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Syntheses, characterization and molecular structures of monomeric selenolato complexes of mercury with nitrogen-containing chelating ligands

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Intramolecularly stabilized divalent mercury selenolates of empirical formula $Hg(SeR)_2$ [R = $2\text{-}Me_2NCH_2C_6H_4$ **1**, (*S*)-$2\text{-}Me_2NCHMeC_6H_4$ **2**, (*R*,*S*)-$(C_5H_5)Fe(2\text{-}Me_2NCHMeC_5H_3)$ **3** and (*S*,*R*)-$(C_5H_5)Fe(2\text{-}Me_2NCHMeC_5H_3)$ **4**] have been synthesized in high yield by treating the corresponding diselenides with elemental mercury. The compounds show excellent solubility in non-polar solvents. They were characterized by elemental analysis, ^1H, ^{13}C, ^{77}Se NMR, IR, Fourier-transform Raman and mass spectral techniques. The single-crystal structures of **1** and **4** were determined. Both are monomeric and the Hg atom is four-co-ordinate, being bound to a pair of chelating aminoselenolate ligands with both the six-membered rings having Se–Hg–N co-ordination adopting an envelope conformation. The bond configuration about Hg in **1** can be approximated to distorted tetrahedral, while in **4** it is more square planar with the two Se atoms being mutually *trans* and the Se–Hg–Se angle 168.6(2)°. Compounds **1** and **2** vaporize without decomposition at atmospheric pressure and decompose at higher temperatures to give HgSe while **3** decomposes to HgSe.

The synthesis and structural characterization of single-source stoichiometric precursors to Group 12–16 semiconductors has continued to be an area of intense recent interest. Several research groups have demonstrated that $M(ER)_2$ complexes (M = Zn, Cd or Hg; E = S, Se or Te; R = aryl) can be used as such precursors.[1] However, these compounds are generally polymeric in the solid state, rather difficult to isolate in the crystalline form, relatively insoluble in hydrocarbon solvents and hence difficult to purify and characterize.[2] The low thermal stability and low volatility of these precursors hinder the production of high-quality thin films of Group 12–16 materials by chemical vapour deposition (CVD).

Much effort has been directed towards isolating stable, monomeric precursors with a view to enhance compound stability. The concept of steric shielding of reactive metal centres by means of bulky ligands has been widely used but has met only with limited success. For example, for metal selenolates with (R = Me) only polymeric compounds $[M(SeC_6H_2R_3\text{-}2,4,6)_2]_\infty$ (M = Zn, Cd or Hg) were obtained.[3] With sterically demanding ligands, *e.g.* R = Bu^t, stable monomeric complexes were characterized in solution.[3] Bulky trialkylsilyl substituents, $Si(SiMe_3)_3$, have been similarly used to obtain dimeric compounds of the type $\{M[TeSi(SiMe_3)_3]_2\}_2$ where M = Zn or Cd. In contrast, the mercury analogue was monomeric in solution.[4] However these compounds decompose *via* reductive elimination to mercury metal and diaryl dichalcogenide. This limits their usefulness as precursors to Group 12–16 solid-state materials *via* thermolysis. Adduct formation with neutral donor ligands has been another strategy to achieve co-ordinative saturation of the metal centre and to reduce the polymerization process. Steigerwald and co-workers[5] have isolated phosphine-substituted metal chalcogenides by addition of bidentate phosphine ligands to $M(ER)_2$ compounds (M = Zn, Cd or Hg; E = S, Se or Te) in different ratios. When an excess of the phosphine was added organometallic co-ordination polymers were obtained. However, at a 1:1 ratio only dimeric compounds were obtained. The utility of these compounds as precursors in CVD is restricted as ligand dissociation precedes neutral complex sublimation. Very recently, monomeric compounds $Zn(ER)_2L$ (E = S or Se; R = $C_6H_2\text{-}Bu^t_3\text{-}2,4,6$; L = 2,6-dimethylpyridine, tetrahydrothiophene, PMe_3 or $PMePh_2$) have been obtained by treating N-, S- or P-donor compounds with dimeric complexes containing bulky substituents.[6]

In our approach to the problem, the donor functionality and chalcogenolate are combined within the same ligand, *viz.* $2\text{-}Me_2NCH_2C_6H_4Se^-$, (*S*)-$2\text{-}Me_2NCHMeC_6H_4Se^-$ and both (*R*,*S*) and (*S*,*R*) enantiomers of $Fe(C_5H_5)(C_5H_3CHMeNMe_2\text{-}2\text{-}Se\text{-}1)$. This approach had been previously applied successfully to obtain intramolecularly stabilized monomeric organyl tellurenyl/selenyl halides ($2\text{-}Me_2NCHRC_6H_4EX$; E = Se or Te; R = H or Me, X = Cl, Br or I)[7,8] which are otherwise unstable. It was hoped that the stabilizing interaction of the chalcogen and internal tertiary amine observed in these chelating ligands would interrupt the formation of chalcogenolato bridges and prevent polymerization, resulting in increased volatility. A related compound of Cd, *viz.* $Cd(TeC_6H_4CH_2NMe_2\text{-}2)_2$ has been reported.[9] However, there was no conclusion about its molecularity and stability.

This paper reports the syntheses of monomeric, hydrocarbon-soluble mercury(II) selenolates stabilized by internal chelation resulting in the formation of a six-membered ring with Hg. Some examples of six-membered rings with Se–Hg–N co-ordination are known.[10] The use of diferrocenyl diselenide offered the prospect of getting volatile precursors as ferrocene itself is known to sublime. It also offered the prospect of mixed systems containing Fe, Hg and Se. During the course of this work a pyridineselenolate complex of Hg^{II} was reported[11] in which the chelate effect has been used effectively to obtain a low-co-ordinate complex possessing high volatility. In contrast, however, the cadmium(II) analogue was polymeric.

Experimental

Materials and methods

The compounds $(2\text{-}Me_2NCH_2C_6H_4Se)_2$,[8] [(*S*)-$2\text{-}Me_2NCHMeC_6H_4Se]_2$,[8] [(*R*,*S*)-$Fe(C_5H_5)(C_5H_3CHMeNMe_2\text{-}2\text{-}Se\text{-}1)]_2$[12] and [(*S*,*R*)-$Fe(C_5H_5)(C_5H_3CHMeNMe_2\text{-}2\text{-}Se\text{-}1)]_2$[12] were prepared following the literature procedures. Solvents were purified by standard techniques[13] and were freshly distilled prior to use. Mercury was purified prior to use.[13] Melting points were recorded in capillary tubes and are uncorrected. Proton (299.94), ^{13}C (75.42) and ^{77}Se (57.22

MHz) NMR spectra were recorded on a Varian VXR 300S spectrometer. Chemical shifts are cited with respect to $SiMe_4$ as internal (^1H and ^{13}C) and Me_2Se (^{77}Se) as external standard. Elemental analyses were performed on a Carlo-Erba model 1106 elemental analyser. Infrared spectra were recorded for KBr pellets on a Perkin-Elmer 681 spectrometer and for polyethylene pellets on a Bruker IFS 66V FT-IR spectrometer. Fourier-transform Raman spectra were recorded for crystalline samples on a Dilor Z24 Raman spectrometer, using argon laser excitation at 514.5 nm, with laser powers of 100 and 20 mW, respectively. Only single scans were recorded. The DTA and TGA measurements were performed on a Shimadzu DT 30 thermal analyser in a nitrogen atmosphere at atmospheric pressure. The heating rate was 5 °C min^{-1}. Fast atom bombardment (FAB) mass spectra were recorded at room temperature on a JEOL SX 102/DA-6000 mass spectrometer/data system using xenon (6 kV, 10 mV) as the bombarding gas. The acceleration voltage was 10 kV and *m*-nitrobenzyl alcohol was used as the matrix with positive-ion detection. In case of isotopic patterns the value given is for the most intense peak. Optical rotations were measured on a JASCO model DIP 370 digital polarimeter.

Syntheses

$Hg(SeC_6H_4CH_2NMe_2\text{-}2)_2$ 1. To a solution of $(2\text{-}Me_2NCH_2C_6H_4Se)_2$ (0.19 g, 0.45 mmol) in methanol (50 cm^3) was added an excess of mercury (0.75 g, 4 mmol) at room temperature. A slight decomposition occurred and a black powder settled out. The mixture was stirred till it became almost colourless (24 h) and then filtered to remove the unreacted mercury and the black powder. The filtrate was concentrated by slow evaporation at room temperature to give a minor amount of compound **1**. The residue was washed with aliquots of chloroform (2 × 50 cm^3), and the washings concentrated separately to give more **1**. The compound was recrystallized from methanol as colourless shiny prisms (0.26 g, 92%), m.p. 129 °C (Found: C, 33.6; H, 3.4; N, 4.4%; *m*/*z*, 627. $C_{18}H_{24}HgN_2Se_2$ requires C, 34.5; H, 3.8; N, 4.4%; *M*, 626); $\tilde{\nu}_{max}/cm^{-1}$ 2831s, 2701m, 1586m, 1473s, 1377m, 1010s, 848s, 645m, 464s (M–N) (KBr); 404w (N–M–N), 241s [ν_{asym}(M–Se)], 218w, 169m (polyethylene); Raman $\tilde{\nu}_{max}/cm^{-1}$ 270w, 238m[ν_{sym}(M–Se)], 198s (M–Se), 153s; $\delta_H(CDCl_3)$ 7.82 (2 H, d, aryl H), 7.12–7.03 (4 H, m, aryl H), 6.98–6.95 (2 H, m, aryl H), 3.56 (4 H, s, CH_2) and 1.87 (12 H, s, NMe_2); $\delta_C(CDCl_3)$ 139.4 (C^6, *ortho*), 137.6 (C^2), 131.7 (C^5), 131.5 (*ipso*-C), 128.2 (C^4), 126.1 (C^3), 66 (CH_2) and 45.2 (NMe_2); $\delta_{Se}(CDCl_3)$ 27 [^1J(Se–Hg) = 1634 Hz]; *m*/*z* 627 (M^+, 25%), 427 (*M* – Hg, 5), 214 ($SeC_6H_4CH_2NMe_2$, 100), 198 ($SeC_6H_4CH_2NMe$, 2), 170 ($C_6H_4CH_2Se$, 7), 134 ($C_6H_4CH_2NMe_2$, 10), 91 (C_7H_7, 9) and 58 (CH_2NMe_2, 12).

$Hg[(S)\text{-}SeC_6H_4CHMeNMe_2\text{-}2]_2$ 2. To a solution of $[(S)\text{-}2\text{-}Me_2NCHMeC_6H_4Se]_2$ (0.6795 g, 1.5 mmol) in methanol was added an excess of mercury (3 g, 15 mmol). Work-up as described for compound **1** yielded colourless crystals of **2** (0.95 g, 98%), m.p. 121 °C (Found: C, 36.9; H, 4.3; N, 4.1%; *m*/*z*, 655. $C_{20}H_{28}HgN_2Se_2$ requires C, 36.7; H, 4.3; N, 4.2%; *M*, 655); $\tilde{\nu}_{max}/cm^{-1}$ 2947m, 2301s, 1375m, 1094s (KBr); 505s, 362s, 332w, 259m, 233vs [ν_{asym}(M–Se)], 190s, 142m (polyethylene); Raman $\tilde{\nu}_{max}/cm^{-1}$ 202vs [ν_{sym}(M–Se)], 188s [ν_{sym}(M–Se)], 148s; $\delta_H(CDCl_3)$ 7.84–7.81 (2 H, dd, aryl H), 7.10–7.0 (6 H, m, aryl H), 4.51–4.45 (2 H, q, CH), 1.79 (12 H, s, NMe_2) and 1.25–1.23 (6 H, d, CH_3); $\delta_C(CDCl_3)$ 143.7 (C^6, *ortho*), 137.9 (C^2), 131.0 (*ipso*-C), 127.9 (C^5), 127.2 (C^4), 126.1 (C^3), 61.92 (CH), 40.1 (NMe_2) and 8.2 (CH_3); $\delta_{Se}(CDCl_3)$ 36.81; *m*/*z* 655 (M^+, 9%), 228 ($SeC_6H_4CHMeNMe_2$, 100), 212 (228 – CH, 5), 183 ($C_6H_4CHMeSe$, 14), 148 ($C_6H_4CHMeNMe_2$, 6), 72 ($CHMeNMe_2$, 14) and 44 (Me_2N). $[\alpha]^{29}_{589} = -297.99$ (*c* 0.5, $CHCl_3$).

$Hg[(R,S)\text{-}(SeC_5H_3CHMeNMe_2\text{-}2)Fe(C_5H_5)]_2$ 3. To a solution of $[(R,S)\text{-}Fe(C_5H_5)(C_5H_3CHMeNMe_2\text{-}2\text{-}Se\text{-}1)]_2$ (0.165 g, 0.25 mmol) in methanol (50 cm^3) was added mercury (0.75 g, 4 mmol). A yellow orange powder precipitated which was found to stick to the unreacted mercury. When a nearly colourless solution was obtained the residue was filtered off and washed with dichloromethane. The dichloromethane washings were collected separately. Most of the yellow residue dissolved to leave unreacted mercury on the filter-paper. Concentration of the solution gave golden-yellow flakes of the desired compound **3** which was recrystallized from benzene (0.26 g, 92%). It decomposes without melting at 168 °C (Found: C, 38.35; H, 4.3; N, 2.3%; *m*/*z*, 871. $C_{28}H_{36}Fe_2HgN_2Se_2$ requires C, 38.6; H, 4.2; N, 3.2%; *M*, 871); $\tilde{\nu}_{max}/cm^{-1}$ 2838s, 1453s, 1361s, 1034s (KBr), 449s (M–N), 414m (M–N), 384m, 334s, 298s, 230m, 208m (M–Se), 195vs (polyethylene); $\delta_H(CDCl_3)$ 4.27–3.98 (6 H, m, C_5H_3), 4.12–4.08 (2 H, q, CH), 4.04 (10 H, s, C_5H_5), 1.9 (12 H, s, NMe_2) and 1.30–1.28 (6 H, d, CH_3); $\delta_C(CDCl_3)$ 91.7 (C^5, *ortho*), 74.2 (C^2), 72.5 (*ipso*-C), 70.5 (C_5H_5), 67.3 (C^4), 66.1 (C^3), 57.7 (CH), 39.8 (NMe_2) and 7.4 (CH_3); $\delta_{Se}(CDCl_3)$ −64.67; *m*/*z* 871 (M^+, 16%), 827 (871 – NMe_2^+, 12), 782 (827 – NMe_2^+, 4), 758 (5), 708 (7), 671 (M^+ – Hg, 15), 644 (12), 612 (9), 581 (782 – Hg, 50), 527 (25), 506 (10), 460 (20), 444 (12), 424 [$(C_5H_3SeCHMeNMe_2)_2$, 12], 379 (12), 337 (54), 307 (78), 292 ($C_5H_3SeSeCHMeNMe_2$, 100), 273 (24), 226 (12), 212 ($C_5H_3SeCHMeNMe_2$, 48), 202 (10), 165 (21), 154 (C_5H_3SeCH, 100), 120 (30), 107 (64), 89 (56) and 65 (C_5H_5, 18); $[\alpha]^{29}_{589} = +751$ (*c* 0.25, $CHCl_3$).

$Hg[(S,R)\text{-}(SeC_5H_3CHMeNMe_2\text{-}2)Fe(C_5H_5)]_2$ 4. Compound **4** was similarly prepared starting from $[(S,R)\text{-}Fe(C_5H_5)(C_5H_3CHMeNMe_2\text{-}2\text{-}Se\text{-}1)]_2$. Golden-yellow crystals were obtained (89%) (Found: C, 37.8; H, 4.1; N, 3.8%); $[\alpha]^{29}_{589} = -759°$ (*c* = 0.25, $CDCl_3$). Other data as for **3**.

Crystal-structure determinations of compounds 1 and 4

Compound **1** was obtained as shiny white prisms from a methanol solution after slow evaporation for 2 d at room temperature. While attempts to grow good-quality crystals of **4** from various solvents like dichloromethane, toluene, chloroform and methanol were unsuccessful and gave only flakes, slow evaporation of a benzene solution gave golden-yellow rod-shaped crystals.

Data collection, structure solution and refinement. All diffraction measurements were performed at room temperature (295 K) on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.7107 Å) employing the ω–2θ scan technique. The unit cell was determined from 25 randomly selected reflections using the automatic search index and least-squares routine. The data were corrected for Lorentz, polarization and absorption effects. The maximum and minimum transmission values of the correction factors for compound **1** (dimensions 0.425 × 0.25 × 0.15 mm) were 0.998 and 0.455 and for **4** (0.25 × 0.25 × 0.20 mm) were 0.998 and 0.310, respectively. The data were monitored by measuring two standard reflections every 60 min of X-ray exposure time. Both structures were solved by routine heavy-atom (using SHELXS 86[14]) and Fourier methods and refined by full-matrix least squares with the non-hydrogen atoms anisotropic and hydrogens with fixed isotropic thermal parameters of 0.07 Å^2 using the SHELX 76 program.[15]

The hydrogens were partially located from difference electron-density maps and the rest were fixed at calculated positions. In the case of compound **4** the hydrogens H(4) and H(22) on the chiral carbons were located from the difference map. The correct absolute structure of **4** was confirmed by computing the Flack parameter [0.20(2)] using the SHELXL 93 program.[16] The value for the other enantiomorph was 0.80(3). In addition the lower *R* values (*R*1 = 0.052, *wR*2 =

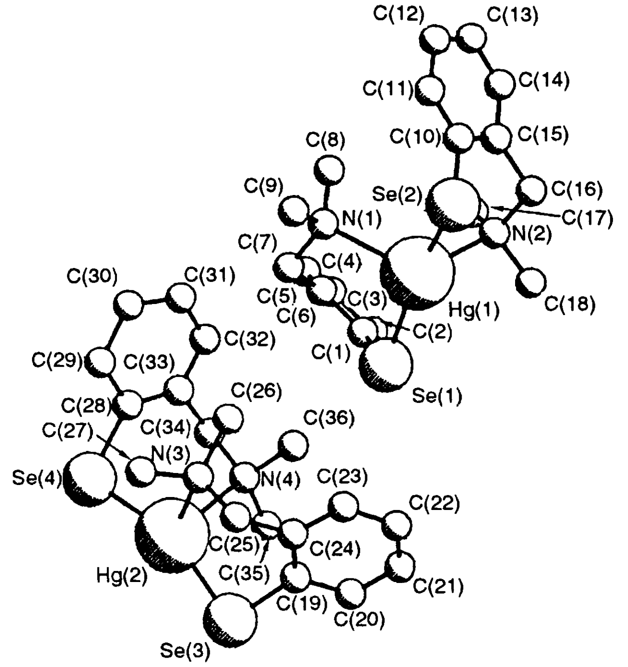

Fig. 1 Molecular structure of $Hg(SeC_6H_4CH_2NMe_2\text{-}2)_2$ **1**

0.162) than for the other enantiomorph ($R1 = 0.066$, $wR2 = 0.222$) confirmed the correctness of the absolute structure. Moreover, the chirality of the starting material is known[12] and could not have changed during the reaction. The weighting scheme employed was $w = K/[\sigma^2(F) + g(F)^2]$ where K and g refined to 3.044 and 0.000 77 for **1** and 3.752 and 0.000 556 for **4**, respectively. The scattering factors of Hg, Se and Fe were from ref. 17, while those for the remaining atoms were as incorporated in the SHELX 76 program. All calculations were carried out on an ND 500 computer. The crystal data and refinement details are given in Table 5.

Complete atom coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Results and Discussion

Syntheses, properties and thermal behaviour

The mercury selenolates $Hg(SeC_6H_4CH_2NMe_2\text{-}2)_2$ **1**, $Hg[(S)\text{-}SeC_6H_4CHMeNMe_2\text{-}2]_2$ **2**, $Hg[(R,S)\text{-}(SeC_5H_3CHMeNMe_2\text{-}2)Fe(C_5H_5)]_2$ **3** and $Hg[(S,R)\text{-}(SeC_5H_3CHMeNMe_2\text{-}2)Fe(C_5H_5)]_2$ **4** were prepared in excellent yields (> 90%) by stirring the corresponding diselenides with mercury in methanol at room temperature. Initial stirring in the presence of mercury produced, in the cases of **1** and **2**, a black powder which was found to stick to the unreacted mercury. For **3** and **4** on the other hand the formation of a yellowish brown precipitate was observed. (Since **3** and **4** show identical behaviour we will discuss the results in the context of **3** alone.) Initially, these observations were related to slight decomposition and hence a variety of reaction conditions including stirring in the dark and in the presence of a nitrogen atmosphere were tested. However, the formation of black precipitates is observed irrespective of these variations. In all cases the completion of the reaction is indicated by the formation of almost colourless solutions.

The products show remarkable stability to light and moisture and have excellent solubility in both non-polar (benzene and hydrocarbons) and slightly polar solvents. They are, however, almost insoluble in highly polar solvents like Me_2SO and methanol. This is especially true for **3** where there is complete precipitation of the product in methanol. Compounds **1** and **2**, on the other hand, are recrystallized from methanol.

Compounds **1** and **2** are colourless, crystalline solids with low melting points (< 130 °C). The high volatility of **2** is reflected by the vaporization temperature of 190 °C (100% weight loss) at atmospheric pressure. The compound is thermally stable under these conditions and does not leave any residue. Compound **1** on the other hand showed a phase transition (without weight loss) at 129 °C, which corresponded to its melting, and a complete weight loss at 330 °C. The TGA behaviour of **3** is markedly different and showed the loss of the ferrocene unit at 300 °C (42%), leaving a black microcrystalline solid which corresponds to HgSe.

Spectroscopic behaviour

The ^1H NMR chemical shifts of compounds **1**–**3** are significantly different from those of the starting diselenides.[8,12] The NMe_2 resonances in each case (**1**, δ 1.87, 2.26;[8] **2**, 1.79, 2.30[8] and **3**, 1.90, 2.19[12]) showed an upfield shift compared to those of the starting diselenides. At ambient temperature, however, no anisochronous signals are observed for NMe_2. The signals are sharp and well defined, probably suggesting, in addition to a monomeric nature, the presence of a two-co-ordinate Hg atom in solution. The same behaviour was also reflected in the ^{13}C chemical shifts. The *ipso*-carbon resonances are very weak and observed with difficulty. The ^{77}Se shifts for the diselenides are typically in the range δ 400–500[18] and metal-bound selenium typically resonates in the range δ 500–1100, where M = Mo, W, Ni, Pd or Pt.[19] The resonances observed for the mercury selenolates in our case are in the range δ +27 to −65. All these observations can be correlated if we assume that the intramolecular co-ordination of the nitrogen to selenium observed in the starting diselenide is broken. Also, oxidative addition of mercury across the selenium–selenium bond leads to a shielding of the ^{77}Se nucleus. Since selenium bonded to a d^{10} species cannot donate sufficient electrons to the metal atom due to absence of vacant d orbitals a significant shielding of the ^{77}Se nucleus occurs. The observations are consistent with similar reports on related compounds.[20] In addition (*a*) the shielding of the ^{77}Se nucleus and (*b*) the ^1H NMR behaviour suggest a two-co-ordinate mercury atom in solution.

The IR and Raman data also suggest compounds **1**–**3** are monomers. The spectra are well resolved. Typically, the mercury–nitrogen vibrations occur in the region 470–400 cm^{-1} and those of mercury selenide in the region 240–200 cm^{-1}. The observation of both the mercury–nitrogen and –selenium vibrations suggests a four-co-ordinate mercury atom in the solid state. Assignments are based on a comparison with the IR spectra of the starting diselenides.[8] The Fourier-transform Raman spectra are even more complex and contain numerous bands due to aryl substituents. Hence a rigorous assignment of M–Se vibrations was not attempted. For compounds **3** and **4**, attempts to record the Raman spectra even at the lowest laser powers led only to sample decomposition. Further close similarity observed in the trends of the ^1H, ^{13}C, ^{77}Se NMR and IR spectra suggests that the compounds probably possess similar structures.

The mass spectra of compounds **1**–**3** showed no peaks higher than the expected molecular mass which is in agreement with the proposed monomeric structure. The molecular ion peaks and the peaks due to other fragments containing Se and Hg exhibit the expected isotope patterns. The most dominent features were the cleavage of the Se–Hg bond, loss of Se and CH_3. Furthermore, the stable tropylium cation ($C_7H_7^+$, m/z 91), the Schiff-base fragments (Me_2NCH_2, m/z 58; Me_2NCHMe, 72) and the cyclopentadienyl fragments (C_5H_5, m/z 65) are also observed. The monomeric nature was unambiguously confirmed by X-ray crystallographic analyses of **1** and **4**.

Table 1 Selected bond lengths (Å) and angles (°) for compound **1** with estimated standard deviations (e.s.d.s) in parentheses

Hg(1)–Se(1)	2.477(2)	Hg(1)–Se(2)	2.475(2)	Hg(2)–Se(3)	2.456(2)	Hg(2)–Se(4)	2.461(3)
Se(1)–C(1)	1.92(2)	Se(2)–C(10)	1.92(2)	Se(3)–C(19)	1.91(2)	Se(4)–C(28)	1.92(2)
C(6)–C(7)	1.52(3)	C(15)–C(16)	1.52(3)	C(24)–C(25)	1.51(2)	C(33)–C(34)	1.51(3)
C(7)–N(1)	1.50(2)	C(16)–N(2)	1.48(2)	C(25)–N(3)	1.46(2)	C(34)–N(4)	1.51(3)
N(1)–C(8)	1.47(2)	N(2)–C(17)	1.46(3)	N(3)–C(26)	1.50(2)	N(4)–C(35)	1.50(3)
N(1)–C(9)	1.46(3)	N(2)–C(18)	1.48(3)	N(3)–C(27)	1.48(3)	N(4)–C(36)	1.47(3)
N(1)–Hg(1)	2.61(1)	N(2)–Hg(1)	2.63(1)	N(3)–Hg(2)	2.72(2)	N(4)–Hg(2)	2.63(2)
Hg(1)–N(1)–C(9)	102(1)	Hg(1)–N(2)–C(18)	103(2)	Hg(2)–N(3)–C(27)	101(1)	Hg(2)–N(4)–C(36)	118(1)
C(9)–N(1)–C(8)	109(1)	C(18)–N(2)–C(17)	106(2)	C(27)–N(3)–C(26)	110(1)	C(36)–N(4)–C(35)	112(1)
C(8)–N(1)–C(7)	110(1)	C(17)–N(2)–C(16)	115(1)	C(26)–N(3)–C(25)	106(1)	C(35)–N(4)–C(34)	111(1)
C(7)–N(1)–Hg(1)	109(1)	C(16)–N(2)–Hg(1)	108(1)	C(25)–N(3)–Hg(2)	105(1)	C(34)–N(4)–Hg(2)	108(1)
C(8)–N(1)–Hg(1)	118(1)	C(17)–N(2)–Hg(1)	118(1)	C(26)–N(3)–Hg(2)	122(1)	C(35)–N(4)–Hg(2)	101(1)
C(9)–N(1)–C(7)	109(1)	C(18)–N(2)–C(16)	106(1)	C(27)–N(3)–C(25)	111(1)	C(36)–N(4)–C(34)	107(1)
N(1)–C(7)–C(6)	112(1)	N(2)–C(16)–C(15)	111(1)	N(3)–C(25)–C(24)	117(1)	N(4)–C(34)–C(35)	113(1)
C(7)–C(6)–C(1)	122(1)	C(16)–C(15)–C(10)	124(1)	C(25)–C(24)–C(19)	121(1)	C(34)–C(33)–C(28)	122(2)
C(7)–C(6)–C(5)	117(1)	C(16)–C(15)–C(14)	122(1)	C(25)–C(24)–C(23)	119(1)	C(34)–C(33)–C(32)	113(2)
C(6)–C(1)–Se(1)	124(1)	C(15)–C(10)–Se(2)	120(1)	C(24)–C(19)–Se(3)	125(1)	C(33)–C(28)–Se(4)	124(2)
C(2)–C(1)–Se(1)	119(1)	C(11)–C(10)–Se(2)	118(1)	C(20)–C(19)–Se(3)	116(1)	C(29)–C(28)–Se(4)	117(2)
Hg(1)–Se(1)–C(1)	95.8(6)	Hg(1)–Se(2)–C(10)	97.0(6)	Hg(2)–Se(3)–C(19)	98.0(6)	Hg(2)–Se(4)–C(28)	95.0(8)
Se(2)–Hg(1)–N(2)	90.1(4)	N(1)–Hg(1)–N(2)	100.9(6)	Se(3)–Hg(2)–N(3)	90.0(4)	N(4)–Hg(2)–Se(4)	90.4(4)
Se(1)–Hg(1)–Se(2)	159.3(1)	Se(1)–Hg(1)–N(2)	103.5(4)	Se(3)–Hg(2)–Se(4)	159.9(1)	Se(4)–Hg(2)–N(3)	103.0(4)
N(1)–Hg(1)–Se(1)	89.9(4)	Se(2)–Hg(1)–N(1)	103.0(4)	N(3)–Hg(2)–N(4)	96.6(6)	Se(3)–Hg(2)–N(4)	103.5(4)

Table 2 Atomic coordinates for non-hydrogen atoms of compound **1** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Hg(1)	0.591 2(1)	0.871 9(1)	0.184 59(2)	Hg(2)	0.048 4(1)	0.212 8(1)	0.036 38(2)
Se(1)	0.397 5(2)	0.763 4(3)	0.164 8(1)	Se(3)	−0.127 5(2)	0.293 6(2)	0.069 4(0)
Se(2)	0.734 6(2)	1.053 7(2)	0.206 6(1)	Se(4)	0.167 4(2)	0.116 9(4)	−0.011 4(1)
C(1)	0.467(2)	0.585(2)	0.151 6(4)	C(19)	−0.041(2)	0.366(2)	0.108 4(5)
C(2)	0.423(2)	0.457(3)	0.166 9(5)	C(20)	−0.076(2)	0.311(2)	0.140 7(4)
C(3)	0.468(2)	0.330(2)	0.157 4(6)	C(21)	−0.023(2)	0.360(2)	0.170 4(5)
C(4)	0.554(2)	0.318(2)	0.133 3(6)	C(22)	0.062(2)	0.460(2)	0.168 7(5)
C(5)	0.598(2)	0.440(2)	0.118 1(6)	C(23)	0.103(2)	0.516(2)	0.137 6(5)
C(6)	0.557(1)	0.571(2)	0.127 5(4)	C(24)	0.047(1)	0.470(2)	0.107 3(4)
C(7)	0.607(2)	0.698(2)	0.108 3(4)	C(25)	0.084(2)	0.537(2)	0.073 8(5)
N(1)	0.697(1)	0.781(2)	0.129 3(3)	N(3)	0.168(1)	0.456(2)	0.052 5(3)
C(8)	0.810(2)	0.699(2)	0.133 7(6)	C(26)	0.288(2)	0.457(2)	0.071 1(6)
C(9)	0.725(2)	0.916(2)	0.111 8(6)	C(27)	0.180(2)	0.521(3)	0.018 2(6)
C(10)	0.875(2)	0.932(2)	0.210 8(4)	C(28)	0.322(2)	0.131(3)	0.012 2(6)
C(11)	0.976(2)	0.968(2)	0.194 3(5)	C(29)	0.411(2)	0.213(3)	−0.003 5(7)
C(12)	1.085(2)	0.894(2)	0.198 2(5)	C(30)	0.531(2)	0.224(3)	0.013 7(6)
C(13)	1.087(2)	0.780(2)	0.219 5(6)	C(31)	0.545(2)	0.159(3)	0.044 6(9)
C(14)	0.986(2)	0.740(2)	0.235 8(5)	C(32)	0.457(2)	0.067(3)	0.058 4(7)
C(15)	0.873(2)	0.813(2)	0.233 0(4)	C(33)	0.350(2)	0.059(2)	0.042 2(5)
C(16)	0.761(2)	0.767(3)	0.252 9(5)	C(34)	0.260(2)	−0.035(2)	0.060 1(6)
N(2)	0.674(1)	0.690(2)	0.230 3(3)	N(4)	0.167(1)	0.048(2)	0.079 8(4)
C(17)	0.718(2)	0.552(2)	0.218 2(5)	C(35)	0.066(2)	−0.045(2)	0.091 7(5)
C(18)	0.566(3)	0.660(3)	0.251 3(8)	C(36)	0.231(2)	0.115(2)	0.108 9(6)

Crystal structure of compound 1

A PLUTO[21] view of compound **1** is shown in Fig. 1, selected bond distances and angles in Table 1 and atomic coordinates in Table 2. The compound crystallizes with two symmetry-independent molecules in the asymmetric unit. The co-ordination around mercury is distorted tetrahedral with an angle of 98(1)° between the mean planes through atoms Hg(1), N(1), N(2) and Hg(1), Se(1), Se(2), while in the second moiety the angle between the Hg(2)N(3)N(4) and Hg(2)Se(3)Se(4) planes is 81(1)°. Further, all the four, six-membered metallocycles are puckered and exist in an envelope conformation. The average bite angle of the chelating ring in both moieties is 90.0(3)°.

The two independent molecules differ significantly in the N–Hg–N angle [N(1)–Hg(1)–N(2) 100.9(6) and N(3)–Hg(2)–N(4) 96.6(6)°]. Mercury valency angles deviate considerably from the typical tetrahedral value. The largest angle Se–Hg–Se [159.9(1)°] exhibits a strong tendency towards linear co-ordination. Another peculiarity is shorter Hg–Se [2.475(2)–2.477(2) Å] compared to Hg–N bond lengths [2.61(1)7–2.63(1) Å] in spite of a considerable difference between the covalent radii of selenium (1.17 Å) and nitrogen (0.70 Å). However, the average Hg–Se bond lengths of 2.476(2) [Hg(1)–Se(1), Hg(1)–Se(2)] and 2.459(2) Å [Hg(2)–Se(3), Hg(2)–Se(4)] respectively are similar to those reported previously,[11,22] while the average Hg–N bond length of 2.64(1) Å is intermediate between those reported for related structures, *viz.* $Hg(SeNC_5H_4)_2$ (Hg–N 2.98 Å)[11] and HgCl(py)(SeEt) (py = pyridine) (Hg–N 2.45 Å).[23] The crystal structure consists of discrete molecules and there are no significant intermolecular contacts.

Crystal structure of compound 4

A PLUTO view of compound **4** is shown in Fig. 2, selected bond lengths and angles are in Table 3 and atomic coordinates in Table 4. The crystal structure shows a distinct monomer with two molecules per unit cell. The absolute configuration was shown to be *S*,*R* where the configuration around the ferrocene axis is *R*. The mercury atom is again four-co-ordinate. However the structure is close to square planar with the Se–Hg–Se angles approaching linearity [168.6(2)°] and the similar nitrogen and selenium atoms being mutually *trans*. The Hg–Se bond lengths are 2.458(2) and 2.469(2) Å and the Hg–N bond lengths 2.61(1) and 2.90(1) Å lie intermediate between those reported[22] earlier and in the recently reported $Hg(SeNC_5H_4)_2$.[11] The bite of the chelate ring involving the Se(1),N(1) donors [93.1(4)°] is significantly different from that involving Se(2),N(2) [85.0(4)°]. Interestingly, the two cyclopentadienyl rings are eclipsed at both Fe(1) and Fe(2) atoms and are slightly tilted with respect to each other, the dihedral angles being 3.0 and 2.2°, respectively.

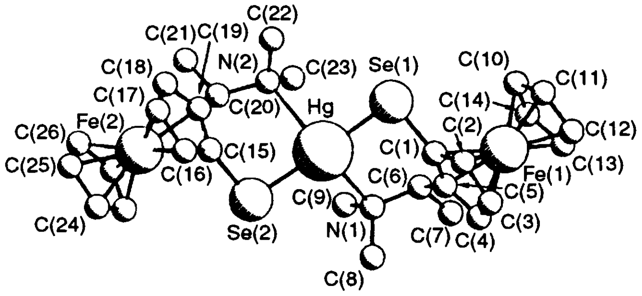

Fig. 2 Molecular structure of $Hg[(S,R)\text{-}(SeC_5H_3CHMeNMe_2\text{-}2)\text{-}Fe(C_5H_5)]_2$ **4**

Table 3 Selected bond lengths (Å) and angles (°) for compound **4** with e.s.d.s in parentheses

Hg(1)–Se(1)	2.458(2)	Hg(1)–Se(2)	2.469(2)
Hg(1)–N(1)	2.61(1)	Hg(1)–N(2)	2.90(1)
Se(1)–C(1)	1.91(1)	Se(2)–C(15)	1.95(1)
C(5)–C(6)	1.53(2)	C(19)–C(20)	1.48(2)
C(6)–C(7)	1.52(2)	C(20)–C(21)	1.52(2)
C(6)–N(1)	1.47(2)	C(20)–N(2)	1.50(2)
N(1)–C(8)	1.51(2)	N(2)–C(22)	1.46(3)
N(1)–C(9)	1.47(2)	N(2)–C(23)	1.40(2)
Hg(1)–Se(1)–C(1)	94.7(5)	Hg(1)–Se(2)–C(15)	94.9(5)
Se(1)–C(1)–C(5)	126.8(9)	Se(2)–C(15)–C(19)	123.5(9)
C(5)–C(6)–C(7)	110(1)	C(19)–C(20)–C(21)	112(1)
C(5)–C(6)–N(1)	109.3(9)	C(19)–C(20)–N(2)	109(1)
C(7)–C(6)–N(1)	114(1)	C(21)–C(20)–N(2)	116(1)
C(6)–N(1)–C(8)	113(1)	C(20)–N(2)–C(22)	111(1)
C(6)–N(1)–C(9)	113(1)	C(20)–N(2)–C(23)	110(1)
C(8)–N(1)–C(9)	111(1)	C(22)–N(2)–C(23)	100(1)
Hg(1)–N(1)–C(6)	109.2(9)	Hg(1)–N(2)–C(23)	110(1)
Hg(1)–N(1)–C(8)	111(1)	Hg(1)–N(2)–C(20)	113(1)
C(1)–C(5)–C(4)	109(1)	C(15)–C(19)–C(18)	104(1)
Se(1)–C(1)–C(2)	125(1)	Se(2)–C(15)–C(16)	126(1)
Se(1)–C(1)–Fe(1)	124.2(8)	Se(2)–C(15)–Fe(2)	122.2(8)
Se(1)–Hg(1)–N(1)	93.1(4)	N(2)–Hg(1)–Se(2)	85.0(4)
Se(1)–Hg(1)–N(2)	98.5(4)	Se(2)–Hg(1)–N(1)	95.0(4)
N(1)–Hg(1)–N(2)	116.5(5)	Se(1)–Hg(1)–Se(2)	168.6(2)

Conclusion

Nitrogen-containing chelating ligands of selenium can be used to prepare low-melting, volatile, stable, discrete monomeric mercury selenolates. A convenient synthesis which does not involve the use of large, bulky, sterically hindered ligands and

Table 4 Atomic coordinates for non-hydrogen atoms of compound **4** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Hg(1)	1.045 0(1)	0.020 0	0.754 54(5)
Se(1)	0.812 4(2)	0.027 2(2)	0.732 9(1)
Se(2)	1.276 0(2)	0.052 4(2)	0.768 6(1)
Fe(1)	0.661 9(2)	−0.110 3(2)	0.487 4(2)
Fe(2)	1.423 8(2)	0.181 1(2)	1.019 7(2)
C(1)	0.805(1)	−0.016(1)	0.567(1)
C(2)	0.741(2)	0.043(1)	0.471(1)
C(3)	0.757(2)	−0.018(1)	0.362(1)
C(4)	0.825(1)	−0.116(1)	0.393(1)
C(5)	0.853(1)	−0.113(1)	0.519(1)
C(6)	0.930(1)	−0.197(1)	0.594(1)
C(7)	0.926(2)	−0.307(1)	0.530(2)
N(1)	1.058(1)	−0.154(1)	0.620(1)
C(8)	1.130(2)	−0.130(2)	0.507(2)
C(9)	1.134(2)	−0.225(2)	0.704(2)
C(10)	0.540(2)	−0.141(2)	0.618(2)
C(11)	0.481(2)	−0.082(2)	0.527(2)
C(12)	0.488(2)	−0.138(2)	0.416(2)
C(13)	0.551(2)	−0.242(2)	0.448(2)
C(14)	0.584(2)	−0.236(2)	0.571(2)
C(15)	1.270(1)	0.154(1)	0.905(1)
C(16)	1.304(1)	0.268(1)	0.902(1)
C(17)	1.294(2)	0.307(1)	1.018(2)
C(18)	1.255(2)	0.220(1)	1.095(2)
C(19)	1.239(1)	0.121(1)	1.025(1)
C(20)	1.202(1)	0.011(2)	1.065(1)
C(21)	1.222(2)	−0.004(2)	1.201(2)
N(2)	1.070(1)	−0.013(1)	1.014(1)
C(22)	0.978(2)	0.058(2)	1.068(2)
C(23)	1.033(2)	−0.123(2)	1.022(2)
C(24)	1.601(2)	0.212(2)	0.964(2)
C(25)	1.592(2)	0.244(2)	1.083(2)
C(26)	1.558(2)	0.155(2)	1.153(2)
C(27)	1.543(2)	0.059(2)	1.075(2)
C(28)	1.569(2)	0.097(2)	0.957(2)

Table 5 Crystal data and structural refinement for $Hg(SeC_6H_4CH_2NMe_2\text{-}2)_2$ **1** and $Hg[(S,R)\text{-}(SeC_5H_3CHMeNMe_2\text{-}2)Fe(C_5H_5)]_2$ **4***

Empirical formula	$C_{18}H_{24}HgN_2Se_2$	$C_{28}H_{36}Fe_2HgN_2Se_2$
M	629.9	870.8
Space group	$P2_1/c$	$P2_1$
a/Å	10.994(2)	10.558(3)
b/Å	9.426(1)	12.220(3)
c/Å	38.959(4)	11.041(3)
β/°	90.74(1)	92.65(2)
U/Å^3	4037.00	1423.09
Z	8 (2 molecules per asymmetric unit)	2
D_c/g cm^{-3}	2.06	2.03
F(000)	1176	836
μ/cm^{-1}	38.62	63.94
hkl Ranges	0–12, 0–14, −13 to 13	0–13, 0–11, −46 to 46
Total reflections collected	6381	2712
No. reflections with $I > 2.5\sigma(I)$	4055	2503
No. parameters refined	560	315
R	0.048	0.048
R'	0.075	0.065
Residual electron density (Δρ) (≈1 Å from Hg)/e Å^{-3}	1.17	2.83
$(\Delta/\sigma)_{max}$	0.56	0.377

* Details in common: monoclinic; θ range 2–25°.

without the addition of external neutral ligands is described. Compounds **1** and **2** vaporize without decomposition at convenient temperatures and do not leave any residue. For the ferrocene complexes, the favoured decomposition pathway involves loss of the ferrocene unit leaving behind HgSe. The thermal behaviour under reduced pressure will have to be probed to get an insight into its utility for deposition of thin films *via* CVD. The formation of the six-membered chelate ring in each case seems to be an important factor in deciding the molecular nature of these compounds. The solution behaviour (NMR spectroscopy) of these compounds at ambient temperature suggests that the Hg atom is two-co-ordinate. However solid-state studies (X-ray crystallography, Fourier-transform IR) reveal it to be four-co-ordinate.

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