Journal of Organometallic Chemistry, 395 (1990) 167–175
Elsevier Sequoia S.A., Lausanne

JOM 20969

2-(2-Pyridyl)phenyl selenium compounds: synthesis and properties. The crystal structure of 2-(2-pyridyl)phenylselenium(II) tribromomercurate(II)

Shaaban A. Mbogo, Tarlok S. Lobana, William R. McWhinnie, Martin R. Greaves

Department of Chemical Engineering and Applied Chemistry, Aston University, Aston Triangle, Birmingham B4 7ET (U.K.)

and Thomas A. Hamor

Department of Chemistry, University of Birmingham, P.O. Box 363, Birmingham B15 2TT (U.K.)

(Received March 9th, 1990)

Abstract

The reaction of RHgCl (R = 2-(2-pyridyl)phenyl-) with SeX_4 (X = Cl, Br) involves both *trans*-metallation and redox processes, the final product being 2-(2-pyridyl)phenylselenium(II) tribromomercurate(II). Variation of the reaction conditions allows isolation of materials that appear to be intermediates in the *trans*-metallation process; the nature of these intermediates is discussed. Routes to compounds of the types $RSeBr_3$ and RR′Se (R′ = *p*-ethoxyphenyl–) are described.

The crystal and molecular structure of the title compound was determined. Disorder in the structure prevented differentiation of the C–Se and N–Se bonds, which apparently had the same length of 1.91(3) Å within the cation, which can be regarded as electronically equivalent to dibenzoselenophene. The packing of the tribromomercurate ions [Hg–Br 2.52(1), 2.49(1) Å] results in two additional Hg · · · Br contacts (3.43(1) Å) that complete trigonal bipyramidal co-ordination. There are weak (3.21(1) Å) Se · · · Br contacts.

Introduction

The synthesis was recently reported of some 2-pyridyl-functionalised organotellurium ligands [1] prepared by reaction of appropriate tellurium compounds with 2-(2-pyridyl)phenylmercury(II) chloride, a reagent that is known to be tetrameric [2]. Subsequent investigation of the ligand properties of *p*-ethoxyphenyl-2-(2-pyridyl)phenyl telluride revealed that there was considerable lability of organic groups between metal centres, particularly when mercury(II) [3] or palladium(II) and

0022-328X/90/$03.50

platinum(II) [4] salts were used as Lewis acids. It was decided to prepare *p*-ethoxyphenyl-2-(2-pyridyl)phenyl selenide for a comparative study. Although the same basic methodology was used, some significant differences in the synthetic pathways for selenium and tellurium were noted. In this paper the new selenium compounds are reported, differences from the tellurium series noted, and the crystal structure of one intermediate presented.

Experimental and results

Preparations

The reaction of $SeBr_4$ and $SeCl_4$ with 2-(2-pyridyl)phenylmercury(II) chloride. A solution of 2-(2-pyridyl)phenylmercury(II) chloride [1] (0.79 g, 0.002 mol) in dry 1,4-dioxane (15 cm^3) was added to a solution of selenium tetrabromide (0.8 g, 0.002 mol) in dry 1,4-dioxane (10 cm^3). The mixture was stirred under reflux for 2h during which a yellow compound **1** separated. This was filtered off and then dried in vacuo. Yield 64%, m.p. 181–182°C. Found: C, 21.5; H, 1.71; N, 1.95. $C_{13}H_{12}Br_3HgNOSe$ (i.e. $C_{11}H_8Br_3HgNSe \cdot 1/2$ dioxane) calc.: C, 21.7; H, 1.67; N, 1.95%.

Treatment of compound **1** with ethanol affords an orange product **2**, which on washing with ethanol and drying in vacuo, gives m.p. 214–216°C. Found: C, 19.6; H, 1.2; N, 1.99. $C_{11}H_8Br_3HgNSe$ calc.: C, 19.6; H, 1.19; N, 2.08%.

A product **3**, shown to be identical to **2**, is obtained directly if the initial reaction with the organo mercurial is carried out in chloroform in place of 1,4-dioxane: found, C, 19.9; H, 1.23; N, 2.09%.

When selenium tetrachloride (0.44 g, 0.002 mol) in dry 1,4-dioxane was used in place of the solution of $SeBr_4$, and the mixture stirred under reflux for 4 h, a solid was formed. This was filtered off and recrystallised from acetonitrile/ethanol (1 : 1 v/v) to give pale yellow crystals, **4**, in 72% yield with m.p. 175–178°C. Found: C, 26.1; H, 1.40; N, 4.15. $C_{37}H_{30}Cl_9Hg_3N_5Se_3$ (i.e. $3(C_{11}H_8Cl_3HgNSe) \cdot 2CH_3CN$) calc.: C, 26.1; H, 2.76; N, 4.11%.

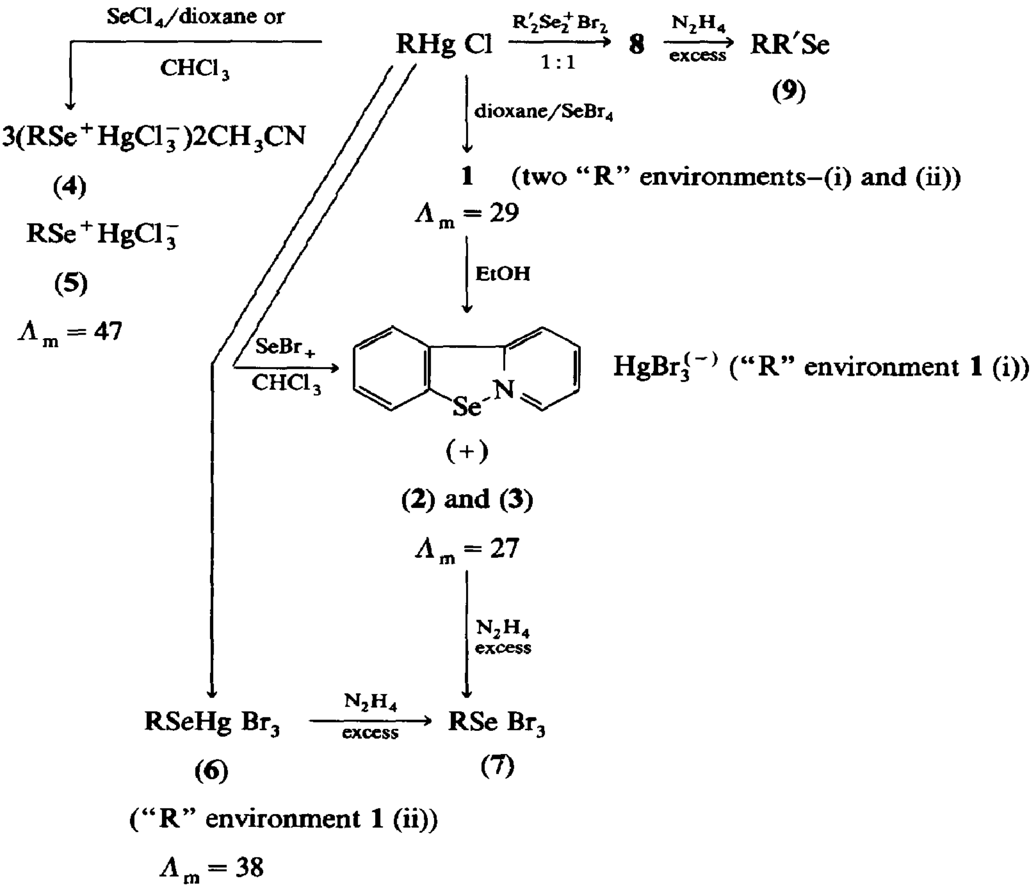
Use of chloroform as a solvent for the above reaction gave directly a solvent free yellow product, **5**, in 60% yield, with m.p. 159–161°C. Found: C, 23.9; H, 1.51; N, 2.50. $C_{11}H_8Cl_3HgNSe$ calc.: C, 24.4; H, 1.48; N, 2.60%.

The reaction of p*-ethoxyphenyl selenium tribromide (prepared in situ) with 2-(2-pyridyl)phenylmercury chloride*

A solution of bis(*p*-ethoxyphenyl) diselenide (2.0 g, 0.005 mol), prepared by a published method [5], in carbon tetrachloride was treated with a six-fold molar excess of bromine at 0°C. under nitrogen. To this solution was added a chloroform (25 cm^3) solution of 2-(2-pyridyl)phenyl mercury chloride, and the mixture was stirred for 2 h at room temperature. A white compound, **6**, with m.p. 126–128°C. was formed. Found: C, 20.0; H, 1.13; N, 1.98. $C_{11}H_8Br_3HgNSe$ calc.: C, 19.6; H, 1.19; N, 2.08%.

Treatment of products 2, 3 and 6 with hydrazine hydrate.

Treatment of compounds **2**, **3** or **6** as suspensions in ethanol with an excess of hydrazine hydrate gave the same pale yellow compound **7**, m.p. 178–180°C. Found: C, 26.2; H, 1.55: N, 2.67. $C_{11}H_8Br_3NSe$ calc.: C, 27.9; H, 1.69; N, 2.95%.



Scheme 1. Preparative scheme (R = 2-(2-pyridyl)phenyl-, R′ = *p*-ethoxyphenyl-. Molar conductivity data (Λ_m) for DMSO solutions (10^{-3} *M*), units are ohm^{-1} mol^{-1}).

Preparation of p-*ethoxyphenyl 2-(2-pyridyl)phenyl selenide.* A solution of 2-(2-pyridyl)phenylmercury chloride (4.0 g, 0.01 mol) in chloroform (25 cm^3) was added to a solution of *p*-ethoxyphenylselenium monobromide prepared in situ by treatment of bis(*p*-ethoxyphenyl) diselenide (2.0 g, 0.05 mol) with bromine (0.8 g, 0.005 mol) at 0 °C in carbon tetrachloride solution under nitrogen. The mixture was stirred at room temperature for 2 h, during which a white material, **8**, m.p. 228–230 ° C. was formed. **8** was suspended in ethanol (30 cm^3) and treated dropwise with an excess of hydrazine hydrate. The mixture was stirred for 15 min then treated with water (50 cm^3) and the solid product, **9**, filtered off. The product was recrystallised from ethanol/acetone (1 : 1 v/v) to give a 50% yield of pale yellow crystals having m.p. 102–104 °C. Found: C, 64.9; H, 4.83; N, 4.05. $C_{19}H_{17}NOSe$ calc.: C, 64.3; H, 4.79; N, 3.94%.

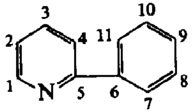
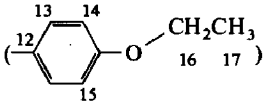
The preparative sequence is summarised in Scheme 1.

Physical measurements

Melting points (uncorrected) were determined with a Gallenkamp electrically-heated apparatus. Molar conductance measurements were made at room tempera-

Table 1

^{13}C NMR data for 2-(2-pyridyl)phenylselenium compounds (ppm vs TMS)

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)
	149.1	119.1	136.2	121.5	156.7	138.8	127.1	128.9	128.1	128.8	126.3
RHgCl	149.7	120.8	138.6	123.4	155.9	141.3	147.6	137.6	128.1	129.4	127.0
1 [a]	141.8	122.9	140.4	124.0	151.8	128.2	142.0	132.3	126.3	127.3	–
	144.5	125.5	143.5	126.3	153.0	121.4	133.2	132.2	129.3	131.9	127.4
2 and **3**	141.8	122.7	140.4	124.0	151.9	129.3	142.0	132.4	126.3	127.3	–
6	144.3	125.9	143.9	127.8	152.5	121.4	134.6	133.2	132.0	132.6	128.2
5	141.4	121.9	139.9	123.9	151.3	130.5	142.3	132.1	126.9	127.8	129.8
9	147.8	122.3	137.2	122.5	157.4	138.2	135.2	129.6	128.9	129.1	125.6
	(C(12))	(C(13))	(C(14))	(C(15))	(C(16))	(C(17))					
	120.8	138.0	115.8	159.1	63.1	14.6					

[a] See Scheme 1 for structural formulae

Table 2

Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses

Hg(1)–Br(1)	2.518(6)	C(2)–C(3)	1.53(6)
Hg(1)–Br(2)	2.492(8)	C(3)–C(4)	1.22(6)
Se(1)–NC(1)	1.91(3)	C(4)–C(5)	1.39(7)
NC(1)–C(2)	1.33(5)	C(5)–C(6)	1.37(6)
NC(1)–C(6)	1.29(5)	C(2)–C(2′)	1.41(7)
Br(1)–Hg(1)–Br(2)	121.9(2)	NC(1)–C(2)–C(2′)	115(4)
Br(1)–Hg(1)–Br(1′)	116.2(3)	C(3)–C(2)–C(2′)	131(4)
NC(1)–Se(1)–NC(1′)	84(2)	C(2)–C(3)–C(4)	123(5)
Se(1)–NC(1)–C(2)	113(2)	C(3)–C(4)–C(5)	121(5)
Se(1)–NC(1)–C(6)	126(3)	C(4)–C(5)–C(6)	117(6)
C(2)–NC(1)–C(6)	121(3)	NC(1)–C(6)–C(5)	124(4)
NC(1)–C(2)–C(3)	114(3)		

ture with a Mullard bridge and a dip cell with bright platinum electrodes (type E 7591/B). Infrared spectra were recorded for KBr discs with a Perkin Elmer 1710 FTIR spectrophotometer (model PP-1), NMR (^{1}H and ^{13}C) spectra were recorded with a Bruker AC-300 instrument using TMS as internal standard. Mass spectra were obtained through the SERC Service at University College, Swansea.

Some ^{13}C NMR data are listed in Table 1.

Crystal and molecular structure of 2-(2-pyridyl)phenylselenium(II) tribromomercurate(II) (2). An irregular shaped crystal of size ca. 0.3 mm^3 was mounted on an Enraf–Nonius CAD-4 diffractometer. Final cell dimensions and reflection intensities were measured with graphite monochromated Mo-K_α radiation with the diffractometer operated in the ω–2θ scan mode. 1295 unique reflections were scanned within $2 < \theta < 25°$ of which 612, [$F > 5\sigma(F)$], were used in the analysis. Three standard reflections were measured every 2 h to monitor the stability of the system.

The structure was determined by Patterson and Fourier methods and refined by least squares. Anisotropic thermal parameters were used for heavier atoms Hg, Se,

Table 3

Fractional atomic coordinates ($\times 10^4$) and isotropic temperature factors (Å$^2 \times 10^3$) with e.s.d.'s in parentheses

	x	*y*	*z*	*U*
Hg(1)	0	955(2)	2500	83[a]
Br(1)	−1377(4)	1920(5)	1420(11)	100[a]
Br(2)	0	−851(5)	2500	108[a]
Se(1)	0	3660(4)	2500	40[a]
NC(1)	819(20)	4692(22)	3041(49)	40(8)[b]
C(2)	455(23)	5566(28)	2811(58)	44(9)
C(3)	1102(28)	6405(34)	3199(66)	61(11)
C(4)	1876(31)	6275(35)	3696(76)	70(13)
C(5)	2217(36)	5346(37)	3907(81)	81(15)
C(6)	1645(24)	4591(28)	3581(61)	47(10)

[a] Refined anisotropically. U_{eq} given, where $U_{eq} = \frac{1}{3}$ (trace of the orthogonalized U_{ij} tensor). [b] Due to disorder NC(1) represents 50% C and 50% N.

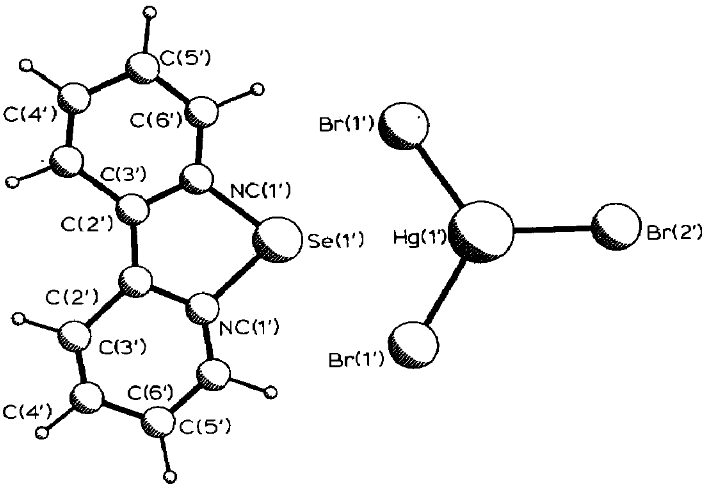


Fig. 1. The molecular structure of 2-(2-pyridyl)phenylselenium(II) tribromomercurate(II).

and Br only. Carbon atoms were refined isotropically and hydrogen atoms were placed in calculated positions riding on their respective bonded atom. The weighting scheme used was $w = 1/[\sigma^2(F) + 0.0001F^2]$. The least squares refinement was terminated when all calculated shifts were $< 0.01\sigma$ and $R = 0.093$. The molecule appears to be disordered about a two-fold axis, the carbon atom bonded to selenium and the 2-pyridyl-nitrogen atom becoming equivalent. Refinement in space group *Cc* without allowing for disorder did not converge satisfactorily.

Computations were carried out on the Birmingham University Honeywell computer with the SHELX [6] suite of programmes. An empirical absorption correction was applied using DIFABS [7] and diagrams were drawn by PLUTO [8] at the University of Manchester regional computer centre.

Crystal data. $C_{11}H_8Br_3HgNSe$, $M = 673.5$, Monoclinic space group $C2/c$, $a = 16.427(4)$, $b = 13.794(7)$, $c = 6.863(2)$ Å, $\beta = 109.07(10)°$, $U = 1469.8$ Å^3, $Z = 4$, $D_c = 3.044$ g cm^{-3}, $F(000) = 1200$, Mo-K_α radiation ($\lambda = 0.71069$ Å), $\mu = 21.97$ mm^{-1}.

Bond lengths and bond angles are listed in Table 2, and fractional atomic co-ordinates in Table 3. The structure is shown in Fig. 1 and the packing diagram in Fig. 2.

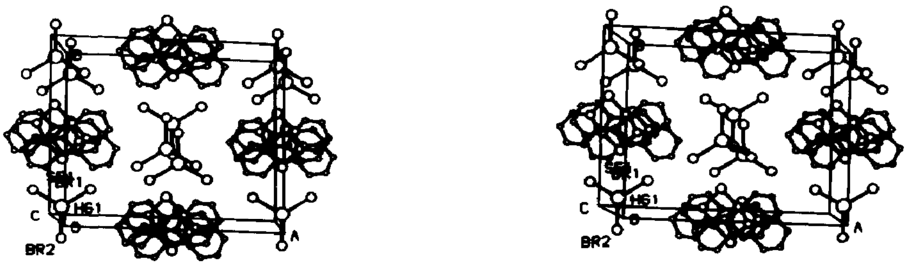
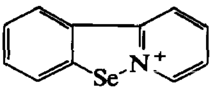


Fig. 2. Stereoscopic packing diagram showing the co-ordination about mercury(II).

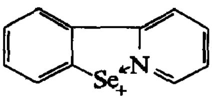
Discussion

The reaction of selenium tetrahalides (Cl, Br) with 2-(2-pyridyl)phenyl mercury chloride follows a different path to that clearly established for the reaction with $TeBr_4$ [1]. Thus a redox process is involved in addition to the *trans*-metallation reaction and the products (Scheme 1: **2**, **3**, **4**, **5**) contain selenium(II). When the reaction between RHgCl (R = 2-(2-pyridyl)phenyl-) and $SeBr_4$ is carried out in 1,4-dioxane, a compound **1** is obtained which analyses as $RSeHgBr_3 \cdot 1/2$dioxane. The presence of dioxane was confirmed by IR spectroscopy, and integration of the ^1H NMR spectrum confirmed the R:dioxane ratio of 1 : 0.5. Of particular interest is that both the ^1H and ^{13}C NMR spectra (Table 1) show *two* environments for R (1 : 1), which are denoted by (i) and (ii) (see Scheme 1 and Table 1). Treatment of **1** with ethanol removes dioxan and gives **2**, which has R in a single environment, (i). If the initial reaction is carried out in chloroform **3**, shown to be identical with **2**, is obtained. The structure of **2** was determined by an X-ray diffraction study (vide infra), which showed it to be an ionic compound and indeed, the conductivity of the compound in dimethylsulfoxide (DMSO) (see Scheme 1) is close to that expected for a 1 : 1 electrolyte. Treatment of **2** or **3** with hydrazine hydrate gives a selenium(IV) product, but no precipitate of either Se or Hg was noted. It is suggested that reduction of $HgBr_3^-$ to a mercury(I) species occurs, with release of halogen, which oxidises selenium(II) to selenium(IV) (compound **7**); compound **7** is $RSeBr_3$ analogous to the well defined $RTeBr_3$ [1], and no further discussion is required.

The nature of product **1** is of some interest. Serendipitously it was discovered that when R'_2Se_2 (R′ = *p*-ethoxyphenyl-) is treated with a six molar excess of bromine, rupture of the R′–Se bond occurs. Subsequent reaction with RHgCl gives a *white* compound, **6**, containing no R′. This material gives ^1H and ^{13}C (Table 1) NMR spectra identical with set (ii) of compound **1**. Compound **6** is a 1 : 1 electrolyte in DMSO and treatment with an excess of hydrazine gives **7**. The FAB mass spectrum shows RSe^+ as the dominant fragment, further, the spectrum is identical to that of **2**. Whatever the nature of **6**, the compound is converted into **2** under the conditions of the FABMS experiment. Since the NMR measurements and the conductivity measurements for **6** are both made on DMSO solutions, it is reasonable to suppose that the data relate to the same species; thus an ionic model is required for **6**. Two such models may be considered; (a) $RSe^+HgBr_3^-$ in which canonical form **2(b)** is dominant, as opposed to form **2(a)** for compound **2**; (b) an extremely labile $RHg^+SeBr_3^-$. Model (**a**) is unconvincing and hence, model (**b**) is preferred. Thus both **1** and **6** may be considered to be intermediates in the *trans*-metallation process. Compound **1**, on available evidence, must be formulated as a 1 : 1 mixture or inclusion compound of **2** and **6**; possibly some stability is conferred on the component **6** by dioxane–mercury co-ordination. The reaction of $SeCl_4$ with RHgCl follows a similar pattern except that no intermediates comparable to **1** to **6** are isolated. Thus, the solvent-free **5** and the acetonitrile solvate



2(a)



2(b)

(confirmed by IR spectroscopy) **4** are seen as the trichloromercurate(II) analogues of **2** and **3**. In accord with this view, **5** is a 1 : 1 electrolyte in DMSO.

The initial synthetic objective was the preparation of *p*-ethoxyphenyl 2-(2-pyridyl)phenyl selenide, R′RSe. This was achieved by bringing RHgCl into reaction with "R′SeBr" produced in situ from the reaction of R'_2Se_2 and Br_2 (1 : 1). The reaction proceeds via an ill-defined white intermediate **8**, which, on treatment with hydrazine hydrate affords R′RSe **9** which has been the subject of independent crystallographic investigation [9].

The crystal and molecular structure of 2-(2-pyridyl)phenylselenium tribromomercurate(II)

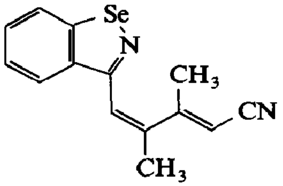
Owing to disorder within the structure, it was not possible to distinguish between the nitrogen atom and the carbon atom bonded to selenium and, hence the NC–Se distances are equivalent (1.91(3) Å). This bond length is close to the sum of the Pauling [10] single bond covalent radii of Se (1.14 Å) and sp^2 hybridised carbon (0.74 Å). Furthermore, a search of the Cambridge Structural Database [11] for Se–C(sp^2) distances revealed 843 bond lengths with a mean distance of 1.898(2) Å, which is in close agreement with the value found here; for example, in the structure of 9,10-diselenoanthracene [12] the C–Se distances are in the range 1.89(5) to 1.908(5) Å.

The sum of the Pauling covalent radii of Se (1.14 Å) and N (0.72 Å), is 1.86 Å [10]. The Se–N distance in **2** is slightly longer, indicating that if this is not a formal bond then it is at least a strong co-ordinate interaction. This interaction holds the organic ligand in a planar geometry. The Cambridge Structural Database [11] yielded 34 Se–N single bond distances, with a mean of 1.82 Å. In the analogous compound 5-(1-2 benzoselenazol-3-yl)-3,4-dimethyl-pentadienonitrile, the Se–N bond distance is 1.833(7) Å [13]. Values of 2.19(2) and 2.20(2) Å for a non-bonded Se- - -N interaction have been reported for $SeOCl_2 \cdot 2C_5H_5N$ [14].

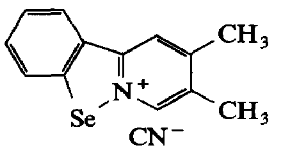
The $HgBr_3$ anion is accurately planar and the RSe^+ cation is planar to within ±0.07 Å. The whole complex is planar to within ±0.2 Å. The Hg–Br distances of 2.518(6) and 2.492(8) Å are in agreement with analogous Hg–Br distances in tetramethylammonium tribromomercurate(II) (2.48–2.56 Å) [15], bis(tetramethylammonium) tetrabromomercurate(II) [16] [2.585(3)–2.589(3) Å] and $HgBr_2$ [17] (2.48 Å). A histogram of the Hg–Br distance in the literature peaks in the range 2.45–2.55 Å. The mercury atom has two additional Br atoms as close neighbours, Br(2′) and Br(2″), completing a trigonal bipyramidal co-ordination geometry about mercury (see Fig. 2) with Hg- - -Br(2′) and Br(2″) 3.43(1) Å. These distances are similar to those found in $HgBr_2$ [17].

The value of 3.21(1) Å for the Se- - -Br(1) distance is outside the Pauling single bond length of 2.31 Å, but well within the van der Waals distance of 3.75 Å [10] implying a moderately strong secondary interaction. This interaction may be responsible for the slightly longer Hg-Br(1) bond length relative to the Hg–Br(2) value. The Br(1) atoms related by the two-fold axis lie almost exactly trans to the NC atoms with the NC1–Se–Br(1) angle 177.9 °. Also noteworthy is the Hg- - -Se distance of 3.73(1) Å.

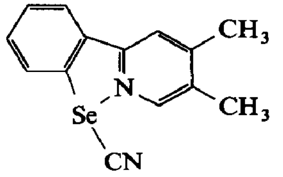
The demonstration of the existence of the 2-(2-pyridyl)phenyl selenium(II) cation (compound **2(a)**), which is isoelectronic with dibenzoselenophene, in this structure is of interest in the context of earlier work. Thus Bryce et al. [13] suggested that compound 5 (b) is an intermediate in the conversion of 5(a) into 5(c).



5(a)



5(b)



5(c)

Acknowledgements

S.A.M. thanks the University of Dar-es-Salaam for study leave and NORAD for financial support. T.S.L. thanks Guru Nanak Dev. University for study leave and the Royal Society and the Indian National Science Academy for support. M.R.G. thanks the SERC and RSRE (Malvern) for a CASE award.

References

1 N. Al-Salim, A.A. West, W.R. McWhinnie and T.A. Hamor, J. Chem. Soc., Dalton Trans., (1988) 2363.
2 E.C. Constable, T.A. Leese and D.A. Tocher, J. Chem. Soc. Chem. Commun., (1988) 570.
3 S.A. Mbogo, W.R. McWhinnie and T.S. Lobana, J. Organomet. Chem., 385 (1990) 115.
4 S.A. Mbogo, W.R. McWhinnie and T.S. Lobana, Unpublished observations.
5 W. Fred, S. Haller and K.J. Irgolic, J. Organomet. Chem., 38 (1972) 97.
6 G.M. Sheldrick, SHELX 76 Program for Crystal Structure determination, University of Cambridge, 1978; SHELX 86 Program for Crystal Structure Solution, University of Göttingen, 1987.
7 N. Walker and D. Stuart, Acta Crystallogr., A39 (1983) 158.
8 W.D.S. Motherwell and W. Clegg, Pluto, Program for Drawing Crystal and Molecular Structures, University of Cambridge (1978).
9 S.A. Mbogo, W.R. McWhinnie, T.S. Lobana and E.R.T. Tiekink, J. Organomet. Chem., 388 (1990) 273.
10 L. Pauling, "The Nature of the Chemical Bond", 3rd Edn., Cornell University Press, Ithaca, New York, 1960.
11 F.H. Allen, S. Bellard, M.D. Brice, B.A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B.G. Hummelink-Peters, O. Kennard, W.D.S. Motherwell, J.R. Rogers and D.G. Watson, Acta Crystallogr., B35 (1979) 2331.
12 E.A. Meyers, E.J. Irgolic, R.A. Zingaro, T. Junk, R. Chakravorty, N.L.M. Dereu and K. French, Phosphorus and Sulphur, 38 (1988) 257.
13 M.R. Bryce, C.E. Reynolds, P. Hanson and J.M. Vernon, J. Chem. Soc., Perkin Trans. I., (1981) 607.
14 I. Lindqvist and G. Nahringbauer, Acta Crystallogr., 12 (1959) 638.
15 J.G. White, Acta Crystallogr., 16 (1963) 397.
16 B. Kamenar and A. Nagl, Acta Crystallogr., B 32 (1976) 1414.
17 H.J. Verweel and J.M. Bijvoet, Z. Kristallogr., 77 (1932) 122; H. Braekken, Z. Kristallogr., 81 (1932) 152.