A Study of the Shapes of the Isoelectronic Species Antimony Pentafluoride (Monomer), Tellurium Tetrafluoride Oxide (Dimer), and Iodine Trifluoride Dioxide (Polymer)†

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The vibrational spectrum of (assumed) monomeric antimony pentafluoride can be assigned acceptably on the basis of a D_{3h} model. In agreement with earlier work tellurium tetrafluoride oxide dimer is found to be strongly oxygen bridged, in sharp contrast to tungsten tetrafluoride oxide which is weakly fluorine bridged in the solid state but readily dissociates to a square pyramidal monomer. Despite variable-temperature i.r. and Raman studies no trace of reversible equilibria involving a terminal Te–O bond was detected. Iodine trifluoride dioxide was found to be polymeric. On the basis of physical studies including n.m.r. and vibrational spectra together with molecular-weight studies it is likely that the principal constituent of the vapour is a centrosymmetric oxygen bridged dimer with 'axial' fluorines. The similarity of the Raman spectra of the solid, melt, and gas strongly suggests the same basic unit to be present in all states.

The interesting comparison between the oxygen bridging of fluoride oxides of the non-transition elements compared with the fluorine bridging of the fluoride oxides of the transition elements is discussed.

WITH the notable exceptions of xenon and iodine few well characterized fluoride oxides of the non-transition elements are known. Where the compounds have been prepared, structural information is frequently lacking. By contrast many fluoride oxides of the transition elements have been synthesized and studied crystallographically. The majority of them are polymeric in the solid state and form fluorine bridges in preference to oxygen bridges. Non-transition element species such as $(BFO)_3$, $(SiF_2O)_3$, and $(PFO_2)_3$ are likely to be based on a planar distribution about boron or a tetrahedral distribution about silicon or phosphorus, with oxygen bridges.[1] The preference for oxygen bridges is expected in view of the considerable stability of B–O–B, Si–O–Si, and P–O–P linkages. It appeared to us that it would be of interest to extend our knowledge to non-transition element fluoride oxides more closely related to the known transition-metal fluoride oxides.

Oxides, fluoride oxides, or fluorides of the post-transition elements In, Sn, Sb, Te, I, Xe where the central atom of the monomer would be surrounded by less than four ligand atoms ‡ are likely to form polymeric solids. :SnO Has an unusual structure in which the tin atom lies above a square of four oxygen atoms.[2] The apical position of this 'square pyramid' could be regarded as being occupied by a lone pair. The structure of the isoelectronic :InF is unknown, but that of :TlF has recently been determined.[3] Again the structure appears to be grossly affected by the lone pair. Each thallium is surrounded by a distorted octahedron of fluoride ions of which two (in *cis*-positions) are much more distant than the others. This leads to four close neighbours. Crystalline SnO_2 has the rutile structure [2] but the matrix isolated monomer is linear $D_{\infty h}$.[4] The compounds InF_3, SnF_2O, $:SnF_2$, and TeO_3 are known but have not been structurally studied. Surprisingly $:TeO_2$ is reputedly known in the rutile form as well as in a brookite and a tetragonal modification.[2] The discrete molecule has, as expected, been reported to be bent (C_{2v}) in a matrix.[5] Formally four-ligand monomers are SnF_4, $:SbF_3$, $:XeO_3$, and XeO_4. (The compounds $:IFO_2$ and IFO_3 are also well characterized [6] but structural data are lacking.) Of these solid SnF_4 [7] is polymeric with an octahedral distribution about tin and

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† No reprints available.

‡ Here we regard a lone pair of electrons (· ·) as a ligand.

[1] See for example B. Latimer and J. P. Devlin, *Spectrochim. Acta*, 1965, **21**, 1437; K. G. Sharp and J. L. Margrave, *J. Inorg. Nuclear Chem.*, 1971, **33**, 2813.

[2] A. F. Wells, 'Structural Inorganic Chemistry,' Clarendon, Oxford, 1962.

[3] N. W. Alcock and H. D. B. Jenkins, *J.C.S. Dalton*, 1974, 1907.

[4] A. Bos and J. S. Ogden, *J. Phys. Chem.*, 1973, **77**, 1513.

[5] M. Spoliti, S. N. Cesaro, and A. Coffari, *J. Chem. Thermodynamics*, 1972, **4**, 507.

[6] H. A. Carter and F. Aubke, *Inorg. Chem.*, 1971, **10**, 2296; M. Schmeisser and K. Brändle, *Adv. Inorg. Radiochem.*, 1963, **5**, 41.

[7] R. Hoppe, *Angew. Chem.*, 1957, **69**, 399.

trans-terminal fluorines. The substitution of F by a lone pair, yielding $:SbF_3$, lowers the tendency to polymerization.[8] The species $\ddot{X}eO_3$ and XeO_4 are monomeric [9] in contrast to SnF_4.

In the case of five-ligand mononuclear species more information is available: SbF_5, $\ddot{T}eF_4$, $\ddot{I}F_3O$, $\ddot{X}eF_2O_2$, XeF_2O_3, and $:\ddot{X}e:F_2$ are all known. Of these SbF_5 [10] and $\ddot{T}eF_4$ [11] are polymeric, the introduction of a lone pair not being sufficient (in the presence of four fluorines *and* a co-ordination number of five) greatly to affect the tendency towards polymerization; $\ddot{X}eF_2O_2$ [12] and $\ddot{I}F_3O$ [13] are much more weakly bridged. More extensive oxygen substitution or lone-pair substitution leads to monomeric [14] XeF_2O_3 (isoelectronic with SbF_5) or $:\ddot{X}e:F_2$.[9]

A sweeping generalization of the above data is that the polymerization tendency is reduced by substitution of fluorine by lone pairs (lowering of the formal oxidation state) or by oxygen (raising of the formal oxidation state). Put in an alternative way, lower Lewis acid character leads to a reduced tendency towards polymerization.* It appeared to us that the compounds TeF_4O and IF_3O_2 were of great interest in the study of polymer–monomer equilibria. When we started this work the compound TeF_4O was unknown, and the compound IF_3O_2 had only recently [15] been made. In this paper we shall deal with SbF_5, TeF_4O, and IF_3O_2.

TABLE 1

The i.r. spectra (frequencies in cm^{-1}) of antimony pentafluoride under various experimental conditions [a]

Polymer		Monomer		
Gas (25 °C)	Solid (15 K)	Gas (~250 °C)	N_2 matrix [b]	Ar matrix [c]
230(sh), br	230w br			
252vs, sharp		263vs, br	254m	258ms
270mw		285mw (PQR?)	279ms	281mw
302mw, br				
339w, br	336w	726vs, br	721.1s	727vs
	412vw		722.5s	
440w, br	447m			
519ms, br				
	613w			
678ms, br	673mw			
711vs, sharp	716s			
726vs, sharp	731(sh)			
~748(sh)	751ms			
759vs, sharp				

[a] For the matrix spectra weak bands and bands which increased on diffusion have been omitted. [b] Splitting of 722 cm^{-1} band may be due to antimony isotopes ^{121}Sb and ^{123}Sb in roughly equal abundances. [c] Band at 273 cm^{-1} assigned to impurity (no apparent change on diffusion).

Antimony Pentafluoride.—Crystalline antimony pentafluoride contains [10] the now familiar tetrameric *cis*-fluorine bridged species with Sb–F–Sb bond angles of 170 and 141°. It is interesting to note that the larger bridge bond angle in $(SbF_5)_4$ is similar to the angle for $(NbF_5)_4$, which may be considered to arise because the niobium atoms occupy one fifth of the octahedral holes in a *cubic* close packed arrangement of fluoride ions.[16] By contrast for $(RuF_5)_4$ the packing [17] is approximately hexagonal close packed leading to a bond angle near to the *smaller* angle for $(SbF_5)_4$. Thus the bond angles in $(SbF_5)_4$ may be considered to be a function of the packing. An ordered combination of close packed layers in hexagonal *and* cubic systems leads theoretically to bond angles of 180 and 132°.

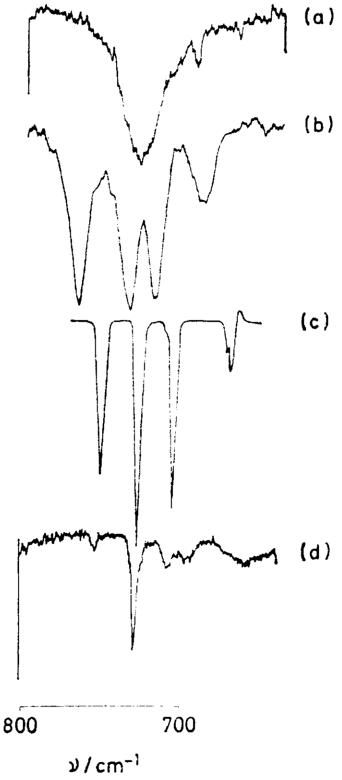

FIGURE 1 The vibrational spectrum of antimony pentafluoride (a) gas at *ca.* 250 °C, (b) gas at room temperature,[22] (c) matrix isolated [23] (assumed by us to be polymeric), (d) matrix isolated (assumed by us to be monomeric); small peaks in (a) due to BF_3 694 cm^{-1} and CO_2 667 cm^{-1}

Antimony pentafluoride melts [18] at 8.3 °C and boils at 150 °C. The melt has been studied using ^{19}F n.m.r. techniques,[19] the results in both cases being interpreted

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* Ionic compounds of the type $Cs_2[F_5SbOSbF_5]$ have not been included in the above discussion as the counter ion could have a great influence on the polymerization.

[8] A. J. Edwards, *J. Chem. Soc.* (*A*), 1970, 2751.

[9] See for example, J. Holloway, 'Noble Gas Chemistry,' Methuen, London, 1968.

[10] A. J. Edwards and P. Taylor, *Chem. Comm.*, 1971, 1376.

[11] A. J. Edwards and F. I. Hewaidy, *J. Chem. Soc.* (*A*), 1968, 2977.

[12] S. W. Peterson, R. W. Willett, and J. L. Huston, *J. Chem. Phys.*, 1973, **59**, 453; see also H. H. Claassen, E. L. Gasner, H. Kim, and J. L. Huston, *ibid.*, 1968, **49**, 253.

[13] J. W. Viers and H. W. Baird, *Chem. Comm.*, 1967, 1093; see also A. J. Edwards, *J. Flourine Chem.*, 1974, **4**, 173 .

[14] H. H. Claassen and J. L. Huston, *J. Chem. Phys.*, 1971, **55**, 1505.

[15] A. Englebrecht, P. Peterfy, and E. Schandara, *Z. anorg. Chem.*, 1971, **384**, 202.

[16] A. J. Edwards, *J. Chem. Soc.*, 1964, 3714.

[17] J. H. Holloway, R. D. Peacock, and R. W. H. Small, *J. Chem. Soc.*, 1964, 644.

[18] C. J. Hoffman and W. L. Jolly, *J. Amer. Chem. Soc.*, 1957, **61**, 1574.

[19] C. J. Hoffman and W. L. Jolly, *J. Phys. Chem.*, 1958, **62**, 364; J. Bacon, P. A. W. Dean, and R. J. Gillespie, *Canad. J. Chem.*, 1970, **48**, 314.

in terms of a *cis*-fluorine bridged structure with approximately octahedral co-ordination about antimony. Studies of the gas-phase using mass spectrometric techniques have again shown the presence of polymers.[20] Problems of ion-molecule reactions (leading to the synthesis of higher polymer ions in the mass spectrometer) or fragmentation reactions during ionization by an electron beam (leading to the synthesis of lower polymers and monomer ions in the mass spectrometer) appear to be at a minimum in the molecular-beam work of Vasile *et al.*[20]

Studies of the vibrational spectra of the melt and gas have been extensive [21,22] and include a normal co-ordinate analysis and a matrix-isolation study.[23] The later papers adopt a *cis*-fluorine bridged polymer model for the liquid and for the gas at lower temperatures. High temperature Raman gas-phase studies show a reversible equilibrium with no formation of fluorine and suggest the compound is exclusively monomeric at temperatures in excess of 350 °C and at pressures close to atmospheric. The proposal of a C_{4v} monomer from matrix-isolation studies [23] appears untenable in the light of these results.[22] We have attempted to complete the observation and assignment of the vibrational spectrum of monomeric antimony pentafluoride.

Table 1 summarises our observations on the i.r. spectra of antimony pentafluoride. Figure 1 shows sequentially the i.r. spectrum of: the gas at high temperature, the gas at room temperature, the compound in a matrix, and the monomer in a matrix. These results reinforce the earlier Raman observations of a reversible polymer–monomer equilibrium. They also show the earlier assignment of C_{4v} symmetry of the monomer to have been based on the spectrum of polymeric species, not of monomer.

The i.r. and Raman spectra of the gas change gradually with increasing temperature as the overall degree of polymerization changes. Whereas the spectrum of a low polymer is likely to be only subtly different from that of a high polymer that of the monomer is likely to differ from that of any polymeric species. It is difficult to estimate the shapes of, for example, tetramer and trimer since it is by no means clear what the bond angle Sb–F–Sb is likely to be. Electron diffraction on related species [24] suggests a value close to 180° for the tetramer, but the uncertainties are likely to be large. Presumably for the dimer the angle will approach 90°. On this basis we believe that the highest frequency bridge 'stretching' modes are likely to follow the frequency order tetramer > trimer > dimer in the i.r. effect. (In an elementary way with a bridge-force constant one half the terminal-force constant, for an angle at 90° the frequency of the bridge mode is at $2^{-\frac{1}{2}}$ that of the terminal frequency while for an angle of 180° bridge and terminal frequencies coincide.)

Our results on the i.r. spectrum of gaseous SbF_5 at room temperature (Table 1) are similar to those obtained previously. The most likely candidates for bridge-stretching modes are the bands at 440 and 519 cm^{-1}. As the temperature is increased the 519 cm^{-1} band disappears much more rapidly than the 440 cm^{-1} band. Similarly, the matrix-isolation work of Aljibury and Redington shows bands at 411, 447, and 524 cm^{-1} at high matrix ratios, but only the first two bands (slightly shifted in frequency) at low matrix ratios, which presumably correspond to the lowest polymer obtainable in those experiments. The 447 cm^{-1} band is appreciably more intense than the 411 cm^{-1} band in all the matrix spectra shown.

We note that for the species $[Sb_3F_{12}O_3]^{3-}$ and $[As_2F_8O_2]^{2-}$ (both of which contain cyclic M–O–M rings) [25] antisymmetric stretching modes of the ring have been assigned at 870 and 700 cm^{-1} respectively. Although the assignment at 700 cm^{-1} is open to some question, it is interesting that the change in frequency from trimer (ν_t) to dimer (ν_d) gives a ratio ν_d/ν_t of 0.80. Because the M–O force constant is likely to decrease slightly from arsenic to antimony the ratio will have been slightly over-estimated relative to the species where no change of the metal (antimony) occurs. Our postulate for SbF_5 gives a ratio of 0.84 although we do not know whether the species were properly identified as dimer and trimer.

The terminal Sb–F stretching modes for polymeric SbF_5 from this and earlier gas-phase work are as follows:

I.r.: 759vs (sharp), 748(sh), 726vs (sharp), 711vs (sharp), 678ms, br (cm^{-1})
Raman: 720vs (pol), 672vs (pol) (cm^{-1})

It is surprising that the 678 cm^{-1} band is broad in the i.r. effect if it is a coincidence with the 672 cm^{-1} band. However comparison with the *ca.* 15 K i.r. and Raman data for the solid from deposition on a cold tip suggests the coincidences are real:

I.r.: 751ms, 731sh, 716s, 673mw (cm^{-1})
Raman: 717vs, 671vs (cm^{-1})

The additional bands in the gas-phase spectra may be due to the presence of several polymers, as may the broadness of the 678 cm^{-1} band. It is possible that deposition *in vacuo* leads to essentially one polymer type under the conditions of our experiment.

With a complex molecule it is doubtful if it is worth attempting a further analysis. The four principal Sb–F stretching modes may be attributed to a C_{2v} MF_4 residue.

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[20] A. Müller, H. W. Roesky, and D. Böhler, *Z. Chem.*, 1967, **7**, 469; E. W. Lawless, *Inorg. Chem.*, 1971, **10**, 2084; M. J. Vasile, G. R. Jones, and W. E. Falconer, *Chem. Comm.*, 1971, 1355; see also M. J. Vasile and W. E. Falconer, *Inorg. Chem.*, 1972, **11**, 2282.

[21] J. Gaunt and J. B. Ainscough, *Spectrochim. Acta*, 1957, **10**, 57; K. Dehnicke and J. Wiedlein, *Z. anorg. Chem.*, 1963, **323**, 267; I. R. Beattie, K. M. S. Livingston, G. A. Ozin, and D. J. Reynolds, *J. Chem. Soc.* (*A*), 1969, 958; R. A. Condrate and K. Nakamoto, *Bull. Chem. Soc. Japan*, 1966, **39**, 1108.

[22] L. E. Alexander and I. R. Beattie, *J. Chem. Phys.*, 1972, **56**, 5829.

[23] A. L. K. Aljibury and R. L. Redington, *J. Chem. Phys.*, 1970, **52**, 453.

[24] G. V. Romanor and V. P. Spiridonor, *Zhur. Strukt. Khim.*, 1966, **7**, 882.

[25] W. Haase, *Acta Cryst.*, 1974, **B30**, 2465; W. Haase, *Chem. Ber.*, 1974, **107**, 1009.

The data on (assumed) monomeric antimony pentafluoride are summarised in Table 2 relative to PF_5 [26] and AsF_5.[27] The assumption that the bands refer to monomer is based on the following observations. (*a*) The i.r. spectrum of antimony trifluoride matrix-isolated in nitrogen [28] shows bands at 654m, 624s, and 259m. This is in good agreement with the gas-phase Raman data: [29] 666sp, 634m, and 250mp. This is quite different from the pattern of frequencies for antimony pentafluoride shown in Table 2. (*b*) The gas-phase Raman spectra showed no evidence of resonance fluorescence, further the gas at high temperatures showed no evidence of colour. From evidence under (*a*) SbF_3 may be eliminated as the source of the spectra. SbF_4 or SbF_2 is rendered unlikely by (*b*). We note also that the fundamental frequency of SbF lies [30] at 609 cm^{-1}. In addition no evidence for molecular fluorine was found in the Raman spectra (although admittedly this molecule is a weak scatterer). Finally both the gas-phase i.r. and Raman spectra showed *reversible* changes with temperature.

TABLE 2

Comparison of fundamentals of PF_5,[26] AsF_5,[27] and (monomeric) SbF_5; frequencies in cm^{-1}

	PF_5		AsF_5		SbF_5	
	I.r.	R	I.r.	R	I.r.	R[22]
ν_1 (a'_1)		817 (100)p		733 (100)p		683 (100)p
ν_2 (a'_1)		640 (14)p		642 (10)p?		636 (1)p
ν_3 (a''_2)	947vs		787vs		726vs, br	
ν_4 (a''_2)	575m		400s		285mw	
ν_5 (e')	1 024vs	1 025(2)dp	812vs	809(5)dp	726vs, br	~730vbr(1)
ν_6 (e')	533m	534 (5)dp	372s	366 (3)dp	263vs, br	
ν_7 (e')		175m‡	123w			
ν_8 (e'')		514 (13)dp		388 (12)dp		272br (7)

‡ I. R. Beattie, K. M. S. Livingston, and D. J. Reynolds, *J. Chem. Phys.*, 1969, **51**, 4269.

In considering the data of Table 2 it is interesting to remember that (C_{4v}) IF_5, which differs from SbF_5 in possessing an additional 'lone pair' of electrons, shows [31] two intense i.r. bands and also two intense polarized Raman bands in the stretching region—with one coincidence between the i.r. and Raman spectra. It must also be noted that the apical IF bond is likely to be appreciably different in bond character from the four basal bonds. It does not automatically follow, therefore, that square pyramidal SbF_5 would follow an identical pattern. The most worrying feature of the SbF_5 data is the (assumed) coincidence of $\nu_3(a''_2)$ and $\nu_5(e')$ in the matrix–i.r. spectra. However, we note that the frequency difference between ν_3 and ν_5 for PF_5 is 78 cm^{-1} while that for AsF_5 is only 25 cm^{-1}.

Tellurium Tetrafluoride Oxide Dimer.—This compound was prepared by the pyrolysis of $LiTeF_5O$.[32] The lowest established formula unit obtained was the dimer $Te_2F_8O_2$ (molecular weight by the Dumas method 431.1 compared to a calculated ratio of 439.2). The melting point is 28 °C, but the boiling point only 77.5 °C. Our results on this compound from a study of the i.r. and Raman spectra are summarised in Table 3. The liquid Raman and gas-phase i.r. data agree sufficiently well with those of Seppelt [32] to suggest that the same compound is being examined. However our Raman data show a difference of *ca.* 4 cm^{-1} in several bands compared to those of Seppelt. Other differences are probably due to printing errors. However we note that a band at 610 cm^{-1} in the liquid did not appear to be polarized in our experiments. The results confirm the absence of a terminal tellurium–oxygen stretching mode and in conjunction with the solid-state data suggest only minor changes between gas, liquid, and solid.

TABLE 3

Vibrational spectra of $(TeF_4O)_2$; frequencies in cm^{-1}

I.r.	Raman		
Gas	Solid	Liquid	Gas
		147w	
270s, br	188 (5)	185(sh)	$\left.\begin{matrix}185\\192\end{matrix}\right\}$ (35)
280(sh)	195 (7.5)	192 (15)p	
305s	235 (10)	232 (19)p	230 (54)
328s, br			
402s	325 (5)	325 (3)	
636 *(sh)	345 (15)	340 (5)	
696s	365 (9)	360 (6)p	
711vs		475wp	
732vs		600w	
	610w	610 (1)	610(sh)
	656 (30)	660 (42)p	660 (60)
	684 (100)	684 (100)p	686 (100)
	710 (5)	714 (4.7)	710w
	740 (11)	735 (18)p	740 (30)

* Shoulder on band due to silicon window at *ca.* 620 cm^{-1}.

Seppelt [32] studied the pyrolysis of $LiTeF_5O$ in a mass spectrometer. Because of the occurrence of fragmentation reactions the results are not easy to interpret. However they do demonstrate that even under the conditions of this experiment the principal species present in the gas is polymer. We attempted to crack $Te_2F_8O_2$ to monomer at pressures of the order of atmospheric (Raman) and at pressures of the order of a few Torr (i.r.). Temperatures up to 300 °C were used,

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[26] L. P. C. Hoskins and R. C. Lovel, *J. Chem. Phys.*, 1967, **46**, 2402.

[27] H. Selig, J. H. Holloway, J. Tyson, and H. H. Claassen, *J. Chem. Phys.*, 1970, **53**, 2559.

[28] C. J. Adams and A. J. Downs, *J. Chem. Soc.* (*A*), 1971, 1534.

[29] L. E. Alexander and I. R. Beattie, *J.C.S. Dalton*, 1972, 1745.

[30] G. Herzberg, 'Spectra of Diatomic Molecules,' Van Nostrand, London, 1950.

[31] L. E. Alexander and I. R. Beattie, *J. Chem. Soc.* (*A*), 1971, 3091.

[32] K. Seppelt, *Z. anorg. Chem.*, 1974, 406, 287.

together with techniques which enabled us to introduce fresh compound rapidly into the thermally equilibrated cell. In no case did we find any evidence for a terminal tellurium–oxygen stretching mode. It is apparent that the dimer is strongly oxygen bridged.*

It is not easy to give a detailed assignment of a molecule such as $Te_2F_8O_2$ without isotopic data. However a few general considerations are useful and will help in understanding IF_3O_2 in the next section. For a centrosymmetric oxygen-bridged dimer there will be six polarized bands. Four of these (two stretches and two deformations) will be associated with the terminal tellurium–fluorine bonds. The remaining two will be associated with the Te_2O_2 ring and, unfortunately, one of these is likely to occur in the same region as the tellurium–fluorine symmetric stretching modes. Clearly the polarized bands at 660, 686, and 740 cm^{-1} (gas-phase data) correspond to two terminal fluorine modes and one bridge mode (all coupled as they are of the same symmetry). All these bands are i.r. inactive because the molecule has a centre of symmetry. Other bands likely to occur in the 600—700 cm^{-1} region are outlined schematically in Figure 2 in terms of symmetry co-ordinates applicable to movement of O or F. Thus, in addition to the three polarized Raman bands we expect three depolarized bands (600, 610, and 714 cm^{-1}, taken from the spectrum of the liquid). In addition to this up to five non-coincident i.r.-active bands may occur (635m, 641s, 698s, 719vs, and 736s cm^{-1} from the gas i.r. data of Seppelt[32]).† Thus, in an elementary manner, the i.r. and Raman spectra are in accord with the structure proposed by Seppelt.

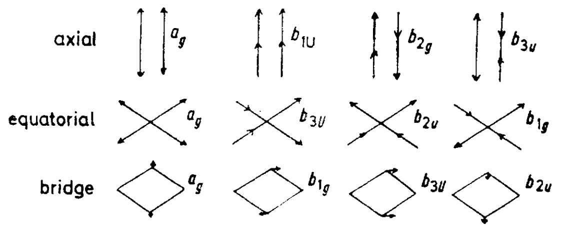

FIGURE 2 Schematic drawing of 'stretching vibrations' of $(TeF_4O)_2$. Motions of only terminal fluorine atoms or bridge atoms shown

Iodine Trifluoride Dioxide.—IF_3O_2 Is a rather difficult compound to work with as it is thermally and photolytically unstable. The melting point is 42.5 °C and the extrapolated boiling point *ca.* 150 °C (closely similar to that of SbF_5, but appreciably higher than that of $Te_2F_8O_2$).[15] Figure 3 shows vapour pressure measurements on IF_3O_2 for three samples of material. The agreement is good for all the samples (ΔH_v for the liquid = 42.5 kJ mol^{-1}). Of the eleven experimental points where the material is likely to be completely in the gas phase nine, lying within the frame A of Figure 3, correspond to a degree of polymerization of 2.00 ± 6%.

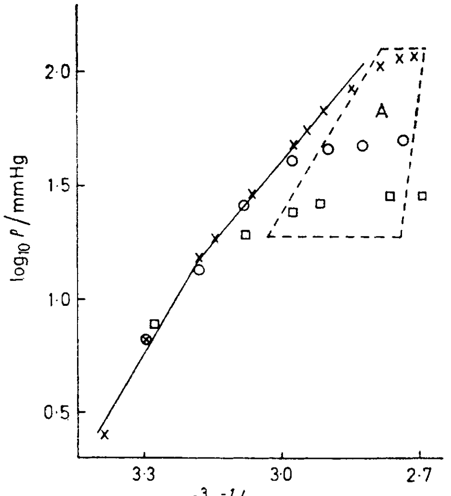

FIGURE 3 Vapour pressure data for IF_3O_2. Points lying within frame labelled A have molecular weights within 6% of that for $(IF_3O_2)_2$; ×, ○, and □ refer to three different samples

The points lying outside this range are one at high temperature (97 °C) where decomposition is becoming serious and the other where not all the material may be in the gas phase. It is apparent that this material is polymeric as a gas and hence will also be polymeric in the melt. Preliminary measurements by Falconer and Vasile[33] using a chopped molecular-beam mass spectrometer and phase-sensitive detection system suggest that the principal constituent of the vapour is dimer under the conditions of their experiment. Further, molecular-beam electric-deflection studies of this dimer suggest that it is centrosymmetric.

TABLE 4

Vibrational spectrum of IF_3O_2; frequencies in cm^{-1}

Infrared	Raman		
Gas	Solid	Melt	Gas
285w	110vvw	106vw	
306w	158w	155vw	
332m	195w		
576w	206m	206mp	205w
619m	239w	242w, p	
666s	260m	260mw, p	260w
684s	284w	285vw	
703s	342w	346w	340w
740mw, br	370w	375mw	370w
794w	377w		
828w, br	605w		
838w, br	630vs	631s, p	630sp
895m	662vs	665mp	665mp
915vs	687w	692wp	
	917vs	917mp	920mp

In Table 4 we report the Raman and i.r. spectra of IF_3O_2. Where the data overlap with that of Engelbrecht, Mayr, Zeller, and Schandara[34] or Carter,

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* *Note added in proof*: When $LiTeF_5O$ was decomposed by heating *in vacuo* to *ca.* 100 °C and the products condensed in an argon matrix at *ca.* 10 K, the i.r. absorptions of the deposit corresponded very closely in both frequency and intensity to the $Te_2F_8O_2$ features listed above, and there was no evidence for monomeric TeF_4O (personal communication, Dr. J. S. Ogden).

† A band reported at 660 cm^{-1} may be due to an impurity.

[33] W. Falconer and M. J. Vasile, personal communication.

[34] A. Englebrecht, O. Mayr, G . Ziller, and E. Schandara, *Monatsh Chem.*, 1974, **105**, 796.

Ruddick, Sames, and Aubke [35] the agreement is only fair. In particular the gas-phase i.r. spectra show a discrepancy of *ca.* 5 cm^{-1} in many of the bands. Figure 4 shows the Raman spectra of the gas, liquid, and solid. The results are closely similar and suggest the presence of the same basic structural unit in all cases. Careful experiments were carried out to examine the effect of temperature on the Raman spectrum and, in particular, on the i.r. spectrum of the gaseous compound. No reversible changes were observed as the temperature was varied in the range 25—150 °C.

We have examined the ^{19}F n.m.r. spectrum of IF_3O_2 as a melt and as a solution in several solvents, over a wide range of temperatures (roughly 90 to −100 °C). In all cases the signals are broad (at least 40 Hz). This is shown in Figure 5 where we include data for $Te_2F_8O_2$ under similar conditions. The excellent resolution of the $Te_2F_8O_2$ spectrum contrasts sharply with that of IF_3O_2. We note that IF_5O shows broad resonances [36] ascribed to quadrupole broadening, the central iodine atom being in an approximately electrically symmetrical environment. Whereas a similar explanation might be expected to pertain in this case, the longitudinal relaxation time, T_1, is *ca.* 2 s. Hence the width of the signals is a reflection of either unresolved coupling to the iodine nucleus or to some exchange process.*

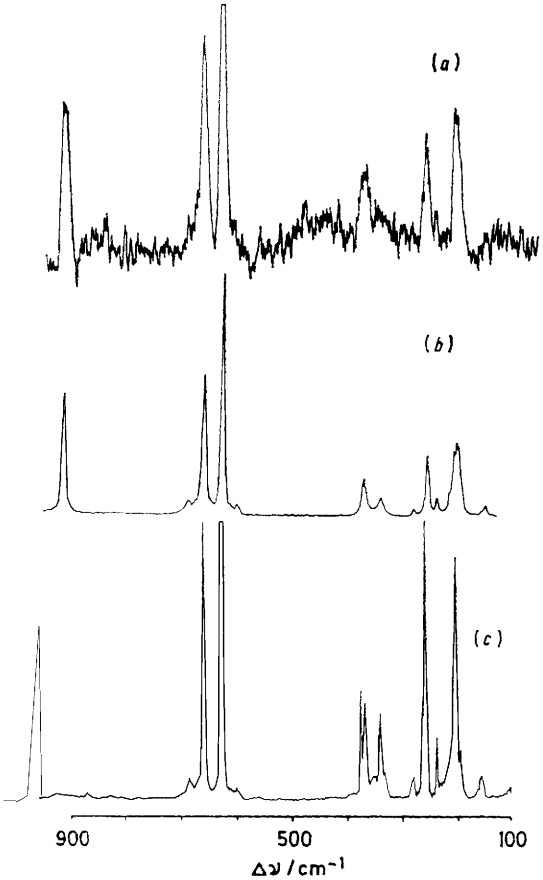


FIGURE 4 Raman spectra of IF_3O_2 (a) gas, (b), melt, and (c) solid

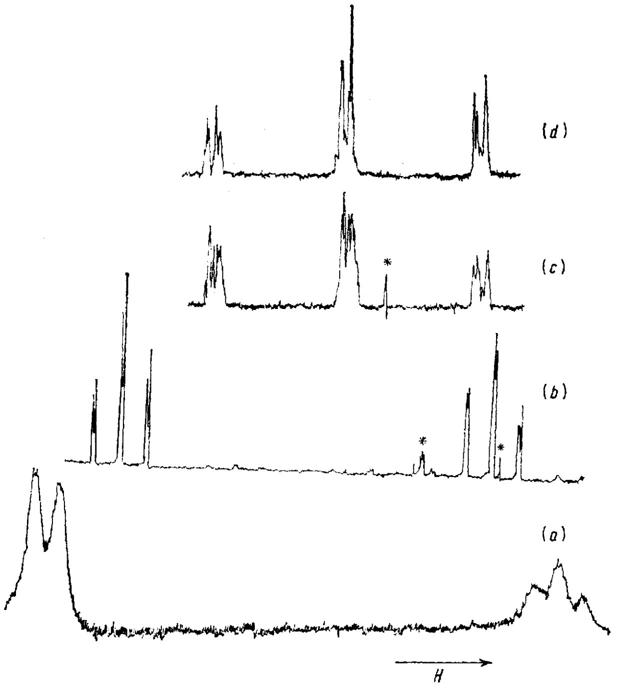
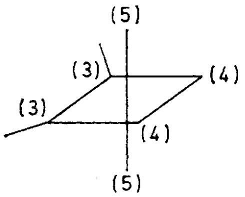


FIGURE 5 ^{19}F N.m.r. spectra at 31 °C in $CFCl_3$ of (a) IF_3O_2, (b) $(TeF_4O)_2$, (c) high-field signal of $(TeF_4O)_2$ on expanded scale, and (d) low-field signal of $(TeF_4O)_2$ on expanded scale. Signals marked * are due to impurities. (For numerical values see Table 5)

TABLE 5

^{19}F Resonances (p.p.m.) from $CFCl_3$ for SbF_5, $(TeF_4O)_2$, and IF_3O_2

Atom number	(3)	(4)	(5)
SbF_5 [a]	88.4	132.7	106.7
$(TeF_4O)_2$ [b]		51.0 (53.5)	22.8 (25.6)
IF_3O_2		−70.9	−109.1



[a] The data of Hoffman, Holder, and Jolly as reassigned by Bacon, Dean, and Gillespie assuming $\delta_{CF_3CO_2H} = \delta_{CFCl_3}$ −79.9.
[b] Results of Seppelt (assigned by us) in parentheses.

The complex splitting pattern of $Te_2F_8O_2$ is due to the presence of eight fluorines which are not magnetically equivalent. Table 5 summarises the ^{19}F chemical shifts

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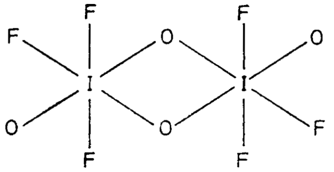
* We thank Dr. J. Emsley for suggesting the measurement of T_1.

[35] H. A. Carter, J. N. Ruddick, J. R. Sames, and F. Aubke, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 29.

[36] N. Bartlett, S. Beaton, L. W. Reaves, and E. J. Wells, *Canad. J. Chem.*, 1964, **42**, 2531.

for SbF_5, TeF_4O, and IF_3O_2 relative to $CFCl_3$, using the numbering scheme shown. The assignment of resonances to fluorines (4) or (5) in IF_3O_2 and TeF_4O is to some extent intuitive, but it provides an excellent sequence for an isoelectronic series.

The vibrational data confirm the close similarity of the basic structural units in gas, melt, and solid for IF_3O_2. The molecular-weight data and mass-spectral evidence suggest at least an appreciable concentration of dimer. The ^{19}F resonance spectra show that fluorine does not act as a bridge in these compounds. The electric deflection data[33] suggest the dimer is centrosymmetric. This information, together with the chemical-shift data of Table 5 leads to the structure



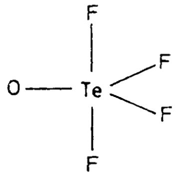
Fortunately, this is the structure that is chemically most satisfying and results rather easily from the linking of two IF_3O_2 (C_{2v}) monomers. Contrary to the recent statement that IF_3O_2 is weakly oxygen bridged,[35] we believe that both TeF_4O and IF_3O_2 are strongly bridged by oxygen.

It is now possible to reconsider briefly the vibrational data. $(IF_3O_2)_2$ is isoelectronic with $(TeF_4O)_2$. On the basis of similar diagrams to those given for $(TeF_4O)_2$ (see Figure 2), for the proposed centrosymmetric species there will be only minor changes associated with the change in point group of the molecule. Pictorially only the ' equatorial ' modes are affected, there now being a symmetric and an antisymmetric stretch associated with the pair of terminal oxygens and also with the pair of fluorines. This introduces one more polarized band in the Raman. The 920 cm^{-1} band is the symmetric terminal-oxygen stretch. The other high-frequency polarized bands are at 630 and 665 cm^{-1} (gas) plus a band in the liquid at 692 cm^{-1}. (These may be compared with polarized bands at 660, 686, and 740 cm^{-1} for $Te_2F_8O_2$.) Similarly, there will be one high-frequency i.r. band (915 cm^{-1}) associated with the terminal-oxygen antisymmetric stretch. In addition up to five noncoincident i.r. bands are expected in the 600—700 cm^{-1} region. The observed bands occur at 619m, 668s, 684s, 703s, and 740mw,br cm^{-1} (comparable with[32] 635m, 641s, 698s, 719vs, and 736s for $Te_2F_8O_2$). In general all the data are acceptable apart from the observation of two i.r. bands in the 900 cm^{-1} region. However the intensity of one of these bands (895 cm^{-1}) appeared to be variable and it may therefore be due to an impurity.

DISCUSSION

It is known that WF_4O[37] and MoF_4O[38] form weakly bound fluorine-bridged polymers in the solid state, but that the vapours are essentially monomeric.[39] Both NbF_5 and TaF_5 are strongly fluorine bridged, and it is difficult to obtain monomers even in the gas phase at temperatures of the order of 500 °C and pressures near atmospheric.[40] The ease of dissociation for the pentafluorides appears to be $V \gg Nb > Ta$. Antimony pentafluoride is also quite strongly fluorine bridged and at room temperature the material is essentially polymeric in the gas phase even at pressures of the order of a few Torr. By contrast both $(TeF_4O)_2$ and $(IF_3O_2)_2$ are strongly oxygen bridged, while XeF_2O_3 is apparently monomeric (it distils rapidly out of a trap at -80 °C when pumped on).[14] It is reasonable to assume that monomeric TeF_4O would, like SF_4O and very probably SeF_4O, have C_{2v} symmetry with a structure derived from a trigonal bipyramid with an equatorial oxygen atom.[32] The molecular shape of WF_4O is square pyramidal (C_{4v}) with an apical oxygen.[39,41] It is likely that monomeric NbF_5, TaF_5, and SbF_5 are all trigonal bipyramidal.

We shall consider the non-transition elements first and utilise only *s*- and *p*-orbitals. Where oxygen is present we shall assume the metal–oxygen bond has extensive *s*-character as it is the shorter bond (relative to fluorine). This is a gross over-simplification but it is helpful. For MF_5 the molecule is conveniently regarded as trigonal bipyramidal with s,p_x,p_y bonding in the MF_3 plane and p_z bonding in the MF_2 direction perpendicular to this plane. (The difference in energy between a square pyramidal and a trigonal bipyramidal distribution for identical ligands is small. However, for the non-transition elements the trigonal bipyramidal shape is clearly favoured.) Using the *s*-orbital for the oxygen of TeF_4O leaves a framework of p_x, p_y, and p_z for the fluorines leading to the preferred structure. We have assumed no multiple bonding to the oxygen, leading essentially to a formal negative charge on this atom and a positive charge on the tellurium. On this basis dimerization affords two new Te–O bonds.



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[37] A. J. Edwards and G. R. Jones, *J. Chem. Soc.* (*A*), 1968, 2074; I. R. Beattie and D. J. Reynolds, *Chem. Comm.*, 1968, 1531; M. J. Burnett, T. E. Haas, and J. T. Purdham, *Inorg. Chem.*, 1972, **11**, 207.

[38] A. J. Edwards and B. R. Steventon, *J. Chem. Soc.* (*A*), 1968, 2507.

[39] L. E. Alexander, I. R. Beattie, A. Bukovszky, P. J. Jones, C. J. Marsden, and G. J. Van Schalkwyk, *J.C.S. Dalton*, 1974, 81.

[40] L. E. Alexander, I. R. Beattie, and P. J. Jones, *J.C.S. Dalton*, 1972, 210; I. R. Beattie, S. B. Brumbach, D. Everett, R. Moss, and D. Nelson, Faraday Symposia of the Chemical Society, 1973, 108.

[41] A. Robiette, personal communication.

For WF_4O we introduce *d*-orbitals and assume strong d_π–p_π bonding in W–O, with use of d_{xz} and d_{yz}. Thus the molecular shape is dominated by this cylindrically symmetrical multiple bond. This leads to a high electron-density region above the WF_4 plane so that the four fluorines are depressed back (O–W–F 105°) leading to ' protection ' of the sixth octahedral position, and reducing the possibility of polymerization.

All this appears to be satisfactory except that XeF_2O_3 is monomeric. (We note also that XeO_4 is monomeric and isoelectronic with polymeric SnF_4.) Presumably the change in behaviour is associated with the increased formal charge leading to a region of high electron density in the equatorial plane. The molecule is effectively dominated by the planar XeO_3 group analogous to the planar SO_3 molecule—but in the case of xenon, having axial fluorines.

EXPERIMENTAL

Reagents.—Commercial H_6TeO_6 was used without further purification. $CFCl_3$ Was distilled from CaH_2; HSO_3F was fractionally distilled at atmospheric pressure. MeOH was dried using Mg.

Preparation of Compounds.—(*a*) Antimony pentafluoride was prepared by the fluorination of freshly sublimed SbF_3 at 300 °C, followed by distillation *in vacuo*.

(*b*) Tellurium tetrafluoride oxide dimer was prepared by the method developed by Seppelt. The following notes on the procedure result from help given to us by Dr. Seppelt, coupled with our own experience. $Te(OH)F_5$ Was prepared by treating H_6TeO_6 (0.2 mol) with HSO_3F (2.4 mol), followed by distillation. The resultant slurry was treated with H_2SO_4 followed by fractional distillation (60 ± 1 °C) to yield $Te(OH)F_5$ (m.p. 40 ± 1 °C). A known amount of LiOMe was taken either by starting with a known weight of Li metal, or by weighing out the LiOMe. It is essential to remove the residual MeOH *in vacuo* at 50 °C for several hours. A batch of 5—6 g of LiOMe required a drying time of *ca.* 6 h. A solution of $Te(OH)F_5$ (0.1 mol) in $CFCl_3$ (20 ml) was added slowly to a suspension of LiOMe (0.1 mol) in $CFCl_3$ (100 ml). The reaction mixture was stirred for 2—3 h under anhydrous conditions during which time a precipitate settled out. The mixture was centrifuged, the solvent decanted off, and the $LiOTeF_5$ dried *in vacuo* at 50 °C for 30 h. The dried salt, which is very moisture sensitive, was heated *in vacuo* and the product formed during decomposition in the temperature range 120—170 °C was collected. This product was treated several times with H_2SO_4 followed by filtration and vacuum sublimation. The product $(TeF_4O)_2$ had m.p. 28 ± 0.5 °C.

(*c*) Iodine trifluoride dioxide was prepared by the method given by Englebrecht, Peterfy, and Schandara.[15] Again we initially had some difficulty with this preparation. $Ba_3(H_2IO_6)_2$ was prepared by the method of Brauer[42] (Found: Ba, 47.3. Calc. for $Ba_3H_4I_2O_{12}$: Ba, 47.8%). Anhydrous $Ba_3(H_2IO_6)_2$ (0.05 mol) was added in small portions during several hours to HSO_3F (60 ml) under nitrogen in a 250-ml flask, the whole being stirred thoroughly and each batch of solid being allowed almost completely to dissolve before the addition of more. The mixture was allowed to warm to room temperature and the flask was evacuated. By the use of warm water (40—60 °C) the HSO_3F–$HOIOF_4$ mixture was distilled into another flask at liquid nitrogen temperature. The first flask was removed, the product was allowed to warm to room temperature, and 60% oleum was added in small portions (*ca.* 1 ml) *via* a greaseless tap. After each addition the mixture was heated with a hot-air blower, when yellow crystals formed in an attached U-tube cooled in ice–salt. The IF_3O_2 was purified by treatment with anhydrous K_2SO_4 and vacuum sublimation (Found: F, 27.0. Calc. for F_3IO_2; F, 26.4%).

Molecular-weight Determination.—An apparatus of known volume containing a known weight of IF_3O_2 was held in a thermostat bath. Pressures were measured using a mercury manometer and spiral gauge.

Spectra.—Perkin-Elmer 225 and Beckman IR11 or FS 720 i.r. spectrometers were used together with Cary 82 or Spex 1401 Raman spectrometers in conjunction with argon ion or krypton ion lasers. I.r. spectra were taken either in borosilicate glass cells containing fused-in silicon windows or in silica cells with diamond windows sealed *via* thin polytetrafluoroethylene gaskets. Raman spectra were taken in borosilicate glass, fused silica, or sapphire cells depending on temperature and reactivity of the sample. For the $(TeF_4O)_2$ Raman experiments at variable temperature a sapphire tube was sealed to borosilicate glass *via* intermediate sealing glasses. The central portion of the sapphire was heated to high temperature while the ends were kept cool. Compound was admitted to and pumped from the system *via* greaseless taps.

We are very grateful to Dr. Seppelt for the helpful comments made to us about the preparation of TeF_4O dimer. We also thank the S.R.C. and the Royal Society for financial support and de Beers for the loan of diamond windows. In addition, we would like to record that Mr. P. J. Tyrell obtained similar results to ours while studying the i.r. spectrum of (monomeric) SbF_5 isolated in a matrix (Part II, Thesis, Oxford, 1971). These results were kindly made available to us during the course of this work. We thank Mr. K. Walkling for assistance during the preparation of IF_3O_2 and Dr. Warren Falconer for making available to us unpublished work on this compound.

[5/1595 *Received*, 13*th August*, 1975]

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[42] G. Brauer, ' Handbook of Preparative Inorganic Chemistry,' Academic Press, London, 1963, vol. 1, p. 326.