Secondary Bonding. Part 6.[1] Distorted Octahedral Geometry in Seleninyl Dichloride–Dioxan (1/1) and Iodylbenzene

By **Nathaniel W. Alcock*** and **Jeffery F. Sawyer**, Department of Chemistry and Molecular Sciences, University of Warwick, Coventry CV4 7AL

The crystal structures of the title compounds have been determined from diffractometer data by the heavy-atom method. Crystals of $SeOCl_2 \cdot C_4H_8O_2$ (1) are orthorhombic, space group $Pna2_1$, with a = 8.884(2), b = 12.066(3), c = 8.410(3), Z = 4, and R = 0.052 for 640 observed reflections. Crystals of $C_6H_5IO_2$ (2) are monoclinic, space group $P2_1$, with a = 12.904 1(23), b = 6.402 3(14), c = 4.011 5(7), β = 99.018(14)° at −100 °C, Z = 2, and R = 0.048 for 755 observed reflections. Compounds (1) and (2) have primary pyramidal co-ordination with, respectively, bond lengths Se–O 1.572(1), Se–Cl 2.235(5) and 2.202(7) Å, and I–C 2.014(2), I–O 2.021(9), and 1.924(8) Å. For (1), the three weaker interactions are Se · · · O 2.614(13), 2.724(15), and 2.902(11) Å, and for (2), I · · · O 2.578(8), 2.660(10), and 2.733(9) Å. The interactions in (2) are the stronger, and produce significant distortion of the primary geometry, with an O–I–O angle of 147.8(4)°. The packing of (1) involves infinite layers of seleninyl dichloride bridged by dioxan molecules and further cross-linked by Se–O · · · Se interactions. In (2) the molecules form layers linked by I–O · · · I interactions.

APPLICATION of the Gillespie–Nyholm theory to the molecules of seleninyl dichloride, $SeOCl_2$, and iodylbenzene, $C_6H_5IO_2$, leads to the same prediction for each: pyramidal geometry with the fourth position of a tetrahedron occupied by a lone pair. However, more detailed study of many non-metal compounds containing lone pairs has shown that the Gillespie–Nyholm approach gives an incomplete description of the bonding. The central atoms very frequently form additional bonds, of greater length than the primary covalent links. In the case of pyramidal molecules, it has been found that there are often three of these secondary bonds, completing a distorted octahedron around the central atom.[2] Striking conformation of this has come from complexes (or solvates) of $SeOCl_2$.[3] All show Se · · · O and Se · · · Cl secondary bonds, with distorted octahedral geometry, although in some cases the third secondary bond opposite the Se–O bond may be significantly longer than the other two secondary bonds. Furthermore, there are rare examples where a secondary bond has been replaced by two longer contacts, and it may be inferred from these results that the steric importance of the lone pair of electrons on $SeOCl_2$ varies. In those cases where an octahedron can be observed, the angles X–Se · · · Y (X, Y = O or Cl) have been found to lie in the range 142—173°, and there appears to be no clear way of deciding which atoms, chlorine or oxygen, are going to form the secondary bonds. The present structure of $SeOCl_2 \cdot C_4H_8O_2$ is, however, the first in which $SeOCl_2$ is involved in three secondary bonds to oxygen with the $SeOCl_2$ being classed as amphoteric.

The commonest oxo-compounds of I^V, the iodates, show very similar behaviour to $SeOCl_2$. They also are pyramidal, and in virtually every example the IO_3^- group is completed to give distorted octahedral geometry around I by three longer I · · · O secondary bonds.[2] Apart from a few halogenoiodates, the only substituted iodine(v) oxo-compound whose structure has been examined is *p*-chloroiodylbenzene.[4] This determination is not of high accuracy, but shows the same I · · · O links. The present study includes the structure of iodylbenzene itself, and it is significant that the detailed pattern of secondary bonding is not the same as in the chloro-compound, nor in the parent iodates or the $SeOCl_2$ complexes. It seems that this difference can be correlated with the extent of involvement of the lone pair on the central atom.

EXPERIMENTAL

$SeOCl_2 \cdot C_4H_8O_2$ (1).—Dropwise addition of a carbon tetrachloride (dried over $CaCl_2$) solution of seleninyl dichloride (B.D.H. Chemicals Ltd.) to a carbon tetrachloride solution of dioxan (dried over sodium) gave immediate precipitation of clear, colourless needle-shaped crystals of the 1 : 1 solvate. These crystals are extremely moisture sensitive and needed to be mounted in Lindemann capillaries baked for several hours *in vacuo* to minimize crystal decomposition.

Crystal data. $C_4H_8Cl_2O_3Se$, M = 253.96, Orthorhombic, a = 8.884(2), b = 12.066(3), c = 8.410(3) Å, U = 901.5(5) Å^3, D_c = 1.870 g cm^{-3}, Z = 4, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 50.10 cm^{-1}, $F(000)$ = 496.0. Systematic absences $0kl$, $k + l \neq 2n$ and $h0l$, $h \neq 2n$ indicate space groups *Pnam* (no. 62, non-standard) or $Pna2_1$ (no. 33).

Unit-cell dimensions and data were collected using a diffractometer, with a crystal of size 0.194 × 0.104 × 0.093 mm. Reflections were measured using θ—2θ scans to a maximum 2θ of 55°. A variable scan rate of 3.0° min^{-1} to 29.3° min^{-1} depending on the intensity of a preliminary 2 s count was used. Background counts were recorded at each end of the scan, each for one quarter of the scan time. The intensities of four standard reflections were recorded every 55 reflections. These showed gradual crystal decomposition complicated by slight movements of the crystal in the capillary. The effects of the crystal movement were reduced by recentring at frequent intervals and increasing the scan range of ($K_{\alpha1}$ − 1.0°)—($K_{\alpha2}$ + 1.0°) to ($K_{\alpha1}$ − 2.0°)—($K_{\alpha2}$ + 2.0°) after 480 reflections had been collected. To correct for crystal decomposition, the collected data were scaled in sections, using linear equations of the form $F = F_0\,(1 + at)$ where a is a constant and t = time.

A total of 1 190 unique reflections were collected, of which

640 were considered observed [$I/\sigma(I) \geqslant 3.0$] and used in refinement. Lorentz, polarization, and absorption corrections were applied, the last with the program ABSCOR.[5]

Iodylbenzene (2).—The preparation of many organoiodine(III) compounds proceeds *via* iodosylbenzene, which is conveniently prepared by treating iodobenzene dichloride with aqueous sodium hydroxide.[6] During one such preparation, using an excess of water, several thin, clear, approximately hexagonal crystalline plates were noticed amongst the yellow powdery product after the solution had been left overnight. Some of these were separated and seen to extinguish sharply under polarized light. Many were too thin, however, to scatter *X*-rays well. A much thicker, roughly hexagonal crystal of size *ca.* 0.19 × 0.16 mm and thickness 0.021 mm was eventually found and in the hope that this might be crystalline iodosylbenzene, a low-temperature data set was collected. The structure solution, however, showed the compound to be iodylbenzene, produced by disproportionation. As a precaution against the known tendency of organoiodine compounds to undergo rapid photodecomposition in *X*-rays, it was decided to cool the crystal to −100 °C using the LT-1 attachment of the Syntex diffractometer.

Crystal data. $C_6H_5IO_2$, $M = 236.0$, Monoclinic, $a = 12.904\,1(23)$, $b = 6.402\,3(14)$, $c = 4.011\,5(7)$ Å, $\beta = 99.018(14)^\circ$, $U = 327.32(11)$ Å^3, at −100 °C, $D_c = 2.394$ g cm^{-3}, $Z = 2$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 48.66 cm^{-1}, $F(000) = 220.0$. Systematic absence $0k0$, $k = 2n$ indicates space group $P2_1$ (no. 4).

Unit-cell dimensions and data were collected using the diffractometer. Reflections were measured using θ—2θ scans to 2θ of 60° in three shells, using a scan range ($K_{\alpha 1} - 0.75$)—($K_{\alpha 2} + 0.75$) and scan speed 0.7—29.3° min^{-1}. Four standards collected every 60 reflections showed only statistical fluctuations throughout the data collection. In all, 1 080 reflections were collected and processed as for (1); 775 were considered to be observed [$I/\sigma(I) \geqslant 3.0$].

Structure Solution and Refinement.—(*a*) $SeOCl_2{\cdot}C_4H_8O_2$. Initially, the centric space group *Pnam* was assumed but was rejected at an early stage. The selenium atom was located in a Patterson map and Fourier maps revealed the remaining light atoms. Hydrogen atoms in the dioxan molecule were placed in calculated positions (C–H = 0.95 Å) with temperature factors of 0.06 Å^{-2}. In the final cycles of least-squares refinement, anisotropic temperature factors were used for all non-hydrogen atoms with the hydrogen-atom parameters fixed. The weights used were given by $w = X{\cdot}Y$ where, if $\sin\theta < 0.35$, $X = (\sin\theta)/0.35$ otherwise $X = 1$, and if $F_{obs} > 27.0$ then $Y = 27.0/F_{obs}$ otherwise $Y = 1$. This scheme gave unit weights to most reflections, but downweights those reflections with large F_{obs} and/or low $\sin\theta$.

The refinement, including corrections for anomalous dispersion, converged to a final *R* of 0.052 and a weighted *R* of 0.064. The final difference Fourier was featureless except for residual peaks near the selenium. There was virtually no difference in refinement between the two enantiomers possible in this space group, and they gave negligible differences in bond distances and bond angles.

(*b*) *Iodylbenzene.* The co-ordinates of the iodine atom were readily located from the Harker plane U½V in the Patterson map, with the *y* co-ordinate arbitrarily fixed ($y = 0$) to define the position of the molecule with respect to the polar axis. Despite the mirror plane in the Fourier synthesis based on I, it was immediately clear that the compound was not iodosylbenzene as expected, but iodylbenzene. Although most atoms could easily be located, some difficulties were encountered before the final atomic arrangement was obtained, because the positions of the carbons in the phenyl ring did not help discriminate between the alternative oxygen positions; all four alternatives (with + or − co-ordinates relative to the mirror plane) gave similar *R* factors when refined. However, of the alternatives, two sets of oxygen positions resulted in a bad O · · · O contact of *ca.* 1.75 Å and a third resulted in a close C · · · O contact, leaving the present arrangement as the most chemically reasonable.

Hydrogen atoms for the phenyl ring were included in calculated positions with fixed temperature factors. In the final cycles of least-squares refinement, anisotropic temperature factors were used for the iodine and oxygen atoms and the reflections were weighted by $w = X.\,Y.\,[1/\sigma(F)]^2$ where $X = F/10.0$ if $F < 10.0$, otherwise $X = 1$, and $Y = (\sin\theta)/0.30$ if $\sin\theta < 0.30$, otherwise $Y = 1$. The refinement, including corrections for anomalous dispersal and extinction, converged to a final *R* of 0.048 and weighted *R* of 0.046.

TABLE 1

Atomic co-ordinates (× 10^4) with standard deviations in parentheses

Atom	*X*	*Y*	*Z*
(*a*) $SeOCl_2{\cdot}C_4H_8O_2$			
Se	5 350(1)	2 554(1)	7 500(0)
Cl(1)	5 070(7)	4 263(4)	6 522(9)
Cl(2)	5 111(10)	3 093(5)	10 011(8)
O	7 090(12)	2 370(11)	7 300(40)
O(1)	5 152(18)	474(10)	8 342(18)
O(2)	4 905(22)	−1 692(12)	9 519(18)
C(1)	6 426(22)	−95(17)	9 102(29)
C(2)	6 236(22)	−1 283(18)	8 881(31)
C(3)	3 653(25)	−1 126(17)	8 833(32)
C(4)	3 773(21)	104(16)	9 019(28)
H(11)	6 347	10	10 364
H(12)	7 324	174	8 854
H(21)	6 225	−1 384	7 754
H(22)	7 075	−1 681	9 309
H(31)	2 762	−1 408	9 322
H(32)	2 653	−1 260	7 749
H(41)	2 913	458	8 668
H(42)	3 748	246	10 259
(*b*) Iodylbenzene			
I	572.3(5)	0.0	3 182.2(14)
O(1)	1 097(7)	2 586(15)	5 807(21)
O(2)	468(7)	−1 561(17)	−955(18)
C(1)	2 053(9)	−968(21)	3 098(28)
C(2)	2 268(11)	−2 952(26)	4 128(35)
C(3)	3 263(12)	−3 761(32)	4 200(38)
C(4)	4 023(13)	−2 502(28)	3 065(41)
C(5)	3 804(11)	−506(25)	1 995(34)
C(6)	2 800(8)	331(29)	1 973(24)
H(2)	1 728	−3 810	4 791
H(3)	3 440	−5 157	5 000
H(4)	4 716	−3 036	3 080
H(5)	4 334	320	1 225
H(6)	2 640	1 750	1 277

Calculations for both structures were carried out with the '*X*-ray '76' programs,[7] and scattering factors (in the analytical form) were from ref. 8. Final positional parameters for all atoms in both structures are listed in Table 1. Anisotropic temperature factors for these atoms and the final structure factors for each compound are available as Supplementary Publication No. SUP 22652 (19 pp.).*

---

* See Notices to Authors No. 7, *J.C.S. Dalton*, 1979, Index issue.

TABLE 2

Significant bond lengths (Å), contact distances, and related bond angles (°) with standard deviations in parentheses

(*a*) $SeOCl_2 \cdot C_4H_8O_2$ [a]

Se–Cl(1)	2.235(5)	O(1)–C(1)	1.47(3)
Se–Cl(2)	2.202(7)	O(1)–C(4)	1.42(3)
Se–O	1.571(11)	O(2)–C(2)	1.39(3)
Se · · · O	2.902(11)	O(2)–C(3)	1.43(3)
Se · · · O(1)	2.614(13)	C(1)–C(2)	1.46(3)
Se · · · O(2)	2.724(15)	C(3)–C(4)	1.50(3)
Cl(1)–Se–Cl(2)	95.6(3)	Se–O · · · Se	166.2(14)
Cl(1)–Se–O	101.6(7)	Se · · · O(1)–C(1)	121.0(11)
Cl(2)–Se–O	103.6(12)	Se · · · O(1)–C(4)	117.9(11)
Cl(1)–Se · · · O(1)	168.1(4)	Se · · · O(2)–C(4)	124.2(14)
Cl(2)–Se · · · O(2)	167.5(4)	Se · · · O(2)–C(3)	119.3(14)
O–Se · · · O	168.6(12)	C(1)–O(1)–C(4)	110.0(15)
O–Se · · · O(1)	87.7(7)	C(2)–O(2)–C(3)	109.7(16)
O–Se · · · O(2)	85.9(12)	O(1)–C(1)–C(2)	108.3(17)
O(1) · · · Se · · · O(2)	82.9(4)	C(1)–C(2)–O(2)	113.5(18)
O · · · Se · · · O(1)	88.8(5)	O(2)–C(3)–C(4)	112.2(18)
O · · · Se · · · O(2)	82.9(7)	C(3)–C(4)–O(1)	109.3(16)

(*b*) Iodylbenzene [b]

(*i*) Around iodine

I–O(1)	2.021(9)	I · · · O(1^{I})	2.733(9)
I–O(2)	1.924(8)	I · · · O(2^{II})	2.578(8)
I–C(1)	2.014(12)	I · · · O(2^{III})	2.660(10)
I · · · C(2)	2.872(15)		
O(1)–I–C(1)	91.1(4)	C(1)–I–O(1^{I})	126.9(4)
O(1)–I–O(2)	147.8(4)	C(1)–I–O(2^{II})	94.7(4)
O(1)–I–O(1^{I})	126.4(3)	C(1)–I–O(2^{III})	132.8(4)
O(1)–I–O(2^{II})	84.5(3)	O(1′)–I–O(2^{II})	59.4(3)
O(1)–I–O(2^{III})	66.9(3)	O(1′)–I–O(2^{III})	98.6(3)
O(2)–I–C(1)	76.4(4)	O(2″)–I–O(2^{III})	122.1(3)
O(2)–I–O(1^{I})	83.3(3)	I–O(1)–I^{IV}	109.5(3)
O(2)–I–O(2^{II})	125.4(4)	I–O(2)–I^{V}	125.4(5)
O(2)–I–O(2^{III})	100.2(3)	I–O(2)–I^{VI}	133.1(4)
		I^{V}–O(2)–I^{VI}	96.3(2)

(*ii*) Phenyl ring

C(1)–C(2)	1.351(21)	C(2)–H(2)	0.96
C(2)–C(3)	1.380(22)	C(3)–H(3)	0.96
C(3)–C(4)	1.400(26)	C(4)–H(4)	0.96
C(4)–C(5)	1.364(24)	C(5)–H(5)	0.95
C(5)–C(6)	1.400(19)	C(6)–H(6)	0.96
C(6)–C(1)	1.401(19)		
I–C(1)–C(2)	115.7(10)	C(2)–C(3)–C(4)	118.3(17)
I–C(1)–C(6)	121.7(10)	C(3)–C(4)–C(5)	121.3(16)
C(6)–C(1)–C(2)	122.6(13)	C(4)–C(5)–C(6)	120.5(15)
C(1)–C(2)–C(3)	120.3(15)	C(5)–C(6)–C(1)	116.9(15)

[a] The C–H bond lengths range from 0.89 to 1.07 Å; C–C–H angles range from 103.6 to 115.8°, O–C–H angles from 107.5 to 116.0°, and H–C–H angles from 103 to 111°. [b] Symmetry transformations are: I $-x, -\frac{1}{2}+y, -z$; II $x, y, 1+z$; III $-x, \frac{1}{2}+y, -z$; IV $-x, \frac{1}{2}+y, 1-z$; V $x, y, -1+z$; VI $-x, -\frac{1}{2}+y, 2-z$.

Significant bond lengths, contact distances, and related angles for both compounds are included in Table 2 and information on the dihedral angles in the dioxan molecule of the solvate and molecular planes in iodylbenzene are included in Tables 3 and 4 respectively. Two views of the molecular packing in the solvate and the co-ordination sphere of the Se atom are given in Figures 1—3; the molecular packing of iodylbenzene and the co-ordination of the iodine atom are similarly shown in Figures 4 and 5.

TABLE 3

Dihedral angles (°) in the dioxan molecule

C(1)–O(1)–C(4)–C(3)	57.5	C(3)–O(2)–C(2)–C(1)	−57.5
O(1)–C(4)–C(3)–O(2)	−56.4	O(2)–C(2)–C(1)–O(1)	59.1
C(4)–C(3)–O(2)–C(2)	55.0	C(2)–C(1)–O(1)–C(4)	−58.5

TABLE 4

Equations of the least-squares mean planes $PI + QJ + RK = S$ [a] in orthogonal angstrom space for iodylbenzene

(*a*)

Plane	Defining atoms	*P*	*Q*	*R*	*S*
1	I, C(1)–C(6)	0.129 0	0.334 2	0.933 6	1.248 7
2	I, O(1), O(2)	0.811 1	−0.469 8	0.348 5	0.876 1
3	C(1), I, O(1)	−0.144 8	−0.493 7	0.857 5	1.003 1
4	C(1), I, O(2)	0.260 9	0.833 0	−0.487 9	−0.474 6

(*b*) Angles (°) between planes

(1)—(2)	74.16	(2)—(3)	65.58
(1)—(3)	51.91	(2)—(4)	69.53
(1)—(4)	81.75	(3)—(4)	29.84

(*c*) Atomic displacements (Å) from these planes [b]

Plane 1: O(1) 1.59, O(2) −1.85, O(1^{I}) −0.43, O(2^{II}) 1.77, O(2^{III}) −0.24
Plane 2: C(1) 1.83, O(1^{I}) 0.87, O(2^{II}) −0.93, O(2^{III}) −2.32
Plane 3: O(2) −0.93, O(1^{I}) 1.43, O(2^{II}) 2.56, O(2^{III}) −1.67
Plane 4: O(1) 1.01, O(1^{I}) −2.06, O(2^{II}) −2.10, O(2^{III}) 1.95

[a] The orthogonal unit vector *I* is parallel to *a*, *J* is perpendicular to *a* in the *ac* plane, and *K* is perpendicular to the *ac* plane. [b] Symmetry transformations are as in Table 2.

DISCUSSION

$SeOCl_2 \cdot C_4H_8O_2$.—The crystal structure of the solid solvate of dioxan with seleninyl dichloride contains infinite layers of seleninyl dichloride molecules bridged by dioxan molecules. These layers are linked into a polymeric lattice by further interactions *via* Se–O · · · Se bridges forming chains parallel to *c* (Figures 1 and 2).

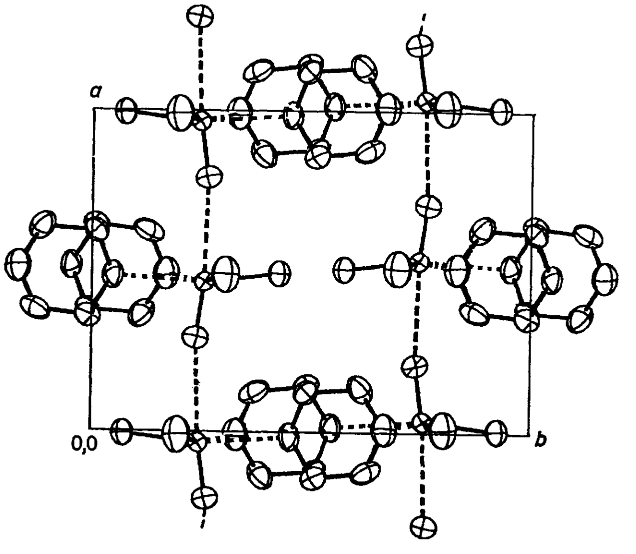

FIGURE 1 Packing diagram for $SeOCl_2 \cdot C_4H_8O_2$ viewed down *c*, showing the primary (full) and secondary (broken) bonds around Se

The co-ordination about each selenium atom is a distorted octahedron of three primary and three secondary bonds. The primary co-ordination consists of two Se–Cl bonds of 2.235(5) and 2.202(7) Å and an Se–O bond of 1.571(11) Å with the octahedron completed by three *fac* Se · · · O contacts of lengths 2.614(3), 2.724(15), and 2.902(11) Å. Two involve different dioxan molecules with Cl–Se · · · O angles of 168.1(4) and 167.5(4)°. The third, from the oxygen atom of an adjacent seleninyl chloride molecule, links the layers together with the O–Se ··· O and Se–O ··· Se angles being 168.6(12) and 166.2(14)° (Figure 3). The Se ··· O contact distances should be compared with the sums of the covalent and van der Waals radii for oxygen and selenium (1.80 and 3.42 Å respectively).

In the seleninyl dichloride moiety, the two Se–Cl bonds appear to be significantly different but this is almost certainly due to anisotropy of the thermal motion of Cl(2). No corrections for this effect have been made. The average Se–Cl bond length of 2.22 Å should be compared to a value of 2.204(5) Å determined in a gas-phase electron-diffraction study of seleninyl dichloride. In the same study, the Se–O bond length was determined as 1.612(5) Å and the angles Cl–Se–Cl and Cl–Se–O were found to be 96.8(7) and 105.8(7)° respectively.[9] The present study has found a Cl–Se–Cl angle of 95.6(3)° and Cl–Se–O angles of 101.6(7) and 103.6(12)°. Clearly, the differences between the seleninyl dichloride in the solvate and the parameters observed for the molecule in the gas phase are slight.

In other solvates the Se–Cl bond length has an average value of 2.123 Å when $SeOCl_2$ acts as a base [based on six measurements in the range 2.09(1)—2.141(9) Å] and 2.235 Å when $SeOCl_2$ acts as an acid [based on 16 measurements in the range 2.17(1)—2.251(6) Å].[10] In the present case, the $SeOCl_2$ is amphoteric in using the lone pair on oxygen in one Se ··· O secondary bond (that is, acting as a Lewis base) whilst at the same time accepting electron density from the bridging dioxan molecules (Lewis acid behaviour). The Se–Cl distance would, however, indicate that the Lewis acid behaviour is more significant.

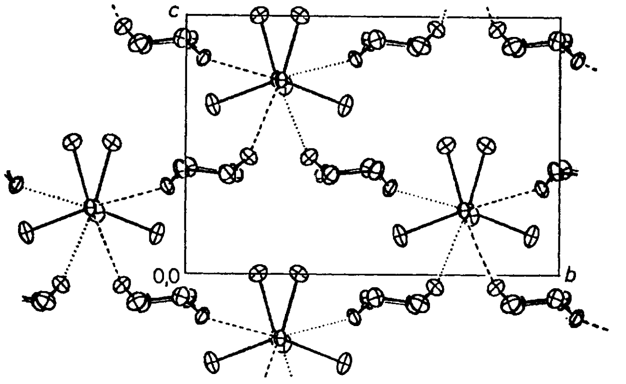

FIGURE 2 Packing of $SeOCl_2 \cdot C_4H_8O_2$, viewed down *a*. Secondary bonds from dioxan to Se at $z = \frac{1}{4}$ and $\frac{3}{4}$ are shown as dashed and dotted lines respectively

The Se–O bond lengths in the $SeOCl_2$ moiety depend on its function. Thus, in those solvates where it acts as a Lewis base forming a co-ordinate bond *via* the oxygen atom, the Se–O bonds are lengthened, 1.67(1) Å in $SnCl_4 \cdot 2SeOCl_2$ [11] and 1.685(24) Å in $SbCl_5 \cdot SeOCl_2$ [12] compared with other solvates where lengths of 1.57—1.62 Å have been observed. It is difficult to see further correlations between the individual values and the strength of the other intermolecular contacts, partly because of the limited accuracy of some of these values. However, in the present structure, considering that the Se–O bond is involved in bridging interactions, the Se–O bond length [1.57(1) Å] appears somewhat short. The Se ··· O distances in $SeOCl_2 \cdot C_4H_8O_2$ fall in the middle of the range (2.47—3.14 Å) observed in other $SeOCl_2$ solvates, and in the intramolecular Se ··· O contact distances found in several other selenium compounds.[13]

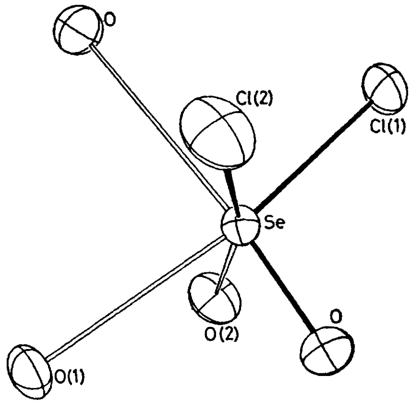

FIGURE 3 Co-ordination sphere and atomic numbering around Se

The dihedral angles for the dioxan molecule, which exists in the chair conformation, are in Table 3. The distances and angles in the molecules are similar to those of dioxan itself.[14] The bridging role of the dioxan giving polymeric layers here has similarly been noted in several other structures of dioxan with molecules such as iodine, bromine, and oxalyl chloride where infinite chains occur. In the present example, the Se ··· O contacts involve the equatorial lone pairs of the oxygen atoms.

The overall octahedral geometry including both short and long bonds is comparatively regular; however, it is noticeable that the angles Y–Se–Y between the *fac* oxygen contacts are less than 90°. This is somewhat surprising as the lone pair of the $SeOCl_2$ molecule would point in a direction bisecting the three Y contacts, and as a consequence the angles Y–Se–Y would be expected to be greater than 90° because of repulsive interactions. Furthermore, as the Cl–Se–Cl and Cl–Se–O angles are also intermediate between tetrahedral angles of 109.5° and angles of 90° based on an octahedron, the stereochemical role of the lone pair may be reduced in the present example and should be considered partly inert.

Iodylbenzene.—Individual molecules of $PhIO_2$ can be distinguished in the crystal, but they show an unusual arrangement of bonds around iodine (Figure 4) consisting of primary bonds to a phenyl ring [I–C = 2.014(12) Å] two oxygen atoms [I–O = 2.021(9) and 1.924(9) Å], and three I ··· O secondary bonds of lengths 2.578(8), 2,660(10), and 2.733(9) Å. The overall effect is to produce a very striking packing (Figure 5). The molecules are linked into layers in the *bc* plane, with the phenyl rings projecting above and below these layers, and forming all the inter-layer contacts. Exactly similar packing is found for *p*-chloroiodylbenzene,[4] although the pattern of I · · · O bonding is apparently different. These secondary bonds are comparatively short, and the distortion they produce can be seen in the angles between the primary bonds. Instead of a tetrahedral AX_3E arrangement typical of iodine(v) structures (as found in iodates [15]) the O–I–O angle has opened to 147.8(4)° with the C–I–O closing to 91.1(4) and 76.3(4)° so that the geometry is intermediate between AX_3E and AX_3E_2.

In chemical terms the present geometry should perhaps be regarded as polymeric, for the primary I–O bond lengths, which are long compared with other IO_3^- structures based on an octahedron of three primary and three secondary bonds, are similar in length to bridging I–O distances in other polymeric ions such as HI_3O_8.[16]

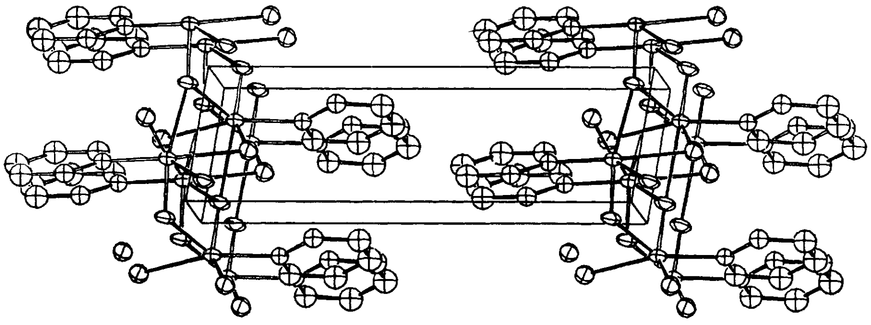

FIGURE 4 Packing diagram of iodylbenzene, viewed almost down *b*

The deviation of the present geometry from an ideal T-shaped arrangement appears in the angle O–I–O (147.8°), the sum of the two C–I–O angles (167.4°), and the displacement (1.83 Å) of C(1) from the O–I–O plane. The considerable distortion in the primary geometry also forces a close intramolecular I · · · C(2) repulsive contact. Other evidence of this repulsive contact can be seen from the I–C–C angles, which are significantly different [116(1) and 122(1)°].

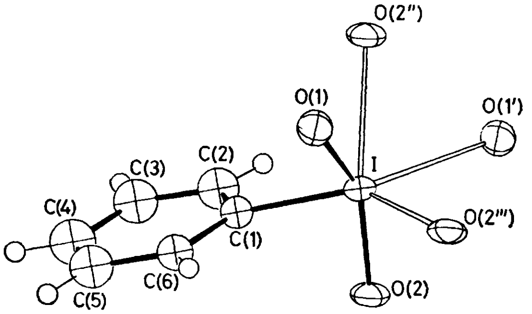

FIGURE 5 A molecule of iodylbenzene, showing the atomic numbering and the shorter and longer I–O bonds

As a result of the pseudo-symmetry present in the refinement, the other distances and angles in the phenyl ring are less accurate and no conclusions can be drawn, although the effect of the iodine atom would be expected to alter some of the ring angles slightly.

The observed I–C distance is very close to the normal I–C distances observed in other complexes,[1] and the sum of the covalent radii (2.10 Å). The I–C distance in the closely related *p*-chloroiodylbenzene [4] is 1.93(5) Å, although this determination is of limited accuracy. The I–O distances are also close to *single* bond distances observed in several other complexes although the I–O distances observed in *p*-chloroiodylbenzene are considerably shorter at 1.60 and 1.65(5) Å and it was suggested that those represented double bonds.[4] The other significant difference between iodylbenzene and *p*-chloroiodylbenzene is the O–I–O and C–I–O angles which are close to tetrahedral values (O–I–O = 103°; C–I–O = 94 and 95°) in the latter. Similarly, the closest intermolecular I · · · O contact in the latter is only 2.72 Å.

The feature of the present arrangement of I · · · O secondary bonds is that none of these contacts is co-linear with a primary bond as has been found in the majority of secondary bonded examples. The largest A–I · · · O (A = C or O) angles are in fact only 125—133°. This must be directly attributable to the non-bonded lone pairs in the present compound being substantially more important than in compound (1). It is also noticeable that other compounds which show polymeric O-bridged chains have their secondary X · · · O bonds arranged less regularly than in similar monomers; examples include $Na_2[Sb_4O_7]$,[17] $TeO_3{\cdot}SO_3$,[18] and $Sb_2[SO_4]_3$.[19]

We thank the S.R.C. for a research studentship (to J. F. S.).

[9/286 *Received, 23rd February,* 1979]

REFERENCES

[1] Part 5, N. W. Alcock, R. M. Countryman, S. Esperas, and J. F. Sawyer, *J.C.S. Dalton*, 1979, 854.

[2] N. W. Alcock, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 1.

[3] I. Lindquist, 'Inorganic Adduct Molecules of Oxo-Compounds,' Springer-Verlag, 1963; J. Jackson and G. B. L. Smith, *J. Amer. Chem. Soc.*, 1940, **62**, 544; M. J. Frazer, *J. Chem. Soc.*, 1961, 3165; J. C. Sheldon and S. Y. Tyree, *J. Amer. Chem. Soc.*, 1959, **81**, 2290; B. Edgington and J. B. Firth, *Chem. and Ind.*, 1936, 192.

[4] E. M. Archer, *Acta Cryst.*, 1948, **1**, 64.

[5] N. W. Alcock in 'Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970.

[6] F. G. Mann and B. C. Saunders, 'Practical Organic Chemistry,' Longmans, London, 1936.

[7] J. M. Stewart, Technical Report TR-446, Computer Science Centre, University of Maryland, 1976.

[8] 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.

[9] D. Gregory, I. Hargittal, and M. Kolonits, *J. Mol. Structure*, 1976, **31**, 261.

[10] A. W. Cordes in 'Selenium,' eds. R. A. Zingaro and W. C. Cooper, Van Nostrand-Reinhold, New York, 1974.

[11] Y. Hermoddson, *Acta Cryst.*, 1960, **13**, 656.

[12] Y. Hermoddson, *Acta Chem. Scand.*, 1967, **21**, 1313.

[13] R. Eriksen, *Acta Chem. Scand.*, 1975, **A29**, 517; M. Balwir, G. Llabres, O. Dideberg, L. Dupont, and J. L. Piette, *Acta Cryst.*, 1975, **B31**, 2188; A. Atkinson, A. G. Brewster, S. V. Ley, R. S. Osborn, D. Rogers, D. J. Williams, and K. A. Woode, *J.C.S. Chem. Comm.*, 1977, 325.

[14] M. Davies and O. Hassel, *Acta Chem. Scand.*, 1963, **17**, 1181.

[15] I. D. Brown, *J. Solid State Chem.*, 1974, **11**, 214.

[16] Y. D. Feikema and A. Vos, *Acta Cryst.*, 1966, **20**, 769.

[17] P. Maraine and G. Pérez, *Acta Cryst.*, 1977, **B33**, 1158.

[18] G. B. Johansson and O. Lindquist, *Acta Cryst.*, 1976, **B32**, 2720.

[19] R. Mercier, J. Douglade, and J. Bernard, *Acta Cryst.*, 1976, **B32**, 2787.