

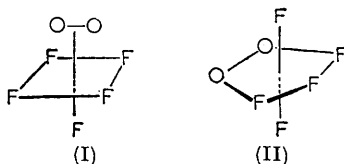
388. Studies on Transition-metal Peroxy-complexes. Part IV.¹ Peroxyfluoro-complexes

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The fluorine magnetic resonance spectra of the ions $(\text{TaO}_2\text{F}_5)^{2-}$, $(\text{MoO}_5\text{F}_2)^{2-}$, and $(\text{WO}_3\text{F}_4)^{2-}$ 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 reported² and are of the form $(\text{M}^{\text{IV}}\text{O}_2\text{F}_5)^{3-}$ ($\text{M} = \text{Ti}$), $(\text{M}^{\text{VO}}\text{O}_2\text{F}_5)^{2-}$ ($\text{M} = \text{Nb}$ or Ta), $(\text{M}^{\text{VI}}\text{O}_3\text{F}_4)^{2-}$ ($\text{M} = \text{W}$ or Mo), $\text{M}^{\text{VI}}\text{O}_5\text{F}_2)^{2-}$ ($\text{M} = \text{Mo}$). Infrared spectra have shown¹ that these complexes have low molecular symmetries, but no definite conclusions could be drawn as to their structures, beyond the demonstration that the $(\text{MO}_3\text{F}_4)^{2-}$ and $(\text{MO}_5\text{F}_2)^{2-}$ 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.

$(\text{TaO}_2\text{F}_5)^{2-}$.—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 $(\text{TaO}_2\text{F}_5)^{2-}$ must have seven co-ordination for which the two most likely structures are (I) and (II). (I) is the C_{2v} structure⁵ found for $\text{K}_2(\text{TaF}_7)$ and⁶ $[\text{Mn}(\text{EDTA})\text{OH}]^-$ and (II) is the pentagonal bipyramidal structure⁷ found for $\text{K}_3(\text{ZrF}_7)$. 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 AX_4 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 $\text{K}_2(\text{TaO}_2\text{F}_5) \cdot \text{H}_2\text{O}$ is not isomorphous with $\text{K}_3(\text{TiO}_2\text{F}_5)$, whereas the latter is isomorphous with $\text{K}_3(\text{ZrF}_7)$, which has a pentagonal bipyramidal anion.⁸ In a solution of $\text{K}_2(\text{NbO}_2\text{F}_5)$ the fluorine-19 lines were very broad, probably owing to exchange

¹ Part III, Griffith, *J.*, 1964, 5248.

² Piccini, *Z. anorg. Chem.*, 1892, **1**, 52; **2**, 21; Balke and Smith, *J. Amer. Chem. Soc.*, 1908, **30**, 1664.

³ Packer and Muettterties, *J. Amer. Chem. Soc.*, 1963, **85**, 3035.

⁴ Muettterties 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.

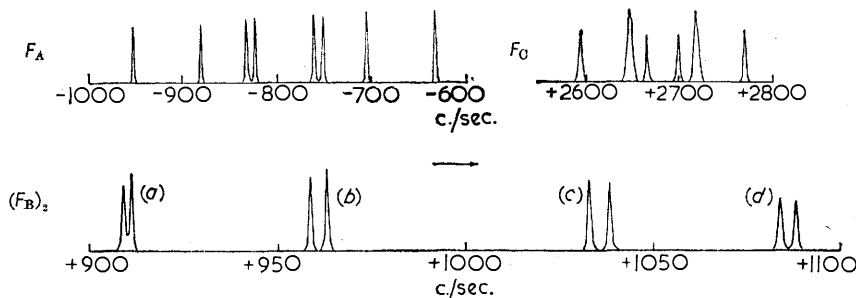
⁸ Peyronel, *Gazzetta*, 1941, **71**, 620.

measured at 56.45 and [for $(\text{WO}_3\text{F}_4)^{2-}$] 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.

$(\text{TaO}_2\text{F}_6)^{2-}$ AX_4 system. $F_A = -65.5$ p.p.m., $F_X = -51.7$ p.p.m.; $J_{\text{AX}} = 64.0$ c./sec.

$(\text{MoO}_5\text{F}_2)^{2-}$ AX system. F_A (non-exchanging) = 58.6 p.p.m. and F_X (exchanging) = (approx.) 51.6 p.p.m.

$(\text{WO}_3\text{F}_4)^{2-}$ AB_2C system. $F_A = -14.01$, $F_B = 17.72$, and $F_C = 47.49$ p.p.m.; $J_{\text{AB}} = \pm 125$ c./sec., $J_{\text{BC}} = \pm 52$ c./sec., $J_{\text{AC}} = \pm 71$ c./sec. The AB_2C spectra were calculated with a Mercury computer from the formulæ given by Abraham, Bishop, and Richards.¹⁰



Fluorine-19 resonance spectrum of $[\text{WO}_3\text{F}_4]^{2-}$ 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.