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Tetramethylammonium Tetrakis(4-chlorobenzenethiolato)mercurate(II). Synthesis and Molecular Structure

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The title member of the almost unknown class of anionic tetrathiolatomercurate(II) complexes can be easily crystallised in good yield from the stoichiometric mixture of components. The $[Hg(SC_6H_4Cl)_4]^{2-}$ *complex has approximately* D_{2d} *symmetry: Hg–S 253.7, 255.2 pm; S–Hg–S ranges 101.8–119.8°. Crystal data: monoclinic* C2, a = *1220.9(3),* b = *1451.5(1),* c = *1149.5(2) pm,* β = *111.83(1)°,* Z *= 2,* R *= 0.025 (2131 data).*

Introduction

Many aspects of mercury–thiolate chemistry have been investigated since the discovery of mercaptans in 1834 [1]. In recent years interest has centred on the bio-thio-chemistry of mercury, with emphasis on organomercury and aminoacid–mercury compounds [2–5]. Despite this, the fundamental class of anionic complexes generally formulated $[Hg_x(SR)_y]^{(2x-y)}$ involving mono-functional organothiolates RS^-, is not well known. The perhalobenzenethiolate compounds $(Et_4N)_2[Hg(SC_6F_5)_4]$ [6] and $(Ph_4As)_2[Hg(SC_6Cl_5)_4]$ [7] have been described. Klar *et al.* [8, 9] have described the preparation of $[Hg(SPh)_3]^-$ and $[Hg(SPh)_4]^{2-}$ by reaction of $Hg(SPh)_2$ with $Ph_4P^+PhS^-$ in liquid ammonia. They have also synthesised analogous selenolates and tellurolates and $[Hg_2(SePh)_7]^{3-}$ and $[Hg_3(TePh)_{11}]^{5-}$, and reported [10] the trigonal planar structure of $[Hg(TePh)_3]^-(Ph_4P^+)$. Bowmaker and Dobson [11] have prepared $(Et_4N)[Hg(SR)_3]$, R = Me, Bu^t and $[(Ph_3P)_2N][Hg(SBu^t)_3]$, and have concluded from vibrational spectra that $[Hg(SBu^t)_3]^-$ is trigonal pyramidal and that $[Hg(SMe)_3]^-$ is associated in the solid state. The dimeric structure $[(MeS)_2Hg(\mu\text{-}SMe)_2Hg(SMe)_2]^{2-}$ has been confirmed crystallographically [12].

We have discovered that $[Hg(SC_6H_4Cl\text{-}p)_4]^{2-}$ can easily be prepared and isolated with Me_4N^+ in good yield. This paper also reports the pseudo-D_{2d} molecular structure of the anion in crystalline $(Me_4N)_2[Hg(SC_6H_4Cl)_4]$.

Experimental

Preparation

All solutions were deoxygenated with nitrogen. A solution of $Hg(NO_3)_2H_2O$ (3.4 g, 10 mmol) in methanol (30 ml) was added to a solution containing 4-chlorobenzenethiol (5.7 g, 40 mmol), triethylamine (4.0 g, 40 mmol), and tetramethylammonium chloride (2.9 g, 27 mmol) in methanol (70 ml) at room temperature. Flocculent precipitation of $Hg(SC_6H_4Cl)_2$ during the addition quickly redissolved. Propanol (70 ml) was added, and methanol removed by distillation at room temperature until crystallisation began. The mixture was heated to dissolve the product, sealed, and allowed to crystallise slowly, first at room temperature and then at 0 °C. The large well-formed crystals, almost colourless, were filtered, washed with propanol, and vacuum dried. Yield 6.2 g (67%). Further solvent removal yields additional product contaminated with Me_4NNO_3, which can be removed by washing the mixture with cold water.

Anal.: Found: C, 42.03; H, 4.55; N, 2.91%. Calcd. for $C_{32}H_{49}N_2HgS_4Cl_4$: C, 41.63; H, 4.37; N, 3.03. This compound is soluble in acetonitrile, slightly soluble in acetone and the lower alcohols, and not soluble in toluene, diethylether. It can be recrystallised from acetonitrile/propanol or acetonitrile/toluene. The crystals are moderately stable in air.

Crystallography

Photography of crystals from the preparative reaction mixture revealed frequent twinning, and the occurrence of a monoclinic C-centred lattice. All

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TABLE I. Atomic Coordinates.

Atom	x/a	y/b	z/c
Hg	0	0	0
S1	0.1392(1)	−0.0873(1)	0.1866(1)
S2	−0.1432(1)	0.0952(1)	0.0655(1)
Cl1	−0.1381(1)	−0.4117(1)	0.3172(2)
Cl2	0.1348(2)	0.4081(1)	0.4373(2)
C11	0.0605(4)	−0.1776(3)	0.2188(4)
C12	0.1147(5)	−0.2352(4)	0.3212(5)
C13	0.0572(5)	−0.3056(4)	0.3540(4)
C14	−0.0591(5)	−0.3226(3)	0.2835(5)
C15	−0.1220(5)	−0.2659(4)	0.1795(5)
C16	−0.0612(4)	−0.1946(4)	0.1495(4)
C21	−0.0610(4)	0.1819(4)	0.1654(5)
C22	−0.1208(4)	0.2468(4)	0.2099(5)
C23	−0.0656(4)	0.3139(4)	0.2922(5)
C24	0.0576(5)	0.3205(4)	0.3319(5)
C25	0.1222(5)	0.2574(4)	0.2924(5)
C26	0.0594(5)	0.1894(4)	0.2070(5)
NI	0.0017(9)	0.0128(6)	0.5049(7)
C1N1	−0.0737(16)	0.0387(13)	0.5725(16)
C2N1	0.0664(16)	−0.0710(9)	0.5596(17)
C3N1	−0.0708(16)	−0.0037(12)	0.3736(9)
C4N1	0.0850(15)	0.0869(11)	0.5139(16)
N2	0.0092(8)	0.4898(7)	0.0004(8)
C1N2	0.0879(16)	0.4114(12)	0.0146(20)
C2N2	0.0790(17)	0.5723(11)	0.0509(20)
C3N2	−0.0613(17)	0.5036(16)	−0.1322(10)
C4N2	−0.0686(16)	0.4719(16)	0.0681(18)
HC12	0.196(3)	−0.224(2)	0.369(3)
HC13	0.098(3)	−0.343(2)	0.427(3)
HC15	−0.204(3)	−0.276(2)	0.132(3)
HC16	−0.106(3)	−0.156(2)	0.075(3)
HC22	−0.203(3)	0.243(2)	0.180(3)
HC23	−0.109(3)	0.356(2)	0.322(3)
HC25	0.207(3)	0.261(2)	0.326(3)
HC26	0.104(3)	0.146(2)	0.177(3)

subsequent measurements were made with a single crystal on a CAD4 diffractometer. Crystal data: a = 1220.9(3), b = 1451.5(1), c = 1149.5(2) pm, β = 111.83(1)°, Space-group $C2$; crystal faces {100}, {001}, {110}, {021}, dimensions 0.13 X 0.23 X 0.26 mm, d_{obs} (flotation) = 1.62(2) g cm^{-3}, $Z = 2 \times HgS_4Cl_4N_2C_{32}H_{40}$, d_{calc} = 1.62 g cm^{-3}; CuK$_\alpha$ radiation, μ = 127.4 cm^{-1}, 2131 independent intensity measurements, $2\theta_{max}$ = 150°, 2117 observed ($I > 3\sigma(I)$) data; absorption corrections applied.

Patterson and Fourier methods revealed all atoms of the structure in space-group $C2$, except the cation carbon atoms. After refinement to R = 0.045 a difference map indicated that both Me_4N^+ groups were disordered and librating about twofold sites. At this stage the crystal enantiomer was determined by assessment of the better agreement of refined structure factors and the better geometry of the ligands.

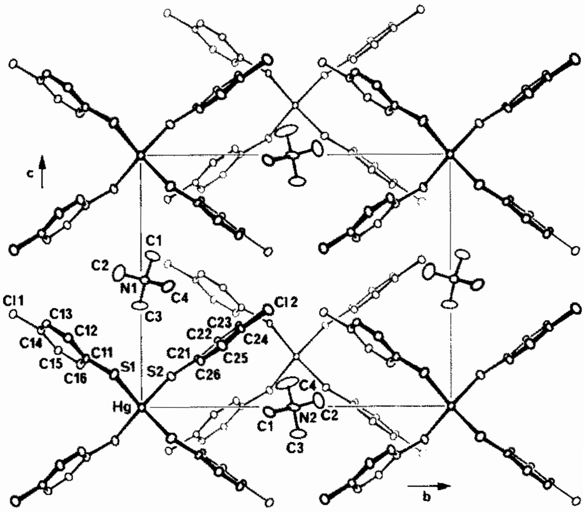

Fig. 1. Part of the lattice of $(Me_4N)_2[Hg(SC_6H_4Cl)_4]$, viewed perpendicular to the bc plane which is a layer of cations (disordered) and anions. Two anions of the lower layer generated by C-centering are shown. Twofold axes are parallel to b.

The refinement was continued using constrained least squares to define the two independent Me_4N^+ groups [13]. Three rotational and three translational displacement parameters and one parameter describing the C–N bond length described the atoms of each of the Me_4N^+ groups, and the C–N bond lengths of the two groups were slack constrained to approach equality [14]. A TLX model was used to describe the thermal motion of the Me_4N^+ groups. Third order cumulant terms and corrections to atom positions associated with the TLX model were applied [15]. All other atomic parameters were unconstrained. The constrained refinement procedure allowed the idealised tetrahedral Me_4N^+ groups to be readily refined without forcing the nitrogen atoms to lie exactly on the twofold axes. Hydrogen atoms of the methyl groups were not located.

Refinement converged with R = 0.025, R_w = $[\Sigma w|\Delta F|^2/\Sigma w|F_o|^2]^{1/2}$ = 0.034, $[\Sigma w|\Delta F|^2/(m - n)]^{1/2}$ = 1.51, $w = [\sigma(F_o)]^{-2}$ for all 2131 observed data.

Scattering factors, for uncharged atoms, were from International Tables [16].

Atomic coordinates are listed in Table I. The Figure shows part of the lattice structure, the atom labelling, and the disordered Me_4N^+ groups close to the twofold axes. The crystal structure is effectively comprised of layers perpendicular to a^*, each layer containing alternating cations and anions along a rectangular network 1452 X 1150 pm. In the Figure the view down a^* shows one such layer, and includes two anions of an adjacent layer related by the C-centering.

The Me_4N^+ groups are disordered about b. In the two crystallographically distinct Me_4N^+ sites a twofold axis of the tetrahedron lies at 5.1° or 3.1° from the a^* direction, and so an approximate D_2 symmetry (axes a^*, b, c) occurs at the cation sites. The complete $[Hg(SC_6H_4Cl)_4]^{2-}$ ion, on a crystallographic twofold axis, has approximate D_{2d} symmetry, associated with the same directions a^* (principal axis), b, c (subsidiary axes).

Crystal Twinning

Weissenberg photographs of twinned crystals show that the twin components overlap perfectly in the hk0 net, showing that the c directions of both components align exactly. The C-centering offsets one layer of the structure relative to the next (Fig. 1). The twinning can be regarded as a modification of this interlayer arrangement. Comparison of the morphology of twinned and untwinned crystals shows that either 2_c (a twofold axis parallel to c) or a mirror plane perpendicular to a^* is the twinning operation, rather than alternatives such as a mirror plane perpendicular to c. Both options are in agreement with the alignment of the c direction and the change in stacking of layers. The twofold axis parallel to c is a pseudosymmetry element of all the ion sites, and would appear to be the preferred option. The twinning changes the unit cell repeat from a, b, c to $2_c(a,b,c) = 2_c\,a,\ -b,\ c$. In reciprocal space, a^*, b^*, c^* changes to $2_c(a^*,b^*,c^*) = -a^*,\ -b^*,\ 2_cc^*$, where $2_cc^* = -0.7900a^* + c^*$. Had 2_cc^* been exactly $-0.8a^* + c^*$ the reflections hkl would overlap exactly with the twin related $h'k'l'$ reflections whenever $h' = -h - 0.8l$, $k' = -k$, $l' = l$, *i.e.* when $h' = -h - 4n$, $k' = -k$, $l = l' = 5n$. Equi-inclination Weissenberg photographs show the approximate overlap of such reflections for layers with $l = 5n$, while layers with $l \neq 5n$ show no overlap of twin related reflections. The relatively high symmetry and non-polar environments of the ion sites are consistent with the twinning and disorder observed.

TABLE II. Distances (pm) and Angles (deg) in the $[Hg(SC_6H_4Cl)_4]^{2-}$ Ion.

Hg–S1	253.7(1)	Hg–S2	255.2(1)
S1–Hg–S1′[a]	119.79(6)	S2–Hg–S2′	114.43(7)
S1–Hg–S2	109.84(4)	S1–Hg–S2′	101.76(4)
S1–C11	174.5(5)	S2–C21	174.7(5)
Hg–S1–C11	107.9(2)	Hg–S2–C21	107.2(2)
C11–C12	139.3(7)	C21–C22	140.0(7)
C12–C13	136.9(8)	C22–C23	135.0(8)
C13–C14	137.1(7)	C23–C24	140.3(8)
C14–C15	141.9(7)	C24–C25	139.0(8)
C15–C16	139.0(7)	C25–C26	140.2(8)
C16–C11	142.1(7)	C26–C21	137.1(7)
C14–Cl1	174.1(5)	C24–Cl2	176.7(6)
S1–C11–C12	120.2(3)	S2–C21–C22	118.4(4)
S1–C11–C16	123.7(4)	S2–C21–C26	124.5(4)
C12–C11–C16	116.0(4)	C22–C21–C26	117.1(5)
C11–C12–C13	123.3(5)	C21–C22–C23	123.3(5)
C12–C13–C14	119.7(5)	C22–C23–C24	118.2(5)
C13–C14–C15	120.7(5)	C23–C24–C25	121.2(5)
C13–C14–Cl1	122.7(4)	C23–C24–Cl2	120.4(4)
C15–C14–Cl1	116.6(4)	C25–C24–Cl2	118.4(4)
C14–C15–C16	118.0(5)	C24–C25–C26	117.6(5)
C15–C16–C11	122.2(4)	C25–C26–C21	122.4(5)

[a] ′ ≡ −x, y, −z

Results and Discussion

Well-formed colourless crystals of $(Me_4N)_2[Hg(SC_6H_4Cl\text{-}p)_4]$ are readily obtained in good yield from a stoichiometric mixture of mercuric nitrate, thiol and trialkylamine, and tetramethylammonium halide, dissolved in the lower alcohols. The compound is soluble in acetonitrile, from which it can be recrystallised by addition of toluene or alcohols. The presence of water causes $[Hg(SC_6H_4Cl)_4]^{2-}$ in solution to dissociate to $[Hg(SC_6H_4Cl)_2]$, which is much less soluble in all solvents.

The $[Hg(SC_6H_4Cl)_4]^{2-}$ ion is tetrahedral. In the crystal studied, with Me_4N^+, the anion has crystallographic symmetry C_2, but the conformations of the ligands are such that the complete anion approximates the higher symmetry of group D_{2d}. As can be seen from Fig. 1, the principal twofold axis of the D_{2d} idealisation is not the crystallographic twofold axis (b) but the axis (a^*) perpendicular to the b c plane. The subsidiary twofold axes of $[Hg(SC_6H_4Cl)_4]^{2-}$ are b and c.

Intra-ion dimensions are given in Table II. This is the most accurate structure determination for a mercury complex with one type of thiolate ligand only, and the first structure report for non-bridging $Hg(SR)_4$ coordination. The Hg–S distances, 253.7(1), 255.2(1) pm, may be compared with values of 236 pm (in $Hg(SMe)_2$ [7]), 245 pm (in $Hg(SEt)_2$ [18]), 233 pm ($2,6\text{-}Me_2C_6H_3SHgPh$ [19]) and 236 pm ($Ph_3CSHgCH_2Ph$ [20]), all for two coordinate mercury, and 259, 266 pm for $Hg(\mu\text{-}SR)_4$ coordination in $Hg(SBu^t)_2$ [21].

Least squares planes calculations are provided in Table III. The two ligand ring planes are inclined by 14.8, 13.6° to the two principal (D_{2d}) S–Hg–S coordination planes, between which the angle is 95.4°.

In the crystal $[Hg(SC_6H_4Cl)_4]^{2-}$ ions are surrounded by six Me_4N^+ cation sites in approximately octahedral array. Each cation is nestled between the planes of four SC_6H_4Cl ligands from two anions with the same x coordinate (see Fig. 1). The cations are disordered about the crystallographic twofold axes.

TABLE III. Molecular Planes and Interplane Angles.

Plane	Composition	Mean Atomic Displacement (pm)
A	S1, Hg, S2′[a]	–
B	S2, Hg, S1′	–
C	ligand 1, SC_6Cl	0.88
D	ligand 2, SC_6Cl	1.48
E	Hg, S1, C11	–
F	Hg, S2, C21	

Interplane Angles (deg)

	A	D	E
B	95.4	13.6	
C	14.8	78.2	1.5
F		4.3	

[a] ′ ≡ −x, y, −z

There are no unusual non-bonding contacts in the crystal.

The HgS_4 coordination contains angular distortions from the tetrahedral ideal. Referring to the more realistic D_{2d} ideal for the anion, the S–Hg–S angles are distinguished as to whether they include the principal or subsidiary twofold axes. The two S–Hg–S angles about the principal axis are S1–Hg–S2′ and S1′–Hg–S2, crystallographically equivalent at 101.8°, and the smallest of the S–Hg–S angles. The four S–Hg–S angles at the subsidiary axes are comprised of two at 109.8° (about the crystal *c* axis) and two at larger values 114.4 and 119.8° (about the crystal *b* axis). There is some parallel between these angles and the similar distribution in $(Ph_4P)_2[Cd(SPh)_4]$ which also approximates D_{2d} molecular symmetry [22, 23]. The S–Cd–S angles, with the comparable Hg values in parentheses, are: principal axis, 98.7 (101.8), 108.5 (101.8); subsidiary axes, 110.2 (109.8), 110.8 (109.8), 114.0 (114.4), 120.0 (119.8). It is claimed that in a series of isostructural crystals $(Ph_4P)_2[M(SPh)_4]$ the angular distortions just described can be attributed to interactions between phenyl ring ortho-hydrogen atoms and sulfur atoms, but there is ambiguity as to whether these interactions are attractive or repulsive [24]. We shall publish separately further analysis of the conformations of phenyl rings in tetrahedral $M(SAr)_4$ complexes and other compounds with terminal arenethiolate ligands.

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