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Crystallographic characterisation of dihalogenodimethylselenium compounds, Me_2SeX_2 (X = Cl, Br or I) and the dependence of their structures on the nature of the halogen

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The reaction of Me_2Se with I_2 in diethyl ether produced the charge-transfer complex $Me_2Se{-}I{-}I$, which has a short I–I distance of 2.916(3) Å, when compared to the analogous Group 16 compound $Me_3As{-}I{-}I$, reflecting the weaker donor power of Se compared to As towards diiodine. Dimethyl selenide reacted with Br_2 to produce the regular trigonal-bipyramidal molecule Me_2SeBr_2 with Se–Br bond lengths of 2.546(4) and 2.551(4) Å, *i.e.* virtually identical. However, the dichloro-compound, Me_2SeCl_2, prepared from the reaction of SO_2Cl_2 with Me_2Se, shows significant variations in Se–Cl bonds [2.349(5), 2.408(6), 2.351(6) and 2.405(5) Å (two inequivalent molecules in the asymmetric unit)]. This is due to significant long Se $\cdots$ Cl contacts which lie within the van der Waals radii. These results illustrate the structural changes observed for the Me_2SeX_2 (X = I, Br or Cl) series in the solid state upon changing the nature of the halogen.

The nature of the products formed between diorganoselenium compounds and dihalogens has been of interest for over sixty years,[1] and, although some spectroscopic data are available, few compounds have been studied by single-crystal X-ray diffraction. No compound of formula Me_2SeX_2 has been crystallographically characterised, but those of stoichiometry R_2SeX_2 containing other organic groups have been studied by single-crystal X-ray diffraction. For example, the diphenyl derivatives, Ph_2SeX_2 (X = Cl[2] or Br[3]), both adopt a ψ-trigonal-bipyramidal geometry, as does bis(2-chloroethyl)selenium dichloride.[4]

From spectroscopic evidence, mainly infrared and Raman, it appears that two distinct structural motifs occur and are dependent on the nature of the halogen. For example, Hayward and Hendra[5] concluded that Me_2SeBr_2 adopts a ψ-trigonal-bipyramidal structure, shown by X-ray crystallography to occur for Ph_2SeBr_2, but that Me_2SeI_2 adopts the charge-transfer $Me_2Se{-}I{-}I$ structure. The latter motif has been identified crystallographically for $C_4H_8OSeI_2$ and $C_4H_8SeI_2$ by McCullough and co-workers.[6,7] More recently, Nakanishi *et al.*[8] have studied a variety of *o*-, *m*- and *p*-substituted diphenylselenium dihalogen adducts and concluded that in all cases the dichlorine adducts were ψ-trigonal bipyramidal and that the diiodine adducts had the charge-transfer structure $R_2Se{-}I{-}I$. However, the dibromine adducts represent an intermediate position. Thus, ^{13}C and ^1H NMR studies showed that for the compounds R_2SeBr_2 (R = 4-NCC_6H_4, 4-$O_2NC_6H_4$, 3,5-$Cl_2C_6H_3$, 2-ClC_6H_4 or 2,6-$Cl_2C_6H_3Ph$) a charge-transfer $R_2Se{-}Br{-}Br$ compound occurs, whereas when R = 3-ClC_6H_4, 4-ClC_6H_4, 4-$EtO_2CC_6H_4$ or 4-$O_2NC_6H_4Ph$ a ψ-trigonal-bipyramidal compound was produced. The structure of Me_2SeF_2 has also been studied[9] by proton NMR spectroscopy and a ψ-trigonal-bipyramidal structure was postulated.

It is thus surprising that, despite the interest in diorganoselenium dihalides, so little crystallographic information is available particularly for the dibromine compounds which, it seems, can adopt either a charge-transfer, $R_2Se{-}Br{-}Br$, or a ψ-trigonal-bipyramidal structure. We therefore decided to characterise crystallographically the series of compounds Me_2SeX_2 (X = Cl, Br or I) in order to investigate the change in structural type upon change in dihalogen and seek possibly to verify the spectroscopic data of Hayward and Hendra.[5]

Our interest in this area stems from our discovery that triorgano Group 15 dihalides, R_3EX_2 (E = P, As or Sb; $X_2 = Br_2$, I_2 or IBr) isolated from diethyl ether, illustrate a structural change from trigonal bipyramidal to charge transfer, $R_3E{-}X{-}X$. Where E = P and $X_2 = Br_2$, I_2 or IBr, X-ray crystallography shows that the charge-transfer species $R_3P{-}X{-}X$ prevails;[10–14] however, where E = Sb the trigonal-bipyramidal species occurs.[15] In the case of the arsenic analogues, R_3EX_2, where X = I, the charge-transfer compound, $R_3As{-}I{-}I$, is adopted, but when X = Br a structural change is observed which is dependent on R. Where R = Ph or Me_3C the trigonal-bipyramidal R_3AsBr_2 compound is revealed, but where R = Me the charge-transfer complex $Me_3As{-}Br{-}Br$ is observed.[16]

It is thus apodictic that there exist structural parallels between the diorgano Group 16 dihalides and the triorgano Group 15 dihalides; the selenium– and the arsenic–bromine compounds illustrate the structural dependency of these adducts on the nature of R. Another reason for our interest in the diorgano Group 16 dihalides is that it is clear from our studies of the Group 15 analogues that the solvent of preparation is critical in determining the nature of the product formed. For example, Ph_3PI_2 prepared in diethyl ether has been shown by single-crystal X-ray diffraction[10] and ^{31}P-{H} magic angle spinning (MAS) NMR spectroscopy[12] to be a molecular four-co-ordinate charge-transfer complex, Ph_3PI_2, whereas the same compound prepared in nitrobenzene, a more polar solvent, was shown by solid-state ^{31}P-{H} NMR spectroscopy[17] to be ionic $[Ph_3PI]I$. For this reason the solid-state structures of these compounds must yield important information.

Furthermore, if Me_2SeI_2 were to adopt the molecular three-co-ordinate spoke structure, $Me_2Se{-}I{-}I$, the I–I bond length would be of interest to compare to analogous Group 16 systems and give an insight into the donor power of the selenium atom, since we have already observed significant differences in I–I bond lengths upon changing the nature of the donor atom. For example, in Ph_3PI_2, the I–I bond length is 3.142(5) Å[10] whereas for Ph_3AsI_2 it is 3.005(4) Å. Finally, it has previously been shown[18] by X-ray crystallographic methods that for certain organotellurium–halogen systems there exist significant Te–I and I–I contacts linking discrete molecules into a more extended structure. The possibility that such linkages may prevail for analogous selenium systems in the solid state can also be investigated in the present study.

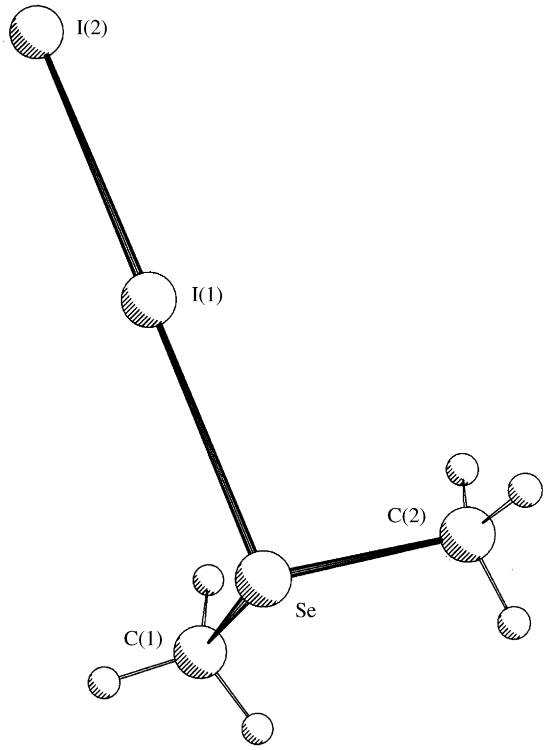

Fig. 1 Crystal structure of Me_2SeI_2

Table 1 Selected bond lengths (Å) and angles (°) for Me_2SeI_2

I(1)–I(2)	2.916(3)	I(1)–Se	2.768(4)
I(2)–I(1)–Se	174.30(9)	I(1)–Se–C(2)	97.6(9)
I(1)–Se–C(1)	94.8(8)	C(1)–Se–C(2)	99(1)

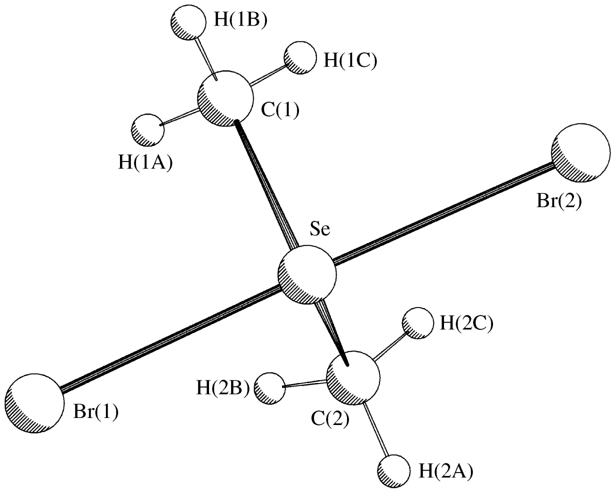

Fig. 2 Crystal structure of Me_2SeBr_2

Table 2 Selected bond lengths (Å) and angles (°) for Me_2SeBr_2

Br(1)–Se	2.546(4)	Br(2)–Se	2.551(4)
Br(1)–Se–Br(2)	177.7(2)	Br(2)–Se–C(1)	90.6(7)
Br(1)–Se–C(1)	91.3(7)	Br(2)–Se–C(2)	89.4(8)
Br(1)–Se–C(2)	91.7(8)	C(1)–Se–C(2)	98(1)

Results and Discussion

Apart from Me_2SeCl_2, all the compounds described were synthesized at room temperature (r.t.) from the direct reaction of dimethyl selenide with the appropriate dihalogen (X = Br or I), equation (1); Me_2SeCl_2 was obtained from the reaction of

$$Me_2Se + X_2 \xrightarrow[\text{Et}_2\text{O}]{ca.\ 2\ \text{d},\ \text{N}_2} Me_2SeX_2 \qquad (1)$$

dimethyl selenide with SO_2Cl_2, equation (2). All the compounds

$$Me_2Se + SO_2Cl_2 \xrightarrow[\text{Et}_2\text{O, r.t.}]{ca.\ 2\text{d},\ \text{N}_2} Me_2SeCl_2 + SO_2 \qquad (2)$$

were isolated in essentially quantitative yield. In the case of the reaction of Me_2Se with I_2, recrystallisation of the red powder from diethyl ether at 60 °C produced red crystals on standing at *ca.* 0 °C for 2 d.

The structure of Me_2SeI_2 is illustrated in Fig. 1, and selected bond lengths and angles are shown in Table 1. This compound represents the first crystallographically characterised molecular 'spoke' structure for a diorgano Group 16–halogen compound, which we have previously established for Group 15 compounds Ph_3PX_2 ($X_2 = Br_2$,[11] I_2[10] or IBr[13]), Ph_3AsI_2[14] and Me_3AsX_2[14] (X = Br or I). Two cyclic systems containing Se–I–I linkages are also known, $C_4H_8OSeI_2$[6] and $C_4H_8SeI_2$,[7] which exhibit I–I bond lengths of 2.956(4) and 2.914(4) Å, respectively, the latter value being very close to that of Me_2SeI_2, 2.916(3) Å, described here. Additionally, the related compound $C_4H_7NSSeI_2$, which contains a C=Se bond, has been crystallographically characterised by Devillanova and co-workers.[19] The I–I bond distance of this charge-transfer adduct was shown to be 2.983(1) Å, significantly longer than for Me_2SeI_2, thus illustrating the increased donor power towards diiodine of *N*-methylthiazolidine-2(3*H*)-selone compared to dimethyl selenide. There are also some examples of selenium donors to interhalogen compounds, for example 1-oxa-4-selenacyclohexane iodine monochloride[20] and 1-thia-4-selenacyclohexane iodine monochloride.[21] Such compounds also show a lengthening of the interhalogen bond, in common with the diiodine adducts and the Group 15 analogue Ph_3PIBr, described by us,[13] which exhibited an I–Br bond of 3.062(3) Å (van der Waals radius for iodine monobromide is 4.1 Å). We[10–14,16,22] and other workers[18] have previously reported a variety of analogous Group 15 derivatives of stoichiometry R_3E–I–I (E = P or As) and have shown by crystallographic methods that the I–I bond lengths are dependent on both the R groups and the donor atom E. It is thus clear that the I–I bond length increases with increasing basicity of the parent tertiary phosphine or arsine, as expected since increased electron density is donated into the σ^* antibonding orbital of the diiodine with increasing basicity of the donor. The I–I bond length in Me_2SeI_2 thus illustrates the weaker donor powder of the Group 16 donor atom when compared to its Group 15 analogue. There is little evidence of any extended solid-state structure for Me_2SeI_2, the closest Se $\cdots$ I contact being 3.910(4) Å; this compares to a combined van der Waals radius of 4.05 Å for selenium and iodine.

The reaction of Me_2Se with Br_2 produced after *ca.* 2 d a yellow product which was recrystallised from diethyl ether at 60 °C yielding a large quantity of yellow crystals on cooling to 0 °C. The structure of Me_2SeBr_2 is illustrated in Fig. 2, and selected bond lengths and angles are given in Table 2. In agreement with the spectroscopic studies of Hayward and Hendra,[5] the compound adopts a ψ-trigonal-bipyramidal structure, illustrating a halogen-dependent structural change. This again mirrors our previous studies of Group 15 analogues, R_3EX_2 (E = P or As, X = Br or I),[10–14,16] where Ph_3AsI_2 adopts the charge-transfer structure Ph_3As–I–I[21] and Ph_3AsBr_2 is ψ-trigonal bipyramidal.[16] We have explained this phenomenon by considering the acidity of the E atom in R_3EX_2 compounds (E = P

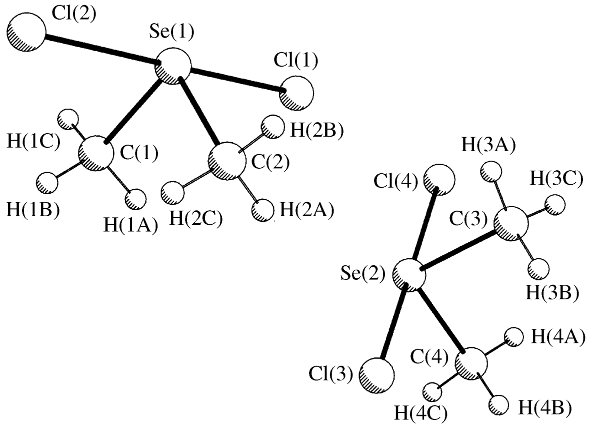

Fig. 3 Crystal structure of Me_2SeCl_2

Table 3 Selected bond lengths (Å) and angles (°) for Me_2SeCl_2

Se(1)–Cl(1)	2.349(5)	Se(1)–Cl(2)	2.408(6)
Cl(1)–Se(1)–Cl(2)	177.6(2)	Cl(3)–Se(2)–C(3)	89.2(5)
Cl(1)–Se(1)–C(1)	89.5(6)	Cl(4)–Se(2)–C(4)	89.2(6)
Cl(1)–Se(1)–C(2)	99.0(8)	C(3)–Se(2)–C(4)	98.6(9)
Cl(3)–Se(2)–Cl(4)	178.0(2)		

or As). We thus propose that the initial interaction of R_3E or R_2E' (E = P or As; E′ = Se or Te) with X_2 (X = Cl, Br or I) depends on the basicity of the R_3E or R_2E' species. The more acidic the E or E′ atom in R_3EX_2 or $R_2E'X_2$, the more likely is the ψ-trigonal-bipyramidal structure. Clearly, as we have already seen for the R_3AsX_2 compounds, the acidity of the selenium is affected by the nature of the X atom co-ordinated to it and thus a structural change is observed between adducts of I_2 and Br_2, the former exhibiting the charge-transfer 'spoke' structure, Me_2Se–I–I and the latter the trigonal-bipyramidal structure Me_2SeBr_2.

There is slightly more evidence of an extended solid-state structure for Me_2SeBr_2 compared to Me_2SeI_2. The Se···Br contacts are 3.604(4) and 3.630(4), shorter than the combined van der Waals radius of 3.85 Å for selenium and bromine but still indicating limited interaction between the discrete molecules.

The reaction of Me_2Se with SO_2Cl_2 produced after *ca.* 3 d a white product which was recrystallised from diethyl ether at 50 °C yielding colourless crystals on cooling to 0 °C. The structure of Me_2SeCl_2 is illustrated in Fig. 3, and selected bond lengths and angles are given in Table 3. Although this compound has not been the subject of any spectroscopic study, a ψ-trigonal-bipyramidal geometry is revealed, as expected and in agreement with the previous structural characterisation of R_2SeCl_2 (R = Ph or ClC_6H_4).[2,4] The Se–Cl distances for these two compounds are 2.30(5) for Ph_2SeCl_2 and 2.376(2) and 2.360(3) Å for $(ClC_2H_4)_2SeCl_2$. This compares with values of 2.349(5), 2.408(6), 2.351(6) and 2.405(5) Å for Me_2SeCl_2, *i.e.* similar values are observed for all three compounds. Interestingly, for R_2SeCl_2 (R = Ph or ClC_2H_4) no extended interactions within the solid state are observed, any contact between atoms lying outside the van der Waals radius of selenium and chlorine. For Me_2SeCl_2, however, significant interaction is observed: the Se···Cl contacts between discrete ψ-trigonal-bipyramidal units are 3.406(6), 3.411(6), 3.410(6) and 3.614(7) Å. This compares to a combined van der Waals radius for selenium and chlorine of 3.7 Å. These long Se···Cl contacts, similar to Te···I contacts observed in organotellurium iodides,[22] link the discrete Me_2SeCl_2 molecules into a network, the selenium atoms adopting distorted-octahedral geometry, Fig. 4. The reason these long-range contacts are observed for Me_2SeCl_2 but not for R_2SeCl_2 (R = Ph or ClC_6H_4)[2,4] is, presumably, because the smaller methyl groups on the selenium allow the selenium and chlorine atoms to pack more closely and thus interact in the solid state. The fact that they are more pronounced for Me_2SeCl_2 compared to Me_2SeBr_2 may be responsible for the loss of symmetry and the non-uniformity of the Se–Cl bonds. The compound Me_2SeBr_2 crystallises in the monoclinic space group with Se–Br 2.546(4) and 2.551(4) Å, *i.e.* virtually identical. On the other hand, Me_2SeCl_2 is triclinic with Se–Cl 2.349(5), 2.408(6), 2.351(6) and 2.405(5) Å and contains two molecules in the asymmetric unit, Fig. 3.

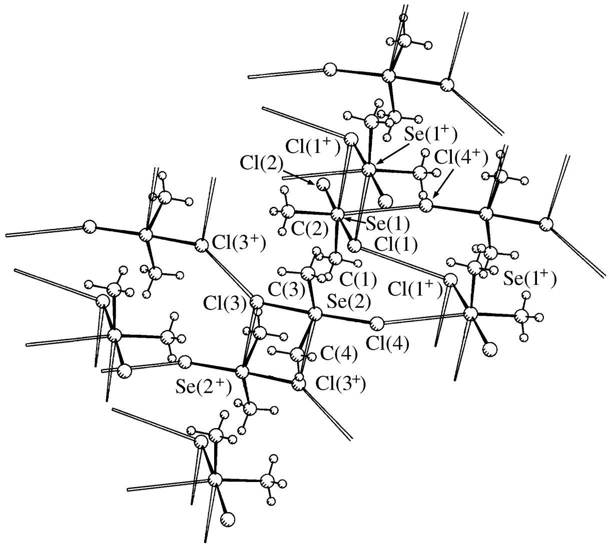

Fig. 4 Crystal packing of Me_2SeCl_2 illustrating the long-range Se···Cl contacts

Conclusion

The solid-state structure of Me_2SeX_2 (X = Cl, Br or I) illustrates interesting structural and geometrical changes upon changing X. In agreement with previous spectroscopic studies, Me_2SeI_2 adopts the molecular charge-transfer 'spoke' structure, also established for the analogous Group 15 compounds R_3EX_2 (R_3 = Ph_3, Bu^t_3 or $PhMe_2$) E = P, X = I; R_3 = Ph_3, E = P, X_2 = Br_2 or IBr; R = Ph or Me, E = As, X = I).[10–14,16] The I–I distance for Me_2SeI_2, 2.916(3) Å, is rather shorter than those observed for the analogous Group 15 compounds [3.005(3)–3.3912(7) Å][16,22] illustrating the weaker donor properties of the Group 16 atom compared to the Group 15 analogues. The structural similarities between R_3EX_2 (E = P, As or Sb)[10–16] and R_2SeX_2 compounds are clearly illustrated, Me_2SeI_2 being a charge-transfer adduct, Me_2Se–I–I, whereas Me_2SeBr_2 is trigonal bipyramidal. This is analogous to the arsenic compounds Ph_3AsX_2:[16,21] Ph_3AsI_2, is a charge-transfer adduct, but Ph_3AsBr_2 is ψ-trigonal bipyramidal. The compound Me_2SeBr_2 exhibits regular trigonal-bipyramidal geometry and virtually identical Se–Br bond lengths, whereas Me_2SeCl_2 shows considerable variation in Se–Cl bond lengths. This may be due to significant secondary Se···Cl interaction in the solid state, destroying the symmetry of the molecule; this phenomenon has previously been observed for organotellurium–diiodine compounds.

Experimental

The Me_2SeX_2 compounds (X = Cl, Br or I) described are moisture sensitive, especially the diiodine adduct. Therefore, strictly anaerobic and anhydrous conditions must be observed for their successful synthesis. Any subsequent manipulation of the compounds was performed in a Vacuum Atmospheres He-493

Table 4 Crystal data and details of refinement for Me_2SeX_2 (X = Cl, Br or I)

	Me_2SeI_2	Me_2SeBr_2	Me_2SeCl_2
Formula	$C_2H_6I_2Se$	$C_2H_6Br_2Se$	$C_2H_6Cl_2Se$
M	362.84	268.84	179.94
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$
a/Å	8.078(5)	8.574(3)	10.381(8)
b/Å	7.923(5)	8.124(5)	10.925(8)
c/Å	12.001(8)	9.640(4)	6.344(4)
α/°	—	—	88.00(6)
β/°	93.95(6)	91.82(3)	99.54(6)
γ/°	—	—	120.62(4)
U/Å^3	766(2)	671(9)	610(2)
Z	4	4	4
D_c/g cm^{-3}	3.145	2.661	1.961
F(000)	632	488	344
μ/cm^{-1}	127.15	172.03	68.36
Crystal size/mm	0.15 × 0.15 × 0.10	0.25 × 0.20 × 0.10	0.20 × 0.20 × 0.10
Decomposition (%)	8	1	32
Maximum 2θ/°	50.20	50.00	50.10
Maximum, minimum transmissions	0.78, 1.15	0.86, 1.08	0.90, 1.11
Total data measured	1574	1363	2295
Number unique reflections	1466	1330	2158
Number observed reflections [$I > 3.00\sigma(I)$]	677	410	881
Number parameters	47	47	91
Minimum, maximum electron density/e Å^{-3}	−1.25, 1.02	−0.61, 0.72	−0.72, 0.68
Maximum least-squares shift/error ratio	0.03	<0.01	0.01
Weighting scheme parameter g in $w = 1/[\sigma^2(f) + gF^2]$	0.02	0.02	0.03
Final R	0.047	0.045	0.050
Final R'	0.051	0.045	0.057

glove-box. Dimethyl selenide was obtained commercially (Strem Inc.) and used as received. Diiodine, dibromine and sulfuryl chloride were obtained commercially (Aldrich) and 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 three compounds described here were synthesized by the direct reaction of dimethyl selenide with dihalogen, or sulfuryl chloride in the case of Me_2SeCl_2. The synthesis of Me_2SeI_2 is typical: diiodine (2.00 g, 7.87 mmol) was dissolved in diethyl ether (*ca.* 50 cm^3) and subsequently dimethyl selenide (0.86 g, 7.87 mmol) was added. After *ca.* 48 h the resultant bright orange solid was isolated by standard Schlenk techniques and dried *in vacuo.* The reaction product was then transferred to pre-dried argon-filled ampoules which were flame sealed. Elemental analyses were performed by the Microanalytical Laboratory of this department [Found (Calc.): C, 6.5 (6.6); H, 1.4 (1.6); I, 71.0 (70.0). C, 8.8 (8.9); H, 2.3 (2.2); Br, 58.8 (59.5). C, 13.0 (13.3); H, 3.3 (3.3); Cl, 38.6 (39.2%)].

Crystallography

Crystals of each compound were independently mounted in Lindemann tubes under an atmosphere of dry argon. All measurements were performed at 298 K on a Rigaku AFC6S diffractometer employing graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) and ω–2θ scans. All the structures were solved using direct methods. Unit-cell dimensions were derived from the setting angles on 125 accurately centred reflections. Lorentz polarisation corrections were applied as well as an absorption correction using the azimuthal scan technique. Details of the X-ray measurements and subsequent structure determinations are presented in Table 4. Hydrogen atoms were confined to chemically reasonable positions. Neutral atom scattering factors were taken from ref. 23. Anomalous dispersion effects were taken from ref. 24. All calculations were performed using the TEXSAN[25] crystallographic software package.

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 186/377.

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