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Structural characterisation of the diorganoselenium interhalogen compounds R_2SeIBr (R = Ph or Me) and the ionic compound $[Me_3Se][IBr_2]$

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The reaction of R_2Se (R = Ph or Me) with iodine monobromide in diethyl ether solution produced the charge-transfer complexes $R_2SeI{-}Br$. In the case of Ph_2Se, Ph_2SeIBr was produced quantitatively. However, for Me_2Se, both Me_2SeIBr and the ionic product $[Me_3Se][IBr_2]$ were produced indicating ease of methyl migration for Me_2SeIBr and that it lies close to the ionic/covalent structural borderline. The other product from this autoionisation is believed to be $Me_2Se_2I_2$, although this was not extensively characterised. The compounds Ph_2SeIBr and Me_2SeIBr show markedly different d(I−Br) 2.640(2) and 2.797(5) Å, respectively, illustrating how the R groups on the selenium affect its donor power towards iodine monobromide. The three compounds Ph_2SeIBr, Me_2SeIBr and $[Me_3Se][IBr_2]$ have been characterised by single-crystal X-ray diffraction.

Although diorganoselenium dihalides, R_2SeX_2 ($X_2 = F_2$, Cl_2, Br_2, I_2, ICl or IBr), have been studied by spectroscopic methods,[1,2] there are few examples of their characterisation by single-crystal X-ray diffraction. From results reported so far, where X = F or Cl, the compounds are exclusively Ψ-trigonal bipyramidal, R_2SeX_2[3–5] (this geometry takes account of the stereochemically active lone pair of electrons on the selenium atom), whereas where X = I, a charge-transfer species results, $R_2Se{-}I{-}I$.[5–7] For the dibromine compounds, R_2SeBr_2, limited X-ray crystallographic data indicate that these compounds are also trigonal bipyramidal.[5,8] However, a recent ^1H and ^{13}C NMR spectroscopic[9] and cyclic voltammetry study[10] strongly suggests that a charge-transfer complex, $R_2Se{-}Br{-}Br$, is also formed for certain dibromine adducts of diaryl selenides which contain electron-withdrawing substituents, particularly if they are at the *ortho* position. Previous workers have concluded that both electronic and steric factors play a part in the geometry (charge-transfer Ψ-trigonal bipyramidal) of the R_2SeBr_2 compound formed.[9] Interhalogen compounds of diorganoselenides have also received some limited study; thus, Me_2SeIBr was assigned a charge-transfer structure from vibrational spectroscopic studies[1] and this geometry was confirmed for the cyclic iodine monochloride adducts 1-oxa-selenacyclohexane[11] and 1,4-selenothiane[12] iodine monochloride by single-crystal X-ray crystallographic studies. No compound of formula R_2SeIBr has been crystallographically characterised with accuracy, determination of the structure of the 1:1 adduct of 1,4-selenothiane with iodine monobromide was attempted[11] but decomposition of the compound affected the accuracy; in addition, 1:2 1,2-selenothiane:X_2 ($X_2 = I_2$, IBr or ICl) complexes were also crystallographically characterised.[13] Such compounds were again found to have a charge-transfer structure where one molecule of dihalogen or interhalogen is co-ordinated to both the selenium and sulfur atoms. Unfortunately, little information regarding bond lengths and angles is reported. The iodine monobromide adduct of the related compound, *N*-methyl-1,3-thiazolidine-2,3*H*-selone, $C_4H_7NSSeIBr$, which contains a C=Se bond has also been reported by Devillovana and co-workers[14] and proved to be a solid solution of $C_4H_7NSSeIBr$ and $C_4H_7NSSeI_2$, having the composition $C_4H_7NSSeI_{1.25}Br_{0.75}$ with a d(I−Br) of 2.908(1) Å. We have previously observed this phenomenon in the reaction of Ph_3P with IBr; the composition of the adduct studied by X-ray crystallography was shown to be $Ph_3PI_{1.29}Br_{0.71}$.[15] The d(I−Br) distance in this compound, 3.062(3) Å, being significantly longer than in $C_4H_7NSSeI_{1.25}Br_{0.75}$, reflecting the greater donor power of the phosphorus compared to selenium towards iodine monobromide.

Our interest in this area was stimulated by our discovery that, contrary to the conclusions of earlier workers, which were based on spectroscopic studies, single-crystal X-ray diffraction studies have shown that R_3EX_2 compounds ($R_3 = Ph_3$ or $PhMe_2$, E = P, X = I;[16–18] R = Ph, E = P, X = Br;[19] R = Ph, E = P or As, $X_2 = I_2$[20] or IBr[21]) adopt a molecular charge-transfer structure in the solid state and not the ionic formulation $[R_3EX]X$ previously proposed. Additionally, certain R_3PX_2 compounds lie close to the molecular/covalent borderline and their geometry is influenced by the relative permittivity of the solvent in which they are prepared. For example, Ph_3PI_2 prepared in diethyl ether and characterised by single-crystal X-ray diffraction was shown to be a molecular charge-transfer species, $Ph_3P{-}I{-}I$,[16] but when prepared in nitrobenzene was shown to be ionic, $[Ph_3PI]I$, by solid-state ^{31}P-{H} NMR studies.[22]

Previous studies have indicated that the geometry of R_2SeX_2 compounds is halogen dependent, the diiodine and interhalogen adducts being charge-transfer compounds, $R_2Se{-}X{-}X'$ (X = I, X′ = I, Br or Cl),[1,5,7,8,11,12] the difluorine[2] and dichlorine[1,3–5] adducts being Ψ-trigonal bipyramidal and the dibromine adducts apparently representing an intermediate,[1,4,8–10] the structure of the R_2SeBr_2 compound being dependent on R, according to ^1H, ^{13}C NMR spectroscopy[9] and cyclic voltammetric studies. Similarly, we have shown that analogous Group 15 compounds also exhibit this phenomenon; for example, Ph_3AsI_2 is a charge-transfer compound, $Ph_3AsI{-}I$, whereas Ph_3AsBr_2 is trigonal bipyramidal.[20] Additionally, Me_3AsBr_2 is charge transfer, $Me_3AsBr{-}Br$, thus illustrating the geometrical dependency of R_3AsX_2 compounds on both R and X.[20] [An alternative interpretation of the structure of Me_3AsBr_2 as ionic has been proposed by Wang *et al.*;[23] whilst we can appreciate this, we draw attention to the fact that d(Br−Br) for this compound is 3.377(4) Å, which lies within the van der Waals radius of dibromine, and therefore constitutes a genuine, albeit weak, covalent bond.] Our preliminary investigations on dimethylselenium dihalides, Me_2SeX_2 (X = Cl, Br or I), have shown that Me_2SeI_2 adopts the three-co-ordinate molecular-spoke structure $Me_2Se{-}I{-}I$ and Me_2SeX_2 (X = Cl or Br) adopt a Ψ-trigonal bipyramidal structure.[5] We were thus intrigued to

Table 1 Selected bond lengths (Å) and angles (°) for Ph_2SeIBr

I–Br	2.640(2)	I–Se	2.809(2)
Br–I–Se	177.29(7)	I–Se–C(7)	104.0(5)
I–Se–C(1)	96.6(4)	C(1)–Se–C(7)	97.7(6)

Table 2 Selected bond lengths (Å) and angles (°) for Me_2SeIBr

I–Br	2.797(5)	I–Se	2.664(5)
Se–I–Br	175.8(2)	I–Se–C(2)	91(1)
I–Se–C(1)	100(1)	C(1)–Se–C(2)	99(2)

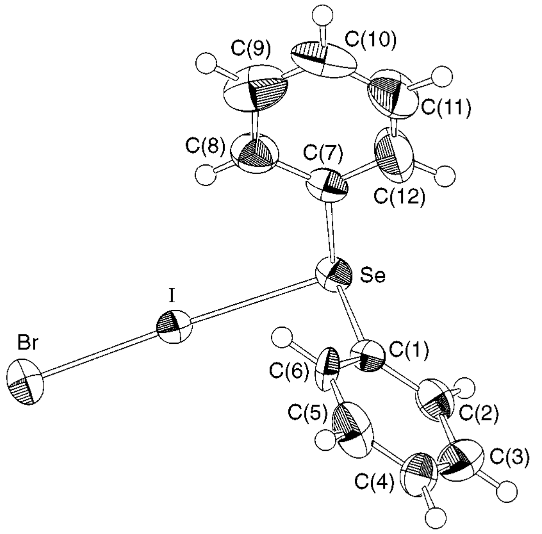

Fig. 1 Molecular structure of Ph_2SeIBr

know what structure the interhalogen compounds of Me_2Se and Ph_2Se would adopt.

Results and Discussion

The compounds Ph_2SeIBr and Me_2SeIBr were both prepared by the direct reaction of the diorganoselenide with iodine monobromide in anhydrous diethyl ether under inert conditions at room temperature, equation (1) (R = Ph or Me; r.t. = room

$$R_2Se + IBr \xrightarrow[N_2\ \mathrm{r.t.}]{2d,\ Et_2O} R_2SeIBr \tag{1}$$

temperature). In the case of Ph_2Se, reaction with IBr produced Ph_2SeIBr in quantitative yield. The reaction of Me_2Se with IBr produced Me_2SeIBr in *ca.* 30% yield (see below). These resultant yellow-orange powders were independently recrystallised by dissolving them in diethyl ether at 50 °C; subsequent cooling of the solutions to 0 °C produced crystals of each material after standing for *ca.* 4 d. The crystal structure of Ph_2SeIBr is illustrated in Fig. 1 and selected bond lengths and angles are displayed in Table 1. As expected, Ph_2SeIBr exists as a molecular charge-transfer species with *d*(I–Br) of 2.640(2) Å, slightly lengthened with respect to iodine monobromide (2.52 Å). The crystal structure of Me_2SeIBr is illustrated in Fig. 2 and selected bond lengths and angles are displayed in Table 2. It is seen that Me_2SeIBr also adopts the molecular charge-transfer structure but with a considerably lengthened I–Br bond, 2.797(5) Å. This lengthening is over twice that observed for the compound Ph_2SeIBr (0.277 *vs.* 0.12 Å) and reflects the greater donor power of Me_2Se compared to Ph_2Se, as expected, since the electron density from the lone pair on the selenium atom is donated into the σ^* orbital of the iodine monobromide. However, both compounds have much shorter I–Br distances than observed for Ph_3PIBr (3.062 Å) and Ph_3AsIBr [2.902(9) Å], thus illustrating the greater donor power of Group 15 compared to Group 16 donor atoms towards iodine monobromide. For Ph_2SeIBr and Me_2SeIBr there is also a commensurate difference in the Se–I distances, 2.809(2) and 2.664(5) Å, respectively. The Se–I–Br bond angle is almost linear being, 177.29(7) Å for Ph_2SeIBr and 175.8(2) Å for Me_2SeIBr.

Table 3 Selected bond lengths (Å) and angles (°) for $[Me_3Se][IBr_2]$

I(2)–Br(2)	2.740(6)	I(1)–Br(1)	2.688(3)
I(2)–Br(3)	2.742(6)	Se(1)–C(1)	1.92(2)
Br(2)–I(2)–Br(3)	179.4(2)	C(1)–Se(1)–C(2)	102(1)
Br(1)–I(1)–Br(1)	178.5(2)	C(2)–Se(1)–C(3)	96(2)

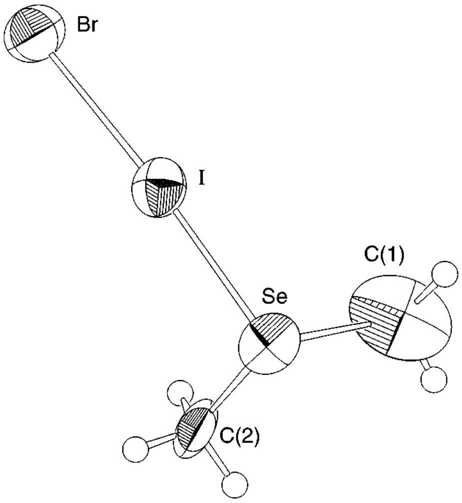

Fig. 2 Molecular structure of Me_2SeIBr

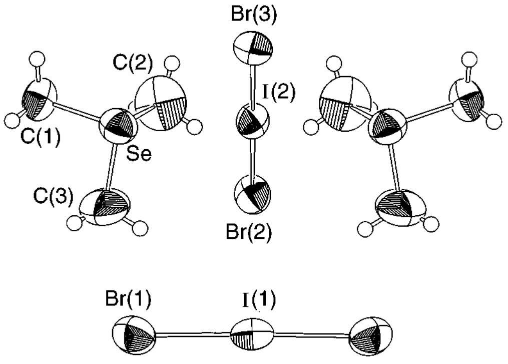

Fig. 3 Ionic structure of $[Me_3Se][IBr_2]$

The major product of the reaction (*ca.* 50% yield) of Me_2Se with IBr in diethyl ether surprisingly proved to be the ionic complex $[Me_3Se][IBr_2]$, Fig. 3. Clearly, Me_2SeIBr lies close to the covalent/ionic structural borderline. Methyl migration occurs to produce the selenium cation $[Me_3Se]^+$ and the mixed trihalide anion IBr_2^-. The structure of the cation $[Me_3Se]^+$ has previously been investigated in an X-ray crystallographic study of $[Me_3Se]I$ by Hope.[24] We have previously observed phenyl migration for the compound Ph_3SbI_2 dissolved in acetonitrile producing $[Ph_4Sb][I_3]$.[25] Clearly, the greater lability of Group 16– compared to Group 15–carbon bonds is demonstrated, since no alkyl or phenyl migration is observed in analogous arsenic compounds, R_3AsX_2.[20] The cation $[Me_3Se]^+$ is unremarkable, but the anion, $[IBr_2]^-$, shows great asymmetry, two I–Br bond lengths being very similar, 2.740(6) and 2.742(6) Å, whereas the third is much shorter, 2.688(2) Å (Table 3). This can be explained by the fact that the structure contains two

Table 4 Crystal data and details of refinement for R_2SeIBr (R = Ph or Me) and $[Me_3Se][IBr_2]$*

	Ph_2SeIBr	Me_2SeIBr	$[Me_3Se][IB_2r]$
Formula	$C_{12}H_{10}BrISe$	C_2H_6BrISe	$C_3H_9Br_2ISe$
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	*C*2/*c* (no. 15)	$P2_1/n$ (no. 14)	*Pnma* (no. 62)
a/Å	12.830(6)	9.607(4)	16.194(4)
b/Å	12.262(7)	7.466(2)	13.680(4)
c/Å	17.261(4)	10.360(4)	9.189(5)
β/°	99.02(2)	108.26(3)	–
U/Å^3	2682(3)	705.7(9)	2036(2)
Z	8	4	8
D_c/g cm^{-3}	2.179	2.973	2.680
F(000)	1632	560	1472
μ/cm^{-1}	79.70	150.83	143.56
Crystal size/mm	0.3 × 0.3 × 0.1	0.2 × 0.25 × 0.1	0.2 × 0.2 × 0.15
Maximum/minimum transmissions	0.57, 1.00	0.69, 1.00	0.13, 1.00
Total data measured	2608	1438	1868
No. unique reflections	2485	1406	
No. observed reflections [$I > 3.00\sigma I$]	1166	365	461
No. parameters	136	47	69
Minimum, maximum residual electron density/Å^{-3}	−1.05, 0.80	−0.90, 1.04	−0.75, 0.93
Maximum least-squares shift to error ratio	0.03	0.03	<0.01
Weighting scheme parameter g in $w = 1/\sigma^2(F) + gF^2$]	0.03	0.02	0.03
Final *R*	0.043	0.076	0.046
Final *R′*	0.050	0.075	0.051

* Details in common: maximum 2θ 50°, 293K.

crystallographically independent $[IBr_2]^-$ anions. One such $[IBr_2]^-$ species lies in a mirror plane, whilst for the other only the iodine atom sits in the mirror plane. A significant variation in *d*(I–Br) is probably caused by significant non-bonded interactions {*d*[I(1)···Br(3)] is 3.98(1) Å which lies just within the van der Waals radius for IBr (4.10 Å)}. The electron density removed from I(1) could therefore explain the shorter *d*(I–Br) for I(1)–Br(1). However, caution must be exercised when discussing *d*(I–Br) for $[IBr_2]^-$ species, since a considerable variation in bond lengths is seen for other crystallographically characterised compounds containing this anion.[26]

Conclusion

The reaction of iodine monobromide with R_2Se (R = Ph or Me) has been studied and the products formed are clearly dependent on R. Where R = Ph the charge-transfer complex Ph_2Se–I–Br is produced in quantitative yield. No crystallographic mixed sites were observed, the sites I and Br being of 100% iodine and bromine character, respectively. Mixed-halogen occupancy of crystallographic sites has previously been observed for Ph_3PI-Br[15] and C_4H_7NSSe·IBr.[14] The value of *d*(I–Br) for Ph_2SeIBr is 2.640(2) Å, only slightly lengthened with respect to free IBr (2.52 Å), reflecting the weaker donor power of Group 16 compared to Group 15 donors [*d*(I–Br) for Ph_3AsIBr is 2.902(9) Å]. The reaction of iodine monobromide with Me_2Se produced several products: the major product proved to be the ionic $[Me_3Se][IBr_2]$, indicating methyl migration during the reaction with IBr. The charge-transfer complex, Me_2Se–I–Br, was also isolated in approximately 30% yield. This compound has *d*(I–Br) of 2.797(5) Å, considerably longer than for Ph_2SeIBr, illustrating the important effect of the R groups on the donor power of the selenium atom towards iodine monobromide. The other product of this reaction was shown to be $Me_2Se_2I_2$ from microanalytical data.

Experimental

The compounds R_2SeIBr (R = Ph or Me) and $[Me_3Se][IBr_2]$ are all moisture sensitive. Therefore strictly anaerobic and anhydrous conditions must be observed for their successful synthesis. Any subsequent manipulation of the complexes was carried out inside a Vacuum Atmospheres HE-493 glove-box. The compounds R_2Se (R = Ph or Me) were obtained commercially (Strem) and used as received. Iodine monobromide was again obtained commercially (Aldrich) and also used as received.

Diethyl ether (BDH) was dried over sodium wire for *ca.* 1 d and subsequently distilled over CaH_2 in an inert atmosphere (N_2). The compound Ph_2SeIBr was synthesized from the direct reaction of Ph_2Se with IBr in diethyl ether solution: diphenyl selenide (2.00 g, 8.58 mmol) was dissolved in diethyl ether (*ca.* 50 cm^3) and subsequently iodine monobromide (1.78 g, 8.58 mmol) was added. After *ca.* 2 d the resultant orange solid was dried *in vacuo* and isolated by standard Schlenk techniques. The product was then transferred to pre-dried argon-filled ampoules which were flame-sealed. The compound Ph_2SeIBr was produced in quantitative yield.

The synthesis of Me_2SeIBr and $[Me_3Se][IBr_2]$ was from the direct reaction of Me_2Se with IBr in diethyl ether, directly analogous to the synthesis of Ph_2SeIBr. However, the product initially formed was the pale yellow $[Me_3Se][IBr_2]$ in approximately 50% yield. Retention and concentration of the filtrate produced an orange solid which proved to be Me_2SeIBr (approximately 30% yield). Complete removal of the solvent produced a little more Me_2SeIBr and a black oil which analysed as 'MeSeI' and is presumed to be $Me_2Se_2I_2$, analogous to $Ph_2Se_2I_2$ described by Du Mont and co-workers;[27] however, other than elemental analysis, no further characterisation of the product was possible due to the very low yield. Elemental analyses were performed by the Microanalytical Laboratory of this department: Ph_2SeIBr [Found (Calc.): C, 33.0 (32.8); H, 2.5 (2.3); Br, 18.4 (18.2); I, 28.0 (28.8)]; Me_2SeIBr [Found (Calc.): C, 7.2 (7.2); H, 1.8 (1.9); Br, 24.8 (25.3); I, 39.8 (40.2)%].

Crystallography

Crystal data and details of refinement for all three structures are presented in Table 4. Crystals of the three structures were independently mounted in Lindemann tubes under an atmosphere of dry argon. All measurements were performed on a Rigaku AFC6S diffractometer employing graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) and ω–2θ scans. The structures were solved by direct methods using SHELXS 86[28] and refined by full-matrix least-squares based on *F* using TEXSAN.[29] All hydrogen atoms were confined to chemical reasonable positions (C−H 0.95 Å) with isotropic thermal parameters set at 120% of the equivalent *B* values of the bonded atoms. There was a slight disorder of a methyl group in [Me_3Se][IBr_2] as indicated by a relatively high U_{11} (0.2 $Å^2$). The split-atom model was not as successful as anisotropic refinement. Neutral atom scattering factors were used throughout and taken from ref. 30(*a*). Anomalous dispersion effects were taken from ref. 30(*b*). Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/572.

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