Molecular Structure of Chromyl Fluoride, CrO_2F_2; an Electron Diffraction Study

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Summary The molecular structure of CrO_2F_2 has been determined in a gas-phase electron diffraction study; the relative magnitudes of the O–Cr–O and F–Cr–F interbond angles are inconsistent with the predictions of V.S.E.P.R. theory, in contrast to the situation in SO_2F_2.

Although several chemical and physical properties of chromyl fluoride, CrO_2F_2, have been known for some time,[1] no investigation of its molecular structure has thus far been reported. As part of a survey of the molecular structures of transition-metal oxo-complexes we have completed such a study.

CrO_2F_2 was prepared according to the method of Engelbrecht and Grosse,[2] distilled pure (m.p. 31 °C), and stored over dried sodium fluoride. Electron-diffraction data at nozzle to plate distances of 100, 50, and 25 cm were collected photographically on Ilford N60 plates using a Balzers KDG2 gas diffraction apparatus.[3] The intensities were converted into digital form using a fully automated Joyce–Loebl microdensitometer. All calculations were carried out on the ICL 1906A computer at the Manchester Regional Computing Centre using established procedures.[4]

The four geometrical parameters Cr–F, Cr–O, ∠F–Cr–F, and ∠O–Cr–O were used to define a C_{2v} structure for CrO_2F_2. The values of these parameters after refinement to $R_g = 11{\cdot}7\%$ are given in the Table, together with the calculated values of the rotational constants. In view of the small difference between oxygen and fluorine as electron scattering centres, the quality of the refinement was tested with the relative magnitudes of the O–Cr–O and F–Cr–F interbond angles reversed. This alternative model gave significantly poorer agreement with the experimental data than that described in the Table.

The results of this test are important in two respects. Firstly such a geometry ($\angle$O–Cr–O = 110°; $\angle$F–Cr–F = 98°) was assumed[5] to explain the microwave spectrum of CrO_2F_2; this interpretation appears to be incorrect.[6] Secondly, a distortion from tetrahedral geometry in the sense F–Cr–F $<$ O–Cr–O would be expected by the V.S.E.P.R. theory[7] which is so successful in rationalising the structures of simple covalent species containing a *p*-block element as the central atom. Thus in SO_2F_2 the O–S–O and F–S–F interbond angles are 123·97(0·20) and 97·12(17)°, respectively,[8] consistent with the electron pairs of the multiple S–O bonds occupying more space around sulphur than those of the S–F bonds. An important difference between CrO_2F_2 and SO_2F_2 is that the charge separation is greater in the former than the latter; *ab initio* molecular orbital calculations[9] suggest that the charges on the atoms in CrO_2F_2 are: Cr, $+2{\cdot}1$, O $-$ 0·39, and F $-$ 0·62, and in SO_2F_2, S $+$ 0·69, O $-$ 0·09, and F $-$ 0·26. These charge separations, when taken with the molecular geometries of the molecules, suggest that ligand–ligand repulsions are more important than electron-pair repulsions in determining the detailed stereochemistry of CrO_2F_2, whereas the opposite situation obtains in SO_2F_2. A similar difference appears to be exhibited by the pair of molecules CrO_2Cl_2 and SO_2Cl_2, the former[10] having $\angle$O–Cr–O *ca.* 105·1° and $\angle$Cl–Cr–Cl *ca.* 113·3° and the latter[11] $\angle$O–S–O = 123·5 (0·8)° and $\angle$Cl–S–Cl = 107·7 (0·4)°.

TABLE

Values of the geometrical parameters (Å and degrees) and calculated rotational constants (cm^{-1}) for CrO_2F_2.

Cr–O	= 1·579 (0·004)	O ------- O	= 2·456
Cr–F	= 1·739 (0·004)	F ------- F	= 2·995
$\angle$ O–Cr–O	= 102·14 (0·36)	O ------- F	= 2·696
$\angle$ F–Cr–F	= 118·91 (0·46)		
B_z	= 0·1264		
B_x	= 0·1542		
B_y	= 0·1152		

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