Mercury(II) Selenolates. Crystal Structures * of Polymeric $Hg(SeMe)_2$ and the Tetrameric Pyridinates $[\{HgCl(py)(SeEt)\}_4]$ and $[\{HgCl(py)_{0.5}(SeBu^t)\}_4]$

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The crystal structures of the title compounds have been determined by single-crystal *X*-ray diffraction at 295 K and refined by least squares to residuals of 0.044, 0.046, 0.058 for 818, 1 678, 2 016 independent 'observed' reflections respectively. For all compounds, crystals are monoclinic, space group $P2_1/c$. For $Hg(SeMe)_2$, a = 8.440(4), b = 10.732(3), c = 6.681(3) Å, β = 96.14(4)°, and Z = 4. For $[\{HgCl(py)(SeEt)\}_4]$ (py = pyridine), a = 8.044(5), b = 17.387(14), c = 15.585(21) Å, β = 101.75(2)°, and Z = 2. For $[\{HgCl(py)_{0.5}(SeBu^t)\}_4]$ a = 12.151(5), b = 16.738(7), c = 10.138(6) Å, β = 90.93(4)°, and Z = 2. Crystals of $Hg(SeMe)_2$ contain infinite one-dimensional chains along b, the pseudo-tetrahedral mercury atoms being bridged by pairs of selenium atoms; Hg–Se bond distances are in the range 2.614(2)—2.764(2) Å. The complexes $[\{HgCl(py)(SeEt)\}_4]$ and $[\{HgCl(py)_{0.5}(SeBu^t)\}_4]$ were obtained from pyridine solutions containing $Hg(SeR)_2$ and $HgCl_2$, and both contain an eight-membered ring $(-Hg-SeR-)_4$. The former contains two independent pseudo-tetrahedrally co-ordinated mercury atoms, '$Hg(\mu\text{-}SeEt)_2Cl(py)$'; the latter contains two inversion related mercury atoms, '$Hg(\mu\text{-}SeBu^t)_2Cl(py)$', and two other inversion related mercury atoms linked by a dichloro-bridge '$Hg(\mu\text{-}SeBu^t)_2(\mu\text{-}Cl)_2$'. The structure of $[\{HgCl(py)_{0.5}(SeBu^t)\}_4]$ is very similar to those of $[\{HgCl(L)_{0.5}(SBu^t)\}_4]$ (L = py or 4-methylpyridine) and is isomorphous with the 4-methylpyridine analogue. Mercury–selenium bond distances are slightly shorter than expected by comparison with covalent radii of sulphur and selenium.

SEVERAL thiolate complexes of stoicheiometry $Hg(SR)_2$ [1-4] and HgX(SR) [4-10] have been examined by *X*-ray diffraction but structural studies of analogous selenolates have not been reported, although recent results suggest that there may be interesting differences in the structural chemistry of $Hg(SR)_2$ and $Hg(SeR)_2$.[11] In addition, structural studies of analogous mercury(II) selenolates should allow direct comparison between Hg–S and Hg–Se bond lengths, not possible so far as complexes containing Hg–Se bonds studied by *X*-ray diffraction do not have directly comparable sulphur analogues.[12-15]

Mercury(II) thiolates $Hg(SR)_2$ have two-co-ordinate mercury {R = Me [1] or Et;[3] $Hg[SCH_2CH(NH_3)CO_2H][SCH_2CH(NH_3)CO_2]Cl\cdot\frac{1}{2}H_2O$[4]}, except for $Hg(SBu^t)_2$ which has distorted-tetrahedral co-ordination for mercury resulting from the presence of bridging thiolate groups.[2] The complexes $Hg(XBu^t)_2$ (X = S or Se) are isomorphous but $Hg(XMe)_2$ are not, and vibrational spectra of $Hg(SeMe)_2$ cannot readily be assigned to either linear [as in $Hg(SMe)_2$] or four-co-ordination for mercury [as in $Hg(XBu^t)_2$], although Hg–Se stretching modes for $Hg(SeR)_2$ (R = Me or Et) do occur in the same region as for $Hg(SeBu^t)_2$.[11] Apart from $Hg(SBu^t)_2$,[16] vibrational spectra of a considerable number of mercury(II) thiolates are consistent with linear geometry,[16-20] and thus the indication, from vibrational spectra, that $Hg(SeR)_2$ (R = Me or Et) may be polymeric is of interest since it suggests that polymeric structures may be more common for mercury(II) selenolates.

In contrast to $Hg(SR)_2$, all 1 : 1 thiolates HgX(SR) examined crystallographically are polymeric,[4,6-10] *e.g.* $Hg(O_2CMe)(SR)$ (R = Me,[7] Pr^n,[6] or Bu^n [6]) and HgX(SMe) (X = Cl [9] or Br [8]), and form complexes with pyridine (py) and 4-methylpyridine (4Me-py) which are polymeric, *e.g.* $Hg(O_2CMe)(py)(SMe)$,[7] or tetrameric, $[\{HgCl(L)_{0.5}(SBu^t)\}_4]$ (L = py [7] or 4Me-py [8]). The complexes $Hg(O_2CMe)(XMe)$ (X = S or Se) are isomorphous,[11] and since the thiolates readily form crystalline complexes from pyridine,[7,8,21] analogous selenolates were sought in this way, resulting in the isolation of tetrameric $[\{HgCl(py)(SeEt)\}_4]$ and $[\{HgCl(py)_{0.5}(SeBu^t)\}_4]$.

EXPERIMENTAL

Preparation of Crystals.—$Hg(SeMe)_2$. The complex was prepared as reported and crystals grown from pyridine. Powder diffraction data reported earlier [11] could be satisfactorily indexed using the cell dimensions obtained from the single crystal used for data collection.

$[\{HgCl(py)(SeEt)\}_4]$. A pyridine solution containing equimolar amounts of $Hg(SeEt)_2$ (prepared as described [11]) and mercury(II) chloride gave crystals which were recrystallized from 50% pyridine in ethanol (Found: C, 20.2; H, 2.5; Hg, 47.4; N, 3.5. Calc. for $C_7H_{10}ClHgNSe$: C, 19.9; H, 2.4; Hg, 47.4; N, 3.3%). An i.r. spectrum (Nujol mull, 400—4 000 cm^{-1}) is consistent with the presence of ethaneselenolate and pyridine groups, and has pyridine bands shifted in the usual manner observed on co-ordination, *e.g.* absorption at 405 cm^{-1} [22] occurs at 413 cm^{-1} in the spectrum of the complex.

$[\{HgCl(py)_{0.5}(SeBu^t)\}_4]$. A similar procedure, omitting recrystallization, gave colourless crystals having an i.r. spectrum similar to that reported [21] for $[\{HgCl(py)_{0.5}(SBu^t)\}_4]$ with pyridine bands shifted from free-ligand values, *e.g.* the complex has an absorption at 410 cm^{-1}. Since the crystals readily lose pyridine they were not analysed, but preliminary oscillation and Weissenberg photographs suggested that the crystals (in capillaries) are isomorphous with $[\{HgCl(4Me\text{-}py)_{0.5}(SBu^t)\}_4]$.

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* *catena*-Bis-μ-methaneselenolato-mercury(II), *cyclo*-tetrakis-[chloro-μ-ethaneselenolato-pyridinemercury(II)], and 1,3;1,3-di-μ-chloro-2,4-dichloro-1,2;1,4;2,3;3,4-tetrakis-μ-1′,1′-dimethylethaneselenolato-2,4-bis(pyridine)-*quadro*-tetramercury(II).

Structure Determinations.—Unique data sets were measured within $2\theta_{max.}$ limits determined by the scope of the data, using a Syntex $P2_1$ four-circle diffractometer in the conventional θ—2θ scan mode; monochromatic Mo-K_α radiation was used ($\lambda = 0.7106_9$ Å) and T was 295 K. N Independent reflections were measured, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the least-squares refinement after analytical absorption correction. Structures were solved by the heavy-atom method and refined by full-matrix least squares, with anisotropic thermal parameters for the non-hydrogen atoms. Hydrogen atoms were included with x, y, z, and U as invariant estimates. Residuals quoted are R,R', with reflection weights being $[\sigma^2(F_o) + 0.0005(F_o)^2]^{-1}$. Neutral atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion (f',f'').[23-25] Computation used the '*X*-RAY '76' program system[26] implemented by S. R. Hall on a Perkin-Elmer 32/40 computer. Atomic co-ordinates are given in Tables 1—3. Material deposited as Supplementary Publication No. SUP 23203 (28 pp.) comprises tables of structure-factor amplitudes, remaining hydrogen-atom parameters and thermal parameters, and least-squares planes.*

TABLE 1

Atomic parameters for $Hg(SeMe)_2$ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Hg	0.457 80(9)	0.141 66(7)	0.118 86(12)
Se(1)	0.371 5(2)	0.365 1(2)	−0.010 0(3)
C(1)	0.143(3)	0.335(2)	−0.072(4)
H(1A)	0.120	0.272	−0.176
H(1B)	0.092	0.310	0.042
H(1C)	0.110	0.414	−0.121
Se(2)	0.733 5(2)	0.039 2(2)	0.077 4(3)
C(2)	0.794(3)	0.131(2)	−0.158(4)
H(2A)	0.721	0.118	−0.276
H(2B)	0.805	0.218	−0.135
H(2C)	0.895	0.094	−0.176

TABLE 2

Non-hydrogen atom co-ordinates for $[\{HgCl(py)(SeEt)\}_4]$ with estimated standard deviations in parentheses

	Section a		
Atom	*x*	*y*	*z*
Hg	0.009 80(13)	0.478 08(6)	0.291 04(7)
Cl	−0.034 4(9)	0.392 7(4)	0.155 9(4)
Se	0.301 6(3)	0.458 9(1)	0.388 0(2)
C(11)	0.373(4)	0.361(2)	0.351(2)
C(12)	0.266(6)	0.301(2)	0.342(2)
N(1)	0.068(3)	0.590(1)	0.210(1)
C(2)	0.109(3)	0.657(2)	0.252(2)
C(3)	0.153(4)	0.718(2)	0.207(2)
C(4)	0.155(4)	0.713(2)	0.121(2)
C(5)	0.115(4)	0.647(2)	0.081(2)
C(6)	0.077(4)	0.586(1)	0.127(1)

	Section b		
Atom	*x*	*y*	*z*
Hg	0.215 25(13)	0.434 68(6)	0.533 69(6)
Cl	−0.086 8(8)	0.384 6(4)	0.518 2(4)
Se	0.288 3(3)	0.503 8(1)	0.680 9(2)
C(11)	0.370(4)	0.417(2)	0.762(2)
C(12)	0.421(5)	0.440(3)	0.854(3)
N(1)	0.353(3)	0.309(1)	0.576(1)
C(2)	0.519(4)	0.306(1)	0.571(2)
C(3)	0.605(3)	0.237(2)	0.581(2)
C(4)	0.518(4)	0.169(2)	0.592(2)
C(5)	0.349(4)	0.175(2)	0.595(2)
C(6)	0.270(4)	0.244(2)	0.585(2)

Atom numbering is shown in the Figures; for hydrogen atoms the numbering follows that of the parent carbon, with distinguishing suffixes A,B,C, as required.

Abnormal Features.—Crystals of the pyridinates blackened badly during data collection, and for $[\{HgCl(py)_{0.5}(SeBu^t)\}_4]$ it was necessary to correct for decomposition by appropriate scaling.

TABLE 3

Non-hydrogen atom co-ordinates for $[\{HgCl(py)_{0.5}(SeBu^t)\}_4]$ with estimated standard deviations in parentheses

	Section a		
Atom	*x*	*y*	*z*
Hg	0.732 30(8)	0.027 06(7)	0.315 74(9)
Cl	0.880 0(6)	0.112 6(6)	0.226 6(8)
Selenol			
Se	0.553 1(2)	0.032 6(1)	0.176 2(2)
C(1)	0.534(2)	0.149(1)	0.126(2)
C(2)	0.417(2)	0.156(2)	0.075(3)
C(3)	0.618(2)	0.158(2)	0.011(2)
C(4)	0.560(3)	0.200(2)	0.235(3)
Pyridine			
N	0.792(2)	−0.097(1)	0.204(2)
C(2)	0.861(2)	−0.094(2)	0.099(3)
C(3)	0.905(3)	−0.157(3)	0.041(3)
C(4)	0.872(4)	−0.232(2)	0.083(4)
C(5)	0.807(3)	−0.237(2)	0.189(4)
C(6)	0.770(2)	−0.168(2)	0.238(3)

	Section b		
Atom	*x*	*y*	*z*
Hg	0.413 21(8)	0.016 82(6)	0.352 81(9)
Cl	0.475 8(5)	0.113 7(4)	0.556 3(6)
Selenol			
Se	0.222 8(2)	0.012 9(2)	0.442 6(2)
C(1)	0.159(2)	−0.085(2)	0.355(2)
C(2)	0.154(3)	−0.067(3)	0.210(3)
C(3)	0.039(2)	−0.090(2)	0.399(3)
C(4)	0.222(2)	−0.155(2)	0.390(4)

Crystal Data.—$Hg(SeMe)_2$,$C_2H_6HgSe_2$, M = 388.6, Monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), a = 8.440(4), b = 10.732(3), c = 6.681(3) Å, β = 96.14(4)°, U = 601.7(4) Å^3, D_c = 4.29 g cm^{-3}, Z = 4, $F(000)$ = 664, μ_{Mo} = 339 cm^{-1}, specimen size 0.10 × 0.16 × 0.16 mm, $2\theta_{max.}$ = 50°, R,R' = 0.044, 0.057, N,N_o = 1 058, 818.

$[\{HgCl(py)(SeEt)\}_4]$,$C_{28}H_{40}Cl_4Hg_4N_4Se_4$, M = 1 692.7, Monoclinic, space group $P2_1/c$, a = 8.044(5), b = 17.387(14), c = 15.585(21) Å, β = 101.75(2)°, U = 2 134(3) Å^3, D_c = 2.63 g cm^{-3}, Z = 2, $F(000)$ = 1 520, μ_{Mo} = 174 cm^{-1}, specimen size 0.11 × 0.07 × 0.06 mm (capillary), $2\theta_{max.}$ = 50°, R,R' = 0.046, 0.049, N,N_o = 3 794, 1 678.

$[\{HgCl(py)_{0.5}(SeBu^t)\}_4]$, $C_{26}H_{46}Cl_4Hg_4N_2Se_4$, M = 1 646.7, Monoclinic, space group $P2_1/c$, a = 12.151(5), b = 16.738(7), c = 10.138(6) Å, β = 90.93(4)°, U = 2 062(2) Å^3, D_c = 2.65 g cm^{-3}, Z = 2, $F(000)$ = 1 480, μ_{Mo} = 180 cm^{-1}, specimen size 0.26 × 0.17 × 0.55 mm (capillary), $2\theta_{max.}$ = 50°, R,R' = 0.058, 0.066, N,N_o = 3 209, 2 016.

RESULTS

$Hg(SeMe)_2$.—The complex $Hg(SeMe)_2$ is polymeric with chains extended along b and formed by selenium atoms

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

bridging pseudo-tetrahedrally co-ordinated mercury atoms, the chain being generated by a succession of inversion centres and two-fold (screw) rotations. The spacings between successive mercury atoms are different and alternating, being 3.538(1) Å for a pair of mercury atoms separated by a pair of Se(2) ligand atoms, and 4.070(2) Å for a pair separated by two Se(1) ligands. The Hg–Se(1) distances are similar [2.625(2), 2.659(2) Å] and comparable to one of the Hg–Se(2) distances [2.614(2) Å] but the other Hg–Se(2) distance is appreciably longer [2.764(2) Å] (Table 4). Moreover, whereas the three angles about Se(1) are very nearly equal [98.6(7)—100.77(7)°] those about Se(2) are much more irregular [82.21(6)—100.7(6)°], the smallest angle [82.21(6)°] being contained between the two mercury atoms while the others are almost equal. The geometrical distortion about Se(2) and the deviation from ideal tetrahedral geometry of the mercury environment may be a consequence of methyl–methyl interactions within the chain about its two-fold symmetry axis, C(2) ··· C(2) ($x, \frac{1}{2} - y, \frac{1}{2} + z$) being 4.21(3) Å, while C(1) ··· C(1) is 3.80(4) Å (Figure 1).

[{HgCl(py)(SeEt)}$_4$].—This complex contains a cyclic (–Hg–SeEt–)$_4$ ring system, with mercury atoms bridged by selenium atoms and having pseudo-tetrahedral co-ordination 'Hg(μ-Se)$_2$ClN' (Figure 2). The molecule is centrosymmetric about a crystallographic symmetry element, and the two independent mercury atoms have very similar geometry, with bond distances within 3σ and bond angles within 3° except for angles N–Hg–Se(b) which differ by 6.8° (Tables 5 and 6).

[{HgCl(py)$_{0.5}$(SeBu^t)}$_4$].—The tetranuclear complex [{HgCl(py)$_{0.5}$(SeBu^t)}$_4$] (Figure 3) is isomorphous with the 4-methylpyridine complex [{HgCl(4Me-py)$_{0.5}$(SBu^t)}$_4$] [a = 12.334(7), b = 17.468(9), c = 9.999(5) Å, β = 91.18(4)°,

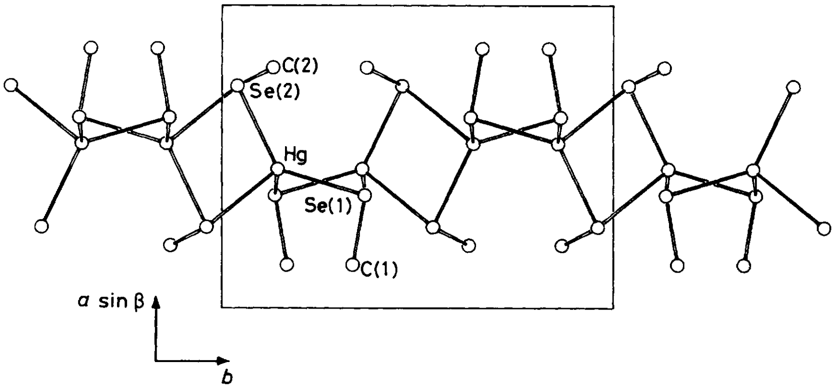

FIGURE 1 Unit-cell contents of Hg(SeMe)$_2$ projected down c

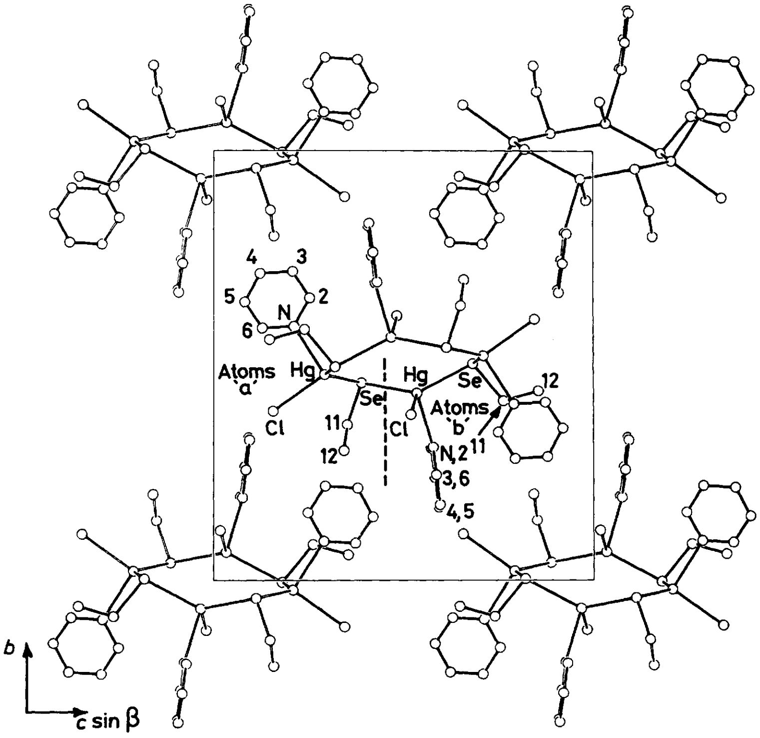

FIGURE 2 Unit-cell contents of [{HgCl(py)(SeEt)}$_4$] projected down a

TABLE 4

Interatomic bonding parameters (non-hydrogen atoms) for $Hg(SeMe)_2$ [a] with estimated standard deviations in parentheses

(*a*) Distances/Å [b]

Hg–Se(1)	2.625(2)
Hg–Se(2)	2.614(2)
Hg–Se(2^{I})	2.764(2)
Hg–Se(1^{II})	2.659(2)
Se(1)–C(1)	1.96(2)
Se(2)–C(2)	1.97(3)

(*b*) Angles/°

Se(1)–Hg–Se(2)	124.63(8)
Se(1)–Hg–Se(2^{I})	111.01(6)
Se(1)–Hg–Se(1^{II})	103.70(7)
Se(2)–Hg–Se(2^{I})	97.79(7)
Se(2)–Hg–Se(1^{II})	115.02(7)
Se(2^{I})–Hg–Se(1^{II})	102.64(6)
Hg–Se(1)–C(1)	98.6(7)
Hg–Se(1)–Hg^{III}	100.77(7)
C(1)–Se(1)–Hg^{III}	99.3(8)
Hg–Se(2)–C(2)	100.7(6)
Hg–Se(2)–Hg^{I}	82.21(6)
C(2)–Se(2)–Hg^{I}	99.3(7)

[a] Atom transformations: I $(1-x, \bar{y}, \bar{z})$; II $(x, \frac{1}{2}-y, \frac{1}{2}+z)$; III $(x, \frac{1}{2}-y, z-\frac{1}{2})$. [b] Hg $\cdots$ Hg^{I} 3.538(1), Hg $\cdots$ Hg^{II} 4.070(2) Å.

TABLE 5

Mercury–selenium geometries for $[\{HgCl(py)(SeEt)\}_4]$. The two entries in each column are for Hg, Se, a,b respectively. Italicized entries involve Se(b) $(x, 1-y, 1-z)$*

(*a*) Distances/Å

Hg–Cl	2.543(7), 2.546(6)
Hg–N	2.42(2), 2.48(2)
Hg–Se(a)	2.542(3), 2.541(4)
Hg–Se(b)	*2.543(3)*, 2.551(3)

(*b*) Angles/°

Cl–Hg–N	92.8(5), 95.0(5)
Cl–Hg–Se(a)	111.9(2), 113.6(2)
Cl–Hg–Se(b)	*103.7(2)*, 106.7(2)
N–Hg–Se(a)	99.3(5), 101.3(6)
N–Hg–Se(b)	*106.2(5)*, 99.7(5)
Se(a)–Hg–Se(b)	*134.7(1)*, 132.2(1)
Hg–Se–C(11)	103.6(8), 101.3(8)

* Also: Hg(b), C(11b)–Se(b)–Hg(a) $(\bar{x}, 1-y, 1-z)$, 99.20(8), 100.7(9)°.

space group $P2_1/c$] but not the analogous pyridinate $[\{HgCl(py)_{0.5}(SBu^t)\}_4]$ [a = 14.399(6), b = 9.893(6), c = 9.597(5) Å, α = 121.82(1), β = 102.52(4), γ = 102.94(4)°, space group $P\bar{1}$]. However, consistent with the presence of py, rather than 4Me-py, the complex has an asymmetric unit volume of 515.5(5) $Å^3$, very similar to that for $[\{HgCl(py)_{0.5}(SBu^t)\}_4]$ [517.8(4) $Å^3$] but not the 4Me-py analogue [538.5(5) $Å^3$]. Molecules of $[\{HgCl(py)_{0.5}(SeBu^t)\}_4]$ are based on an eight-membered ring of alternating Hg and Se atoms $(\text{–Hg–SeBu}^t\text{–})_4$ having a centre of symmetry and two mercury environments, '$Hg(\mu\text{-}Se)_2(\mu\text{-}Cl)_2$' and '$Hg(\mu\text{-}Se)_2ClN$', with a dichloro-bridge linking the former mercury atoms (Table 7).

DISCUSSION

The pseudo-tetrahedral geometry for mercury in $Hg(SeMe)_2$ is similar to that in $Hg(SBu^t)_2$ although the thiolate has an inversion centre between each mercury atom in the chain, rather than a succession of inversion centres and two-fold (screw) rotations. The thiolate groups form angles S–Hg–S of 87 and 90° (within Hg_2S_2 rings) and 121° (between Hg_2S_2 rings) compared with 97.79(7), 103.70(7), and 102.64(6)—124.63(8)° respectively, for $Hg(SeMe)_2$.

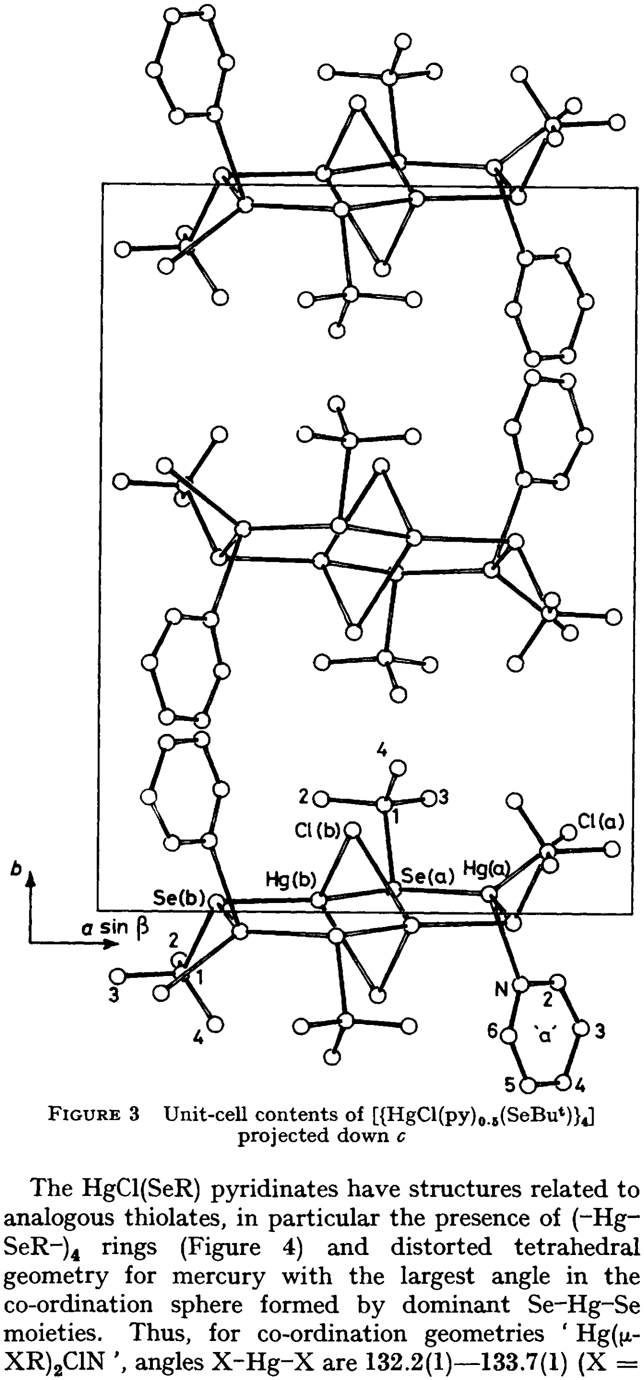

FIGURE 3 Unit-cell contents of $[\{HgCl(py)_{0.5}(SeBu^t)\}_4]$ projected down c

The HgCl(SeR) pyridinates have structures related to analogous thiolates, in particular the presence of $(\text{–Hg–SeR–})_4$ rings (Figure 4) and distorted tetrahedral geometry for mercury with the largest angle in the co-ordination sphere formed by dominant Se–Hg–Se moieties. Thus, for co-ordination geometries '$Hg(\mu\text{-}XR)_2ClN$', angles X–Hg–X are 132.2(1)—133.7(1) (X = Se) and 127.7(3)—130.9(2)° (X = S); [7,8] for '$Hg(\mu\text{-}XR)_2(\mu\text{-}Cl)_2$' 155.0(1) (X = Se) and 158.1(3)—159.9(3)° (X = S).[7,8]

Consideration of the molecular projections of Figure 4(*a*), together with those of Figure 4(*b*) for the related thiolates, suggests that the normal mode of co-ordination

TABLE 6

Ligand geometries for $[\{HgCl(py)(SeEt)\}_4]$

	Ligand a	Ligand b
(*a*) Ethaneselenol		
(*i*) Distances/Å		
Se–C(11)	1.92(3)	1.99(3)
C(11)–C(12)	1.35(5)	1.47(5)
(*ii*) Angles/°		
Se–C(11)–C(12)	120(3)	113(2)
(*b*) Pyridine rings		
(*i*) Distances/Å		
N(1)–C(2)	1.33(4)	1.36(4)
N(1)–C(6)	1.31(3)	1.32(4)
C(2)–C(3)	1.36(5)	1.38(4)
C(3)–C(4)	1.34(5)	1.40(4)
C(4)–C(5)	1.33(4)	1.37(5)
C(5)–C(6)	1.34(4)	1.36(5)
(*ii*) Angles/°		
C(2)–N(1)–C(6)	118(2)	120(2)
N(1)–C(2)–C(3)	120(3)	120(2)
C(2)–C(3)–C(4)	121(3)	120(3)
C(3)–C(4)–C(5)	118(3)	118(3)
C(4)–C(5)–C(6)	119(3)	121(3)
C(5)–C(6)–N(1)	123(2)	122(3)
Hg–N(1)–C(2)	120(2)	114(2)
Hg–N(1)–C(6)	122(2)	125(2)

to be found in these complexes is that of the 'Hg$(\mu\text{-}XR)_2$ClN' unit, linked by the chalcogen atom (X) into a tetrameric ring (although chain polymer structures are also conceivable). In the t-butyl-substituted derivatives, however, steric hindrance permits co-ordination of only two pyridine bases per tetrameric unit instead of four, and the co-ordination spheres lacking the pyridine bases become tetrahedral by virtue of the attached chlorine atoms adopting a bridging role. The disposition of t-butyl methyl groups tends to confirm this, being such as to allow the entry of a pyridine base molecule at two of the centrosymmetrically related mercury atoms when the ring is chlorine bridged, but not at the other two; hence the hemipyridinate nature of these complexes.

Since this is the first report of mercury–selenolate bond distances it is of interest to compare Hg–S with Hg–Se bond distances in closely related complexes. It was noted earlier that Hg–Se bond lengths in $[\{HgCl_2(SePPh_3)\}_2]$ (2.53 Å)[12] and the selenourea complex $[HgMe\{SeC(NH_2)_2\}][NO_3]$ [2.477(3) Å][15] are shorter than expected, although for these complexes suitable sulphur analogues are not available for direct comparison. The covalent radii of sulphur and selenium differ by 0.13 Å (Pauling),[27] although recent determinations of the structures of elemental sulphur,[28] selenium,[29] and R_2X_2 (X = S or Se)[30] result in distances $\{\frac{1}{2}[(Se\text{–}Se) - (S\text{–}S)]\}$ covering the range 0.13(2)—0.182(4) Å. Values of Hg–S and Hg–Se bond distances in closely related complexes are given in Table 8. For 'Hg$(\mu\text{-}XR)_4$' the

TABLE 7

Interatomic distances (Å) and angles (°) for $[\{HgCl(py)_{0.5}(SeBu^t)\}_4]$. Transformation of the asymmetric unit: I $(1 - x, \bar{y}, 1 - z)$

(*a*) Mercury a					
Hg(a)–Cl(a)	2.478(9)	Cl(a)–Hg(a)–Se(a)	112.9(2)	Se(a)–Hg(a)–Se(b$^{\mathrm{I}}$)	133.7(1)
Hg(a)–Se(a)	2.579(3)	Cl(a)–Hg(a)–N	95.6(5)	N–Hg(a)–Se(b$^{\mathrm{I}}$)	99.1(5)
Hg(a)–N	2.49(2)	Cl(a)–Hg(a)–Se(b$^{\mathrm{I}}$)	110.6(2)	Hg(b) · · · Hg(a) · · · Hg(b$^{\mathrm{I}}$)	56.15(2)
Hg(a)–Se(b$^{\mathrm{I}}$)	2.589(3)	Se(a)–Hg(a)–N	91.7(5)		
(*b*) Mercury b					
Hg(b)–Cl(b)	2.723(6)	Cl(b)–Hg(b)–Se(b)	89.4(1)	Hg(a) · · · Hg(b) · · · Hg(a$^{\mathrm{I}}$)	123.85(3)
Hg(b)–Se(b)	2.501(3)	Cl(b)–Hg(b)–Se(a)	107.1(1)	Hg(b$^{\mathrm{I}}$) · · · Hg(b) · · · Hg(a$^{\mathrm{I}}$)	62.10(2)
Hg(b)–Se(a)	2.503(3)	Cl(b)–Hg(b)–Cl(b$^{\mathrm{I}}$)	95.2(2)		
Hg(b)–Cl(b$^{\mathrm{I}}$)	2.720(6)	Se(b)–Hg(b)–Se(a)	155.0(1)		
Hg(b) · · · Hg(a)	3.905(2)	Se(b)–Hg(b)–Cl(b$^{\mathrm{I}}$)	108.2(1)		
Hg(b) · · · Hg(b$^{\mathrm{I}}$)	3.670(2)	Se(a)–Hg(b)–Cl(b$^{\mathrm{I}}$)	89.3(1)		
Hg(b) · · · Hg(a$^{\mathrm{I}}$)	3.892(2)	Hg(a) · · · Hg(b) · · · Hg(b$^{\mathrm{I}}$)			
(*c*) Chlorine b					
		Hg(b)–Cl(b)–Hg(b$^{\mathrm{I}}$)	84.8(2)		
(*d*) Selenol a					
Se(a)–C(1a)	2.03(2)	Hg(b)–Se(a)–Hg(a)	100.4(1)	Se(a)–C(1a)–C(4a)	111(17)
C(1a)–C(2a)	1.51(3)	Hg(b)–Se(a)–C(1a)	102.0(6)	C(2a)–C(1a)–C(3a)	111(2)
C(1a)–C(3a)	1.56(3)	Hg(a)–Se(a)–C(1a)	105.3(7)	C(2a)–C(1a)–C(4a)	114(2)
C(1a)–C(4a)	1.42(4)	Se(a)–C(1a)–C(2a)	105(2)	C(3a)–C(1a)–C(4a)	113(2)
		Se(a)–C(1a)–C(3a)	102(2)		
(*e*) Selenol b					
Se(b)–C(1b)	2.02(3)	Hg(b)–Se(b)–C(1b)	102.3(7)	Se(b)–C(1b)–C(4b)	111(2)
C(1b)–C(2b)	1.50(4)	Hg(a$^{\mathrm{I}}$)–Se(b)–C(1b)	106.3(8)	C(2b)–C(1b)–C(3b)	106(2)
C(1b)–C(3b)	1.54(4)	Hg(b)–Se(b)–Hg(a$^{\mathrm{I}}$)	99.7(1)	C(2b)–C(1b)–C(4b)	115(3)
C(1b)–C(4b)	1.44(4)	Se(b)–C(1b)–C(2b)	106(3)	C(3b)–C(1b)–C(4b)	113(3)
		Se(b)–C(1b)–C(3b)	106(2)		
(*f*) Pyridine					
N–C(2)	1.37(3)	Hg(a)–N–C(2)	120(2)	C(4)–C(5)–C(6)	117(3)
N–C(6)	1.27(5)	Hg(a)–N–C(6)	126(2)	C(5)–C(6)–N	129(3)
C(2)–C(3)	1.33(5)	C(2)–N–C(6)	113(3)		
C(3)–C(4)	1.38(6)	N–C(2)–C(3)	124(3)		
C(4)–C(5)	1.35(6)	C(2)–C(3)–C(4)	118(3)		
C(5)–C(6)	1.33(5)	C(3)–C(4)–C(5)	118(3)		

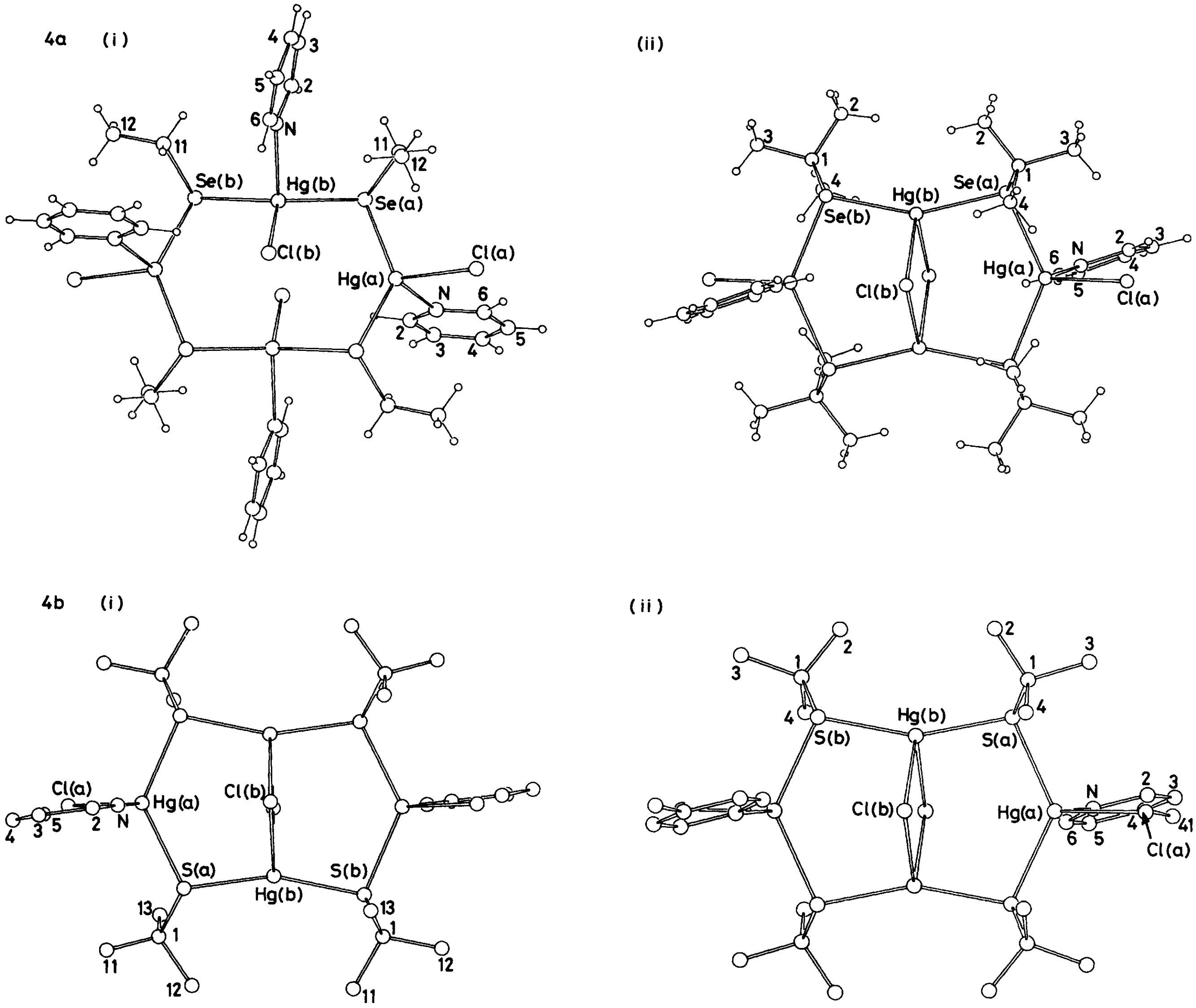

FIGURE 4 (*a*) Single molecules of [$\{HgCl(py)(SeEt)\}_4$] (i) and [$\{HgCl(py)_{0.5}(SeBu^t)\}_4$] (ii) projected normal to the plane of the four selenium atoms; (*b*) the same for (i) [$\{HgCl(py)_{0.5}(SBu^t)\}_4$] and (ii) [$\{HgCl(4Me\text{-}py)_{0.5}(SBu^t)\}_4$]

TABLE 8

Mercury(II)–sulphur and mercury(II)–selenium distances (Å) in closely related complexes

Co-ordination sphere	Hg–S	Hg–Se	Difference [a]
' $Hg(\mu\text{-}XR)_4$ '	2.59, 2.66 [b]	2.614(2)— 2.764(2) [c]	0.04
' $Hg(\mu\text{-}XBu^t)_2(\mu\text{-}Cl)_2$ '	2.38(1), 2.39(1) [d] 2.379(8), 2.395(8) [f]	2.501(3), 2.503(3) [e]	0.12
' $Hg(\mu\text{-}XBu^t)_2ClN$ '	2.488(7), 2.509(9) [d] 2.501(8), 2.505(8) [f]	2.579(3), 2.589(3) [e]	0.08
' $Hg(\mu\text{-}SeEt)_2ClN$ '		2.541(4)— 2.551(3) [g]	

[a] Difference between average values. [b] $Hg(SBu^t)_2$ (ref. 2). [c] $Hg(SeMe)_2$. [d] [$\{HgCl(py)_{0.5}(SBu^t)\}_4$] (ref. 7). [e] [$\{HgCl(py)_{0.5}(SeBu^t)\}_4$]. [f] [$\{HgCl(4Me\text{-}py)_{0.5}(SBu^t)\}_4$] (ref. 8). [g] [$\{HgCl(py)(SeEt)\}_4$].

difference between average values is 0.04 Å and, for [$\{HgCl(py)_{0.5}(SeBu^t)\}_4$] which has bond angles at mercury within 5° of those for both sulphur analogues, the differences are 0.12 [for ' $Hg(\mu\text{-}XBu^t)_2(\mu\text{-}Cl)_2$ '] and 0.08 Å [for ' $Hg(\mu\text{-}XBu^t)_2ClN$ '], indicating that Hg–Se bond distances are slightly shorter than expected from a consideration of covalent radii.

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