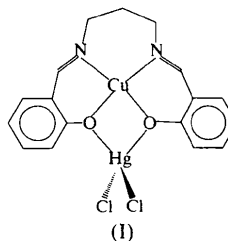


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compounds are therefore very interesting from both toxicological and crystallographic points of view.

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.



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.

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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

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

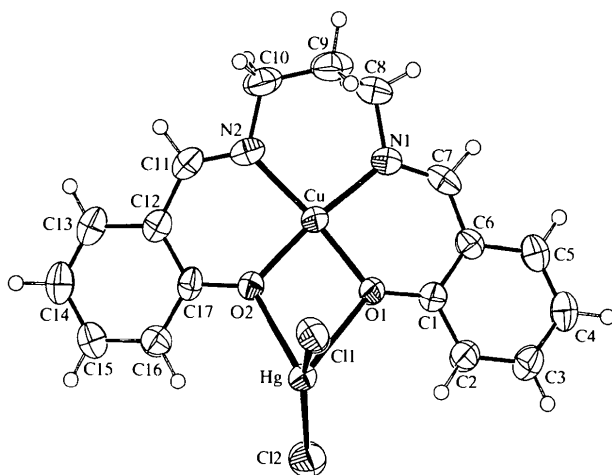


Fig. 1. PLATON (Spek, 1999) drawing of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small circles of arbitrary radii.

Experimental

N,N'-Bis(salicylidene)-1,3-propanediamine (1.120 g, 4 mmol) and ammonia solution (10 ml, 20%) were dissolved in ethanol (60 ml). This solution was heated to boiling and a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.682 g, 4 mmol) in hot water (30 ml) was added. The resulting mixture was left to stand for 2 h. The green copper(II) complex which formed was filtered off and dried at 383 K for 3 h. This complex (0.344 g, 1 mmol) was dissolved in hot dioxane (50 ml). A solution of HgCl_2 (0.271 g, 1 mmol) in hot MeOH (20 ml) was added rapidly to the final mixture. The green crystals which formed after 24 h were filtered off and dried in air.

Crystal data

$[\text{CuHgCl}_2(\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2)]$

$M_r = 615.37$

Triclinic

$P\bar{1}$

$a = 8.9427(12) \text{ \AA}$

$b = 9.4190(13) \text{ \AA}$

$c = 11.9415(12) \text{ \AA}$

$\alpha = 95.977(2)^\circ$

$\beta = 106.464(3)^\circ$

$\gamma = 107.763(2)^\circ$

$V = 898.4(2) \text{ \AA}^3$

$Z = 2$

$D_x = 2.275 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 11.61\text{--}20.89^\circ$

$\mu = 10.04 \text{ mm}^{-1}$

$T = 295 \text{ K}$

Pinakoid

$0.350 \times 0.200 \times 0.125 \text{ mm}$

Green

Data collection

Enraf–Nonius CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

empirical *via* ψ scan (Fair, 1990)

$T_{\min} = 0.103$, $T_{\max} = 0.285$

2687 reflections with

$I > 3\sigma(I)$

$R_{\text{int}} = 0.010$

$\theta_{\max} = 25.02^\circ$

$h = -10 \rightarrow 10$

$k = -11 \rightarrow 11$

$l = -14 \rightarrow 0$

3327 measured reflections
3159 independent reflections

3 standard reflections
frequency: 120 min
intensity decay: -1.47%

Refinement

Refinement on F

$R = 0.019$

$wR = 0.025$

$S = 0.94$

2687 reflections

226 parameters

H-atom parameters constrained

$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.69 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.21 \text{ e \AA}^{-3}$

Extinction correction: none

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

Table 1. Selected geometric parameters (\AA , $^\circ$)

Cu···Hg	3.5301 (8)	Cu—O1	1.920 (3)
Hg—C11	2.343 (1)	Cu—O2	1.926 (2)
Hg—C12	2.325 (2)	Cu—N1	1.966 (3)
Hg—O1	2.516 (2)	Cu—N2	1.986 (4)
Hg—O2	2.421 (3)		
C11—Hg—C12	154.44 (5)	O1—Cu—N1	91.9 (1)
C11—Hg—O1	93.56 (8)	O1—Cu—N2	167.6 (1)
C11—Hg—O2	97.99 (9)	O2—Cu—N1	171.2 (1)
C12—Hg—O1	101.97 (8)	O2—Cu—N2	90.7 (1)
C12—Hg—O2	107.25 (9)	N1—Cu—N2	96.6 (1)
O1—Hg—O2	61.25 (9)	Hg—O1—Cu	104.7 (1)
O1—Cu—O2	81.7 (1)	Hg—O2—Cu	108.1 (1)

Table 2. Comparison of molecular-geometry parameters (\AA , $^\circ$) of the title compound and a mononuclear analogue

Parameter	(I)	(II)†
Cu—O1	1.920 (3)	1.857 (9)
Cu—O2	1.926 (2)	1.878 (11)
Cu—N1	1.966 (3)	1.938 (11)
Cu—N2	1.986 (4)	1.958 (12)
O1—Cu—N2	167.6 (1)	174.1 (8)
O1—Cu—O2	81.7 (1)	82.2 (4)
N1—Cu—O2	171.2 (1)	159.9 (5)
N1—Cu—O1	91.9 (1)	93.3 (5)

† Drew *et al.* (1985).

The H81, H82, H91, H92, H101 and H102 atoms were taken from difference maps, while the remaining H atoms were placed geometrically 0.95 \AA from their parent C atoms. A riding model with $U_{\text{iso}}(\text{H}) = 1.3U_{\text{eq}}(\text{C}, \text{O})$ was then used for the refinement of all H atoms.

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1993). Data reduction: MolEN (Fair, 1990). Program(s) used to solve structure: SIR in MolEN. Program(s) used to refine structure: LSFM in MolEN. Molecular graphics: PLATON (Spek, 1999). 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.

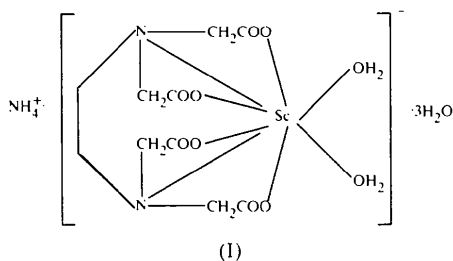
Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1333). Services for accessing these data are described at the back of the journal.

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complex, (I), was synthesized as a precursor compound and its crystal structure has been determined.



Certainly, the following discussions are helpful and meaningful in the understanding of the relationship between the precursor structure and the thermal decomposition reaction in synthesizing the target scandia–zirconia composite oxide. Crystallographic determination has revealed the structural features of the title complex.

Complex (I) has a discrete structure composed of [Sc(edta)(H₂O)₂][−] anions, NH₄⁺ cations and two solvent water molecules. The Sc³⁺ ion has coordination number 8, which includes four O and two N atoms of the ethylenediaminetetraacetate (edta) ligand, and two O atoms of coordinated water. These eight atoms form a distorted square antiprism around the Sc³⁺ ion, in which the two parallel planes contain atoms N1/O1/O3/O9 and N2/O5/O7/O10. Such a high coordination number is common for Sc³⁺ (Willey *et al.*, 1992); it was also observed in a polyaminopolycarboxylic scandium(III) heteronuclear complex with manganese, [Mn–Sc(dtpa)(H₂O)₂].2H₂O (dtpa is diethylenetriaminepentaacetic acid; Zhang *et al.*, 1995), in which the Sc³⁺ ion is coordinated by five O and three N atoms of dtpa. In (I), the mean Sc—O distance is 2.189 (2) Å, which is about 0.27 Å shorter than the mean Sc—N distance [2.458 (2) Å]. The mean Sc—O and Sc—N distances in the title complex are both longer than those in [MnSc(dtpa)(H₂O)₂].2H₂O [2.158 (3) and 2.435 (3) Å, respectively]. On the other hand, in comparison with six-coordinated scandium(III) complexes, the mean Sc—O bond length in (I) is much longer than those in {[Sc₂(Gly)₆](ClO₄)₆]_n (Gly is glycine; Yan *et al.*, 1996) and [Sc(ClCH₂CO₂)₃]_n (Sugita *et al.*, 1987) [2.066 (7) and 2.075 (6) Å, respectively]. This phenomenon arises from the enlargement of the coordination sphere round the Sc³⁺ ions from six-coordinated to eight-coordinated. There are two types of hydrogen bond, namely O—H...O between water of solvation and the carboxylate groups, and N—H...O between NH₄⁺ and the carboxylate groups, with mean *D*...*A* distances of 2.800 (3) and 2.995 (3) Å, respectively. The four carboxylate groups of the edta ligand in (I) are all monodentate, as found in the lanthanum(III)–edta complex Na[La(edta)(H₂O)₄].3H₂O with coordination number 10 (Lind *et al.*, 1965). However, the coordination number of the Sc³⁺ ion in (I)

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Ammonium diaqua(ethylenediaminetetraacetato)scandium(III) trihydrate

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Abstract

The title complex, (NH₄)[Sc(C₁₀H₁₂N₂O₈)(H₂O)₂].3H₂O, was synthesized in aqueous solution as a precursor compound for scandia–zirconia solid composite oxide electrolytes. The structural determination shows that the Sc³⁺ ion is coordinated by four O and two N atoms of the ethylenediaminetetraacetate (edta) ligand, and by two water molecules. All of the four carboxylate groups are monodentate. A distorted square antiprism is formed around the Sc³⁺ ion by the eight ligating atoms.

Comment

The coordination chemistry of scandium with polyaminopolycarboxylic acids such as ethylenediaminetetraacetic acid (EDTA) has been studied in detail for analytical purposes, but no crystal structures of scandium complexes of EDTA have been reported. In our present study, we have exploited the advantages of the thermal decomposition of coordination compounds, *viz.* formation of pure crystalline phases and small homogeneous particles (van Doorn *et al.*, 1998), to synthesize scandia–zirconia composite oxide electrolytes. The title