

**1020. Studies on Transition-metal Peroxy-complexes. Part II.<sup>1</sup>  
Permolybdates and Pertungstates.**

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The structures of the tetraperoxy-dimolybdate and -ditungstate anions have been investigated by means of molecular-weight measurements and by infrared and Raman studies of solid samples and aqueous solutions. The results indicate that the basic formula of these compounds is  $(M_2O_{11})^{2-}$ . Studies on a number of other peroxy-complexes are also reported.

A LARGE number of anionic peroxy-complexes of molybdenum and tungsten have been reported. Although many of the early reports are conflicting, it now seems clear that, in strongly basic solutions, molybdates and tungstates react with an excess of hydrogen peroxide to give the tetraperoxy-species  $(MO_3)^{2-}$  and that in these conditions no other peroxy-compounds are formed. The nature of the products from corresponding reactions in neutral and in acid media is by no means as clear: there have been reports of polynuclear ions as well as of such species as  $(MO_7)^{2-}$ ,  $(MO_6)^{2-}$ ,  $(MO_5)^{2-}$ , and  $(MO_4)^-$ . This paper is concerned chiefly with the complexes in which the peroxide : metal ratio is 2 : 1.

(a) 2 : 1 Permolybdates and Pertungstates.—The complexes obtained by treating acidic solutions ( $\sim N$ ) of molybdates and tungstates with hydrogen peroxide have been variously formulated as containing the  $(M_2O_8)^{2-}$ ,<sup>2</sup>  $(M_2O_9)^{2-}$ ,<sup>3</sup> and  $(MHO_6)^-$  ions, but work by Jahr *et al.*<sup>4</sup> established that the peroxide : metal ratio was 2 : 1, so that they should be formulated as  $(HMO_6)^-$  or as  $(M_2O_{11})^{2-}$ . Dialysis measurements favoured the mononuclear formulation,<sup>4</sup> but cryoscopic determinations on solutions of tungstate ion in hydrogen peroxide under varying conditions of pH indicated that the species was binuclear.<sup>5</sup> More recently, Csanyi<sup>6</sup> reviewed Souchay's<sup>5</sup> cryoscopic work and concluded that the pertungstate ion was mononuclear. Fergusson *et al.*<sup>7</sup> state in a recent paper that the ions are mononuclear but give no evidence for this, while Richardson<sup>8</sup> could find no evidence from conductance measurements for the existence of 2 : 1 peroxytungstates, but concluded that 2 : 1 permolybdates did exist.

*Stoichiometry and molecularity of the complexes.* It is clear that the 2 : 1 permolybdates

<sup>1</sup> Part I, *J.*, 1962, 3948.

<sup>2</sup> Pechard, *Compt. rend.*, 1891, **112**, 1060.

<sup>3</sup> Pissarjewsky, *Z. anorg. Chem.*, 1903, **24**, 108.

<sup>4</sup> Jahr and Lothar, *Ber.*, 1938, **71**, 894, 903, 1127; Jahr, *Ber., Freund. Techn. Hochschule, Berlin*, 1939, 91; Jahr, *Angew. Chem.*, 1940, **53**, 20.

<sup>5</sup> Souchay, *Bull. Soc. chim. France*, 1949, 122; Jahr and Blanke, *Z. anorg. Chem.*, 1953, **272**, 45; Tridot, *Ann. Chim. (France)*, 1955, **10**, 255; Souchay, Chauveau, and Tridot, *Bull. Soc. chim. France*, 1955, 1519.

<sup>6</sup> Csanyi, *Acta Chim. Acad. Sci. Hung.*, 1958, **14**, 69.

<sup>7</sup> Fergusson, Wilkins, and Young, *J.*, 1962, 2136.

<sup>8</sup> Richardson, *J. Less Common Metals*, 1960, **2**, 360.

and pertungstates differ considerably from the formally analogous perchromates,  $(\text{HCrO}_6)^{-1}$ . They are much more stable, are not decomposed by water, and are formed in strongly acid solutions, whereas the perchromates are formed only in neutral or slightly acid solutions.

Analyses confirm the presence of two peroxide groups per metal atom in the potassium salts; the data correspond to the stoichiometries,  $\text{K}_2\text{Mo}_2\text{O}_{11}\cdot 3\text{H}_2\text{O}$  and  $\text{K}_2\text{W}_2\text{O}_{11}\cdot 3\text{H}_2\text{O}$ , and in the case of the pertungstate the water of crystallisation may be removed by dehydration over phosphorus pentoxide. The compounds are diamagnetic and must consequently contain hexavalent molybdenum and tungsten.

Conductometric and spectral data show that these complexes are less polymeric in acid solution than the parent molybdate and tungstate species.<sup>5,6,8</sup> Direct molecularity measurements with solutions of the pure complexes have not been made previously; the results of such determinations are given in Table 1. The technique used was to observe

TABLE I.  
Molecularity measurements of potassium pertungstate.

c (g. atoms of $W/1.$ )	$\Delta T$ Temp.	$c/\Delta T (= k/n)$	$n (= K_0\Delta T/k)$	c (g. atoms of $W/1.$ )	$\Delta T$ Temp.	$c/\Delta T (= k/n)$	$n (= K_0\Delta T/k)$
0.048	0.055	0.87	1.93	0.015	0.019	0.79	2.12
0.0325	0.04	0.81	2.08	0.013	0.017	0.76	2.2
0.026	0.034	0.76	2.2	0.013	0.018	0.72	2.3
0.022	0.03	0.72	2.3	0.011	0.012	0.92	1.84

$$K_0 = 1.68 \text{ (Wiede, Ber., 1897, 30, 2178).}$$

$k$  = molar depression constant ( $K_0$  at infinite dilution).

the depression in eutectic point of an ice-water-potassium nitrate mixture: this method has the advantage of measuring the molecularity of the anion alone, potassium being a common cation.<sup>9</sup> The results indicate that the pertungstate anion is binuclear (similar measurements<sup>1</sup> on the perchromate ion indicated that this was mononuclear). Owing to the low solubility of potassium permolybdate in the eutectic mixture, it was possible to obtain measurements only at very low concentrations, but these indicated that the anion was also binuclear.

*Spectroscopic measurements.* Infrared measurements (Table 2) support the binuclear formulation: the spectra of the anhydrous potassium permolybdate and pertungstate show no absorption in the 2000–4000  $\text{cm}^{-1}$  region (where O–H stretching modes should occur) or near 1600  $\text{cm}^{-1}$  (where the H–O–H deformation mode occurs). Hence the  $\text{K}(\text{HMO}_6)$  formulation must be incorrect, since the proton is likely to be associated with the oxygen atom of an oxy- or peroxy-group and should therefore give rise to an O–H stretching vibration. [In contrast,  $\text{K}(\text{HCrO}_6)$  has a strong band at 3500  $\text{cm}^{-1}$ .<sup>1</sup>] The Raman spectrum of the salt  $\text{Na}_2(\text{W}_2\text{O}_{11})$  in aqueous solution (Table 2) demonstrates that these are true peroxy-complexes and not perhydrates; if they contained hydrogen peroxide of crystallisation a strong band should appear at 877  $\text{cm}^{-1}$  arising from the O–O stretching mode of free hydrogen peroxide.

*Structure of the permolybdate and pertungstate ions.* Analytical data, molecular-weight determinations, and spectroscopic measurements all suggest that the correct formulation for these ions is  $(\text{M}_2\text{O}_{11})^{2-}$ . If we assume that the peroxide group is bonded in a side-on position to the metal atom, as it is in other peroxy-complexes,<sup>10</sup> the most likely structures are those in which two  $\text{MO}_5$  groups are linked by a single oxygen atom; if one regards the peroxide group as forming two bonds to the metal, there will be distorted octahedral co-ordination about each metal atom. It is unlikely that the M–O–M linking chain is linear, and also the coincidence of most of the infrared and Raman bands excludes the possibility of there being a centre of symmetry in the molecule. A structure based on

<sup>9</sup> Jahr, Brechlin, Blanke, and Rubens, *Z. Anorg. Chem.*, 1952, **270**, 240; Jander and Ertel, *J. Inorg. Nuclear Chem.*, 1956, **3**, 149.

<sup>10</sup> Stromber and Brosset, *Acta Cryst.*, 1960, **14**, 441; Swalen and Ibers, *J. Chem. Phys.*, 1962, **37**, 17.

TABLE 2.

K[CrHO <sub>8</sub> ]		K <sub>2</sub> [Mo <sub>2</sub> O <sub>11</sub> ]		K <sub>2</sub> [W <sub>2</sub> O <sub>11</sub> ]			Assignment
Mull	D <sub>2</sub> O solution	Mull	D <sub>2</sub> O solution	Mull	D <sub>2</sub> O solution	Raman	
		971s		963s			} M=O stretch
924s	926vs	961s	961vs	960s	957vs	961vs	
		953s		946s			} O-O stretch
876s	875vs	861s	862vs	860s	841vs		
		847s		836s		854vs	} M-O-M antisym. stretch
		700s, b *		750s, b *	750b	750w	
		580s *		530m, b *		620m, b	} M-O-M symmetric stretch
		353s †		357s †		556s	
		292vs †		330s, b †		326vs	} Deformation mode
		245vs †		294vs †			
		250vs †		250vs †			} Deformation mode
K <sub>2</sub> CrO <sub>8</sub>		K <sub>3</sub> NbO <sub>8</sub>					
Mull	D <sub>2</sub> O solution	Mull	D <sub>2</sub> O solution	Raman			
875s	877vs	818vs	823vs	820s			O-O stretch
670m, b*							
553*s, 424vs†, 294s†		587s*, 530*s, 439†, 300s†, 263†s					

Spectra taken with NaCl optics (650—4000 cm.<sup>-1</sup>) except \* KBr optics (400—650 cm.<sup>-1</sup>) and † far-infrared grating (200—450 cm.<sup>-1</sup>). Raman spectra over the 300—1200 cm.<sup>-1</sup> range for Na<sub>2</sub>W<sub>2</sub>O<sub>11</sub> and 800—1000 cm.<sup>-1</sup> for K<sub>3</sub>NbO<sub>8</sub>.

K<sub>2</sub>MoO<sub>8</sub>: 845vs. K<sub>2</sub>WO<sub>8</sub>: 818vs.

(pyH)<sub>2</sub>[Mo<sub>2</sub>O<sub>11</sub>].H<sub>2</sub>O (from 650 to 2000 cm.<sup>-1</sup>): 1628m, 1607m, 1530m, 1247m, 1197m, 940vs, 890vs, 832s, 757s.

(pyH)<sub>2</sub>[W<sub>2</sub>O<sub>11</sub>].3H<sub>2</sub>O (from 650 to 2000 cm.<sup>-1</sup>): 1650m, 1623s, 1547s, 1260m, 1214m, 965vs, 855m, 833vs, 770vs, 760vs.

that of dichromate ion is proposed, in which the M-O-M angle is less than 180° because of the presence of lone-pairs on the bridging oxygen atom, and in which four of the doubly bonded oxygen atoms in the dichromate-type structure are replaced by four " bidentate " peroxide groups.

*Assignments of bands in the spectra.* Considered as a whole, the (W<sub>2</sub>O<sub>11</sub>)<sup>2-</sup> ion should have thirty-three fundamental modes of vibration, but a reasonable simplifying assumption is that the system may be treated by the methods of local symmetry since the metal atoms have a far greater mass than the ligands. On this basis it may be represented as two equivalent WO<sub>5</sub> groups (point group C<sub>s</sub> or C<sub>1</sub>), associated with twelve fundamental vibrational modes which will be active both in the infrared and Raman region, and as the W-O-W grouping, which will have three fundamentals active both in the infrared and Raman region if the chain is bent.

There will be one W=O stretching vibration, and the band at 957 (infrared) and 961 cm.<sup>-1</sup> (Raman) is assigned to this mode: this compares with a ν<sub>1</sub> of 931 cm.<sup>-1</sup> for the (WO<sub>4</sub>)<sup>2-</sup> ion.<sup>11</sup> The strong infrared and Raman band at 841 and 854 cm.<sup>-1</sup> is assigned to a predominantly O-O stretching vibration; as in the case of the C=C stretching mode in platinous ethylene complexes, this will be activated in the infrared spectrum owing to the one-sided perturbing effect of the metal atom;<sup>12</sup> only one band is observed as the degree of coupling between the two peroxy-groups bonded to each metal is likely to be small owing to the large mass of the tungsten atom. The bands at 750 and 556 cm.<sup>-1</sup> may be attributed to the antisymmetric and symmetric W-O-W stretching modes (the corresponding frequencies in dichromate ion<sup>13</sup> are at 772 and 558 cm.<sup>-1</sup>). On this assumption,

<sup>11</sup> Woodward and Roberts, *Trans. Faraday Soc.*, 1956, **52**, 615.

<sup>12</sup> Powell and Sheppard, *Spectrochim. Acta*, 1958, **13**, 69; *J.*, 1960, 2519.

<sup>13</sup> Stammreich, Bassi, Sala, and Siebert, *Spectrochim. Acta*, 1958, **13**, 192; Dupusi and Viltange, *Compt. rend.*, 1962, **255**, 2582.

it is significant that the intensity of the antisymmetric infrared stretching band is greater than that of the symmetric band, while the reverse is true in the Raman effect (in dichromate spectra these pairs of bands are of comparable strength); this may indicate that the W-O-W angle is larger than the corresponding angle in dichromate, owing perhaps to the bulkiness of the peroxide groups. If this angle were to be unusually large the symmetric W-O-W stretch would produce only a small dipole change and its activity in the infrared region would be correspondingly diminished; in the case of disilyl ether, where the Si-O-Si angle is as large as  $140^\circ$ , the symmetric stretch is not observed in the infrared spectrum at all, and the antisymmetric stretch is active only in the infrared region.<sup>14</sup>

(b) *Other 2 : 1 Permolybdates and Pertungstates.*—A number of salts of the  $(\text{MO}_6)^{2-}$  ion have been reported: e.g.,  $\text{Na}_2(\text{MoO}_6)$  is claimed as a decomposition product of  $\text{Na}_2(\text{MoO}_8)$ ,<sup>15</sup> and salts of  $(\text{WO}_6)^{2-}$  and  $(\text{MoO}_6)^{2-}$  are alleged to be formed by the action of hydrogen peroxide on molybdates and tungstates.<sup>16</sup> Since these species are precipitated from basic solution they may well contain the mononuclear  $(\text{MO}_6)^{2-}$  ions, although Csanyi<sup>6</sup> regards them as derivatives of  $\text{MoO}_2(\text{OO}^-)(\text{OOH})$ . It seems likely that the decomposition of the salt  $\text{Na}_2(\text{MoO}_8)$  yields a mixture of  $\text{Na}_2(\text{Mo}_2\text{O}_{11})$  and  $\text{NaOH}$ —our analyses of the products gave variable results. Pyridinium complexes of the form  $\text{pyH}_2(\text{MoO}_6)$  and  $\text{pyH}_2(\text{WO}_6)$  have been reported;<sup>17</sup> they are made by the action of hydrogen peroxide on acid solutions of molybdates and tungstates containing the pyridinium ion. The infrared spectra of these complexes (Table 2) have bands which are typical of the  $(\text{pyH})^+$  ion rather than of co-ordinated pyridine groups, according to the criteria of Gill *et al.*<sup>18</sup> The compounds have ultraviolet spectra which are almost identical with those of the corresponding potassium salts (above  $260 \text{ m}\mu$ ), and it seems likely that these are in fact better formulated as  $(\text{pyH})_2[\text{Mo}_2\text{O}_{11}]$  and  $(\text{pyH})_2[\text{W}_2\text{O}_{11}]$ .

(c) *3 : 1 and 4 : 1 Permolybdates and Pertungstates.*—There is little evidence for the existence of true 3 : 1 permolybdates and pertungstates. The salt  $\text{Na}_2(\text{MoO}_7)$  reported by Melikoff and Pissarjewsky<sup>19</sup> is identical in properties with  $\text{Na}_2(\text{MoO}_8)$ ; the complex  $\text{Sr}(\text{MoO}_7)\cdot 4\text{H}_2\text{O}$  is believed to be  $\text{SrMoO}_6\cdot \text{H}_2\text{O}_2\cdot 3\text{H}_2\text{O}$ .<sup>16</sup> It has recently been claimed that compounds  $\text{pyH}_2(\text{MoO}_7)$  and  $\text{pyH}_2(\text{WO}_7)$  are true 3 : 1 per-complexes;<sup>17</sup> the preparations have been repeated but only the molybdenum compound could be obtained with a peroxide : metal ratio of 3 : 1 (the tungsten product has a 2.5 : 1 ratio). In both cases the peroxy-groups were easily removable *in vacuo* to leave, in both cases, the  $(\text{pyH})_2(\text{M}_2\text{O}_{11})$  species. The infrared and the ultraviolet absorption spectra are identical with those of  $(\text{pyH})_2(\text{Mo}_2\text{O}_{11})$  and  $(\text{pyH})_2(\text{W}_2\text{O}_{11})$ , and it seems likely from the chemical properties and analyses that they simply contain molecules of hydrogen peroxide of crystallisation, replacing water in the  $(\text{pyH})_2(\text{M}_2\text{O}_{11})$  compounds: thus, from  $(\text{pyH})_2(\text{Mo}_2\text{O}_{11})\cdot \text{H}_2\text{O}$  the perhydrate  $(\text{pyH})_2(\text{MoO}_{11})\cdot 2\text{H}_2\text{O}_2$  is formed, and from  $(\text{pyH})_2(\text{W}_2\text{O}_{11})\cdot 3\text{H}_2\text{O}$ , only one water molecule is replaced to give  $(\text{pyH})_2(\text{W}_2\text{O}_{11})\cdot \text{H}_2\text{O}_2\cdot 2\text{H}_2\text{O}$ .

The infrared spectra of a number of tetraperoxy-complexes have already been reported.<sup>1,7</sup> The outstanding feature is a sharp, intense band in the  $800\text{--}900 \text{ cm.}^{-1}$  region; in the case of the niobate  $\text{K}_3\text{NbO}_8$  this band is also Raman-active (Table 2) (Raman spectra could not be taken of the salt  $\text{K}_3\text{CrO}_8$  owing to its yellow colour in solution, but  $\text{K}_3\text{NbO}_8$  and  $\text{K}_3\text{CrO}_8$  are isomorphous.<sup>7,20</sup>) The Raman spectrum also shows that

<sup>14</sup> Lord, Robinson, and Schumb, *J. Amer. Chem. Soc.*, 1956, **78**, 1327; Ebsworth, Taylor, and Woodward, *Trans. Faraday Soc.*, 1959, **55**, 211; McKern, Taylor, and Woodward, *Proc. Chem. Soc.*, 1959, 321.

<sup>15</sup> Kobosev and Sokolov, *Z. anorg. Chem.*, 1933, **214**, 324; *Zhur. fiz. Khim.*, 1933, **4**, Nos. 3 and 4.

<sup>16</sup> Bogdanov, Berkenzeim, and Prokhorova, *Zhur. fiz. Khim.*, 1956, **30**, 1223; Scherbinin and Bogdanov, *Russ. J. Inorg. Chem.*, 1959, **4**, 112.

<sup>17</sup> Beiles, Safina, and Beiles, *Russ. J. Inorg. Chem.*, 1961, **6**, 825.

<sup>18</sup> Gill, Nuttall, Scaife, and Sharp, *J. Inorg. Nuclear Chem.*, 1961, **18**, 79.

<sup>19</sup> Melikoff and Pissarjewsky, *Z. anorg. Chem.*, 1898, **18**, 79.

<sup>20</sup> Bohm, *Z. Krist.*, 1926, **63**, 319.

no free peroxide is present in solution, there being no band at 877  $\text{cm}^{-1}$ . These high-frequency bands in tetraperoxy-complexes are assigned to predominantly O—O stretching modes (they lie very close to the O—O stretch of hydrogen peroxide itself, at 877  $\text{cm}^{-1}$ ); again, only one band is seen, owing to lack of coupling between peroxy-group stretches. The lower-frequency bands are to be associated with M—O stretching and bending modes.

## EXPERIMENTAL

*Salts.*—Potassium tetraperoxydioxymolybdate(vi),  $\text{K}_2\text{Mo}_2\text{O}_{11}\cdot 3\text{H}_2\text{O}$ , was prepared as pale yellow crystals by Jahr's method<sup>4</sup> (Found: K, 15.1; Mo, 39.1;  $\text{O}_2^{2-}$ , 25.7.  $\text{H}_6\text{K}_2\text{Mo}_2\text{O}_{14}$  requires K, 15.6; Mo, 38.4;  $\text{O}_2^{2-}$ , 25.6%). An aqueous solution of the complex had  $\lambda_{\text{max}}$  311 ( $\epsilon$  1400) and 237  $\text{m}\mu$  ( $\epsilon$  4000).

Potassium tetraperoxydioxytungstate(vi),  $\text{K}_2\text{W}_2\text{O}_{11}\cdot 3\text{H}_2\text{O}$ , was prepared as white crystals by Jahr's method<sup>4</sup> (Found: K, 11.2; W, 54.6;  $\text{O}_2^{2-}$ , 18.9;  $\text{H}_2\text{O}$ , 7.9.  $\text{H}_6\text{K}_2\text{O}_{14}\text{W}_2$  requires K, 11.6; W, 54.3;  $\text{O}_2^{2-}$ , 18.9;  $\text{H}_2\text{O}$ , 8.0%).

Dehydration *in vacuo* over phosphorus pentoxide or by gentle heating gave the anhydrous product (Found: K, 11.6;  $\text{O}_2^{2-}$ , 20.6.  $\text{K}_2\text{W}_2\text{O}_{11}$  requires K, 12.6;  $\text{O}_2^{2-}$ , 20.6%). An aqueous solution had  $\lambda_{\text{max}}$  238  $\text{m}\mu$  ( $\epsilon$  2500).

Dipyridinium tetraperoxydioxymolybdate(vi),  $(\text{pyH})_2\text{Mo}_2\text{O}_{11}\cdot \text{H}_2\text{O}$ , was made by the method of Beiles and Safina<sup>17</sup> (Found: C, 21.5; H, 3.0; N, 4.7; Mo, 36.1;  $\text{O}_2^{2-}$ , 23.2.  $\text{C}_{10}\text{H}_{14}\text{Mo}_2\text{N}_2\text{O}_{12}$  requires C, 21.3; H, 3.2; N, 4.6; Mo, 35.2;  $\text{O}_2^{2-}$ , 23.1%). There was one band in the ultraviolet spectrum of the complex above 260  $\text{m}\mu$ , at 311  $\text{m}\mu$  ( $\epsilon$  1200).

Dipyridinium tetraperoxydioxymolybdate(vi) perhydrate,  $(\text{pyH})_2\text{Mo}_2\text{O}_{11}\cdot 2\text{H}_2\text{O}$ , was prepared by the procedure of Beiles and Safina<sup>17</sup> (Found: C, 21.0; H, 3.0; N, 4.7;  $\text{O}_2^{2-}$ , 32.8.  $\text{C}_{10}\text{H}_{13}\text{Mo}_2\text{N}_2\text{O}_{15}$  requires C, 20.2; H, 2.7; N, 4.7;  $\text{O}_2^{2-}$ , 32.2%); the ultraviolet spectrum was identical with that of the previous compound.

Dipyridinium tetraperoxydioxytungstate(vi),  $(\text{pyH})_2\text{W}_2\text{O}_{11}\cdot 3\text{H}_2\text{O}$ , was prepared by the method of Beiles and Safina<sup>17</sup> (Found: C, 16.6; H, 2.2; N, 3.8;  $\text{O}_2^{2-}$ , 16.7.  $\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_{14}\text{W}_2$  requires C, 15.8; H, 2.4; N, 3.7;  $\text{O}_2^{2-}$ , 16.9%). Any absorption due to the peroxy-complex was obscured by the pyridinium charge-transfer bands below 260  $\text{m}\mu$ .

Dipyridinium tetraperoxydioxytungstate(vi) perhydrate,  $(\text{pyH})_2\text{W}_2\text{O}_{11}\cdot \text{H}_2\text{O}\cdot 2\text{H}_2\text{O}$ , was prepared by the method of Beiles and Safina<sup>17</sup> (Found: C, 16.5; H, 2.6; N, 3.8;  $\text{O}_2^{2-}$ , 19.5.  $\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_{15}\text{W}_2$  requires C, 15.3; H, 2.3; N, 3.6;  $\text{O}_2^{2-}$ , 20.7%).

Violet potassium perchromate,  $\text{K}[\text{Cr}(\text{OH})(\text{O}_2)_2\text{O}]$  was prepared as described previously<sup>1</sup> (Found: K, 20.0; Cr, 27.2. Calc. for  $\text{HKCrO}_6$ : K, 20.8; Cr, 27.6%).

Potassium perchromate,  $\text{K}_3\text{CrO}_8$ , was prepared by Reisenfeld's method<sup>21</sup> (Found: K, 39.9; Cr, 17.7. Calc. for  $\text{K}_3\text{CrO}_8$ : K, 39.5; Cr, 17.5%).

Potassium perniobate,  $\text{K}_3\text{NbO}_8\cdot 3\text{H}_2\text{O}$ , was prepared by the method of Balke and Smith<sup>22</sup> (Found: Nb, 24.0. Calc. for  $\text{H}_6\text{K}_3\text{NbO}_{11}$ : Nb, 24.0%).

Potassium permolybdate and pertungstate,  $\text{K}_2\text{MoO}_8$  and  $\text{K}_2\text{WO}_8$ . These were made by adding an excess of hydrogen peroxide to alkaline solutions of molybdate and tungstate at  $-5^\circ$ . They were explosive, in the case of the tungsten compound dangerously so.

*Analyses.*—Potassium was estimated gravimetrically as the tetraphenylboronate, niobium as the pentoxide, chromium and molybdenum spectrophotometrically as the peroxides, tungsten spectrophotometrically as the oxythiocyanato-complex, and peroxide by titration with permanganate. Microanalyses of carbon, nitrogen, and hydrogen were performed by the Microanalytical Department. Infrared spectra were taken on a Perkin-Elmer model 21 recording instrument with sodium chloride and potassium bromide optics;  $\text{D}_2\text{O}$  solution spectra were taken on solution films between silver chloride plates. Raman spectra were taken on a 3M-solution of  $\text{Na}_2\text{W}_2\text{O}_{11}$  in a 10-cm. cell on a Carey recording instrument; far-infrared spectra were taken of Nujol mulls of the complexes, with Polythene plates on a Grubb-Parsons recording instrument. Ultraviolet spectra were taken on a Perkin-Elmer recording spectrophotometer.

<sup>21</sup> Reisenfeld, *Z. Anorg. Chem.*, 1912, **74**, 48.

<sup>22</sup> Balke and Smith, *J. Amer. Chem. Soc.*, 1908, **30**, 1648.

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