

Musa Sari,^{a*} Sefa Durmuş,^b
Orhan Atakol,^b Ingrid Svoboda^c
and Harmut Fuess^c

^aDepartment of Physics Education, Gazi University, Beşevler, 06500 Ankara, Turkey, ^bDepartment of Chemistry, Ankara University, Tandogan, 06100 Ankara, Turkey, and ^cStrukturforchung, FB Materialwissenschaft Technische Hochschule, Darmstadt Petersen Straße 23, 64287 Darmstadt, Germany

Correspondence e-mail: msari@gef.gazi.edu.tr

Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.017 \text{ \AA}$
R factor = 0.040
wR factor = 0.100
Data-to-parameter ratio = 10.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Bis[μ -N,N'-bis(salicylidene)-1,3-propanediamine-copper(II)]diiodolead(II)

In the title compound, bis[μ -N,N'-bis(salicylidene)-1,3-propanediamine]-1 κ^4 N,N',O,O':3 κ^2 O,O';2 κ^4 N,N',O,O':3 κ^2 O,O'-diiodo-3 κ^2 I-dicopper(II)lead(II), $[\{\text{Cu}(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)\}_2\text{PbI}_2]$, the Pb atom is in a distorted octahedral environment coordinated by four O and two I atoms. The phenolic O atoms of the two organic ligands coordinate both Cu and Pb atoms, forming a bridge. The Pb—I bond distances are 3.0945 (9) and 3.1831 (9) Å, and the Pb—O bond distances range from 2.492 (6) to 2.616 (6) Å. The Pb···Cu bridging distances are 3.6331 (14) and 3.5662 (13) Å.

Received 12 March 2001

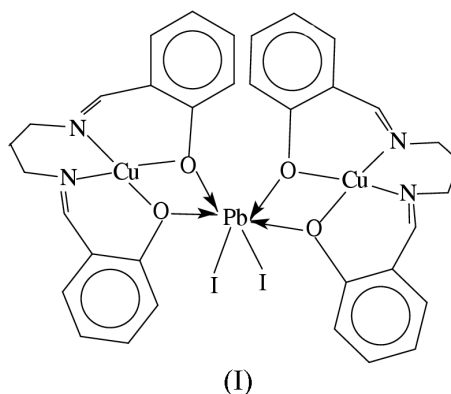
Accepted 18 April 2001

Online 26 April 2001

Comment

Lead is environmentally significant and its solid solutions with other oxides are of great importance in a number of ferroelectric and electronic devices (Lashgari *et al.*, 1998). The coordination sphere of Pb is mainly dominated by oxygen, generally six, seven, eight or ten in number (Virovets *et al.*, 1993; Tahir *et al.*, 1996; Schürman & Huber, 1994; Lashgari *et al.*, 1998). Sometimes Pb is coordinated by weakly bonding N (Inoue *et al.*, 1993; García-Granda *et al.*, 1993). In addition to the above, some Cu–Pb heterodinuclear complexes with macrocyclic ligands have been reported recently (Guerrino *et al.*, 1995; Yonemura *et al.*, 1998).

We report here the crystal structure of a heterotrinary complex, $[\{\text{Cu}(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)\}_2\text{PbI}_2]$, (I), in which the phenolic O atoms of the organic ligands coordinate both Cu and Pb atoms, forming μ_2 bridges.



The coordination of lead(II) in (I) is in the form of a distorted octahedron comprising four O and two I atoms (Fig. 1), with Pb—O distances of 2.492 (6), 2.603 (6), 2.607 (6) and 2.616 (6) Å, and Pb—I distances of 3.0945 (9) and 3.1831 (9) Å. The O—Pb—O bond angles range from 56.7 (2) to 159.6 (2)°. Copper(II) is four-coordinate in a highly deformed square-planar arrangement, consisting of two

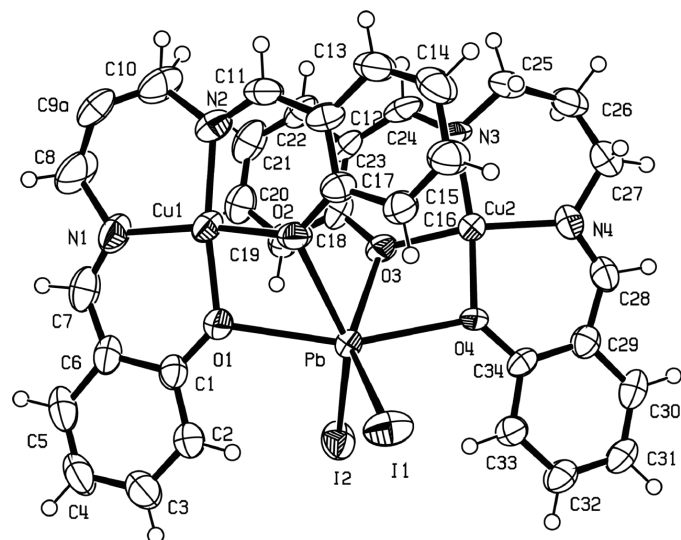


Figure 1
The molecular structure and atomic labelling scheme of the title compound (ORTEP-3; Farrugia, 1997). For clarity, only one component of the disordered C9 atom is shown; the C atom of the other component carries suffix *b* instead of *a*. The displacement ellipsoids are drawn at the 50% probability level.

phenolic O and two N atoms. The four-membered rings Pb—O1—Cu1—O2 and Pb—O4—Cu2—O3 are not entirely planar with, for example, Pb—O1.158 (2) Å out of the plane defined by O1, Cu1 and O2, but the angle between their least-squares planes is 50.80 (2)°. The six-membered Cu1—N1—C8—C9—C10—N2 chelate ring has a boat conformation in which C9 is disordered; the atom with suffix *a* has occupancy 0.564 (16) and that with suffix *b* has an occupancy of 0.436 (16). The Pb···Cu distances [3.6331 (12) and 3.5662 (12) Å] are rather long for a direct interaction.

Experimental

A solution of *N,N'*-bis(salicylidene)-1,3-propanediamine (0.585 g, 0.002 mol) was dissolved in 50 ml hot ethanol. Then a solution of CuCl₂·2H₂O (0.340 g, 0.002 mol) in 30 ml hot water and 10 ml concentrated ammonia was added to it. The green complex [Cu(C₁₇H₁₆N₂O₂)], which precipitated out after a few hours, was filtered off and dried in an oven at 353 K. 0.344 g (0.001 mol) of this complex was then dissolved in 150 ml dimethylformamide (DMF) at 373 K. In another beaker, PbI₂ (0.454 g, 0.001 mol) and 1 g finely ground KI were heated in a mixture of 50 ml acetone and 50 ml DMF until all the PbI₂ was dissolved (KPbI₃ formation) (Hofmann & Rüdorff, 1966). The excess KI was filtered off and the two hot solutions were mixed and stirred and allowed to cool for 48 h. The brown crystals formed were filtered off and dried in air.

Crystal data

[Cu ₂ PbI ₂ (C ₁₇ H ₁₆ N ₂ O ₂) ₂]	Z = 2
<i>M_r</i> = 1148.71	<i>D_x</i> = 2.228 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 10.516 (1) Å	Cell parameters from 25 reflections
<i>b</i> = 11.381 (2) Å	θ = 4.1–14.3°
<i>c</i> = 14.558 (3) Å	μ = 7.98 mm ⁻¹
α = 87.23 (2)°	<i>T</i> = 293 (2) K
β = 79.73 (1)°	Needle, brown
γ = 88.54 (1)°	0.22 × 0.05 × 0.03 mm
<i>V</i> = 1712.2 (5) Å ³	

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (Fair, 1990)
 $T_{\min} = 0.626$, $T_{\max} = 0.787$
 7106 measured reflections
 6685 independent reflections
 4611 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 26.0^\circ$
 $h = -12 \rightarrow 1$
 $k = -14 \rightarrow 14$
 $l = -17 \rightarrow 17$
 3 standard reflections
 frequency: 120 min
 intensity decay: 3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.100$
 $S = 1.01$
 4611 reflections
 423 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0651P)^2 + 3.3407P]$,
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 2.48 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -2.14 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Pb—O1	2.607 (6)	Cu1—O1	1.938 (6)
Pb—O2	2.616 (6)	Cu1—O2	1.924 (6)
Pb—O3	2.492 (6)	Cu2—O3	1.924 (6)
Pb—O4	2.603 (6)	Cu2—O4	1.926 (5)
Pb—I1	3.1831 (9)	Cu1—N1	1.970 (9)
Pb—I2	3.0945 (9)	Cu1—N2	1.985 (8)
Pb—Cu1	3.6331 (12)	Cu2—N3	1.961 (7)
Pb—Cu2	3.5662 (12)	Cu2—N4	1.966 (7)
O1—Pb—O2	56.7 (2)	O3—Pb—I1	142.81 (14)
O3—Pb—O4	59.31 (18)	O4—Pb—I1	91.15 (14)
O3—Pb—O1	101.2 (2)	O1—Pb—I1	103.75 (16)
O4—Pb—O1	159.6 (2)	O2—Pb—I1	96.58 (15)
O3—Pb—O2	74.8 (2)	I2—Pb—I1	109.13 (3)
O4—Pb—O2	108.39 (19)	O2—Cu1—O1	80.0 (3)
O4—Pb—I2	93.01 (15)	O1—Cu1—N1	91.2 (3)
O1—Pb—I2	95.08 (15)	O2—Cu1—N2	91.8 (3)
O2—Pb—I2	146.22 (14)	N1—Cu1—N2	97.7 (4)

H atoms were placed geometrically (C—H = 0.93 and 0.97 Å) based on their parent C atoms and a riding model was used for all H atoms, with $U_{\text{iso}}(\text{H}) = 1.3U_{\text{eq}}(\text{C})$. The disorder of atoms C9*a* and C9*b* was refined, with occupancies of 0.564 (16) and 0.436 (16), respectively. The largest peak and deepest hole in the final difference Fourier map were located 0.90 and 0.99 Å from Pb, respectively.

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1993); cell refinement: CAD-4 EXPRESS; data reduction: X-RED (Stoe & Cie, 1996); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

The authors wish to acknowledge the financial support of the Deutscher Akademischer Austauschdienst of Germany.

References

- Enraf–Nonius (1993). CAD-4 EXPRESS. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
 Fair, C. K. (1990). MolEN. Enraf–Nonius, Delft, The Netherlands.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 García-Granda, S., Díaz, M. R., Gómez-Beltrán, F. & Blanco-Gomís, D. (1993). *Acta Cryst.* **C49**, 884–886.
 Guerrino, P., Tamburini, S. & Vigato, V. (1995). *Coord. Chem. Rev.* **139**, 17–243.

- Hofmann, U. & Rüdorff, W. (1966). *Anorganische Chemie*, 19th ed., p. 543. Braunschweig, Germany: Friedr. Vieweg and Son.
- Inoue, M. B., Fernando, Q., Villegas, C. A. & Inoue, M. (1993). *Acta Cryst.* **C49**, 875–878.
- Lashgari, K., Kritikos, M., Lashgari, K. & Westin, G. (1998). *Acta Cryst.* **C54**, 1794–1797.
- Schürman, M. & Huber, F. (1994). *Acta Cryst.* **C50**, 1710–1713.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Stoe & Cie (1996). *X-RED*. Stoe & Cie, Darmstadt, Germany.
- Tahir, M. N., Ülkü, D., & Mövsümov, E. M. (1996). *Acta Cryst.* **C52**, 2436–2439.
- Virovets, A. V., Naumov, D. Yu, Boldyreva, E. V. & Podberezskaya, N. V. (1993). *Acta Cryst.* **C49**, 1882–1884.
- Yonemura, M., Ohba, M., Takahashi, K., Ökawa, H. & Fenton, D. (1998). *Inorg. Chim. Acta*, **283**, 72–79.