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Preparation of complexes of the 3-trimethylammonio-1-propanethiolato ligand, $[M\{S(CH_2)_3NMe_3\}_2](PF_6)_2$, M = Zn, Cd, Hg. Crystal structures of monomeric and polymeric forms of the mercury complex

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Abstract

Reaction of metal acetates with 3-trimethylammonio-1-propanethiol hexafluorophosphate $[HS(CH_2)_3NMe_3](PF_6)$ in a methanol–acetonitrile–aqueous sodium hydroxide solution gives complexes of formula $[M\{S(CH_2)_3NMe_3\}_2](PF_6)_2$ (M = Zn, Cd, Hg) as crystalline or microcrystalline solids. In the case of mercury, an alternative product, $[M\{S(CH_2)_3NMe_3\}_2](PF_6)_2\cdot\frac{1}{2}[S(CH_2)_3NMe_3]$ is sometimes obtained instead, from an apparently identical procedure. The crystal structures of both mercury complexes have been determined. $[Hg\{S(CH_2)_3NMe_3\}_2](PF_6)_2\cdot\frac{1}{2}[S(CH_2)_3NMe_3]$ contains polymeric chains of mercury atoms bridged by pairs of aminothiolato ligands to give tetrahedral coordination with Hg–S 2.564(3) and 2.567(3) Å. The cation chains run parallel to the tetragonal unit cell *c* axis and are separated by PF_6^- anions. Channels in the structure are probably occupied by the disordered additional ligand molecules in zwitterionic form. $[Hg\{S(CH_2)_3NMe_3\}_2](PF_6)_2$ contains essentially linear mononuclear cations with Hg–S 2.321(9)–2.370(11) Å, which are linked by weaker Hg...S interactions (2.98–3.59 Å) into loose octameric cation units. These are widely separated from each other by the surrounding anions.

Introduction

The coordination of cysteine residues of metallothioneins (MT) and MerR metalloregulatory protein (MerR) to zinc, cadmium [1, 2] and mercury [3] atoms is nowadays well documented and the object of intensive study. However, in contrast to the progress that has been made in the detailed structural elucidation of the Cd(II) and Cd(II)–Zn(II) forms of MT [2], relatively little is known about the details of the coordination geometries of the metal centres in Hg–MT. Recent studies based on the presence of low-energy UV transitions have led to the proposal that Hg(II) adopts both a tetrahedral and a linear coordination in this protein [4].

The study of the molecular details of the mercury(II) resistance response in bacteria at the level of gene activation, where MerR is involved [5], has provided evidence that the coordination geometry around Hg in Hg–MerR is trigonal planar and that three cysteine residues are responsible for metal binding [3b, c].

The occurrence of two-, three- and four-coordinate thiolate complexes in the chemistry of Hg(II) is well known [6, 7]. The question of what determines the coordination of mercury in di(alkylthio)mercury(II) complexes, however, remains as yet unresolved. In the case of simple alkyl groups R in the RS^- ligands, both $[Hg(SMe)_2]$ [8] and $[Hg(SEt)_2]$ [9] contain essentially linearly coordinated Hg, with only weak interactions between molecules, but $[Hg(SBu^t)_2]$ [10] is polymeric, with tetrahedral coordination; here, the obvious difference in the alkyl groups is the degree of substitution on the α-carbon atom. Such a simple explanation does not, however, extend to other thiolate ligands. Complexes with several aliphatic γ-mercaptoamine ligands, which under appropriate conditions behave as monofunctional thiols with a solubilizing amine group, have linear digonal coordination of Hg, as is demonstrated by the crystal structure of bis(4-mercapto-1-methylpiperidi-

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nium)mercury(II) perchlorate [11], but the analogous cadmium(II) complex is polymeric [12], similar to $[Hg(SBu^t)_2]$ [10]. It has been suggested that the effective electronegativity of the sulfur atom determines the stereochemistry around Hg [13], and some of the previous results could be interpreted in accordance with this, but our results reported here indicate that the factors affecting the coordination geometry can not be so easily identified.

As part of our work on Hg(II) aliphatic γ-mercaptoamine complexes [11, 14–16], we have prepared $[Hg\{S(CH_2)_3NMe_3\}_2](PF_6)_2$, together with the Zn(II) and Cd(II) analogues. The mercury complex has been obtained in both mononuclear and polymeric forms, with linear and tetrahedral coordination, respectively, from apparently identical synthetic procedures.

Experimental

All reagents were research grade, and were not further purified. 3-Dimethylamino-1-propanethiol was prepared as already described [17]. All thiolate preparations were carried out under an atmosphere of dry nitrogen, standard Schlenk techniques being used.

3-Trimethylammonio-1-propanethiol hexafluorophosphate

An aqueous solution (20 ml) of 3-dimethylamino-1-propanethiol (1 g, 8.4 mmol) containing hydrogen peroxide (4.3 ml, 3%) was refluxed for 5 min. The resulting disulfide, $[Me_2N(CH_2)_3S]_2$, was extracted 10 times with 10 ml aliquots of diethyl ether and the combined extracts dried over potassium carbonate. To the filtered solution, methyl iodide (1 ml) was added, and the reaction mixture was stirred overnight. Evaporation of the solvent yielded the iodide salt, $[Me_3N(CH_2)_3S]_2X_2$, X = I, which was converted into the choride by adding slowly hydrogen peroxide (4.3 ml, 3%) and hydrochloric acid (5 ml) to an aqueous solution (20 ml) of the iodide. The iodine produced was extracted with diethyl ether and then with carbon tetrachloride until the colour of both phases remained unchanged. This solution became colourless on gentle heating. The chloride of the disulfide (X = Cl) was then reduced by refluxing it for 3 h with an excess of powdered tin in 50 ml of 1 M hydrochloric acid. The compound formed, 3-trimethylammonio-1-propanethiol trichlorostannate(II), was not isolated from solution. Into this was passed hydrogen sulfide until no more precipitation could be seen. Tin(II) sulfide was filtered off. The filtrate was evaporated to dryness under vacuum and the solid residue dissolved in a 1:1 (vol./vol.) mixture of dichloromethane and acetonitrile. An aliquot of this solution was titrated iodometrically in order to calculate the stoichiometric quantity of hexafluorophosphate anion to be added. A solution of potassium hexafluorophosphate (0.23 g, 1.26 mmol) in methanol was added. Potassium chloride was filtered off and the filtrate evaporated to dryness in vacuum. The white solid was washed with dry diethyl ether several times, dried *in vacuo* and kept under nitrogen. 3-Trimethylammonio-1-propanethiol hexafluorophosphate thus formed is hygroscopic. Its purity could only be checked by iodometric determination of the –SH content (97%) [18].

Preparation of $[M\{S(CH_2)_3NMe_3\}_2](PF_6)_2$, *M* = *Zn, Cd, Hg, and* $[Hg\{S(CH_2)_3NMe_3\}_2](PF_6)_2\cdot\frac{1}{2}[S(CH_2)_3NMe_3]$

The same procedure was followed in each case. 3-Trimethylammonio-1-propanethiol hexafluorophosphate (57.6 mg, corresponding to 0.20 mmol of pure thiol) was dissolved in a mixture of acetonitrile (1 ml), methanol (1 ml) and water (1 ml). Aqueous sodium hydroxide solution (12.8 mg, 0.32 mmol in 2 ml) was added, followed by the corresponding metal acetate dihydrate (0.08 mmol) dissolved in 2.0 ml of water. The slightly cloudy solution was filtered and kept under nitrogen at room temperature. After several days the solid product was isolated. For M = Zn, this was a colourless crystalline material (complex **1**); for M = Cd, it was a colourless microcrystalline powder (complex **2**). Of eight repeated preparations for M = Hg, four gave pale yellow crystals (complex **3**), and four gave a colourless microcrystalline solid, which upon recrystallization from concentrated aqueous solutions always yielded colourless crystals (complex **4**). Analytical data are presented in Table 1.

TABLE 1. Analytical data

Complex	C(%)	N(%)	S(%)
$[Zn\{S(CH_2)_3NMe_3\}_2](PF_6)_2$ (**1**)			
Calc.	23.18	4.51	9.96
Found	22.80	4.16	9.88
$[Cd\{S(CH_2)_3NMe_3\}_2](PF_6)_2$ (**2**)			
Calc.	21.55	4.19	9.58
Found	22.21	3.89	9.82
$[Hg\{S(CH_2)_3NMe_3\}_2](PF_6)_2\cdot\frac{1}{2}[S(CH_2)_3NMe_3]$ (**3**)			
Calc.	20.95	4.86	9.32
Found	21.42	4.67	9.34
$[Hg\{S(CH_2)_3NMe_3\}_2](PF_6)_2$ (**4**)			
Calc.	19.04	3.70	8.47
Found	19.34	3.63	8.59

Instrumentation

Microanalyses were performed with a Carlo Erba NA 1500 analyzer. IR spectra were recorded in the range 4000–400 cm^{-1} from KBr pellets on a Perkin–Elmer 1710 spectrophotometer. The far IR spectrum of the ligand and of the corresponding mercury complex were recorded from polyethylene pellets on a Bomem DA3 spectrophotometer. The Raman spectra were recorded on a Dilor spectrophotometer using powdered samples and 514.5 nm excitation. X-ray powder diffraction traces were obtained from a Siemens D-500 diffractometer with nickel-filtered Cu Kα radiation.

X-ray crystallography

All measurements were made on a Stoe-Siemens four-circle diffractometer at room temperature (22 °C) with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Crystal data and other information on the determination of the structures are given in Table 2. Cell parameters were refined from 2θ values (20–25°) of reflections measured at $\pm\omega$. Intensities were measured by ω/θ scans with on-line profile fitting [19]. Corrections were applied for the observed decay in intensity of three standard reflections, and for absorption by a semi-empirical method based on the measurement of sets of equivalent reflections at a range of azimuthal angles [20]. The structures were determined from Patterson and difference syntheses, and refined by blocked-cascade least-squares methods to a minimum of $\Sigma w\Delta^2$, with $\Delta = |F_o| - |F_c|$, $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + A_1 + A_2G + A_3G^2 + A_4H + A_5H^2 + A_6GH$, $G = F_o/F_{max}$, $H = \sin\theta/\sin\theta_{max}$, using reflections with $F_o > 4\sigma_c(F_o)$, (σ_c from counting statistics only) [21].

For complex **3**, all non-H atoms were refined with anisotropic thermal parameters and H atoms were constrained (C–H 0.96 Å, H–C–H 109.5°, $U(H) = 1.2U_{eq}(C)$); the anions were restrained to an ideal octahedral geometry with a common P–F bond length, which refined to 1.544(3) Å. The atoms of the polymeric chain cations and of the PF_6^- anions were all well defined, but the additional half-molecule of ligand per Hg atom was not located; unresolved residual electron density up to 3 eÅ^{-3} in the channels between the cations, running parallel to the *c* axis, probably indicate disorder and partial occupancy over these sites.

For complex **4**, anisotropic thermal parameters were refined for the Hg, S and P atoms only; H atoms were not included. Chemically equivalent C–C and C–N bond lengths and angles at C and N within the ligands were restrained to be equal, and the anions were constrained to ideal octahedral geometry with P–F fixed at 1.544 Å; two-fold disorder of orientation was resolved for one anion, with relative occupancies 57:43(2)%.

For both structures, extinction effects were insignificant. Atomic scattering factors were taken from ref. 22. Refinement of $\eta = 0.28(9)$ for the non-centrosymmetric structure of complex **3** indicates possible partial twinning [23]. The largest electron density features in final difference syntheses were close to Hg atoms and anions, and in the channels of complex **3**.

Refined atomic coordinates for the two structures are given in Tables 3 and 4. See also 'Supplementary material'.

Results and discussion

Synthesis

The same experimental procedure has been followed in the synthesis of the Zn, Cd and Hg complexes of the 3-trimethylammonio-1-propanethiolato ligand; the stoichiometric ligand:metal ratio in the reaction mixture was 2.5:1 in each case. The amount of ligand used was calculated on the basis of its SH content. However, the complexes thus formed have different formulae, as is shown in the scheme:

$$\mathrm{M(CH_3COO)_2} + 2.5[\mathrm{HS(CH_2)_3NMe_3}](\mathrm{PF_6}) \xrightarrow[\mathrm{CH_3CN,\,MeOH,\,H_2O}]{\mathrm{Na(OH)_{aq}}} \left\{\begin{array}{l}[\mathrm{M\{S(CH_2)_3NMe_3\}_2}](\mathrm{PF_6})_2,\ \mathrm{M = Zn,\ Cd,\ Hg}\\ [\mathrm{Hg\{S(CH_2)_3NMe_3\}_2}](\mathrm{PF_6})_2\cdot\tfrac{1}{2}[\mathrm{S(CH_2)_3NMe_3}]\end{array}\right.$$

Thus, the synthetic route leads to hexafluorophosphate salts of complex ions of formula $[\mathrm{M^{II}(SR)_2}]^{2+}$ whichever of the divalent metals Zn, Cd, or Hg is used, but the Hg complex can be obtained in two crystalline forms, one with additional, uncoordinated ligand. The structure of $[\mathrm{Pb_2\{S(CH_2)_2NMe_3\}_5}](\mathrm{PF_6})_4$, with an analogous 2:5 empirical formula to that of complex **3** [24], consists of $[(\mu\text{-SR})_3\mathrm{M}(\mu\text{-SR})_2\mathrm{M}]$ chains and PF_6^- anions. In this case five-coordinate lead atoms are connected alternately by two and three doubly-bridging sulfur atoms.

It should also be noted that the stoichiometric metal:ligand ratio used, 2:5, is that of the adamantanoid cage structure, $(\mathrm{MSR})_4(\mu\text{-SR})_6$, widely known for metals adopting tetrahedral coordination with aromatic thiols [6]. It has not been reported previously for Zn, Cd and Hg when thiol ligands are of aliphatic nature, and it is not observed in the results presented here. Solution equilibria studies with aliphatic γ-mercaptoamine ligands [25] corroborate the difficulties found in obtaining this structural type.

Experimentally measured X-ray powder diffraction patterns for the samples of the mercury complexes

TABLE 2. Crystallographic data

	Complex **3**	Complex **4**
Formula	$[C_{12}H_{30}HgN_2S_2](PF_6)_2\cdot\frac{1}{2}(C_6H_{15}NS)$	$[C_{12}H_{30}HgN_2S_2](PF_6)_2$
M_r	822.1	757.0
Crystal system	tetragonal	triclinic
Space group	$I\bar{4}$	$P\bar{1}$
a (Å)	19.768(1)	15.097(4)
b (Å)		18.968(5)
c (Å)	7.0161(4)	20.365(6)
α (°)		71.74(1)
β (°)		68.50(1)
γ (°)		75.46(2)
V (Å^3)	2741.7(3)	5091(4)
Z	4	8
D_x (g cm^{-3})	1.991	1.975
μ (mm^{-1})	6.00	6.42
F(000)	1606	2928
Crystal size (mm)	0.32×0.36×0.48	0.24×0.28×0.52
No. reflections for cell	24	32
$2\theta_{max}$ (°)	50	45
h range	−23 to 23	−16 to 16
k range	−23 to 23	−20 to 20
l range	−8 to 8	0 to 21
Intensity decay (%)	*c.* 6	*c.* 40
Ratio of max:min transmission	1.67	1.30
Reflections measured	10491	13288
Unique reflections	2408	13288
Observed reflections	2026	7571
R_{int}	0.033	
Weighting parameters A_n	198, 520, 505, −582, 451, −1117	284, 1582, 3430, −677, 461, −3872
R	0.045	0.101
$R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$	0.027	0.099
Goodness of fit	1.23	1.03
No. parameters	141	490
Mean shift/e.s.d.	0.22	0.02
Max., min. el. density (eÅ^{-3})	2.98, −1.21	3.02, −1.22

obtained in the syntheses were compared with patterns calculated from the single-crystal structure determinations for pure complexes **3** and **4**. It was found that the samples prepared were, in each case, pure complex **3** or pure complex **4**, with no observable signs of a mixture of the two complexes being formed.

Description of the structures of complexes 3 and 4

The crystal structure of complex **3** contains one-dimensional cationic chains of formula $[Hg\{S(CH_2)_3NMe_3\}_2]_n^{2n+}$. The Hg atoms are spaced equidistantly along the *c* axis and are bridged by pairs of thiolate ligands (Fig. 1). These chains resemble closely those found in $[Hg(SBu^t)_2]$ [10] and $[Cd(SC_5H_9NHMe)_2](ClO_4)_2\cdot2H_2O$ [12]. In all three complexes, the metal atoms are tetrahedrally coordinated by the doubly-bridging sulfur atoms. Bond lengths and angles for complex **3** are given in Table 5. Table 6 compares the most important geometrical features of all three chain structures; the close similarity is evident.

The aminothiolate ligands radiate from the core of the $Hg(\mu\text{-}SR)_2Hg$ chains, providing them with a positively charged surrounding. The hexafluorophosphate anions, balancing this charge, are positioned so as to separate the positive charges from each other, both within and between the cation chains. A very similar disposition of the aminothiolate ligands towards the $Cd(\mu\text{-}SR)_2Cd$ chains and a comparable role for the anions are found in the structure of $[Cd(SC_5H_9NHMe)_2](ClO_4)_2\cdot2H_2O$ [12, 26]. In complex **3**, however, additional zwitterionic $S(CH_2)_3NMe_3$ molecules apparently lie in the wide channels running parallel to the *c* axis and to the cation chains (Fig. 2). The formulation of half a mole of additional ligand to one mole of salt is based on the experimental analytical results. The additional ligand molecules could not be identified and refined

TABLE 3. Atomic coordinates ($\times 10^4$) for complex **3**

Atom	x	y	z
Hg(1)	0	0	0
Hg(2)	0	0	5000
S	-506(1)	801(1)	2497(6)
C(1)	-1408(3)	633(3)	2638(38)
C(2)	-1628(3)	-90(3)	2545(26)
C(3)	-2380(3)	-149(3)	2624(35)
N	-2667(3)	-844(3)	2416(29)
C(4)	-2464(6)	-1214(6)	805(16)
C(5)	-2450(8)	-1208(10)	4307(24)
C(6)	-3427(4)	-777(6)	2627(53)
P	1040(1)	2878(1)	2480(6)
F(1)	1166(4)	2750(4)	338(9)
F(2)	1213(4)	3634(2)	2202(12)
F(3)	914(5)	3006(5)	4622(7)
F(4)	1792(2)	2726(3)	2903(14)
F(5)	288(2)	3030(4)	2057(14)
F(6)	868(4)	2122(2)	2759(15)

in the structure determination; they are extensively disordered, and possibly lost in some degree from the channels before and/or during data collection.

In the structure of complex **4**, by contrast, each Hg atom is strongly coordinated by two aminothiolate ligands in an essentially linear S–Hg–S arrangement. Important bond lengths and angles are given in Table 7. The Hg–S bond lengths lie in the range 2.321(9)–2.370(11) Å, significantly shorter than 2.564(3)–2.567(3) Å in complex **3**, and comparable to those observed in other approximately linear coordinated Hg thiolate complexes [11, 27]; S–Hg–S angles are in the range 174.8(4)–178.9(3)°. There are four crystallographically independent $[Hg(SR)_2]^{2+}$ cations, which differ in the conformations of the aminothiolate chains (Fig. 3). These cations are linked together by weaker Hg...S interactions of length 2.98–3.59 Å to give loosely bound octameric units as shown in Fig. 4. Each Hg atom forms either two or three such Hg...S interactions, with sulfur atoms which lie approximately at right angles to the primary linear S–Hg–S groups: S–Hg...S angles range from 76.1 to 105.8°. The shortest Hg...S distance between different loose octamers is 9.97 Å, these cation aggregates having an enveloping shell of ligand chains, further surrounded and separated by the hexafluorophosphate anions (Fig. 5). The existence of similar aggregates, but with three and with six RSHgSR units, is known for crystalline $[Hg(SCH_2CH_2NMe_3)_2(ClO_4)_2$ [6]. However, the full crystal structure has not been published, so a comparison with complex **3** is not possible.

Vibrational spectra

IR spectra of the four complexes in the range 4000–400 cm^{-1} are all very similar. They all show

TABLE 4. Atomic coordinates ($\times 10^4$) for complex **4**

Atom	x	y	z
Hg(1)	4764(1)	4300(1)	885(1)
S(11)	4297(7)	5131(5)	1627(5)
C(111)	3795(17)	4473(30)	2464(17)
C(112)	3059(11)	4747(50)	3101(27)
C(113)	3498(6)	4863(7)	3608(5)
N(11)	2869(11)	5143(10)	4245(7)
C(114)	2391(36)	4537(20)	4814(14)
C(115)	2138(29)	5765(26)	4039(19)
C(116)	3451(25)	5418(36)	4530(24)
S(12)	5243(6)	3481(5)	115(5)
C(121)	4152(20)	3585(11)	-168(12)
C(122)	4128(19)	2885(12)	-356(11)
C(123)	4842(8)	2795(4)	-1083(5)
N(12)	5111(6)	2043(5)	-1226(5)
C(124)	4239(9)	1736(10)	-1079(10)
C(125)	5699(9)	2102(8)	-1992(4)
C(126)	5670(14)	1547(8)	-752(7)
Hg(2)	2679(1)	6126(1)	1127(1)
S(21)	2418(6)	6764(5)	2008(5)
C(211)	1447(18)	7567(19)	1927(11)
C(212)	412(16)	7484(28)	2361(6)
C(213)	245(8)	7171(15)	3160(5)
N(21)	-718(8)	7296(6)	3684(5)
C(214)	-1404(8)	6980(9)	3545(11)
C(215)	-1039(19)	8102(5)	3634(12)
C(216)	-658(13)	6915(8)	4423(4)
S(22)	2811(6)	5469(5)	271(4)
C(221)	1789(16)	5048(26)	618(28)
C(222)	953(12)	5592(32)	948(30)
C(223)	49(7)	5619(23)	788(16)
N(22)	-884(9)	5894(12)	1271(10)
C(224)	-961(25)	6702(14)	1183(31)
C(225)	-961(22)	5492(29)	2030(11)
C(226)	-1668(7)	5756(8)	1083(7)
Hg(3)	7283(1)	2818(1)	917(1)
S(31)	6144(6)	3319(4)	1856(4)
C(311)	6632(19)	4062(16)	1937(6)
C(312)	7144(13)	3767(21)	2502(5)
C(313)	6480(7)	3588(7)	3269(3)
N(31)	6878(9)	3217(8)	3872(5)
C(314)	7683(14)	3576(15)	3786(12)
C(315)	7221(20)	2418(7)	3879(14)
C(316)	6120(15)	3280(17)	4564(5)
S(32)	8421(7)	2414(5)	-75(5)
C(321)	8640(25)	1393(19)	268(21)
C(322)	9279(33)	1336(14)	710(28)
C(323)	9835(31)	564(11)	890(24)
N(32)	10491(14)	427(5)	1314(11)
C(324)	11322(24)	819(12)	874(25)
C(325)	9982(33)	706(15)	1974(18)
C(326)	10826(10)	-384(4)	1523(7)
Hg(4)	4675(1)	2281(1)	1741(1)
S(41)	6130(6)	1464(5)	1619(5)
C(411)	6283(26)	1217(13)	2513(19)
C(412)	5571(24)	746(10)	3101(15)
C(413)	5650(18)	-14(7)	2978(5)
N(41)	5097(9)	-567(5)	3578(5)
C(414)	4063(11)	-270(12)	3734(12)

(*continued*)

TABLE 4. (*continued*)

Atom	*x*	*y*	*z*
C(415)	5374(10)	−689(8)	4230(5)
C(416)	5300(10)	−1275(5)	3367(7)
S(42)	3265(6)	3135(6)	1749(6)
C(421)	2412(25)	2945(14)	2606(16)
C(422)	2208(20)	2150(14)	2862(14)
C(423)	1481(22)	1985(15)	3610(12)
N(42)	906(12)	1389(10)	3806(9)
C(424)	1544(26)	667(13)	3771(27)
C(425)	234(26)	1337(22)	4549(14)
C(426)	355(33)	1562(29)	3295(22)
P(1)	1873(5)	1222(4)	8540(4)
F(11)	1920	1596	9097
F(12)	2958	909	8381
F(13)	1826	849	7982
F(14)	2115	1940	7930
F(15)	1630	505	9149
F(16)	787	1536	8698
P(2)	3845(5)	2373(4)	4265(4)
F(21)	4162	3146	4071
F(22)	2810	2765	4286
F(23)	3528	1600	4459
F(24)	3589	2327	5083
F(25)	4102	2419	3447
F(26)	4881	1981	4244
F(21x)	4347	2929	3565
F(22x)	2858	2856	4257
F(23x)	3344	1818	4965
F(24x)	3953	2833	4730
F(25x)	3738	1914	3800
F(26x)	4834	1890	4273
F(3)	8020(5)	220(4)	3991(4)
F(31)	9080	−167	3806
F(32)	7722	−478	4610
F(33)	6960	608	4175
F(34)	7859	−118	3452
F(35)	8180	559	4529
F(36)	8318	919	3371
P(4)	22(5)	4449(4)	3707(4)
F(41)	965	3951	3812
F(42)	−568	3880	4339
F(43)	−921	4946	3602
F(44)	58	4022	3162
F(45)	−14	4875	4252
F(46)	612	5018	3075
P(5)	−81(6)	3148(4)	1391(4)
F(51)	630	3710	923
F(52)	721	2603	1676
F(53)	−792	2586	1858
F(54)	217	2773	753
F(55)	−379	3523	2028
F(56)	−884	3692	1104
P(6)	3920(7)	3875(6)	6656(6)
F(61)	2918	4159	6548
F(62)	3464	3348	7396
F(63)	4921	3592	6764
F(64)	3752	4503	7040
F(65)	4087	3247	6271
F(66)	4375	4403	5916

(*continued*)

TABLE 4. (*continued*)

Atom	*x*	*y*	*z*
P(7)	7931(6)	1810(5)	6158(5)
F(71)	8121	1334	5615
F(72)	7329	1234	6770
F(73)	7741	2286	6701
F(74)	7014	2251	5964
F(75)	8848	1369	6352
F(76)	8533	2386	5546
P(8)	3694(7)	586(5)	1459(5)
F(81)	2848	1229	1384
F(82)	2971	34	1931
F(83)	4540	−56	1535
F(84)	3670	773	2152
F(85)	3718	400	767
F(86)	4417	1139	989

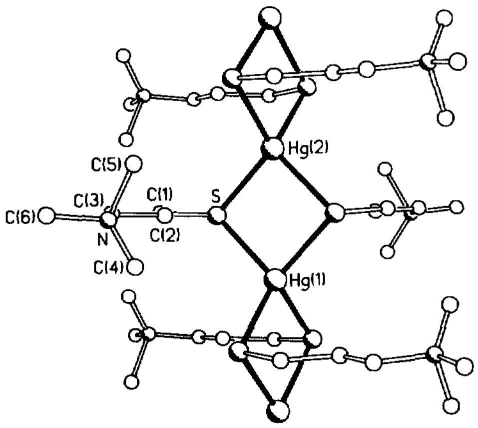

Fig. 1. The cation chains of complex **3**, with crystallographically independent atoms labelled. Hydrogen atoms are omitted.

TABLE 5. Bond lengths (Å) and angles (°) for complex **3**

Hg(1)–S	2.564(3)	Hg(2)–S	2.567(3)
S–C(1)	1.816(6)	C(1)–C(2)	1.495(9)
C(2)–C(3)	1.492(8)	C(3)–N	1.494(9)
N–C(4)	1.404(20)	N–C(5)	1.568(24)
N–C(6)	1.515(10)		
S–Hg(1)–S(a)	93.8(1)	S–Hg(1)–S(b)	117.8(1)
S–Hg(2)–S(a)	93.7(1)	S–Hg(2)–S(c)	117.9(1)
Hg(1)–S–Hg(2)	86.3(1)	Hg(1)–S–C(1)	107.9(6)
Hg(2)–S–C(1)	103.5(6)	S–C(1)–C(2)	117.3(4)
C(1)–C(2)–C(3)	111.3(5)	C(2)–C(3)–N	116.5(6)
C(3)–N–C(4)	116.7(13)	C(3)–N–C(5)	103.7(14)
C(4)–N–C(5)	111.4(9)	C(3)–N–C(6)	106.6(7)
C(4)–N–C(6)	114.0(16)	C(5)–N–C(6)	103.2(17)

Symmetry operators: (a) $-x\ -y,\ z$; (b) $y,\ -x,\ -z$; (c) $y,\ -x,\ 1-z$.

the two strong absorptions of the hexafluorophosphate anion at 835 and 565 cm^{-1}. They give no indication, however, that the two mercury complexes

TABLE 6. Selected geometrical parameters for chain metal(II)–thiolate complexes

Complex	Distances (Å)		Bond angles (°)	
$[Hg\{S(CH_2)_3NMe_3\}_2]^{2+\,a}$	Hg–S	2.564(3)	S–Hg–S	93.8(1)
		2.567(3)		93.7(1)
	Hg...Hg	3.508(2)	Hg–S–Hg	86.3(1)
$[Cd(SC_5H_9NHMe)_2]^{2+\,b}$	Cd–S	2.546(9)	S–Cd–S	98.6(2)
		2.550(9)		98.2(2)
	Cd...Cd	3.330(5)	Cd–S–Cd	81.6(4)
$[Hg(SBu^t)_2]^c$	Hg–S	2.66	S–Hg–S	90
		2.59		87
	Hg...Hg	3.76	Hg–S–Hg	90
				93

[a]This work. [b]Ref. 12. [c]Ref. 10.

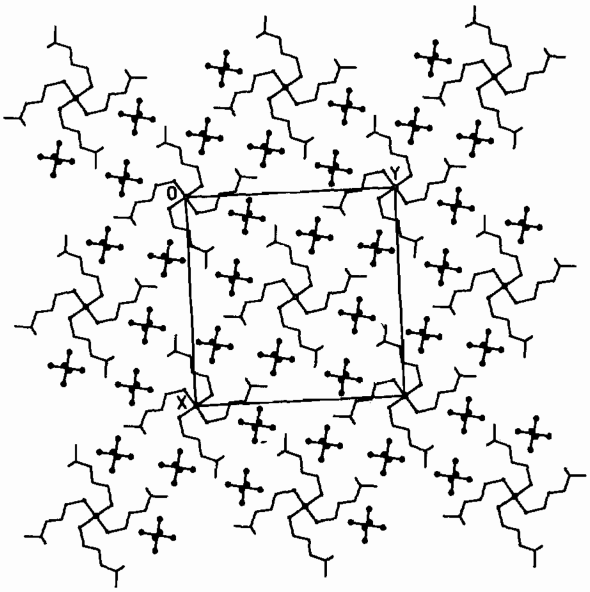

Fig. 2. Packing of the cations and anions in the structure of complex 3, seen in projection down the *c* axis, showing the channels probably occupied by disordered additional ligand molecules. Hydrogen atoms are not shown.

TABLE 7. Selected bond lengths (Å) and angles (°) for complex **4**

Hg(1)–S(11)	2.329(11)	Hg(1)–S(12)	2.351(11)
S(11)–C(111)	1.797(37)	S(12)–C(121)	1.882(34)
Hg(2)–S(21)	2.333(11)	Hg(2)–S(22)	2.370(11)
S(21)–C(211)	1.843(29)	S(22)–C(221)	1.727(37)
Hg(3)–S(31)	2.329(8)	Hg(3)–S(32)	2.321(9)
S(31)–C(311)	1.820(35)	S(32)–C(321)	1.830(34)
Hg(4)–S(41)	2.327(8)	Hg(4)–S(42)	2.327(9)
S(41)–C(411)	1.820(42)	S(42)–C(421)	1.740(29)
S(11)–Hg(1)–S(12)	178.9(3)	Hg(1)–S(11)–C(111)	96.3(18)
Hg(1)–S(12)–C(121)	103.9(8)	S(21)–Hg(2)–S(22)	175.4(3)
Hg(2)–S(21)–C(211)	108.7(11)	Hg(2)–S(22)–C(221)	105.5(20)
S(31)–Hg(3)–S(32)	175.6(3)	Hg(3)–S(31)–C(311)	107.3(7)
Hg(3)–S(32)–C(321)	103.5(12)	S(41)–Hg(4)–S(42)	174.8(4)
Hg(4)–S(41)–C(411)	104.0(10)	Hg(4)–S(42)–C(421)	109.8(11)

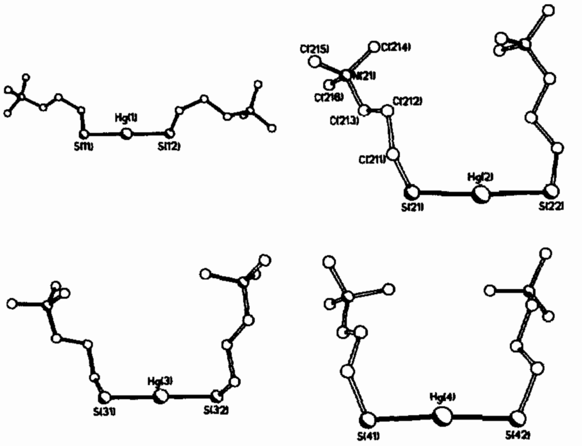

Fig. 3. The four crystallographically independent cations of complex **4**. All ligands follow a numbering scheme analogous to the one shown.

have different metal:ligand ratios and different structures. In the region 3000–2500 cm^{-1}, which is most indicative of ligand behaviour in the case of aliphatic γ-mercaptoamine complexes, the spectra show only one broad band centred at *c*. 2930 cm^{-1}, and two weaker side bands at 2850 and 3040 cm^{-1}. Thus, they are very similar to this region of the spectrum of $[HS(CH_2)_3NMe_3](PF_6)$, except for the band at 2600 cm^{-1}, assigned to ν(S–H). This feature is normally found in complexes where β- [28] or γ-mercaptoamine [29] ligands behave as chelates. The sharing of the free electron pair on the nitrogen atom of the $-NR_2$ group by a metal atom or the quaternization of this nitrogen to give $-NR_3^+$ are reflected in the same way in this region of the spectrum.

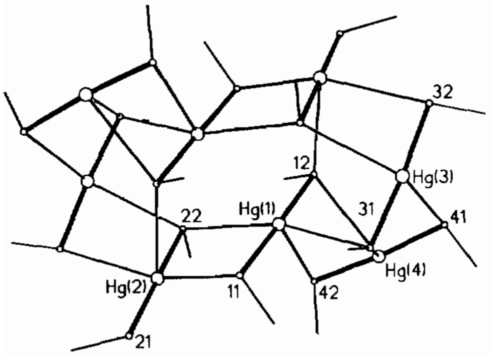

Fig. 4. The loosely bound octameric cation units of complex **4**. Only the α-carbon atom of each ligand chain is shown. Primary Hg–S bonds are shown thick, secondary Hg...S thinner. S atoms are labelled by number only.

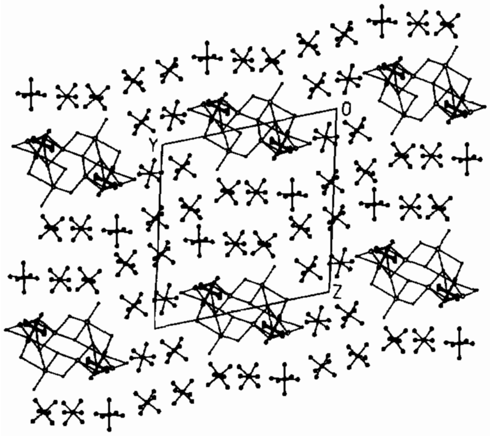

Fig. 5. Projection of the structure of complex **4** along the *a* axis. In the cations, only Hg and S atoms are shown. Each octameric cation unit in this projection is partially obscured by two PF_6 anions.

Comparison of the far IR and Raman spectra (400–200 cm^{-1}) of the two mercury complexes with those of the ligand itself allows the assignment of the ν(Hg–S) vibrations. In the case of complex **3**, with a structure containing polymeric chains having all Hg–S bond lengths essentially equal, there is only one, very intense, absorption in both spectra of the complex, at 244 cm^{-1}. For complex **4**, which contains loosely bound octameric assemblies of essentially digonal S–Hg–S units, there are two bands in the IR (354 cm^{-1}, strong; 279 cm^{-1}, medium) and two bands in the Raman spectrum (326 cm^{-1}, strong; 299 cm^{-1}, medium). Although the presence of secondary interactions in complex **4** makes the correlation between structure and vibrational frequencies rather difficult, these data agree well with the assignments made for related complexes [16].

Supplementary material

Full tables of bond lengths and angles, thermal parameters, and H atom parameters, together with structure factor tables, are available from the authors.

Acknowledgments

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