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Bis(triethylsulfonium) Tetraiodo-mercurate(II)

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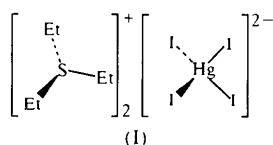
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Abstract

The reaction of an aqueous slurry of HgI₂ and an acetone solution of (Et₃S)I (molar ratio 1:2) gives the title compound, [(C₂H₅)₃S]₂[HgI₄], which contains discrete pyramidal Et₃S⁺ and tetrahedral HgI₄²⁻ ions. The bond distances of the anion (HgI—II and HgI—I2) are 2.780 (1) and 2.790 (1) Å.

Comment

The present work is part of a larger investigation of (R₃S)I_x-HgI₂ (x = 1–7) systems. Some crystalline compounds have been synthesized and structurally characterized in a study of the effects of iodide-accepting cations on the local structure and conductivity properties of trialkylsulfonium-based polyiodide systems. (Et₃S)-[Hg₂I₆]_{1/2}·3I₂(s) was obtained by reaction of (Et₃S)I₇ and HgI₂, and has been shown to consist of dimers of edge-sharing HgI₄²⁻ tetrahedra bridged by iodine molecules into a three-dimensional network (Stegemann *et al.*, 1995). The structural anion motif of Hg₂I₆²⁻ is also present in the I₂-free analogue (Et₃S)[Hg₂I₆]_{1/2}(s) (Bengtsson *et al.*, 1995). The crystal structure of the corresponding trimethylsulfonium compound, (Me₃S)-[HgI₃], on the other hand, has already been shown to consist of trigonal HgI₃⁻ units stacked into one-dimensional chains (Fenn, 1966*a*). Fenn (1966*b*) also determined the crystal structure of (Me₃S)₂[HgI₄]. The crystal structure of (Et₃S)₂[HgI₄], (I), is presented here in order to clarify whether structural effects on the anion similar to those observed for the triiodomercurate compounds are caused by cation exchange. The analogous



cadmium compound, (Et₃S)₂[CdI₄], is isostructural with the title compound (Bengtsson-Kloo *et al.*, 1996).

The title compound consists of discrete pyramidal Et₃S⁺ cations and tetrahedral HgI₄²⁻ anions. Selected distances and angles are listed in Table 2. The intramolecular structural parameters of the Et₃S⁺ cation in (Et₃S)₂HgI₄(s) correspond well with previous results for (Et₃S)₂[CdI₄] (Bengtsson-Kloo *et al.*, 1996), (Et₃S)[Hg₂I₆]_{1/2}(s) (Bengtsson *et al.*, 1995) and (Et₃S)-[Hg₂I₆]_{1/2}·3I₂(s) (Stegemann *et al.*, 1995). The two orientations found for each ethyl group (Fig. 1) coincide at the terminal C atom. The occupancies are 0.63 (2) and 0.37 (2) for the two orientations. The corresponding occupancies in the isostructural cadmium compound were 0.65 (2) and 0.35 (2). The cation–anion arrangement was described as a distorted anti-fluorite-type structure (Bengtsson-Kloo *et al.*, 1996). It is also similar to that in (Et₃S)[Hg₂I₆]_{1/2}, where the S atoms of the triethylsulfonium cations are positioned above the faces of the tetraiodometallate(II) tetrahedra. Also, the I···S distances are of the same magnitude (4.0–5.5 Å) and indicate that the cation–anion interactions are predominantly of the electrostatic and van der Waals types (Bengtsson *et al.*, 1995). Furthermore, the structure of (Et₃S)₂[HgI₄] is very similar to that of (Me₃S)₂[HgI₄] (Fenn, 1966*b*) and no cation-induced structural differences similar to those observed in the corresponding triiodomercurate systems can thus be identified. The tetrahedral HgI₄²⁻ complex is probably one of the most well known coordination compounds and it represents an archetype of an inorganic Werner-type complex. The MI₄²⁻ fragments have been observed as isolated tetrahedra both in solution and the solid state (see Table 3), as edge-sharing tetrahedra in Hg₂I₆²⁻ [recently reviewed by Bengtsson *et al.* (1995)], as well as corner-sharing tetrahedra in Hg₂I₇⁻ dimers and extended layers of tetrahedra, with ion-conducting materials such as M₂HgI₄ being typical examples (M = Ag, Cu, In or Tl). The average Hg—I distances in compounds with isolated HgI₄²⁻ tetrahedra are typically similar to those observed in this study [2.780 (1) and 2.790 (1) Å].

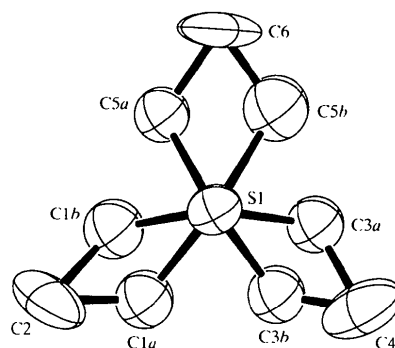


Fig. 1. The molecular structure of the Et₃S⁺ cation showing 50% probability displacement ellipsoids.

Experimental

Bis(triethylsulfonium) tetraiodomercurate(II) was prepared by mixing stoichiometric amounts of an aqueous slurry of HgI₂ (Merck, p.a. grade) with an acetone solution of triethylsulfonium iodide to give a pale-yellow solution. Single crystals were grown by slow evaporation. (Et₃S)I was prepared by alkylation of Et₂S by EtI in chloroform and then purified by recrystallization from hot ethanol before use.

Crystal data

(C₆H₁₅S)₂[HgI₄]M_r = 946.71

Tetragonal

I4₁/a

a = 13.903 (1) Å

c = 25.963 (3) Å

V = 5018 (1) Å³

Z = 8

D_x = 2.506 Mg m⁻³D_m not measured

Mo Kα radiation

λ = 0.7107 Å

Cell parameters from 47 reflections

θ = 19–38°

μ = 11.16 mm⁻¹

T = 295 K

Tetragonal bipyramid

0.29 × 0.28 × 0.28 mm

Yellow

C5a†	0.184 (2)	0.275 (2)	0.483 (1)	0.074 (8)
C5b‡	0.150 (4)	0.205 (4)	0.430 (2)	0.10 (1)
C6	0.143 (1)	0.312 (1)	0.4297 (7)	0.1134

† Site occupancy = 0.631 (19). ‡ Site occupancy = 0.369 (19).

Table 2. Selected geometric parameters (Å, °)

Hg1—I1	2.7799 (9)	C1b—C2	1.68 (5)
Hg2—I2	2.7899 (9)	C1a—C1b	1.23 (5)
S1—C1a	1.83 (3)	C3a—C4	1.54 (3)
S1—C1b	1.87 (5)	C3b—C4	1.36 (5)
S1—C3a	1.83 (3)	C3a—C3b	1.23 (5)
S1—C3b	1.80 (5)	C5a—C6	1.58 (3)
S1—C5a	1.87 (2)	C5b—C6	1.49 (5)
S1—C5b	2.00 (5)	C5a—C5b	1.75 (6)
C1a—C2	1.51 (3)		
I1—Hg1—I1 ⁱ	112.98 (5)	C3a—S1—C5a	102 (1)
I1—Hg1—I1 ⁱⁱ	107.74 (2)	C3b—S1—C5b	96 (2)
I1 ⁱⁱⁱ —Hg1—I1 ⁱⁱⁱⁱ	112.98 (5)	S1—C1a—C2	112 (1)
I2—Hg2—I2 ⁱ	108.65 (4)	S1—C1b—C2	102 (2)
I2—Hg2—I2 ⁱⁱ	109.88 (2)	S1—C3a—C4	105 (1)
C1a—S1—C3a	102 (1)	S1—C3b—C4	115 (3)
C1a—S1—C5a	99 (1)	S1—C5a—C6	105 (1)
C1b—S1—C3b	94 (2)	S1—C5b—C6	103 (2)
C1b—S1—C5b	106 (1)		

Symmetry codes: (i) $-x, \frac{1}{2} - y, z$; (ii) $y - \frac{1}{2}, \frac{1}{2} - x, \frac{5}{2} - z$; (iii) $\frac{1}{2} - y, \frac{1}{2} + x, \frac{5}{2} - z$; (iv) $\frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{2} - z$.Table 3. Average H—I bond distances (Å) of some isolated HgI₄²⁻ ions

HgI ₄ ²⁻ (aq) ^a	2.78	(CH ₃ N) ₂ [HgI ₄](s) ^b	2.78
HgI ₄ ²⁻ (DMSO) ^c	2.79	(C ₃ H ₉ S) ₂ [HgI ₄](s) ^f	2.73
HgI ₄ ²⁻ (DMSO) ^d	2.79	(C ₆ H ₁₅ S) ₂ [HgI ₄](s) ^g	2.79
HgI ₄ ²⁻ (DMSO) ^e	2.80	Ca[HgI ₄].8H ₂ O(s) ^k	2.80
HgI ₄ ²⁻ (DMF) ^b	2.80	Sr[HgI ₄].8H ₂ O(s) ^l	2.78
HgI ₄ ²⁻ (DMF) ^f	2.80	C ₆ (OH) ₁₂ N ₁₈ O ₁₄ S ₁₂ ·[Hg ₃ I ₁₀][HgI ₄](s) ^j	2.83
Cs ₂ [HgI ₄](s) ^e	2.82	(Me ₃ PCH ₂ CN) ₂ [HgI ₄](s) ^m	2.82
Cs ₂ [HgI ₄](s) ^f	2.78	(Me ₃ PCH ₂ CN) ₂ [HgI ₄](s) ^m	2.79
(Cs ₃ I)[HgI ₄](s) ^g	2.77		
(Cs ₃ I)[HgI ₄](s) ^h	2.77		

References: (a) Sandström & Johansson (1977); (b) Gaizer & Johansson (1968); (c) Gaizer & Johansson (1969); (d) Sandström (1978); (e) Pakhomov & Fedorov (1973); (f) Sjövall & Svensson (1988); (g) Fedorov *et al.* (1975); (h) Körfer *et al.* (1986); (i) Fenn (1966b); (j) this work; (k) Thiele *et al.* (1982); (l) Cramer & Carrié (1990); (m) Bellamy *et al.* (1981).

The intensities decreased by an average of 0.44% during the data collection. The values of *I* and $\sigma(I)$ were corrected for Lorentz, polarization and absorption effects. The Laue group is 4/*m* and systematic extinctions (*hkl*: $h+k+l \neq 2n$; *hk0*: $h \neq 2n$; *00l*: $l \neq 4n$) are consistent with space group I4₁/a (No. 88), which was verified by the statistical analysis of intensity distribution, packing considerations and the successful refinement of the structure.

Data collection: local software. Cell refinement: local software. Data reduction: *PREPROCESS* and *PROCESS* in *TEXSAN* (Molecular Structure Corporation, 1993). Program(s) used to solve structure: *MITHRIL* in *TEXSAN*. Program(s) used to refine structure: *LS* in *TEXSAN*. Software used to prepare material for publication: *FINISH* in *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1033). Services for accessing these data are described at the back of the journal.

Refinement

Refinement on *F*

R = 0.037

wR = 0.048

S = 1.633

1351 reflections

85 parameters

H atoms not located

Weighting scheme based

on measured s.u.'s;

 $w = 4F_o^2/\sigma^2(F_o^2)$ $(\Delta/\sigma)_{\max} = 0.060$ $\Delta\rho_{\max} = 0.82 \text{ e } \text{Å}^{-3}$ $\Delta\rho_{\min} = -0.71 \text{ e } \text{Å}^{-3}$

Extinction correction:

Zachariasen (1968) type

2 Gaussian isotropic

Extinction coefficient:

 2.02×10^{-8} Scattering factors from *Inter-**national Tables for X-ray**Crystallography* (Vol. IV)Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

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

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Hg1	0	1/4	5/8	0.0512
Hg2	0	1/4	1/8	0.0484
I1	0.01132 (8)	0.08367 (7)	0.56589 (4)	0.0710
I2	0.04904 (7)	0.09454 (6)	0.06233 (4)	0.0643
S1	0.2744 (2)	0.1806 (2)	0.4656 (1)	0.0605
C1a†	0.307 (2)	0.140 (2)	0.531 (1)	0.080 (8)
C1b‡	0.253 (3)	0.210 (3)	0.535 (2)	0.09 (1)
C2	0.365 (1)	0.215 (1)	0.5594 (7)	0.1061
C3a†	0.199 (2)	0.081 (2)	0.442 (1)	0.079 (8)
C3b‡	0.258 (3)	0.053 (3)	0.474 (2)	0.08 (1)
C4	0.270 (1)	-0.002 (1)	0.4312 (10)	0.1116

References

- Bellamy, A. J., Gould, R. O. & Walkinshaw, M. D. (1981). *J. Chem. Soc. Perkin Trans. 2*, pp. 1099–1104.
- Bengtsson, L. A., Norén, B. & Stegemann, H. (1995). *Acta Chem. Scand.* **49**, 391–398.
- Bengtsson-Kloo, L., Berglund, J., Stegemann, H., Svensson, C. & Svensson, P. H. (1996). *Acta Cryst.* **C52**, 3045–3047.
- Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.
- Cramer, R. E. & Carrié, M. J. J. (1990). *Inorg. Chem.* **29**, 3902–3914.
- Fedorov, P. M., Pakhomov, V. I. & Ivanova-Korfini, I. N. (1975). *Koord. Khim.* **1**, 1569–1574.
- Fenn, R. H. (1966a). *Acta Cryst.* **C20**, 20–24.
- Fenn, R. H. (1966b). *Acta Cryst.* **C20**, 24–27.
- Gaizer, F. & Johansson, G. (1968). *Acta Chem. Scand.* **22**, 3013–3022.
- Gaizer, F. & Johansson, G. (1969). *Magy. Kem. Foly.* **75**, 553–559.
- Körfer, M., Fuess, H. & Bats, J. W. (1986). *Z. Anorg. Allg. Chem.* **543**, 104–110.
- Molecular Structure Corporation (1993). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Pakhomov, V. I. & Fedorov, P. M. (1973). *Kristallografiya*, **17**, 942–948.
- Sandström, M. (1978). *Acta Chem. Scand. Ser. A*, **32**, 627–641.
- Sandström, M. & Johansson, G. (1977). *Acta Chem. Scand. Ser. A*, **31**, 132–140.
- Sjövall, R. & Svensson, C. (1988). *Acta Cryst.* **C44**, 207–210.
- Stegemann, H., Tebbe, K.-F. & Bengtsson, L. A. (1995). *Z. Anorg. Allg. Chem.* **621**, 165–170.
- Thiele, G., Brodersen, K. & Pezzeri, G. (1982). *Z. Anorg. Allg. Chem.* **491**, 308–318.
- Zachariasen, W. H. (1968). *Acta Cryst.* **A24**, 212–216.

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Aqua(diethylenetriamine)(isonicotinato)-copper(II) Hexafluorophosphate

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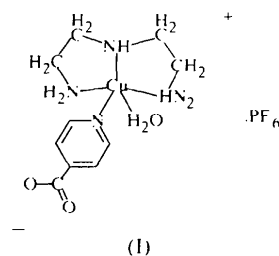
Abstract

The Cu atom in the title complex, [*N*-(2-aminoethyl)-*N*]-1,2-ethylenediamine-*N,N'*]aqua(4-pyridine-carboxylato-*N*)copper(II) hexafluorophosphate, [Cu(C₆H₄NO₂)(C₄H₁₃N₃)(H₂O)]PF₆, is coordinated in a square-pyramidal arrangement by three N atoms

of *N*-(2-aminoethyl)-1,2-ethylenediamine (diethylenetriamine) and one N atom from the pyridine ring of isonicotinate in equatorial positions, and by one water molecule in an axial position.

Comment

Isonicotinate is a ligand with two types of binding site. It can coordinate with transition metal ions *via* one or two O atoms from the carboxylate group or the N atom from the pyridine ring. Only a few structures containing copper(II) and isonicotinate have been reported (Okabe *et al.*, 1993). In the course of our systematic study of the coordination mode of isonicotinate with copper(II) in mixed-ligand systems, we isolated the complex [Cu(dien)(iso)(H₂O)]PF₆ (I), where dien is diethylenetriamine and iso is isonicotinate. We report here its preparation and structure.



The crystal structure of (I) comprises discrete [Cu(dien)(iso)(H₂O)]⁺ cations and hexafluorophosphate anions (Fig. 1). The coordination polyhedron of the Cu atom is a square pyramid whose base is formed by three N atoms from the amine ligand and one pyridine N atom from isonicotinate. A coordinated water molecule occupies the apex of the pyramid with a Cu—O distance of 2.316(2) Å. The Cu atom lies 0.199(1) Å above the mean plane defined by the four basal N atoms. This is in good agreement with the situation found in most square-pyramidal structures where the Cu atom is lifted *ca* 0.2 Å towards the apex of the pyramid (Hathaway & Billing, 1970). The Cu—N bond lengths to dien fall in the range 2.005(2)–2.017(2) Å. Among these, that from the Cu atom to the secondary N atom of the amine ligand is the shortest, as was found by Sato *et al.* (1986) and Hu *et al.* (1997). The Cu to pyridine N (Cu—N₁) bond length is 2.016(2) Å. This is comparable to the Cu—N_{iso} bond length found in the square-planar coordinated Cu^{II} complex [Cu(iso)₂(H₂O)₂].2H₂O (2.004 Å; Okabe *et al.*, 1993). The dihedral angle between the pyridine ring plane and the basal plane of the square pyramid is 61.49(7)°. The hexafluorophosphate anion is below the square pyramid and F1 is close to the Cu atom at a distance of 2.969(2) Å. An extensive hydrogen-bonding network is present in the crystal, with hydro-