

Bis[$[\mu$ -*N,N'*-bis(salicylidene)-1,4-butanediamine-*N,N',O,O'*-copper(II)]- μ -chloro-chloromercury(II)]¹

Ismail Ercan,^a Filiz Ercan,^{b*} Cengiz Arici^b and Orhan Atakol^c

^aAnkara Nuclear Research and Training Center, Beşevler 06100, Ankara, Turkey, ^bDepartment of Engineering Physics, Hacettepe University, Beytepe 06532, Ankara, Turkey, and ^cDepartment of Chemistry, Ankara University, Tandoğan 06100, Ankara, Turkey

Correspondence e-mail: filiz@hacettepe.edu.tr

Received 27 September 2001

Accepted 15 November 2001

Online 31 January 2002

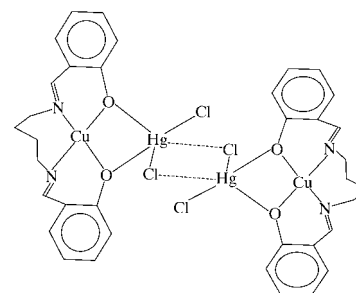
A new tetranuclear Cu^{II}-Hg^{II}-Hg^{II}-Cu^{II} complex, [Cu₂Hg₂Cl₄-(C₁₈H₁₈N₂O₂)₂], has been prepared by means of a copper complex found in the literature. The molecular structure of this complex was determined by X-ray diffraction and the Cu-Hg-Hg-Cu chain was seen to be non-linear. The change in magnetic susceptibility with temperature was recorded for this complex and observed to abide by the Curie-Weiss law. The coordination around the Hg^{II} ions is square pyramidal. The Cu···Hg bridging distance is 3.5269 (7) Å.

Comment

Organic-copper complexes have been used in pharmacology because the Cu^{II} ion is an essential element for all living beings. Mercury is one of the most toxic elements for animals and humans because secretion of mercury from the human body is very difficult. For this reason, copper and mercury complexes are important in bioinorganic chemistry and a complex which contains both ions is very interesting. The most frequently observed coordination of the mercury(II)-organic ligand complexes in the literature is tetrahedral. If the complexes contain halogen ions, either dimerization or formation of planar rings in the structure HgX···HgX (the ring is defined as the Hg-Cl-Hg-Cl ring) can be observed (Canty *et al.*, 1979; Holy *et al.*, 1976; Davidovic *et al.*, 1998).

It has been known for some time that ONNO-type Schiff bases form polynuclear complexes with Cu^{II} and Ni^{II} complexes by reaction with many Lewis acids in non-aqueous solvents (Butcher & Sinn, 1976; Aminabhavi *et al.*, 1986; Yao *et al.*, 1997; Atakol *et al.*, 1999). A Cu-ONNO Schiff base complex previously prepared was reacted with HgCl₂ in the

expectation that a Cu^{II}-Hg^{II} heterometal complex would tend to dimerize, forming planar HgX···HgX coordination rings (Atakol *et al.*, 1999). The molecular structure of the title compound, (I), was found to be tetranuclear through X-ray diffraction studies (Fig. 1). The complex structure was also studied using IR and element analysis techniques. In addition, the magnetic behaviour of the metal complex was measured in the temperature range 2–300 K. The magnetic measurements indicate that the crystals are paramagnetic.



(I)

The seven-component chelate ring is not seen very often and most of the transition metal ions do not form this seven-membered chelate ring. The seven-membered chelate ring composed of atoms Cu^{II}, N1, C8, C9, C10, C11 and N2 has a chair conformation. Similar to the six-component rings, the most stable form of the seven-membered ring is the chair. The Cu^{II} ion has a distorted square-planar coordination involving two O and two N atoms from the salbd (salicylidene-butane-diamine) ligand. The Hg^{II} ion has a distorted square-pyramidal coordination. This coordination of the Hg^{II} ion is unusual (Eliel & Wilen, 1996).

In general, a τ value can be calculated from the angles around the central atom for a coordination number of five; $\tau = (\alpha - \beta)/60$ and α and β are the largest two angles around the central atom. If $\tau = 1$ then the coordination is an ideal trigonal bipyramid, whereas if $\tau = 0$ then the coordination is an ideal

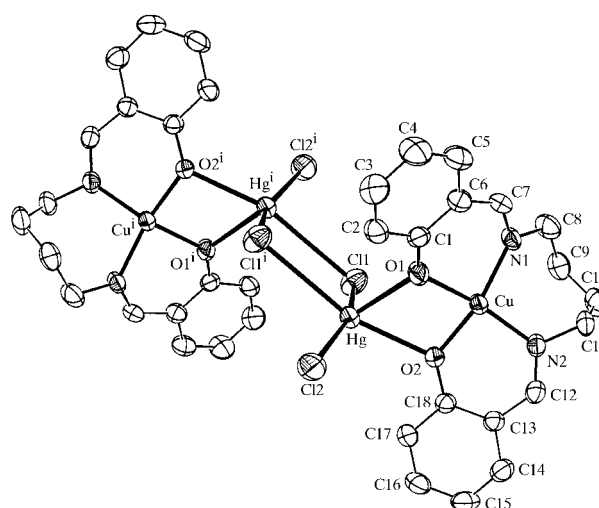


Figure 1
ORTEP (Johnson, 1976) drawing of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) 1 - x, 1 - y, 2 - z.]

¹ Systematic name: di- μ -chloro-2,3 κ^4 -Cl-dichloro-2 κ Cl,3 κ Cl-bis[μ -2,2'-[1,4-butanediyl]bis(nitrilomethylidene)]diphenolato-1:2 κ^6 O,*N,N',O',O',O',3,4 κ^6 O,*O',O,N,N',O'*-dicopper(II)dimercury(II).*

square pyramid (Addison *et al.*, 1984). From the bond angles given in Table 1, τ is 0.176. As this value as close to zero, the coordination around Hg^{II} is a square pyramid. The Cu···Hg and Hg···Hg(1 - x, -1 - y, 2 - z) distances are 3.5269 (7) and 4.3613 (6) Å, respectively. The greatest Hg···Cl distance found in the literature in an Hg-Cl-Hg-Cl ring is 2.976 Å (Davidovic *et al.*, 1998). Although Hg^{II} has been reported as generally having coordination numbers two and four, its coordination number in the tetranuclear complex can be taken as five.

Experimental

Salicylaldehyde, 1,4-butanediamine and the metal salts were obtained from Merck. The solvents were acquired from Carlo Erba and were used without further purification. The magnetic susceptibility of the powdered sample was measured between 2.6–300 K with a Faraday-type magnetometer at 1.2 T. Experimental susceptibility data were corrected for the underlying diamagnetism. The magnetic measurements indicated that the heterometal tetranuclear complex was paramagnetic. The ligand was prepared by the condensation of salicylaldehyde and 1,4-butanediamine in EtOH (m.p. 603 K, yield 94%). The complex was prepared in two steps. Step 1: 0.592 g (0.002 mol) of the ligand was dissolved in 50 ml MeOH with heating. A solution of 0.400 g [Cu(CH₃COO)₂].H₂O in 50 ml hot MeOH was added and the resulting solution mixed and left to stand for 3–4 h. The resulting precipitate was filtered off. C₁₈H₁₈CuN₂O₂, m.p. >603 K, yield 80%. Step 2: 0.358 g of the complex prepared in Step 1 was dissolved at 363–373 K in a mixture of 20 ml DMF (dimethylformamide) and 20 ml dioxane. A solution of 0.272 g HgCl₂ (0.001 mol) in 30 ml hot MeOH was added to this solution. The mixture was left to stand for 3–4 d. The precipitated crystals were filtered off and left to dry in the open. Elemental analysis, calculated for C₃₆H₃₆Cl₄Cu₂Hg₂N₄O₄: C 34.33, H 2.86, N 4.45, Cl 11.27, Cu 10.10%; found: C 34.46, H 2.94, N 4.54, Cl 11.23, Cu 10.0%. IR (cm⁻¹): $\nu(\text{C-H})_{\text{arom}}$ 3029, $\nu(\text{C-H})_{\text{aliph}}$ 2927, $\nu(\text{C-H})_{\text{imin}}$ 2984, $\nu(\text{C=N})_{\text{arom}}$ 1625, $\delta(\text{C-H})_{\text{aliph}}$ 1472, $\delta(\text{C-H})_{\text{arom}}$ 757, $\nu(\text{C-O})_{\text{arom}}$ 1140.

Crystal data

[Cu₂Hg₂Cl₄(C₁₈H₁₈N₂O₂)₂]
M_r = 1258.74
 Triclinic, *P* $\bar{1}$
a = 8.9927 (12) Å
b = 9.4979 (13) Å
c = 13.0245 (14) Å
 α = 72.440 (2)°
 β = 69.285 (3)°
 γ = 73.023 (3)°
V = 970.4 (2) Å³

Z = 1
D_x = 2.154 Mg m⁻³
 Mo *K* α radiation
 Cell parameters from 25 reflections
 θ = 10.2–18.1°
 μ = 9.29 mm⁻¹
T = 301 (2) K
 Prism, dark brown
 0.20 × 0.15 × 0.10 mm

Data collection

CAD-4 EXPRESS diffractometer
 $\omega/2\theta$ scans
 Absorption correction: empirical via ψ scan (MolEN; Fair, 1990)
T_{min} = 0.223, *T_{max}* = 0.395
 4114 measured reflections
 3932 independent reflections
 3482 reflections with *I* > 2 σ (*I*)

R_{int} = 0.036
 θ_{max} = 26.3°
h = -10 → 11
k = -11 → 11
l = 0 → 16
 3 standard reflections
 frequency: 120 min
 intensity decay: 0.3%

Table 1

Selected geometric parameters (Å, °).

Hg—Cl1	2.331 (2)	Cu—O1	1.933 (6)
Hg—Cl1 ⁱ	3.300 (2)	Cu—O2	1.921 (5)
Hg—Cl2	2.321 (2)	Cu—N1	2.001 (6)
Hg—O1	2.420 (5)	Cu—N2	1.955 (7)
Hg—O2	2.562 (5)		
O2—Cu—O1	83.6 (2)	Cl2—Hg—O2	100.32 (15)
N2—Cu—N1	98.1 (3)	Cl1—Hg—O2	96.17 (15)
Cl2—Hg—Cl1	153.80 (12)	Cl1 ⁱ —Hg—O2	164.36 (3)
Cl2—Hg—O1	108.68 (18)	Cl1 ⁱ —Hg—Cl1	79.96 (3)
Cl1—Hg—O1	96.99 (18)	Cl1 ⁱ —Hg—Cl2	88.92 (3)
Cl1 ⁱ —Hg—O1	103.40 (3)	O1—Hg—O2	62.04 (18)

Symmetry code: (i) 1 - x, 1 - y, 2 - z.

Refinement

Refinement on *F*²

R(*F*) = 0.057

wR(*F*²) = 0.149

S = 1.09

3932 reflections

236 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1197P)^2 + 0.1203P]$

where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} = 0.003

$\Delta\rho_{\text{max}} = 0.92 \text{ e } \text{Å}^{-3}$

$\Delta\rho_{\text{min}} = -0.19 \text{ e } \text{Å}^{-3}$

Extinction correction: SHELXL97 (Sheldrick, 1997)

Extinction coefficient: 0.0026 (8)

H atoms were placed geometrically and refined using a riding model; C—H = 0.95 or 0.99 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C).

Data collection: CAD-4 EXPRESS (Enraf-Nonius, 1993); cell refinement: CAD-4 EXPRESS; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPII (Johnson, 1976).

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.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1346). Services for accessing these data are described at the back of the journal.

References

- Addison, A. W., Rao, J. N., Reedijk, J., Von Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.
- Aminabhavi, J. M., Biradar, N. S. & Divakar, M. C. (1986). *Indian. J. Chem. Sect. A*, **25**, 283–284.
- Atakol, O., Arici, C., Tahir, M. N., Kenar, A. & Ülkü, D. (1999). *Acta Cryst.* **C55**, 1416–1418.
- Butcher, R. J. & Sinn, E. (1976). *Inorg. Chem.* **15**, 1604–1608.
- Canty, A. J., Raston, C. L. & White, A. H. (1979). *Aust. J. Chem.* **32**, 1165–1166.
- Davidović, N., Matković-Čalogović, D., Popović, Z. & Dragojević, I. V. (1998). *Acta Cryst.* **C54**, 574–576.
- Eliel, E. L. & Wilen, S. H. (1996). *Stereochemistry of Organic Compounds*, pp. 762–767. New York: John Wiley Interscience.
- Enraf-Nonius (1993). CAD-4 EXPRESS. Version 1.1. Enraf-Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). MolEN. Enraf-Nonius, Delft, The Netherlands.
- Holy, N. L., Baezinger, N. C., Flynn, R. M. & Swenson, D. C. (1976). *J. Am. Chem. Soc.* **98**, 7823–7824.
- Johnson, C. K. (1976). ORTEPII. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Sheldrick, G. M. (1997). SHELXL97 and SHELXS97. University of Göttingen, Germany.
- Yao, H. H., Lo, J. M., Chen, B. H. & Lu, J. H. (1997). *Acta Cryst.* **C53**, 1012–1013.