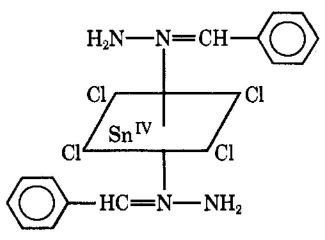

III

obtained from our infrared data. Finally, it should be noted that the similarity of the isomer shifts of the bis hydrazine complex of tin(IV) chloride and bis(benzalhydrazono)tin(IV) chloride does not necessarily imply that the metal–ligand interaction in the two cases is exactly identical.

Attempts to grow stable single crystals of the complexes discussed in this paper have thus far been unsuccessful but one X-ray investigation relating to the tris hydrazine hydrochloride complex of cobalt(II) chloride[2] is in progress.

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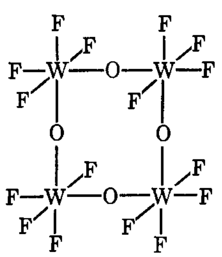
CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

## On the Structure and Bonding in the Tungsten Oxide Tetrafluoride Tetramer

BY M. J. BENNETT,* T. E. HAAS, AND J. T. PURDHAM

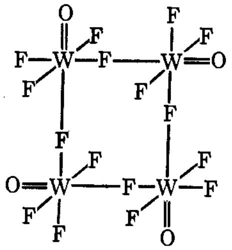
*Received May 21, 1971*

The solid-state structure of tungsten oxide tetrafluoride has been reported[1] as a tetrameric unit with idealized symmetry $D_{4h}$ (I) and site symmetry $C_{2h}$.

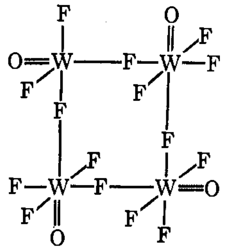


I

The assignment of the oxygen atoms to the bridging positions was based on the symmetry requirements of the space group and the stoichiometry of the compound. This assignment, which assumes an ordered structure, has been criticized[2] on the basis of the infrared and Raman spectra of $(WOF_4)_4$ in the solid state. In addition to the spectroscopic evidence we find that the observed bond lengths are inconsistent with an oxygen-bridged structure. All the data can be interpreted by a disorder of two orientations of an asymmetrically fluorine-bridged structure, II and III. The idealized symmetry of the tetrameric unit is then $C_{4h}$. This disorder of oxygen and fluorine atoms is not without precedent in oxymetal fluoride systems;[3] *e.g.*, in the cesium salt of $CrO_3F^-$, the anion occupies a position with site symmetry $S_4$, and only one bond length (of 1.53 Å) is observed for the weighted average of Cr=O and Cr—F distances.



II



III

The relative merits of oxygen- and fluorine-bridged structures can be evaluated on the basis of expected bond lengths. A simple symmetry-based molecular orbital treatment of the oxygen-bridged structure shows that one might expect significant $\pi$ bonding and hence a short tungsten–oxygen distance. The molecular orbitals, after construction of the $\sigma$ framework, can be briefly described as follows for the $D_{4h}$ oxygen-bridge model. Along each edge of the square array, perpendicular to the plane of the four metal atoms, a three-center W–O–W $\pi$-bonding system, consisting of d$\pi$ orbital from each metal and the corresponding oxygen p$\pi$ orbital, would result in bonding, nonbonding, and antibonding orbitals. Two electrons, those on the oxygen, are available to populate the bonding levels, thus giving an out-of-plane $\pi$-bond order of 0.5. In the plane a more extensively delocalized system results, but briefly the d$\pi$ orbitals transform as $A_{1g} + B_{2g} + E_u'$ and the oxygen p$\pi$ orbitals as $A_{1g} + B_{1g} + E_u$. The metal and oxygen $A_{1g}$ and $E_u$ orbitals give rise to bonding and antibonding combinations of each symmetry. The eight available electrons are housed in the $A_{1g}$ and $E_u$ bonding orbitals and the $B_{1g}$ nonbonding orbital (which remains localized on the oxygen atoms). Thus a total in-plane $\pi$-bond order of 3 is distributed among the eight equivalent W–O linkages. The total $\sigma + \pi$ bond order is then 1.875 for each metal–oxygen bond. The approximate bond order *vs.* bond length curve of Cotton and Wing[4] would suggest a W–O bond of approximately 1.8 Å assuming that W–O distances parallel Mo–O distances. However the observed W–"O" distances are normal (2.10 and 2.12 Å) and correspond to an approximate bond order of 1.0.

Simple electron counting for a fluorine-bridged structure suggests one oxygen per tungsten atom and the pattern of in-plane and out-of-plane tungsten ligand distances[1] suggests that the oxygen atoms lie in the plane of the four tungsten atoms. These requirements allow three structures II, IV, and V. The particular arrangement and orientation of the tungsten atoms in this structure requires either or both of the diagonals to be coincident with symmetry elements, de-

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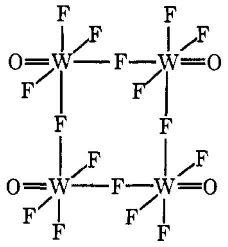
(1) A. J. Edwards and G. R. Jones, *J. Chem. Soc. A*, 2074 (1968).

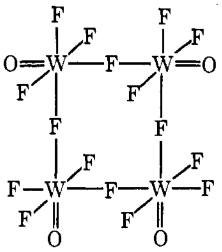
(2) I. R. Beattie and D. J. Reynolds, *Chem. Commun.*, 1531 (1968).

(3) J. A. Ketelaar and E. Wegerif, *Recl. Trav. Chim. Pays-Bas*, **58**, 948 (1939).

(4) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 867 (1965).



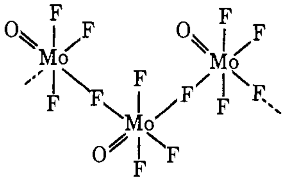
IV



V

pending on the choice of space group *C*2, *Cm*, or *C*2/*m*. Since none of these structures has a strict mirror plane or twofold axis that contains diagonal tungsten atoms, a disorder, and hence the presence of a pseudosymmetry element, has to be postulated in each case. We prefer structure II on the grounds that it is the structure most likely to disorder in that it is based on a square whereas structures V and VI we estimate to contain a rectangle and trapezoid of tungsten atoms, respectively.

The apparent W–F bridge distance, where the fluorine atom is placed at a position corresponding to the average of structures II and III, can be readily assessed from the structure of $MoOF_4$,[5] assuming that Mo–F and W–F distances will be essentially the same. The structure of $MoOF_4$ is different from that found for $WOF_4$ in that it forms infinite chains rather than discrete tetrameric units. However, the essential features of the heavy-atom environment are the same as shown in VI. The average of the two independent Mo–F bridge distances (1.96 and 2.27 Å) in this asymmetrically bridged structure is 2.11 Å, the value observed for bridge bonds in the tungsten compound. The hypothesis of the disordered structure was then tested using the published structure factor amplitudes. Two models were tested: (a) the ordered oxygen-bridge structure I and (b) an average of structuring II and III with two independent half-weight fluorine atoms in each bridge, the terminal in-plane atoms each being treated as a single atom comprising half oxygen and half fluorine. Both models were restricted to isotropic refinement and were refined in space group *C*2/*m* using scattering factors[6] that included the real and imaginary components of anomalous dispersion[7] and the weighting scheme of Edwards and Jones.[1] In model (b) only one half-weight fluorine was refined in each cycle because of the resolution limits of the data set and naturally high correlation coefficients. Both models refined to *R* factors 0.126 (defined by $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$). The refinement of the disordered model produced asymmetric bridges with individual tungsten–fluorine distances 2.04 (7) and 2.19 (7) Å (average values, standard deviation in parentheses). The other parameters were not significantly different from those already published. The X-ray data do not allow the rejection[8] of the ordered model I. This is not surprising in view of the quality of the data used and the relative insensitivity of the structure factors to small changes in the light atoms when a third-row transition metal is present.



VI

Since the X-ray data do not favor either model, the choice must be made on the basis of other evidence. In this case the spectroscopic evidence[2] and the structural arguments presented here favor a fluorine-bridged structure, and of the fluorine-bridged structures, we find II to be the most attractive.

**Acknowledgment.**—We thank the National Research Council of Canada for its financial support.

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[7] D. T. Cromer, *ibid.*, **18**, 17 (1965).

[8] W. C. Hamilton, *ibid.*, **18**, 502 (1965).

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Contribution from Rocketdyne,
a Division of North American Rockwell,
Canoga Park, California 91304

## Selenium Chloride Pentafluoride

By C. J. Schack,* R. D. Wilson, and J. F. Hon

*Received May 24, 1971*

The existence of $SF_5Cl$ has been known[1] for some time, while $TeF_5Cl$ has been reported[2] more recently. However, no report concerning the preparation of the intermediate member of the S–Se–Te triad, $SeF_5Cl$, has appeared. Since the best synthetic routes[3] to $SF_5Cl$ involve chlorination of sulfur fluoride substrates and since this reaction had been found to be enhanced by added alkali metal fluorides,[4] this technique was applied to the formation of $SeF_5Cl$. We wish now to report the synthesis and characterization of this new compound.

### Experimental Section

**Apparatus and Materials.**—The equipment used in this work has been described[5] and was supplemented with a Perkin-Elmer Model 457 Infracord and a 10-cm, stainless steel infrared cell fitted with AgBr windows. Details concerning the preparation or treatment of ClF, $ClSO_3F$, and CsF have been given.[5] Additional materials were purchased and used as received.

**$SeF_4$.**—Selenium tetrafluoride was first prepared from Se powder and ClF according to Pitts and Jache.[6] Later it was determined that $ClF_3$ performed equally well in this reaction, thereby circumventing the need to prepare ClF. Typically, a prepassivated 30-ml stainless steel cylinder was loaded with Se powder (14.2 g-atoms) in the drybox. Chlorine trifluoride (20.3 mmol) was added at −196° from a vacuum line and the cylinder allowed to warm slowly to ambient temperature where it was maintained for 1 day or until needed. Vacuum fractionation through U traps cooled to −30, −78, and −196° furnished $SeF_4$ (12.3 mmol) in the highest temperature trap. The purity and identity of the $SeF_4$ were verified by its vapor pressure[6] and infrared spectrum.[7] Based on the equation $3Se + 4ClF_3$

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[2] G. W. Fraser, R. D. Peacock, and P. M. Watkins, *Chem. Commun.*, 1257 (1968).

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