	120.04 (5)	P1—Ag1—P2	122.99 (2)
N1—Ag1—P2	111.87 (5)	P1—Ag1—N4	119.39 (5)

Table 2. Hydrogen-bonding geometry ($\text{\AA}, ^\circ$)

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
C48—H48A \cdots O4A ⁱ	0.93	2.47	3.36 (1)	160
C49—H49A \cdots O4A ⁱⁱ	0.93	2.56	3.37 (1)	146

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

The perchlorate ion is highly disordered. The O2, O3 and O4 atoms were refined with 60 and 40% occupancies for the two conformers, while the O1 atom was refined with full occupancy.

Data collection: SMART (Siemens, 1996). Cell refinement: SAINT (Siemens, 1996). Data reduction: SAINT. Program(s) used to solve structure: SHELXTL (Sheldrick, 1997). Program(s) used to refine structure: SHELXTL. Molecular graphics: SHELXTL. Software used to prepare material for publication: SHELXTL and PARST (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1429). Services for accessing these data are described at the back of the journal.

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Diamminebis(2,4,6-trichlorophenolato)-copper(II)

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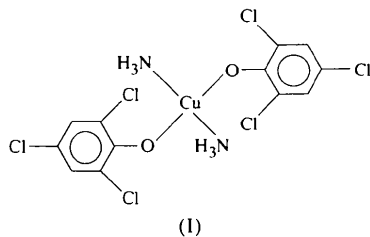
Abstract

The crystal structure of the title compound, [Cu(C₆H₂Cl₃O)₂(NH₃)₂], has been determined by X-ray diffraction. The title monomeric centrosymmetric Cu^{II} complex

crystallizes in the monoclinic system. The CuO₂N₂ coordination sphere is *trans*-planar [Cu—O1 = 1.946 (2) and Cu—N1 = 1.984 (2) Å], with the fifth and sixth coordination sites blocked by Cl atoms from the phenoxide ions [Cu—Cl1 = 2.982 (1) Å] to form a tetragonally elongated octahedral structure for CuO₂N₂Cl₂ coordination. Intermolecular hydrogen bonds hold the complex molecules together in a one-dimensional chain.

Comment

CuL₂(THP)₂-type complexes (where THP is 2,4,6-trihalophenol and *L* is pyridine, tetramethylethylenediamine, 2,2'-dipyridyl or ammonia) are important starting materials for the preparation of poly(dihalophenylene oxide) polymers (Harrod, 1969; Baştürkmen *et al.*, 1993). It is believed that the structure of the complex and the kind of ligand in these Cu^{II} complexes have significant effects on polymerization. This is currently under investigation (Kısakürek, 1996). Although some of the X-ray crystal structures of Cu^{II} complexes with phenolate ligands, such as bis(2,4,6-trichlorophenolato)(*N,N,N',N'*-tetramethylethylenediamine)copper(II), bis(4-formyl-2-methoxyphenolato)bis(pyridine)copper(II) hydrate and bis(2-methoxy-4-nitrophenolato)bis(pyridine)copper(II) (Bullock *et al.*, 1974), have been studied previously, no work has been performed on the simple diamminebis(2,4,6-trichlorophenolato)copper(II) complex, (I). In this work, the crystal structure of (I) has been determined. The polymerization with this complex is currently under investigation.



It was found that the Cu^{II} complex has a tetragonally elongated octahedral structure, with bond angles of 90.66 (9) and 179.99 (1)° for N1—Cu—O1 and Cl1—Cu—Cl1', respectively [symmetry code (i): $-x, -y, -z$] (Fig. 1). The Cu—N1 bond length [1.984 (2) Å] is slightly longer than the Cu—O1 bond length [1.946 (2) Å] in the coordination plane. The Cu—O distance is very close to that in bis(4-formyl-2-methoxyphenolato)bis(pyridine)copper(II) hydrate [1.939 (4) Å], while the Cu—N bond length is slightly shorter than that for a similar complex [2.061 (7) Å; Hobson *et al.*, 1973]. This might be due to the smaller size and more basic character of ammonia compared with pyridine. The Cu—Cl1 distance [2.982 (1) Å] is close to the average value of the Cu—Cl distances found in other complexes

where the Cl atom is coordinated to copper in the axial position as in the title complex (Ladd & Perrins, 1980; Marengo-Rullan & Willett, 1986). The dihedral angle between the coordination plane around copper (N1, O1, N1' and O1') and the trichlorophenol plane (C1—C6) is 81.7 (1)°. The C—C bond lengths in the trichlorophenol ligand range between 1.374 (4) and 1.409 (4) Å. These values are between a C—C single-bond length of about 1.530 Å and a C=C double-bond length of about 1.312 Å (Tahir *et al.*, 1997). This indicates delocalization of the double bonds (Csp²—Csp²) within the trichlorophenol ring.

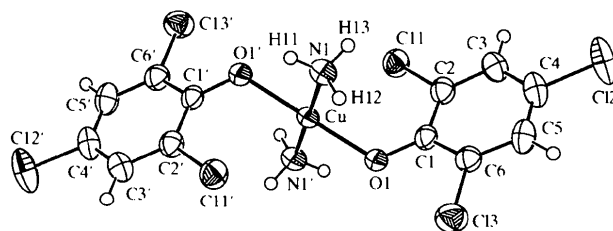


Fig. 1. ORTEP-3 (Farrugia, 1997) drawing of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles with arbitrary radii.

Intermolecular hydrogen bonds hold the complex molecules together in a one-dimensional chain (Fig. 2). The hydrogen bonds are formed between H atoms of ammonia and the chlorine of one 2,4,6 trichlorophenol ligand and the oxygen of the second 2,4,6-trichlorophenol ligand, which are in *trans* positions, *i.e.*

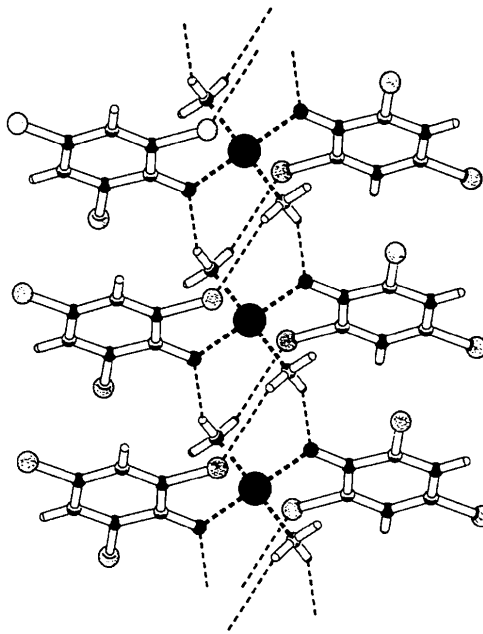


Fig. 2. PLATON (Spek, 1990) drawing illustrating the hydrogen bonding.

H11···Cl1(1 - x, -y, -z) and H13···O1(1 + x, y, z). Hydrogen bonds were calculated with *PLATON* (Spek, 1990) and details are given in Table 3.

Experimental

An aqueous solution (42 ml) of sodium 2,4,6-trichlorophenolate (0.805 g, 0.00408 mol), which was prepared by adding excess concentrated NaOH (0.428 g, 0.01205 mol) to 2,4,6-trichlorophenol in water, was added dropwise to a concentrated aqueous solution (10 ml) of CuSO₄ (0.325 g, 0.00204 mol) with stirring. Immediate formation of a dark-brown precipitate was observed. This dark-brown precipitate turned light blue after addition of the sodium 2,4,6-trichlorophenolate solution was complete. Concentrated ammonia (0.1338 mol, 10 ml) solution was 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 crystals were formed. These crystals were collected, washed with a small amount of cold water and dried in a vacuum overnight and used for X-ray data collection. Elemental analysis found for C₁₂H₁₀Cl₆CuN₂O₂: C 29.50, H 2.16, N 5.68%; calculated: C 29.39, H 2.06, N 5.71%.

Crystal data

[Cu(C₆H₂Cl₃O)₂(NH₃)₂]

M_r = 490.48

Monoclinic

*P*₂/n

a = 4.7711 (7) Å

b = 12.4592 (10) Å

c = 14.9907 (13) Å

β = 94.37 (1)°

V = 888.5 (2) Å³

Z = 2

D_x = 1.833 Mg m⁻³

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 9.55–18.33°

μ = 2.15 mm⁻¹

T = 295 K

Prismatic

0.40 × 0.15 × 0.15 mm

Dark brown

Data collection

Enraf–Nonius CAD-4 diffractometer

ω/2θ scans

Absorption correction:

empirical *via* ψ scans

(Fair, 1990)

T_{min} = 0.690, *T_{max}* = 0.724

1965 measured reflections

1748 independent reflections

1448 reflections with *I* > σ(*I*)

R_{int} = 0.028

θ_{max} = 26.17°

h = -5 → 0

k = -15 → 0

l = -18 → 18

3 standard reflections

frequency: 120 min

intensity decay: 0.107%

Refinement

Refinement on *F*²

R = 0.031

wR = 0.038

S = 1.00

1448 reflections

106 parameters

H atoms: see below

w = 1/[σ(*F*)² + (0.02*F*)²

+ 0.35], except *w* = 0

if *F*² < σ*F*²

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.454 e Å⁻³

Δρ_{min} = -0.496 e Å⁻³

Extinction correction: none

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i \sum_j U^{ij} a^i a^j a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Cu	0	0	0	0.0328 (1)
Cl1	0.2293 (2)	-0.18966 (6)	0.10262 (5)	0.0476 (2)
Cl2	0.3972 (3)	-0.13174 (8)	0.45771 (6)	0.0755 (3)
Cl3	-0.3286 (2)	0.12300 (7)	0.26487 (6)	0.0548 (3)
O1	-0.1777 (4)	-0.0084 (2)	0.1124 (1)	0.0417 (5)
N1	0.2926 (5)	0.0977 (2)	0.0551 (2)	0.0422 (6)
C1	-0.0439 (6)	-0.0355 (2)	0.1888 (2)	0.0360 (6)
C2	0.1563 (6)	-0.1186 (2)	0.1982 (2)	0.0390 (6)
C3	0.2929 (7)	-0.1480 (3)	0.2787 (2)	0.0444 (10)
C4	0.2315 (7)	-0.0938 (3)	0.3546 (2)	0.0483 (10)
C5	0.0393 (7)	-0.0115 (3)	0.3514 (2)	0.0470 (10)
C6	-0.0922 (6)	0.0167 (2)	0.2692 (2)	0.0403 (8)

Table 2. Selected geometric parameters (Å, °)

Cu—O1	1.946 (2)	Cl2—C4	1.747 (3)
Cu—N1	1.984 (2)	Cl3—C6	1.738 (3)
Cu—Cl1	2.982 (1)	O1—C1	1.312 (3)
Cl1—C2	1.742 (3)		
O1—Cu—N1	90.66 (9)	Cl1—C2—C3	118.4 (2)
Cl1—Cu—Cl1'	179.99 (1)	Cl2—C4—C3	119.2 (2)
Cu—O1—C1	123.7 (2)	Cl2—C4—C5	119.3 (2)
O1—C1—C2	123.9 (3)	Cl3—C6—C1	118.0 (2)
O1—C1—C6	122.0 (3)	Cl3—C6—C5	118.4 (2)
Cl1—C2—C1	117.9 (2)		

Symmetry code: (i) -x, -y, -z.

Table 3. Hydrogen-bonding geometry (Å, °)

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N1—H13···O1'	0.87	2.12	2.923 (3)	154
N1—H11···Cl1''	0.86	2.79	3.596 (3)	155

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

Ring H atoms were placed geometrically 0.95 Å from their parent atoms, while the H atoms of ammonia were taken from a difference map. A riding model was used for all H atoms, with *U*(H) = 1.3*U_{eq}*(C).

Data collection and cell parameters: *CAD-4 EXPRESS Software* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MolEN*. Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP-3* (Farrugia, 1997). Software used to prepare material for publication: *MolEN*.

The authors wish to acknowledge the purchase of the CAD-4 diffractometer under grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey. The authors also acknowledge Özlem Saraçoğlu for her help during single-crystal preparation.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1268). Services for accessing these data are described at the back of the journal.

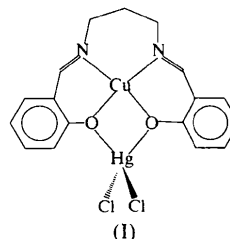
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compounds are therefore very interesting from both toxicological and crystallographic points of view.

The title compound, (I), comprises a novel Cu–Hg hetero-dinuclear complex. The [*N,N'*-bis(salicylidene)-1,3-propanediaminato]copper(II) complex forms different polynuclear complexes with metal salts in non-aqueous media *via* its phenolic O atoms (Fukuhara *et al.*, 1990), and these complexes may be di-, tri- or tetranuclear.



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{[μ -*N,N'*-Bis(salicylidene)-1,3-propanediaminato]copper(II)}dichloromercury(II)†

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Abstract

The title compound, [CuHgCl₂(C₁₇H₁₆N₂O₂)], is a hetero-dinuclear complex containing Cu^{II} and Hg^{II} ions. The Cu^{II} centre has a distorted square-planar coordination involving two O and two N atoms from the imine–phenol ligand, with Cu–O distances of 1.920 (3) and 1.926 (2) Å, and Cu–N distances of 1.966 (3) and 1.986 (4) Å. The coordination around the Hg^{II} centre consists of two chloride ions at distances of 2.343 (1) and 2.325 (2) Å, and two phenolic O atoms of the organic ligand at distances of 2.516 (2) and 2.421 (3) Å. The Cu···Hg separation is 3.5301 (8) Å.

Comment

It has been known since 1926 that mercury is toxic to humans and animals (Greenwood & Earnshaw, 1994). Mercury compounds have interesting crystal lattice structures (Grdenic, 1965; Cotton & Wilkinson, 1967; Holy *et al.*, 1976) and mercury halides tend to dimerize forming planar HgX₂···XHg coordination rings. Mercury

As described in the *Experimental* section, the first step in the synthesis of (I) was the preparation of the [*N,N'*-bis(salicylidene)-1,3-propanediaminato]copper(II) complex, (II) (Drew *et al.*, 1985). When this complex was reacted with HgCl₂ in dry dioxane, the overall coordination of copper was unaltered, but the bond lengths and angles differ between the mononuclear (Drew *et al.*, 1985) and the present dinuclear complexes. The Cu^{II} centre has a distorted square-planar coordination involving two O and two N atoms from the imine–phenol ligand, with Cu–O distances of 1.920 (3) and 1.926 (2) Å, and Cu–N distances of 1.966 (3) and 1.986 (4) Å.

The most significant geometric changes were observed in the coordination around the Hg^{II} centre. Solid HgCl₂ was found to be linear, with Hg–Cl and Hg···Cl(neighbour) distances of 2.25 and 3.34 Å, respectively (Greenwood & Earnshaw, 1994), but the Cl–Hg–Cl angle in (I) is not linear and the Hg–Cl distances are 2.325 (2) and 2.343 (1) Å. In (I), the Hg^{II} centre is further coordinated by two phenolic O atoms at distances of 2.516 (2) and 2.421 (3) Å, making its coordination number 4. The Cl1–Hg–Cl2 and O1–Hg–O2 angles are 154.44 (5) and 61.25 (9)°, respectively. The Cu···Hg separation is 3.5301 (8) Å. This coordination can be considered as an excessively deformed tetrahedral structure.

Although mercury(II) has been reported as having coordination numbers 2, 3, 4, 5, 7 and 8, the most frequently observed of these are 2 and 4. It was reported that the coordination in the symmetric [HgI₄]²⁻ complex (Greenwood & Earnshaw, 1994) was perfectly tetrahedral, with Hg–I bond lengths of 2.78 Å. However, in the solid-state structure of Hg(CN)₂ (Cotton & Wilkinson, 1967), the Hg^{II} centre was reported to have four-coordination, with NC–Hg–CN and CN···Hg···NC angles of 171 and 80°, respectively. The coordination in solid Hg(CN)₂ is therefore very similar to the coordination of the present complex.

† Systematic name: dichloro-2κ²Cl-μ-{2,2'}-[1,3-propanediylbis(nitrilomethylidene)]diphenolato}-1κ⁴O,*N,N',O'*:2κ²O,*O'*-copper(II)-mercury(II).