1005. *Studies on Transition-metal Peroxy-complexes. Part III.*[1]
Peroxy-complexes of Groups IVA, VA, and VIA.

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Infrared and Raman spectra together with molecular-weight measurements and other data have been used to help to elucidate the structures of a number of mono-, di-, and tri-peroxy-complexes.

The nature of the bonding of the peroxide group to metal atoms is discussed, and a " bent bond " scheme suggested.

FOR convenience, the system adopted in Part II [1] is continued of classifying the complexes by their peroxide : metal ratio.

(*a*) 1 : 1 *Peroxy-complexes.*—A wide range of very ill-defined titanium peroxy-complexes appears in the literature. Jere and Patel [2] have reported the infrared spectra of a number of hydrated polymeric peroxy-titanium complexes, and have concluded from their data that two sets of bands near 1000 and 870 cm.[-1] represent, respectively, the asymmetric and symmetric stretching vibrations of the titanium–oxygen bonds in the triangular $Ti(O_2)$ system. Since these assignments differ from those previously suggested in this Series,[1,3] it was decided to examine the infrared spectra of some titanium peroxy-complexes which were less likely to be polymeric, and also to study the spectra of a number of peroxy-fluoro-complexes in which it was hoped that the metal–fluorine vibrations would differ sufficiently in frequency from the metal–peroxide bands in order to render the assignment of the latter easier.

The infrared spectra of $K_2(TiO_2(SO_4)_2),5H_2O$, $K_2[TiO_2(C_2O_4)_2],3H_2O$, and $K_3(TiO_2F_5)$ are reported in Table 1. The sulphato-complex was first prepared pure by Schwarz and Giese; [4] the oxalato-complex is probably identical with the $(K_2C_2O_4,TiO_3)_2,C_2O_3,2H_2O$ of Mazzucchelli,[5] but our analyses fit the simpler formulation above; the fluoro-complex was reported by Piccini [6] as $K_2(TiO_2F_4)$ but his preparation involved contamination of the product with $K_2(TiF_6)$ and oxyfluorides.[7] The formulation $K_3(TiO_2F_5)$ (anhydrous) is confirmed by our analytical data and the fact that the salt is isomorphous with $(NH_4)_3(TiO_2F_5)$; the latter is known to be isomorphous with $(NH_4)_3(ZrF_7)$,[7] and we have confirmed this.

Molecular-weight measurements on $K_3(TiO_2F_5)$ in an ice–water–potassium nitrate eutectic mixture show that the anion is mononuclear in solution (Table 2), while similar measurements on $K_2[TiO_2(C_2O_4)_2]$ show that the anion of this is extensively dissociated in solution. The infrared spectra (Table 1) have, in addition to the absorption normally expected for bidentate oxalate and sulphate groups,[8] intense bands at 862 cm.[-1] for $K_2[TiO_2(SO_4)_2]$, 840 cm.[-1] for $K_2[TiO_2(C_2O_4)_2]$, and 901 cm.[-1] for $K_3(TiO_2F_5)$. Very weak absorption near 1000 cm.[-1] was observed, but since such bands also appear in $K_2[TiO(C_2O_4)_2]$ it seems unnecessary to ascribe them to fundamentals of the peroxide group. The spectra of a number of other peroxyfluorides are also recorded in Table 1 and are very similar to those of $K_3(TiO_2F_5)$; the compounds $K_2(WO_3F_4)$, $K_2(MoO_3F_4)$, and $K_2(MoO_5F_2)$ also have strong bands near 950 cm.[-1] which are likely to be due to a metal–oxygen double bond, so that their structures would be of the form $[M(O_2)(\overset{..}{\cdot}O)F_4]^{2-}$ and $[Mo(O_2)_2(\overset{..}{\cdot}O)F_2]^{2-}$. Complex splitting of the peaks in the metal–fluorine stretching region in $K_3(TiO_2F_5)$ and $K_2[TaO_2F_5]$ is

[1] Part II, *J.*, 1963, 5345.

[2] Jere and Patel, *J. Inorg. Nuclear Chem.*, 1961, **20**, 343; *Canad. J. Chem.*, 1962, **40**, 1576; *Z. anorg. Chem.*, 1962, **319**, 175; Patel and Jere, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1155.

[3] Griffith, *J.*, 1962, 3948; Fergusson, Wilkins, and Young, *J.*, 1962, 2136.

[4] Schwarz and Giese, *Z. anorg. Chem.*, 1928, **176**, 220.

[5] Mazzucchelli, *Gazzetta*, 1907, **37** (II), 545; *Atti Acad. Lincei*, 1907 (5), **16** (II), 265.

[6] Piccini, *Z. anorg. Chem.*, 1895, **10**, 438.

[7] Peyronel, *Gazzetta*, 1941, **71**, 620.

[8] Nakamoto, " Infra-red Spectra of Inorganic and Co-ordination Compounds," Wiley, New York, 1963.

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observed, owing presumably to the low (C_{2v}) symmetry of the complexes. The splitting was partially resolved by using films cooled to liquid-nitrogen temperatures. *X*-Ray powder studies are now in progress on these peroxy fluorides.

TABLE 1.

Infrared and Raman spectra of peroxy-complexes.

Complex	Metal–peroxide group bands	Other bands and suggested partial assignments
$K_2[TiO_2(C_2O_4)_2]$	840s; 615s	1704vs, 1667vs, 1259vs, 1024vw, 904vs, 798vs, 615s, b, 526m, 481b, w (oxalate)
$K_2[TiO_2(SO_4)_2]$	862s; 667m	1250w, 1120s, 1030w, 966 + 938vs, 667m, 615s, 590m (sulphate)
$K_3[TiO_2F_5]$ †	901vs; 597vs	521s,* 510s,* 472s,* 429s * (ν_{Ti-F}); 313vs
$K_4[TaO_2F_5]$	867vs; 634m; 577s	513s, 469s, 459w (ν_{Ta-F})
$K_2[NbO_2F_5]$	929vs; 588b	547vs, 497b, m (ν_{Nb-F})
$K_2[WO_3F_4]$	905vs; 617m, 601s	976 + 954vs ($\nu_{W=O}$), 734w, 617m, 555vs, 516vs, 480m (ν_{W-F}), 439m, b
$K_2[MoO_3F_4]$	933vs, 599vs, 565vs	957vs ($\nu_{Mo=O}$), 734w, 501vs (ν_{Mo-F}), 454w, b
$K_3[MoO_5F_2]$ †	869 + 854vs, 649s, 578s	938vs ($\nu_{Mo=O}$), 734w, 535s, 518s, 493s (ν_{Mo-F}), 283vs
$TiO_3,3H_2O$	856s	3350vs, 1630m, b (H_2O), 1130w, b, 1020w, 620vb
$TiO_3,3D_2O$	856s	2400m, 1230w (D_2O), 1130w, b, 1020w, 620vb
$KNbO_4,7H_2O$	848s	1015vw, 541s, vb
$KNbO_5,2H_2O$ } $NaNbO_5,2H_2O$ }	850vs, 823vs	1028w, 541s, vb
$K_2[Ti(O_2)_3,H_2O]$	825s	990s, 562w
$K_3[TaO_8]$ †	807vs	618vs, 552vs, 527vs, 440vs, 300s
$K_3[NbO_8]$ †	813vs	587vs, 530vs, 439s, 300s, 263s
$K_3[CrO_8]$ †	875s	670m, b, 553vs, 424vs, 294s

All spectra taken in Nujol and hexachlorobutadiene mulls 4000—400 cm.$^{-1}$ except † (4000—200 cm.$^{-1}$); bands due to H_2O not quoted. * Mulls also run at liquid N_2 temperatures (650—400 cm.$^{-1}$).
   Spectra 600—1200 cm.$^{-1}$: $K_4[TiO_8]$, 818vs; $K_4[ZrO_8]$, 854 vs; $K_4[HfO_8]$, 828 vs.
   Raman shifts (solid samples): $K_3[TaO_8]$ (100—1000 cm.$^{-1}$) 184s, 450b, 620b, 820s (strong bands only reported). $K_2[TaO_2F_5]$ (100—1000 cm.$^{-1}$) 190s, 450, 635s, 860m.
   Infrared spectra of related complexes (mulls; 400—4000 cm.$^{-1}$): $K_2[TiO(C_2O_4)_2]$: 1712vs, 1670vs, 1241vs, 1024vw, 902m, 808s, vb, 526s, b, 469w, b. $K_2[NbOF_5]$: 936vs ($\nu_{Nb=O}$), 543vs (ν_{Nb-F}). $K_3[TaF_7]$: 526vs, b (ν_{Ta-F}). $K_2[TiF_6]$: (200—1000 cm.$^{-1}$): 569vs (ν_{Ti-F}).

TABLE 2.

Molecular complexity determinations using a potassium nitrate–ice–water eutectic mixture.

$K_3[TiO_2F_5]$			$K_2[TiO_2(C_2O_4)_2]$			$K_2[Mo_2O_{11}]$		
C	ΔT	n	C	ΔT	n	C	ΔT	n
0·017	0·031	0·9	0·027	0·118	0·4	0·033	0·038	1·5
0·01	0·019	0·9	0·022	0·111	0·3	0·027	0·020	2·2
0·009	0·019	0·8	0·015	0·087	0·3	0·019	0·017	1·9
0·005	0·009	0·9	0·011	0·068	0·3	0·013	0·012	1·8
0·004	0·009	0·8	0·008	0·058	0·25	0·011	0·01	1·8

$K_2[W_2O_{11}]$			$NaNbO_5$		
C	ΔT	n	C	ΔT	n
0·036	0·025	2·4	0·095	0·035	0·5
0·018	0·013	2·3	0·08	0·025	0·5
0·016	0·011	2·4	0·05	0·017	0·5
0·01	0·008	2·1	0·045	0·015	0·5
0·008	0·006	2·3	0·043	0·016	0·45

C = concentration of metal (g.-atom/l.); ΔT = depression (°c); $n = K_0\ C/\Delta T$; $K_0 = 1·68$ (Wiede, *Ber.*, 1897, **30**, 2178).

Infrared Spectra of Monoperoxy-complexes. Taking the metal–peroxide grouping as an isosceles triangle (C_{2v}) and using local symmetry arguments, we expect three infrared- and Raman-active vibrational modes. These are ν_1, the predominantly O–O stretching or

O–M–O deformation vibration (species A_1), the symmetric M–O stretch with some O–O stretching character v_2 (A_1), and the asymmetric M–O stretch v_3 (B_1). The strong bands in the 800—930 cm.$^{-1}$ region observed in all peroxy-complexes are likely to arise from v_1 as they are close to the O–O stretch in hydrogen peroxide at 877 cm.$^{-1}$; thus in the analogous ring systems of cyclopropane,[9] diazirine,[10] and ethylene oxide[11] the frequencies of v_1 are near the normal C≖C, N≎N, and C–C stretches, respectively. For many of the other peroxy-complexes studied (Table 1) one or two other bands in the 500—650 cm.$^{-1}$ region are seen and these are likely to arise from v_3 or possibly v_2 also. Jere and Patel[2] argue that bands in titanium peroxy-complexes near 1000 cm.$^{-1}$ are to be ascribed to v_3, but this seems improbable as they are higher in frequency than v_1, are very weak, and do not appear to be specific to peroxides. Furthermore, they claim that titanium–oxygen single bond stretches are to be found between 1000 and 1150 cm.$^{-1}$ in the spectrum of [Ti(OEt)$_4$][2] but it is clear from more recent work that these must in fact be C–O stretches: thus, in [Ti(OCHMe$_2$)$_4$], the C–O stretching frequency appears at 1005 cm.$^{-1}$ and the Ti–O stretch at 619 cm.$^{-1}$.[12]

Other 1 : 1 *peroxides.* The spectrum of TiO$_3$,3H$_2$O and that of its deuterated form is given in Table 1. It is very similar to that of (TiOF$_2$)$_n$, which has been shown to have this formulation rather than [Ti(OH)$_2$F$_2$],[13] and to other complexes containing the Ti–O–Ti–O– chain. It seems, therefore, that this is a polymer, [Ti(O$_2$)O]$_n$,aq, rather than the simple hydroxy-form [Ti(O$_2$)(OH)$_2$] proposed by Jere and Patel,[2] especially since none of the bands below 1100 cm.$^{-1}$ were shifted by deuteration. The band at 856 cm.$^{-1}$ is assigned to the O–O stretching mode.

The complex KNbO$_4$,nH$_2$O reported by Grigor'eva *et al.*[14] has also been studied. Molecular-weight measurements could not be carried out owing to the insolubility of the compound, but the very strong and broad band at 540 cm.$^{-1}$ suggests that there may well be Nb–O–Nb–O– or Nb–OH–Nb–OH– polymer chains in the complex. Similar broad bands have been reported for alkali-metal niobates.[15] The O–O vibration appears at 848 cm.$^{-1}$; this band does not appear in the spectra of niobates.

(*b*) 2 : 1 *and* 3 : 1 *Peroxy-complexes.*—The complexes KNbO$_4$,H$_2$O$_2$,nH$_2$O and NaNbO$_4$,H$_2$O$_2$,nH$_2$O have been reported recently by Grigor'eva *et al.*[14] The sodium salt is more soluble than the potassium and was used for these studies.

Raman spectra of aqueous solutions of the sodium salt showed no bands at 877 cm.$^{-1}$ due to hydrogen peroxide, though if the compound had contained hydrogen peroxide of crystallisation it should have been present in sufficient concentration to be detected in the Raman. It therefore seems that the peroxide groups are complexed to the niobium atoms. Molecular-weight measurements (Table 2) gave a value close to 0·5 for n, the ratio of the apparent molecular weight to the molecular weight calculated on the assumption that the complex was mononuclear. This result indicates that the anion is mononuclear in solution if complete dissociation to Na$^+$ and NbO$_5^-$ ions is assumed. Titration shows two peroxide groups present to each niobium atoms, as found by Grigor'eva. There are also two molecules of water per niobium in both the sodium and potassium salts, only one of which can be removed *in vacuo* over phosphoric oxide (hydrogen peroxide was not removed under these conditions). The infrared spectra of the compounds are shown in Table 1, and it is of some interest to compare them with that of K$_2$(MoO$_5$F$_2$), which is also a di-peroxide; in the latter case, a strong band at 938 cm.$^{-1}$ is assigned to the Mo=O stretch (see above), but no such band occurs in the niobium complex above 850 cm.$^{-1}$. It is therefore proposed that this compound should be formulated as [Nb(O$_2$)$_2$(OH)$_2$]$^-$,H$_2$O, which accounts for the monomeric nature of the anion, the absence of a Nb=O band and

[9] Wiberg and Nist, *J. Amer. Chem. Soc.*, 1961, **83**, 1226.
[10] Graham, *J. Amer. Chem. Soc.*, 1962, **84**, 1063.
[11] Thompson and Cave, *Trans. Faraday Soc.*, 1951, **43**, 946.
[12] Barraclough, Bradley, Lewis, and Thomas, *J.*, 1961, 2601.
[13] Kharitonov and Buslaev, *Bull. Acad. Sci. U.S.S.R.*, 1962, 366.
[14] Grigor'eva, Selezneva, and Duganova, *Bull. Acad. Sci. U.S.S.R.*, 1962, 875.
[15] Last, *Phys. Rev.*, 1957, **107**, 1740.

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for the easy removal of only one water molecule. The strong band at 540 cm.$^{-1}$, as in the case of the monoperoxy-niobates, probably arises from Nb–OH–Nb–OH– vibrations.

The presence of the Mo=O band in $K_2(MoO_5F_2)$ suggests that this is probably seven co-ordinate with the structure $[Mo(O_2)_2(:O)F_2]^{2-}$ analogous to that of $K_2(Mo_2O_{11})$ and $K_2(W_2O_{11})$. The X-ray crystal structure of the latter salt has recently been determined,[18] and has the structure proposed in Part II [1] with the addition of a molecule of co-ordinated water per tungsten atom to complete the seven co-ordination. It is very likely that $K_2Mo_2O_{11}$ has this structure also; Table 2 gives new molecular-weight data for this complex, and new data for $K_2W_2O_{11}$, since in the previous Paper [1] the *n*-values were incorrectly calculated for this compound. The conclusion that the anions are binuclear is unchanged.

The only established case of a triperoxy-complex is that of a uranium(VI) compound, although perhydrates of diperoxides are known.[1] The decomposition in aqueous solution of tetraperoxytitanate(IV) is found to give a pale yellow triperoxy-complex of titanium(IV),
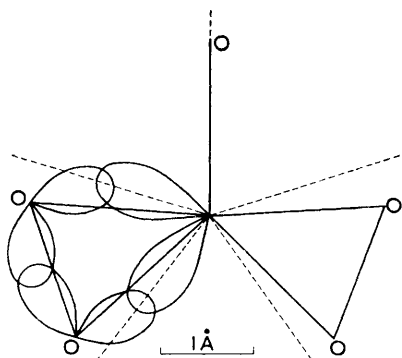

FIG. 1. Pentagonal ring of $K_2W_2O_{11}$.

Solid lines indicate peroxide groups, broken lines normal metal–ligand directions.
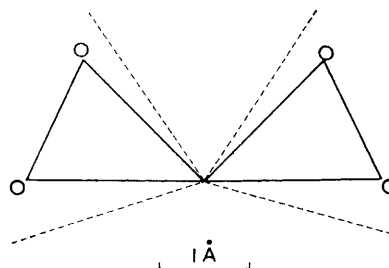
FIG. 2. One of the mirror planes in the D_{2d} structure of $K_3[CrO_8]$.

Solid lines indicate peroxide groups, broken lines normal metal–ligand directions.

which has the stoicheiometry $K_2[Ti(O_2)_3],H_2O$. The infrared spectrum of this complex shows no Ti–O–Ti–O– bands. It is likely that a molecule of water is co-ordinated to the metal atom.

Bonding of the peroxide group. X-Ray studies show that peroxy-complexes have unusual structures: $K_3[CrO_8]$ is dodecahedral (D_{2d});[16] $K_2[W_2O_{11}(H_2O)_2]$ [17] and $[CrO_4(NH_3)_3]$ [18] have pentagonal bipyramidal structures in which the two peroxide groups lie in the pentagonal ring; and $[CrO_5,py]$ [19] is pentagonal pyramidal with both peroxides in the ring. Within the limits of experimental error the MO_2 triangle is isosceles (except for $K_3[CrO_8]$, where the M–O bond lengths differ by about 0·1 Å) [16] and the O–M–O angle is close to 45°.

Tuck and Walters have suggested that the peroxide group bonding ($\pi 2p$) electrons are donated to empty *d* orbitals on the metal atom, and to support this they cite the absorption spectrum of $[CrO_5,py]$ which has bands in the visible with molar extinction cofficients of about 500, which they suggest indicates a distorted tetrahedral structure involving monodentate π-donor peroxide ligands.[20] However, bands of this intensity are

[16] Stomberg, *Acta Chem. Scand.*, 1963, **17**, 1563; Swalen and Ibers, *J. Chem. Phys.*, 1962, **192**, 570; Hoard and Silverton, *Inorg. Chem.*, 1963, **2**, 235.
[17] Einstein and Penfold, *Acta Cryst.*, 1964, **17**, 1127.
[18] Stomberg, *Arkiv Kemi*, 1964, **22**, 49.
[19] Stomberg, *Arkiv Kemi*, 1964, **22**, 29.
[20] Tuck and Walters, *Inorg. Chem.*, 1963, **2**, 428.

common to all peroxy-complexes [21] and in some if not all of these the co-ordination number certainly exceeds four, even if the peroxide were unidentate. Furthermore, the fact that the O–O stretching frequency (ν_1) rises on increasing the electronegativity of the metal atoms by attachment of fluoride ligands (Table 1) is not in accordance with the π-donor theory, since removal of further ($\pi 2p$) density from O_2^{2-} would weaken the O–O bond. The formation of such a bond from O_2^{2-} should cause a slight lengthening of the O–O distance for the same reason, whereas in fact a definite shortening is observed; and finally this model does not explain the unusual stereochemistry of peroxy-complexes.

A " bent-bonding " scheme avoids these difficulties. In undistorted dodecahedral co-ordination, the metal–ligand (A) bond makes an angle of 71° with the metal–ligand (B) bond, as found in $K_4[Mo(CN)_8]$ and $K_4[Zr(C_2O_4)_4]$,[16] and in the undistorted pentagonal pyramid or bipyramid the five metal–ligand orbitals will be at 72° to each other. The structural data available on peroxides show that the O–M–O– (45°) angle of the peroxide group lies neatly between these metal–ligand directions (see Fig. 1). Assuming the metal hybrid orbitals used for σ-bonding in the dodecahedron or pentagonal rings make their normal angles of 71—72°, the σ orbitals on the oxygen atoms in the MO_2 triangles can subtend angles of 15—20° outward from the M–O and O–O directions, the model which has been used to explain the stability of the ring systems of cyclopropane,[22] ethylene oxide, and ethylene sulphide.[23] The angle between the two bonding σ orbitals on each oxygen will now be about 100°, leading to a relatively unstrained configuration.

If such bent bonding occurs, the metal–oxygen and oxygen–oxygen distances should be slightly shorter than normal so that maximum orbital overlap may occur,[22,23] and this is in fact observed. The Cr–O (bridge) distance in $(NH_4)_2[Cr^{VI}_2O_7]$ is 1.91 ± 0.05 Å [24] while in $[CrO_5,py]$ it is 1.81 ± 0.014 Å; [19] the O–O distance in O_2^{2-} (in BaO_2) is 1.49 ± 0.04 Å; [25] in $[CrO_4(NH_3)_3]$ it is 1.429 ± 0.025 Å [18] and in $[CrO_5,py]$ it is 1.404 ± 0.016 Å.[19]

It may be expected that stable peroxide complexes will be found in structures where two or more of the normal metal–ligand bonds are at angles of about 70° to each other. This occurs in the dodecahedral and pentagonal pyramidal structures, and also in the $[TaF_7]^{2-}$ (C_{2v}) structure, where the angle between the two co-ordination positions above the square plane is 75° (in $[Mn(EDTA)OH]^-$),[26] so it is possible that some peroxy-fluorides may have this structure.

EXPERIMENTAL

Potassium peroxydisulphatotitanate(IV), $K_2[TiO_2(SO_4)_2],5H_2O$, was made by Schwarz and Giese's method [4] (Found: K, 18·8; O_2^{2-}, 6·9; S, 14·1. Calc. for $H_{10}K_2TiO_{15}S_2$: K, 17·8; O_2^{2-}, 7·3; S, 14·3%). *Potassium peroxydioxalatotitanate*(IV), $K_2[TiO_2(C_2O_4)_2],3H_2O$, was made by adding an excess of hydrogen peroxide to a solution of potassium titanyl oxalate and adding the deep red solution to alcohol. The yellow precipitate was filtered off and dried with alcohol and ether (Found: K, 20·8; Ti, 13·4; O_2^{2-}, 8·9; C, 11·2; H, 1·7. $H_6K_2TiO_{13}C_4$ requires K, 20·1; Ti, 12·3; O_2^{2-}, 8·3; C, 12·4; H, 1·5%). *Potassium peroxypentafluorotitanate*(IV), $K_3(TiO_2F_5)$, was prepared by treating potassium hexafluorotitanate with an excess of 30% hydrogen peroxide in the presence of a slight excess of potassium hydroxide; it is important that the temperature is not allowed to exceed 45°. The mixture was slowly cooled and the yellow crystals of the salt were recrystallised from 6% hydrogen peroxide (Found: K, 39·6; Ti, 15·8; O_2^{2-}, 11·1; F, 32·1. $K_3TiO_2F_5$ requires K, 40·1; Ti, 16·4; O_2^{2-}, 11·0; F, 32·5%). The corresponding ammonium salt, $(NH_4)_3(TiO_2F_5)$, was made by the method of Schwarz and Giese [4] (Found: N, 18·5; Ti, 21·0; O_2^{2-}, 13·6. Calc. for $H_{12}N_3TiO_2F_5$: N, 18·4; Ti, 20·9; O_2^{2-}, 13·9%). Titanium peroxyoxyhydrate, $[Ti(O_2)O]_n,3nH_2O$, was made by the procedure of Jere and Patel [2]

[21] Palille, Adler, and Hiskey, *Analyt. Chem.*, 1953, **25**, 926.
[22] Coulson and Goodwin, *J.*, 1962, 2851; Coulson and Moffitt, *Phil. Mag.*, 1949, **40**, 1.
[23] Cunningham, Boyd, Myers, and Gwinn, *J. Chem. Phys.*, 1951, **19**, 676.
[24] Bystrom and Wilhelmi, *Acta Chem. Scand.*, 1951, **5**, 1003.
[25] Abrahams and Kalnajs, *Acta Cryst.*, 1954, **7**, 838.
[26] Richards, Pedersen, Silverton, and Hoard, *Inorg. Chem.*, 1964, **3**, 27.

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(Found: Ti, 30·8; O_2^{2-}, 20·7. Calc. for H_6TiO_6: Ti, 31·9; O_2^{2-}, 21·3%). The deutero form was made by using heavy water in excess with the minimum amount of 30% hydrogen peroxide. Potassium peroxyniobate(v), $K(NbO_4),7H_2O$, was made by the method of Grigor'eva *et al.*[14] (Found: K, 11·2; O_2^{2-}, 10·1. Calc. for $H_{14}KNbO_{11}$: K, 12·1; O_2^{2-}, 9·9%). Potassium peroxypentafluoroniobate(v), $K_2(NbO_2F_5),H_2O$, was made by the method of Piccini[27] (Found: K, 24·7; O_2^{2-}, 13·9; H_2O, 5·6; F, 30·1. Calc. for $H_2K_2NbO_3F_5$: K, 24·7; O_2^{2-}, 12·8; H_2O, 5·7; F, 30·0%).

Potassium peroxypentafluorotantalate, $K_2(TaO_2F_5),H_2O$, was made by the method of Balke and Smith[28] (Found: K, 19·9; O_2^{2-}, 8·0; F, 24·5; H_2O, 4·2. Calc. for $H_2K_2TaO_3F_5$: K, 19·4; O_2^{2-}, 7·9; F, 23·5; H_2O, 4·4%).

Potassium oxyperoxytetrafluoromolybdate(vi), $K_2(MoO_3F_4),H_2O$, was made by the method of Piccini[29] (Found: K, 24·8; O_2^{2-}, 10·2; F, 22·4; H_2O, 6·6. Calc. for $H_2K_2MoO_4F_4$: K, 24·7; O_2^{2-}, 10·1; F, 24·0; H_2O, 5·7%). Potassium oxyperoxytungstate(vi), $K_2(WO_3F_4),H_2O$, was made by the method of Piccini[27] (Found: K, 18·4; O_2^{2-}, 8·0; F, 19·0; H_2O, 5·0. Calc. for $H_2K_2WO_4F_4$: K, 19·3; O_2^{2-}, 7·9; F, 18·8; H_2O, 4·5%).

Potassium diperoxyniobate(v), $K(NbO_5),2H_2O$, was made by the method of Grigor'eva[14] (Found: K, 14·3; O_2^{2-}, 25·8; Nb, 38·1; H_2O, 8·5. Calc. for H_4KNbO_6: K, 15·7; O_2^{2-}, 25·8; Nb, 37·5; H_2O (1 mole), 7·3%). The sodium salt was made by the same method[14] (Found: O_2^{2-}, 27·1; Nb, 40·1; H_2O, 8·4. Calc. for H_4NaNbO_7: O_2^{2-}, 27·6; Nb, 40·1; H_2O (1 mole), 7·8%).

Potassium oxydiperoxydifluoromolybdate(vi), $K_2(MoO_5F_2),H_2O$, was made by recrystallising $K_2(MoO_3F_4),H_2O$ twice from 6% hydrogen peroxide (Found: K, 25·0; Mo, 30·1; O_2^{2-}, 21·5; F, 7·8; H_2O, 6·6. Calc. for $H_2K_2MoO_6F_2$: K, 25·2; Mo, 30·9; O_2^{2-}, 20·6; F, 7·7; H_2O, 5·8%).

Potassium triperoxytitanate(iv), $K_2[Ti(O_2)_3],4H_2O$, was made by allowing an aqueous solution of $K_4(TiO_8),6H_2O$ to stand for 6 hr. at room temperature. The product was then isolated by adding the solution to ethanol, filtering off the pale yellow product, and drying it with alcohol and ether (Found: K, 26·6; Ti, 17·9; O_2^{2-}, 32·7. $H_8TiK_2O_{10}$ requires K, 26·6; Ti, 16·3; O_2^{2-}, 32·7%).

Analyses.—Potassium was analysed as the tetraphenylboronate, titanium colorimetrically as the peroxide in acid solution, niobium and zirconium gravimetrically as the oxides. Sulphur, carbon, hydrogen, nitrogen, and fluorine were analysed by the Microanalytical Laboratory of this Department.

Spectra were taken on a Grubb–Parsons Spectromaster (400—4000 cm.$^{-1}$), a Grubb–Parsons D.M. far-infrared spectrophotometer (200—450 cm.$^{-1}$), and a Cary model 81 Raman spectrophotometer. Nujol mulls were used for infrared spectra.

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