388. Studies on Transition-metal Peroxy-complexes. Part IV.¹ Peroxyfluoro-complexes

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The fluorine magnetic resonance spectra of the ions $(TaO_{2}F_{5})^{2-}$, $(MoO_5F_2)^{2-}$, and $(WO_3F_4)^{2-}$ in aqueous solution are reported and discussed in terms of possible structures for these complexes.

Most transition-metal peroxide complexes are unstable, both as solid and especially in aqueous solution, with the exception of the peroxyfluorometallates of the periodic groups IVa, Va, and VIa. A number of the latter complexes have been reported $\frac{2}{3}$ and are of the form $(M^{IV}O_2F_5)^{3-}$ (M = Ti), $(M^{V}O_2F_5)^{2-}$ (M = Nb or Ta), $(M^{VI}O_3F_4)^{2-}$ (M = W or Mo), $M^{VIO_5}F_2)^{2-}$ (M = Mo). Infrared spectra have shown ¹ that these complexes have low molecular symmetries, but no definite conclusions could be drawn as to their structures, beyond the demonstration that the $(MO_3F_4)^{2-}$ and $(MO_5F_2)^{2-}$ ions contain a metal-oxygen doubly bonded group in addition to the peroxide ligands. For a number of complex fluoro-metal ions, some structural information has been obtained from the fluorine nuclear magnetic resonance spectra.^{3,4} Although we have examined the fluorine resonance spectra of all the above-mentioned peroxy-fluorides, useful results could only be obtained with three complexes, the others being too insoluble or too labile towards fluorine exchange.

 $(TaO_{2}F_{5})^{2-}$.—In all the transition-metal peroxy-complexes so far studied by structural methods, the peroxide group is bounded in a side-on position to the metal atom, so that effectively each peroxide group occupies two co-ordination positions of the metal; furthermore, two oxygen atoms of the peroxide group occupy adjacent apices of a pentagonal ring (or of a dodecahedral mirror plane in rarer cases) rather than a square plane.¹ If this is



assumed to hold for peroxyfluoro-complexes, as seems probable from the spectroscopic data,¹ the tantalum in $(TaO_2F_5)^{2-}$ must have seven co-ordination for which the two most likely structures are (I) and (II). (I) is the $C_{2\nu}$ structure ⁵ found for $K_2(TaF_7)$ and ⁶ [Mn(EDTA)OH] - and (II) is the pentagonal bipyramidal structure ⁷ found for $K_3(ZrF_7)$. Since the peroxide group normally subtends an angle of 45° at the metal, it is likely to be bonded in the positions shown in the diagrams rather than, for example, in the square plane of (I).

The fluorine magnetic resonance spectra of an aqueous solution of the potassium salt consists of a doublet and a quintuplet of relative intensities 4:1. This AX₄ pattern clearly favours a structure such as (I), which has four equivalent and one non-equivalent fluorine atoms; for structure (II) a 1:2:2 pattern would be expected. This conclusion is supported by the fact that $K_2(TaO_2F_5), H_2O$ is not isomorphous with $K_3(TiO_2F_5)$, whereas the latter is isomorphous with $K_{3}(ZrF_{7})$, which has a pentagonal bipyramidal anion.⁸ In a solution of $K_2(NbO_2F_5)$ the fluorine-19 lines were very broad, probably owing to exchange

- Part III, Griffith, J., 1964, 5248.
 Piccini, Z. anorg. Chem., 1892, 1. 52; 2, 21; Balke and Smith, J. Amer. Chem. Soc., 1908, 30, 1664.
- ³ Packer and Muetterties, J. Amer. Chem. Soc., 1963, 85, 3035.
 ⁴ Muetterties and Phillips, J. Amer. Chem. Soc., 1959, 81, 1084.
 ⁵ Hoard, J. Amer. Chem. Soc., 1939, 61, 1252.

- ⁶ Richards, Pedersen, Silverton, and Hoard, Inorg. Chem., 1964, 3, 27.
- 7 Zachariasen, Acta Cryst., 1954, 7, 792.
- ⁸ Peyronel, Gazzetta, 1941, 71, 620.

effects, but the solid-state infrared spectrum of the salt is very similar to that of $K_2(TaO_2F_5)$, which suggests that the anions may have similar structures.

 $(MoO_5F_2)^{2-}$.—The fluorine magnetic resonance spectrum of the potassium salt shows two lines, one broad and the other very broad. No extra line was observed on addition of potassium fluoride solution, but the broader line was shifted to lower applied fields and the width of the narrower line decreased further. This indicates non-equivalence of the two fluorine atoms in the ion, and suggests that one of them exchanges with fluoride ion at a much faster rate than the other. The sharpening of the narrower line on the addition of fluoride is presumably due to a more complete averaging out of spin coupling from the " rapidly " exchanging fluorine.

A structure derived from (I) is unlikely for $(MoO_5F_2)^{2-}$, because a peroxide group would have to be accommodated in the square plane or in the equally strained position between the square plane and the C_2 axis. A more likely configuration would be one based on (II) with the pentagonal ring containing the two peroxide groups and one fluorine atom, which has an arrangement very similar to that of the five-membered ring ⁹ in $(NH_3)_3CrO_4$, the second fluorine atom being in the axial position *trans* to the oxide group. It is probably this latter fluoride atom that has the more rapid exchange rate. The non-equivalence of the two fluorine atoms eliminates the alternative structure based on (II), in which the atoms would occupy the two equivalent axial positions.

The tungsten analogue of $(MoO_5F_2)^{2-}$ could not be made by repeated recrystallisation of $(WO_3F_4)^{2-}$ from hydrogen peroxide, although one such treatment is sufficient to convert $(MoO_3F_4)^{2-}$ to $(MoO_5F_2)^{2-}$.

 $(WO_3F_4)^{2-}$.—The fluorine magnetic resonance spectrum of the sodium salt of this ion was measured at 56.45 Mc./sec. (see Figure) and at 40 Mc./sec. It consists of three chemically shifted bands of relative intensities 1:2:1 suggesting that there are three different environments for the fluorine atoms, and that two of the atoms are in equivalent environments. Both the chemical shifts and the spin-coupling constants are large, and the structure of each band is slightly more complicated than a simple first-order analysis would predict. The positions of all the lines in the spectra at both frequencies agree very closely $(\pm 0.5 \text{ c./sec.})$ with the positions calculated for an AB₂C group of fluorine nuclei. As seen in the Table, the calculated values of the small doublet separations in the B group are sensitive to the relative signs of the coupling constants, especially at 40 Mc./sec. It can be concluded that the signs of all three coupling constants are the same.

Doublet in group B (see Figure)		a		b		С		d	
leasuring frequency (Mc./sec.)	56.45	40 ·0	56.45	40 ·0	56.45	40 ·0	56.45	40 •0	
Observed separation (c./sec.)	$2 \cdot 6$	3.8	$4 \cdot 5$	$6 \cdot 3$	5.6	7.7	$4 \cdot 2$	6.0	
Calc., $I_{AB} = \pm$, $I_{BC} = \pm$, $I_{AC} = \pm$	3.1	3.7	4.8	6.5	5.7	8.1	4.1	6.4	
	5.0	6.7	3.0	4.1	3.9	6.0	5.6	$8 \cdot 2$	
"	4.8	6.5	3.1	$4 \cdot 3$	4.1	5.8	5.6	8.0	
" ± ± …	3.3	$4 \cdot 6$	4.4	6.0	6.0	9.0	3.8	4 ∙9	

The presence of an equivalent pair and two non-equivalent fluorine atoms would suggest either a structure derived from (I), with the oxy-group occupying one of the equatorial positions (if it were to be in the axial position *trans* to the midpoint of the peroxide the four fluorine atoms would be equivalent); or a structure based on (II) with the oxy-group occupying one of the axial positions (if it were *trans* to the midpoint of the peroxide group an A_2B_2 pattern would result).

Studies on the $(MoO_3F_4)^{2-}$ ion were inconclusive owing to the low solubility of the salts, but the infrared spectra of $K_2(WO_3F_4)$ and $K_2(MoO_3F_4)$ are very similar, indicating that the anions may have similar structures.

EXPERIMENTAL

The complexes were prepared and analysed as described in the previous Paper.¹

The fluorine magnetic resonance spectra of the aqueous solutions of the complexes were ⁹ Stomberg, Arkiv Kemi, 1964, 22, 49.

measured at 56.45 and [for $(WO_3F_4)^{2-}$] at 40 Mc./sec. on a Varian spectrometer. Chemical shifts are given relative to trifluoroacetic acid as an external reference, negative values being on the low-field side of the reference.

(TaO₂F₅)²⁻ AX₄ system. $F_{\rm A} = -65.5$ p.p.m., $F_{\rm X} = -51.7$ p.p.m.; $J_{\rm AX} = 64.0$ c./sec. (MoO₅F₂)²⁻ AX system. $F_{\rm A}$ (non-exchanging) = 58.6 p.p.m. and $F_{\rm X}$ (exchanging) = (approx.) 51.6 p.p.m.

 $(WO_3F_4)^{2^-}AB_2C$ system. $F_A = -14.01$, $F_B = 17.72$, and $F_C = 47.49$ p.p.m.; $J_{AB} = \pm 125$ c./sec., $J_{BC} = \pm 52$ c./sec., $J_{AC} = \pm 71$ c./sec. The AB₂C spectra were calculated with a Mercury computer from the formulæ given by Abraham, Bishop, and Richards.¹⁰



Fluorine-19 resonance spectrum of $[WO_3F_4]^{2-}$ in aqueous solution, at 56.45 Mc./sec., relative to trifluoroacetic acid as external reference; negative values on low-field side of reference. The vertical scale for the B group is about half that for A and C

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¹⁰ Abraham, Bishop, and Richards, Mol. Phys., 1960, 3, 485.