

Contribution from the Department of Chemistry,  
Georgetown University, Washington, D. C. 20007**Tungstovanadate Heteropoly Complexes. IV. Vanadium(IV) Complexes**C. M. FLYNN, Jr., and M. T. POPE\*<sup>1</sup>

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Three tungstovanadate(IV) heteropoly anions have been isolated as several crystalline salts and characterized by elemental analysis, chemical reaction studies, X-ray diffraction, and infrared, optical, and esr spectroscopy. Pinkish purple  $V^{IV}W_5O_{19}^{4-}$  (stable at pH 5–6) and brown-orange  $H_nV^{IV}W_4O_{19}^{-(6+n)}$  (stable at pH 7–8) appear to possess the Lindqvist-Aronsson  $Nb_6O_{19}^{8-}$ -type structure. Dull wine red  $H_2W_{11}V^{IV}O_{40}^{8-}$  is stable at pH 4–7; the data point to a Keggin structure related to metatungstate. The optical spectra show the three complexes to be analogs of heteropoly blue species, with low-energy intervalence charge transfer as well as the expected d-d transitions. The chemical reactions of the complexes are schematized. A new preparation of metatungstate is also described.

**Introduction**

Recent investigations of tungstovanadates<sup>2,3</sup> have demonstrated the existence of the vanadium(V) complexes  $V_2W_4O_{19}^{4-}$ ,  $VW_5O_{19}^{3-}$ ,  $V_3W_{10}O_{40}^{5-}$ ,  $V_4W_9O_{40}^{6-}$  (formerly thought to be  $V_3W_7O_{31}^{5-}$ ), and  $V_5W_8O_{40}^{7-}$ . Souchay, *et al.*,<sup>4</sup> have reported optical spectroscopic and pH-titration studies of solutions containing tungstate and vanadium(IV) and deduced the existence of  $V^{IV}W_5O_{19}^{4-}$  and  $HV^{IV}W_2W_4O_{18}^{3-}$  (or  $H_3V^{IV}W_2W_4O_{19}^{3-}$ ). We have extended our investigations to tungstovanadates(IV) and report here the preparation and characterization of species with  $W/V = 5/1$  and  $4/2$  as well as a third complex with  $W/V = 11/1$ , which has been described briefly by Tourne and Tourne.<sup>5</sup>

**Experimental Section**

Oxovanadium(IV) sulfate was obtained commercially and had approximate composition  $VOSO_4 \cdot 4H_2O$ . A solution of oxovanadium(IV) chloride was prepared by stoichiometric reaction of  $V_2O_5$  with hydrazine in hydrochloric acid solution. The solution was prepared equimolar in HCl and  $VOCl_2$  (typically 2.0 *F*) and is referred to below as "HVOCl<sub>3</sub>."

Solutions of  $N_2H_5Cl$  and of various organic cations were prepared by stoichiometric reaction of the bases with hydrochloric acid in aqueous solution. Tank nitrogen was passed through aqueous acidic chromium(II) solution to remove oxygen impurity.

Ammonium paratungstate, potassium tungstate ( $K_2WO_4$ ), sodium metatungstate, and tetramethylammonium metatungstate were prepared as described previously.<sup>3</sup> Potassium metatungstate was prepared according to Freedman's<sup>6</sup> procedure with the substitution of potassium tungstate for the sodium salt. However the reaction mixture after being heated still contained much light yellow precipitate. Filtration gave a clear solution which deposited much white, slightly soluble, crystalline material (presumably paratungstate) during evaporation to low volume. After a few days the solution was filtered again and treated with excess ethanol to precipitate potassium metatungstate. After it was filtered, washed with ethanol followed by acetone, and air-dried, the product was dried to constant weight at 110–120° and stored over magnesium perchlorate. The yield was about 55%.

An alternate preparation of potassium metatungstate was carried out as follows. Potassium tungstate (10 ml of 1.0 *F* aqueous  $K_2WO_4$ ) was diluted with 30 ml of hot water treated with 10 ml of glacial acetic acid. The resultant solution was refluxed 2 hr. The solution was then treated with 10 ml more of glacial acetic acid and evaporated on the hot plate. Rod-shaped crystals began to form when the volume decreased below 30 ml. At a volume of 5–10 ml the mixture was allowed to cool. The crystals were then isolated by washing

with ethanol and air-drying. About 2.7 g (nearly 90% yield) of prismatic crystals with a persistent acetic acid odor were obtained. They were dried at 110–120° to constant weight, and an odorless powder which was stored over magnesium perchlorate was obtained.

The ultraviolet spectra of both potassium metatungstate preparations agreed with that reported.<sup>7</sup> From the absorbances and from base titrations, both products were deduced to be  $K_8[H_2W_{12}O_{40}] \cdot 2H_2O$ . Formula weight: calcd: 3118.8; found: Freedman method, 3120, 3118, 3110; acetic acid reflux, 3118, 3115.

In the preparations described below, the crystalline products were usually isolated by washing by decantation with ethanol-water mixtures followed by 95% ethanol and air-drying. The use of plastic containers for the recrystallization of aqueous solutions greatly minimized the formation of crusts due to creeping and drying of the solution. Substances found to be efflorescent were stored over sodium sulfate decahydrate. All products were examined under the microscope. Analyses are given in Table I. The preparations of the three complexes were repeated several times and found to be reproducible.

**5-Tungstovanadate(IV) Salts,  $M_4V^{IV}W_5O_{19} \cdot nH_2O$ .** a. **Methylammonium Sodium Salt.** Sodium tungstate dihydrate (50 mmol, 16.5 g) was dissolved in 50 ml of water and treated with 10 ml of 5 *F* acetic acid and 5 ml of 1 *F*  $N_2H_5Cl$  (to prevent oxidation of vanadium). A solution of 10 mmol of  $VOSO_4$  in 10 ml of water was added, giving a brown mixture containing much precipitate. The mixture was heated at 80–90° and was stirred for up to 1 hr, during which it became reddish purple and nearly clear. The solution was filtered, reheated nearly to boiling, and treated with a solution of 40 mmol of  $CH_3NH_2Cl$  in 20 ml of water. After the solution had been cooled and had been allowed to stand for 2 days, the product was isolated as 13 g (nearly 90% yield) of dark reddish purple crystals of distorted octahedral or rhombohedral habit. The slightly soluble compound was pure by microscopy. The compound may be recrystallized by dissolving it in a solution 0.1 *F* in sodium acetate, 0.02 *F* in acetic acid, and 0.01 *F* in  $N_2H_5Cl$  (6 ml of solution/g of compound with heating to boil) and then making the solution 0.2 *F* in  $CH_3NH_2Cl$ . The product is isolated after allowing the cooled solution to stand for up to 2 days.

b. **Dimethylammonium Sodium Salt.** A solution of the tungstovanadate complex obtained as in part a (scaled to 2 mg-atoms of vanadium) was treated with 10 mmol of  $(CH_3)_2NH_2Cl$  in 10 ml of water. The principal product, dark reddish purple chunky crystals, was isolated after room-temperature evaporation for 1–3 days. (Minor phases were nearly black plate- and rod-shaped crystals.) The desired crystals were separated mechanically and recrystallized by dissolution in 5 ml of solution 0.1 *F* in sodium acetate, 0.02 *F* in acetic acid, and 0.02 *F* in  $N_2H_5Cl$  (heat) and addition of 4 ml of 2 *F*  $(CH_3)_2NH_2Cl$ . When the solution was cooled and allowed to evaporate 1.8 g of complex (about 60% yield) was obtained.

c. **Tetramethylammonium Sodium Sulfate Double Salt.** Preparation was carried out as in part b, substituting  $(CH_3)_4NCl$  for  $(CH_3)_2NH_2Cl$ . The desired product formed platy to tabular crystals, accompanied by some smaller nearly black prisms. The product was separated mechanically from the impurities. Recrystallization gave a product frequently contaminated by slightly soluble yellow octahedral crystals, evidently the  $V^{IV}W_5O_{19}^{3-}$  salt,<sup>3a</sup> despite presence of  $N_2H_5Cl$ . Characterization was therefore carried by using a mechanically separated unrecrystallized product. Solutions of the compound gave an immediate white precipitate with barium ion.

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Table I. Analyses

Compd		%						
		V	W	Inorg cation	C	H or H <sub>2</sub> O	W/V	Cation/anion
(CH <sub>3</sub> NH <sub>2</sub> ) <sub>2</sub> Na <sub>2</sub> (VW <sub>5</sub> O <sub>19</sub> )·6H <sub>2</sub> O	Calcd	3.41	61.6	3.1	1.61	1.62 <sup>a</sup>		1.97 <sup>c</sup>
	Found	3.35 (2)	61.1 (1)	3.1	1.57	1.63	5.05	2.04 <sup>d</sup>
((CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> ) <sub>2</sub> Na <sub>2</sub> (VW <sub>5</sub> O <sub>19</sub> )·6H <sub>2</sub> O	Calcd	3.35	60.5	3.0	3.16	1.86 <sup>a</sup>		1.98 <sup>c</sup>
	Found	3.33 (1)	60.4	3.0	3.13	1.90	5.03	1.98 <sup>d</sup>
((CH <sub>3</sub> ) <sub>4</sub> N) <sub>2</sub> Na <sub>4</sub> (SO <sub>4</sub> )(VW <sub>5</sub> O <sub>19</sub> )·14H <sub>2</sub> O	Calcd	2.73	49.4	4.9	5.16	2.81 <sup>a</sup>		2.13 <sup>c</sup>
	Found	2.70 (1)	49.4	5.0	5.48	2.88	5.06	4.05 <sup>d</sup>
(C(NH <sub>2</sub> ) <sub>3</sub> ) <sub>4</sub> (VW <sub>5</sub> O <sub>19</sub> )·H <sub>2</sub> O	Calcd	3.32	60.0		3.14	1.71 <sup>a</sup>		
	Found	3.35 (2)	60.0		3.28	1.73	4.96	4.18
(C <sub>2</sub> H <sub>4</sub> (NH <sub>2</sub> ) <sub>2</sub> ) <sub>2</sub> (VW <sub>5</sub> O <sub>19</sub> )·2H <sub>2</sub> O	Calcd	3.55	64.1		3.35	1.69 <sup>a</sup>		
	Found	3.54 (2)	64.1		3.10	1.79	5.03	1.85
(CH <sub>3</sub> NH <sub>2</sub> ) <sub>2</sub> Na <sub>2</sub> (V <sup>IV</sup> W <sub>5</sub> O <sub>19</sub> ) <sub>1-x</sub> (V <sup>V</sup> W <sub>4</sub> O <sub>19</sub> ) <sub>x</sub> ·6H <sub>2</sub> O	Calcd <sup>e</sup>	3.95 <sup>f</sup>	60.6	3.1	1.63	1.64 <sup>a</sup>		2.06 <sup>c</sup>
	Found	3.93 (2) <sup>f</sup>	60.3 (1)	3.1	1.67	1.69	4.25 <sub>2</sub>	1.99 <sup>d</sup>
(C(NH <sub>2</sub> ) <sub>3</sub> ) <sub>5</sub> H(V <sub>2</sub> W <sub>4</sub> O <sub>19</sub> )·H <sub>2</sub> O	Calcd <sup>g</sup>	6.97	50.3		4.11	2.28 <sup>a</sup>		
	Found <sup>g</sup>	7.02 (6)	50.8 (1)		4.09	2.38	2.00	4.89
K <sub>8</sub> (H <sub>2</sub> W <sub>11</sub> VO <sub>40</sub> )·13H <sub>2</sub> O	Calcd	1.56	62.0	9.59		7.73 <sup>b</sup>		
	Found <sup>h</sup>	1.56 (1) <sup>i</sup>	62.1	9.30		7.6 (1)	11.04	7.74
(NH <sub>4</sub> ) <sub>7.5</sub> H <sub>0.5</sub> (H <sub>2</sub> W <sub>11</sub> VO <sub>40</sub> )·15H <sub>2</sub> O	Calcd	1.63	64.8	4.33		9.52 <sup>b</sup>		
	Found	1.60 (1) <sup>j</sup>	64.8 (1)	4.33		9.40 <sup>k</sup>	11.19	7.49
((CH <sub>3</sub> ) <sub>4</sub> N) <sub>7</sub> H(H <sub>2</sub> W <sub>11</sub> VO <sub>40</sub> )·16H <sub>2</sub> O	Calcd	1.45	57.4		9.54	3.40 <sup>a</sup>		
	Found <sup>m</sup>	1.44 (1) <sup>l</sup>	57.4		9.41	2.85	11.03	6.91
((CH <sub>3</sub> ) <sub>4</sub> N) <sub>3</sub> H <sub>3</sub> (H <sub>2</sub> W <sub>11</sub> VO <sub>40</sub> )·8H <sub>2</sub> O	Calcd	1.58	62.6		7.43	2.53 <sup>a</sup>		
	Found <sup>n</sup>	1.52	62.5		7.77	2.30	11.41	5.23

<sup>a</sup> Total hydrogen. <sup>b</sup> Total water, including constitutional water. <sup>c</sup> Organic cation/anion. <sup>d</sup> Inorganic cation/anion. <sup>e</sup> Based on  $x = 0.142$  derived from experimental W/V ratio. <sup>f</sup> Vanadium(V): calcd, 0.98; found, 1.04. <sup>g</sup> Nitrogen: calcd, 14.38; found, 14.21. Guanidinium from picrate determination: calcd (CN<sub>3</sub>H<sub>5</sub>), 20.57; found, 20.15 (5). <sup>h</sup> Matter sum 99.6%. Product from W/V = 11 preparation, recrystallized at pH near 5. Products from W/V = 5 gave 1.55 (1)% V. A product recrystallized at pH near 4 gave 1.55% V and 9.35% K. <sup>i</sup> Range for different crops and preparations 1.50–1.56. <sup>j</sup> Range for different crops and preparations 1.58–1.61. <sup>k</sup> By difference. <sup>l</sup> Range for different crops and preparations 1.42–1.45. <sup>m</sup> For product obtained from potassium salt. Found for product obtained from ammonium salt: V, 1.44 (1); W, 57.6; C, 9.55; H, 3.08. Compounds were recrystallized from 1:1 or 2:1 acetate-acetic acid buffer. <sup>n</sup> Product recrystallized from 1:5 acetate-acetic acid buffer.

**d. Guanidinium Salt.** The preparation, carried out as in part b, gave some precipitate on addition of the C(NH<sub>2</sub>)<sub>3</sub>Cl. The solution was heated to boiling and filtered. Rod-shaped crystals of the product separated with some fine precipitate during cooling. The crystals, freed from the fine material by washing, were dissolved by heating them in 15–20 ml of water containing 0.5 mmol of sodium acetate, 0.1 mmol of acetic acid, and 0.1 mmol of N<sub>2</sub>H<sub>5</sub>Cl. Guanidinium chloride (4 mmol in 2 ml of water) was added, and the solution was filtered and allowed to cool and stand. The dark purple needles thus obtained were isolated after a few hours (yield 2.0 g, about 65%). They appeared to be efflorescent.

**e. Ethylenediammonium Salt.** The preparation proceeded like that of the guanidinium salt, with the use of C<sub>2</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>, giving needles and fine precipitate. The product was isolated and recrystallized in the same way, substituting 2 mmol of C<sub>2</sub>H<sub>4</sub>(NH<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub> for the guanidinium chloride. A yield of 2.0 g of apparently efflorescent needles was obtained.

**f. Other Salts.** No sodium salt was obtained because of its high solubility. Attempts to obtain a potassium salt also failed; potassium paratungstate, a yellow-brown fine precipitate, and small dark square crystals of the 11-tungstovanadate(IV) complex (see below) were usually obtained. In another experiment in which less acetic acid was used, some soluble dark purple crystals were obtained in addition to much brown-yellow material. They were not investigated further.

**Solid Solution of V<sup>IV</sup>W<sub>5</sub>O<sub>19</sub><sup>4-</sup> and V<sup>V</sup>W<sub>4</sub>O<sub>19</sub><sup>4-</sup>.** If hydrazine is not used in the preparation of 5-tungstovanadate(IV), some oxidation occurs, leading to formation of V<sup>V</sup>W<sub>4</sub>O<sub>19</sub><sup>4-</sup>. These two complexes form solid solutions and cannot be separated by recrystallization. A sample of the methylammonium sodium salt was prepared in this way and gave crystals which were brown instead of red-purple. Analytical data are given in Table I with the data for the pure complex salts.

**4-Tungsto-2-vanadate(IV) Salts, M'<sub>6-n</sub>H<sub>n</sub>V<sup>IV</sup>W<sub>4</sub>O<sub>19</sub>·xH<sub>2</sub>O.** **a. Guanidinium Salt.** A solution of 16.5 g (50 mmol, 25% excess) of sodium tungstate dihydrate, 40 mmol of guanidinium chloride, 20 mmol of N<sub>2</sub>H<sub>5</sub>Cl, and 10 mmol of sodium hydroxide together in 600 ml of water in a flask was heated to boiling while a stream of nitrogen was passed through it. A solution of 20 mmol of VOSO<sub>4</sub> and 40 mmol of sodium oxalate was added in small portions to the boiling tungstate solution. A clear deep red-brown solution was thus obtained. The solution was then allowed to cool slowly while a slow stream of nitrogen was passed over its surface. After being cooled, the flask was stoppered tightly on removal of the nitrogen line and

allowed to stand 2–3 days. Dark crystals which formed during that time were isolated after the solution was siphoned off under nitrogen. (They were mixed with a little dark fine precipitate which was washed out.) The solid could be washed and dried in the air. A second crop of crystals was obtained by heating the solution to boiling (nitrogen stream) and adding slowly 10 ml of hot 2 *F* guanidinium chloride solution, followed by cooling and standing as for the first crop. A third crop was subsequently obtained similarly. The total yield of product was about 11 g (about 75% based on vanadium). (The third crop was about 2 g.) The crops were kept separate for analyses. The product appeared to be pure and consisted of deep red-brown to black cube-shaped crystals with angular pits and sometimes some octahedral faces. The low solubility combined with the oxidation sensitivity prevented successful recrystallization. While the crystals appeared to resist oxidation by air indefinitely, a powdered sample underwent partial oxidation during several months.

**b. Other Salts.** Solutions of the complex were prepared as described above with the omission of the guanidinium chloride and at higher concentrations. None of the four methylammonium ions gave a salt of low solubility; precipitation of less soluble materials always occurred. Ethylenediammonium ion gave an insoluble product which could not be obtained in a well-crystallized state.

Attempts to obtain sodium or potassium salts by the above method failed. Alternatively, concentrated alkali carbonate solutions (sodium, potassium, or mixtures of these) of vanadium(IV) and tungstate in 1:2 mole ratio (under nitrogen) were carefully acidified with acetic acid to pH 6–8. Again mixtures of crystalline and apparently amorphous materials were obtained. The crystalline products probably included the 2:4 complex, as suggested by vanadium analyses on more nearly pure samples separated mechanically. The other important crystalline phases appeared to be isopolyvanadates(IV), which we are investigating separately.

**11-Tungstovanadate(IV) Salts, M'<sub>8-n</sub>H<sub>n</sub>[H<sub>2</sub>W<sub>11</sub>V<sup>IV</sup>O<sub>40</sub>]·xH<sub>2</sub>O.**

**a. Potassium Salt.** A solution of 8 mmol of "HVOCl<sub>3</sub>" (excess), 8 mmol of oxalic acid, and 4 mmol of N<sub>2</sub>H<sub>5</sub>Cl in about 10 ml of water was added to a solution of 40 mmol of K<sub>2</sub>WO<sub>4</sub> and 60 mmol of formic acid in about 200 ml of water at 80–90°. The initially purple-brown mixture was heated at 80–90° and was stirred for 4 hr, during which it became clear and pinkish purple. During this treatment it was allowed to evaporate to about 100 ml. After the solution had cooled and stood overnight, a black crystalline product mixed with some fine brown precipitate separated. The crystalline solid was isolated and the fine precipitate was washed away. The

crystalline product consisted of small black square blocks, with little or no colorless paratungstate impurity. The remaining reaction solution was reheated at 80–90° for 4 hr more, allowing evaporation to about 80 ml. The second crop of product which had separated from the solution cooled overnight was washed free of some fine brown precipitate and isolated. The remaining solution was recycled through a few more 4-hr heating treatments to obtain additional crops. In the latter treatments the solution was gray-violet to gray-blue after isolation of product; the successive reheating treatments led to progressively less change to purple-pink. (The volume of the solution was maintained at about 60 ml after obtaining the third crop.) Successive crops were smaller and tended to be more contaminated with paratungstate. A total of five to eight such crops was thus obtained.

The crops were examined for paratungstate impurity under the microscope, and those appearing to contain more than 2–4% of impurity were rejected (these were generally the last one or two crops). The purer crops (total yield about 7–7.5 g) were combined and dissolved in about 80 ml of near-boiling 0.1 *F* potassium acetate–0.1 *F* acetic acid–0.01 *F* N<sub>2</sub>H<sub>5</sub>Cl. The dark wine red solution was filtered, reheated, and allowed to cool and stand in a large flat dish. After 1–2 days the first crop of about 5 g of complex was isolated. Room-temperature evaporation of the remaining solution led to isolation of additional crops. The latter crops contained paratungstate impurity and were rejected. About 7 g (50–60% yield based on tungsten) of pure product was obtained as lustrous black square blocks.

The preparation could be scaled up readily by a factor of 5. If the preparation was carried out with stoichiometric proportions of vanadium and tungsten, there was more difficulty with paratungstate impurity. The paratungstate and the vanadate complex have similar solubilities and are not readily separated by recrystallization. For microscopic detection of paratungstate impurity, the compound must be crystallized slowly over a large surface area to give individual crystals. If these conditions are not met, the compound separates as a crust in which the impurity cannot be detected visually.

**b. Ammonium Salt.** When the preparation was carried out in the same way for as the potassium salt (with use of ammonium paratungstate and addition of ammonium hydroxide with the formic acid to obtain the same buffer composition), the product was obtained similarly. However it could not be recrystallized pure despite many variations in conditions. (The product always formed ill-defined crusts and contained paratungstate, which is less soluble than the vanadate complex.)

A successful preparation was carried out by metathesis as follows. A solution of the complex was prepared by using sodium tungstate instead of potassium tungstate in the procedure described above, except that less water was used (reaction solution 200 ml/100 mmol of Na<sub>2</sub>WO<sub>4</sub>). The reaction mixture was allowed to evaporate to about 100 ml during the 4 hr of heating. After the solution had cooled, it was treated with 15 g (100 mmol) of solid ammonium acetate to precipitate the ammonium salt (contaminated with some paratungstate). The solid was isolated by filtration and washed with a little 1:2 ethanol–water mixture. (The pinkish or brownish gray filtrate was discarded.) The solid was redissolved in about 50 ml of 0.1 *F* ammonium acetate–0.1 *F* acetic acid by heating nearly to boiling. If any white solid remained, it was removed. The complex was reprecipitated by adding 5 g of solid ammonium acetate and cooling the mixture in an ice bath for up to 0.5 hr with intermittent agitation. The product was then isolated by filtration as before. It was redissolved a second time in about 100 ml of a solution 0.1 *F* each in ammonium acetate, acetic acid, and ammonium nitrate and 0.01 *F* in N<sub>2</sub>H<sub>5</sub>Cl. The solution was filtered and allowed to cool and stand in a large flat dish. A colorless impurity separated first; it appeared to be (NH<sub>4</sub>)<sub>4</sub>NaHW<sub>6</sub>O<sub>21</sub>·6.5H<sub>2</sub>O.<sup>8,9</sup> It was removed by filtration the next day. Room-temperature evaporation led to the separation of individual dark wine red to black crystals as square blocks or plates or rods, contaminated with a little of the paratungstate (tiny colorless parallelogram-shaped plates). Most of the vanadate complex formed larger crystals which were readily separated mechanically from the impurity. The yield of pure product was about 12 g (about 40% based on tungsten).

The above comments about reaction stoichiometry and recrystallization for the potassium salt apply also to the ammonium salt. The paratungstate salt impurity in the sodium salt metathesis preparation is evidently not the same as that in the attempted direct preparation. Both paratungstates are less soluble than the vanadate complex, but

the one produced in the successful preparation does not interfere with the crystallization of the product.

Attempts to isolate a sodium salt directly from the above reaction mixture failed because of its high solubility.

**c. Tetramethylammonium Salt.** A solution of potassium 11-tungstovanadate(IV) (3.3 g, 1.0 mmol) in about 60 ml of water containing 4 mmol of tetramethylammonium acetate (prepared from aqueous solution of the hydroxide and acetic acid), 2 mmol of acetic acid, and 1 mmol of N<sub>2</sub>H<sub>5</sub>Cl (heated to boil to dissolve the heteropoly salt) was treated with 3.3 g (30 mmol) of solid tetramethylammonium chloride. The mixture was cooled in an ice bath to precipitate the product. After several minutes the solid was isolated by filtration and washed with a little 1 *F* N(CH<sub>3</sub>)<sub>4</sub>Cl. Then it was dissolved by heating in about 60 ml of a solution 0.1 *F* in tetramethylammonium acetate, 0.05 *F* in acetic acid, and 0.01 *F* in N<sub>2</sub>H<sub>5</sub>Cl. The salt crystallized from the cooled solution after about 1 day. A yield of 3.1 g of efflorescent parallelepiped-shaped prismatic crystals was obtained.

If potassium acetate was used instead of tetramethylammonium acetate (e.g., 2 mmol in the preparation), the same product was obtained. However a phase recrystallized from a dilute ~1:5 potassium acetate–acetic acid buffer had a different composition (see Table I).

Since tetramethylammonium ion does not form insoluble paratungstates, impure potassium or ammonium 11-tungstovanadates(IV) may be purified by metathesis to the tetramethylammonium salt as described above.

Preparation of this salt by direct addition of tetramethylammonium ion to the crude reaction mixture (e.g., starting with sodium tungstate) gave products which appeared homogeneous (six-sided plates, laths) but which had low and variable vanadium analyses.

**Analyses.** Elemental analyses were carried out as previously described,<sup>3</sup> with the following modifications in the case of vanadium. One drop of 0.01 *F* CuSO<sub>4</sub> was added with the 5 ml of 1 *F* NaOH in the initial decomposition (color change to light brown). One drop of 30% hydrogen peroxide was then added, and the solution was boiled for 2 min to decompose excess peroxide. The sample was then treated with NaF, acidified, and titrated as described.<sup>3</sup> (The guanidinium salt of the 2:4 complex was dissolved first in a hot bisulfate buffer solution and then treated with the CuSO<sub>4</sub> and NaOH. For guanidinium and NH<sub>4</sub> salts, complete decomposition of peroxide required boiling nearly to dryness, adding 5 ml of water, and boiling nearly to dryness again.) The oxidation could also be performed by treating the water solution of the sample with chlorine. After boiling to expel excess chlorine, the decomposition with NaOH and remaining operations were carried out. (This method was particularly effective for the 1:1 complex, which itself decomposes rather slowly in basic solution. It could not be used for the NH<sub>4</sub> salt, however.)

Oxidation state determinations were based on the titration of any vanadium(V) present in the complex. The sample was decomposed by dissolution with 1–2 ml of 48% HF and 3–5 ml of 6 *F* HCl and warming until no further color change was evident (light blue or green). The sample was treated with 15–20 ml of water and 2 ml of 5 *F* H<sub>3</sub>PO<sub>4</sub> and titrated as in the total vanadium determination. Pure vanadium(IV) products thus gave no consumption of titrant. Attempts to titrate vanadium(IV) in the complexes with permanganate met with interference from reagents used to decompose the complex or were rendered inaccurate because of the intense yellow color of the vanadium(V) species produced.

Guanidinium ion in the 2:4 complex was also determined by precipitation as the picrate by a procedure based on the work of Fainer and Myers.<sup>10</sup> The sample was dissolved in a minimum amount of water, decomposed with LiOH and H<sub>2</sub>O<sub>2</sub>, and neutralized with acetic acid. A moderate excess of hot 0.1 *F* sodium picrate was added; the precipitate was subsequently isolated, dried, and weighed as described.<sup>10</sup>

**Physical Measurements.** Powder and single-crystal X-ray diffraction data, infrared spectra, and optical spectra were obtained as described.<sup>3</sup> Some X-ray data were obtained with Mo K $\alpha$  radiation ( $\lambda$  0.7107 Å). ESR spectra were obtained by using a JEOL Model MES-3X spectrometer; *g* values were obtained by using DPPH and measurement of the field was done with an nmr probe. *g* and *a* values have been corrected with the second-order form of the Breit-Rabi equation. Powder diffraction, infrared, optical, and esr data are given in Tables II, III, IV, and V, respectively, with data for other complexes<sup>3,11–13</sup> included for comparison.

(10) P. Fainer and J. L. Myers, *Anal. Chem.*, **24**, 515 (1952).

(11) J. Selbin, *Chem. Rev.*, **65**, 153 (1965); *Coord. Chem. Rev.*, **1**, 293 (1966).

(12) D. P. Smith, Ph.D. Dissertation, Georgetown University, 1972; D. P. Smith, H. So, J. Bender, and M. T. Pope, *Inorg. Chem.*, **12**, 685 (1973).

(8) M. Hahnert, *Z. Anorg. Allg. Chem.*, **318**, 222 (1962); *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **120**, 216 (1964).

(9) O. W. Rollins, Ph.D. Dissertation, Georgetown University, 1965.

Table II. X-Ray Powder Diffraction Data for  $[M_6O_{19}]^{n-}$  Salts<sup>a</sup>

Methylammonium sodium salts VW <sub>5</sub> O <sub>19</sub> <sup>4-</sup>		Dimethylammonium sodium salts VW <sub>5</sub> O <sub>19</sub> <sup>4-</sup>		Ethylenediammonium salts VW <sub>5</sub> O <sub>19</sub> <sup>4-</sup>		Guanidinium salts VW <sub>5</sub> O <sub>19</sub> <sup>4-</sup>									
V <sub>2</sub> W <sub>4</sub> O <sub>19</sub> <sup>4- b</sup>		V <sub>2</sub> W <sub>4</sub> O <sub>19</sub> <sup>4- b</sup>		V <sub>2</sub> W <sub>4</sub> O <sub>19</sub> <sup>4- b</sup>		V <sub>2</sub> W <sub>4</sub> O <sub>19</sub> <sup>4- b</sup>									
10.2	79	10.1	55	9.93	58	9.85	100	9.06	76	9.03	100	8.51	100		
7.21	100	7.16	100	7.64	100	7.54	77	7.78	46	7.67	87			7.75	56
6.67	30	6.66	21	7.41	42	7.33	38	7.54	84	7.46	88	7.31	24	7.48	100
5.33	18	5.29	21	6.84	8	6.76	11	5.77	39	5.77	77	7.17	18		
3.68	16	3.67	16	6.54	9	6.53	6	3.97	7	3.95	13			6.88	23
3.39	20	3.37	16	5.48	13	5.43	18			3.89	13			6.76	44
3.34	42	3.32	25	4.07	10	4.04	7	3.86	10	3.85	17	5.51	7		
3.17	22	3.15	23	3.86	7	3.81	10	3.76	28	3.72	87	5.25	6	5.30	10
2.826	13	2.812	12	3.71	14	3.69	15	3.54	24	3.53	17			5.14	6
2.760	7	2.746	13	3.41	14	3.38	14			3.50	21			3.90	12
2.659	11	2.647	9	3.31	35	3.28	18	3.46	37	3.44	17	3.63	18		
2.632	10	2.616	3	3.27	24	3.25	15	2.99	10	2.99	8	3.52	16	3.52	26
2.549	13	2.540	15	3.22	12	3.19	13	2.94	7	2.93	12	3.39	7	3.34	19
2.360	14	2.347	8	2.94	9	3.05	7	2.886	22			3.29	6	3.29	9
2.225	13	2.215	18	2.834	14	2.800	6	2.872	26	2.874	22	3.15	11	3.16	12
2.066	11	2.056	9	2.736	7	2.719	9	2.819	7	2.844	12	2.94	9	2.96	7
1.999	27	1.988	9	2.670	12	2.656	4	2.775	16	2.775	21	2.821	10	2.852	8
1.699	11	1.688	8	2.487	10	2.475	8	2.727	15	2.703	11			2.715	9
				2.281	10	2.269	11	2.474	11					2.681	8
				2.164	81	2.150	4	2.461	12	2.441	15			2.376	8
				2.075	4	2.062	11	2.422	11			2.218	11	2.150	7
				2.056	7	2.043	11	2.384	100	2.393	17			2.119	9
				2.001	5	1.985	10			2.378	23				
								2.344	13	2.342	19				
								2.219	11	2.202	11				
								2.187	11	2.175	29				
								2.068	13						
								2.052	22	2.045	21				

<sup>a</sup> Principal diffraction lines; *d* (Å) and relative intensity. <sup>b</sup> Reference 3a.

Table III. Anion Infrared Frequencies

Compd	Freq. <sup>a</sup> cm <sup>-1</sup>						
VIVW <sub>5</sub> O <sub>19</sub> <sup>4-</sup> salts							
Methylammonium sodium	983 sh		967	799	630 b	576, 569	~400
Dimethylammonium sodium	990 sh	974 sh	959	795	630 b	580, 561	~400
Tetramethylammonium sodium <sup>b</sup>	981 sh		954	807	645 sh, b	574, 560	~400
Ethylenediammonium	984 sh		955	800	615 b	575, 560	~400
Guanidinium	982 sh		947	794	635 b	572, 560	~400
VIVW <sub>4</sub> O <sub>19</sub> <sup>6-</sup> salts							
Guanidinium		964 sh	920	793, 735		593, 553, 522	~400
VV <sub>2</sub> W <sub>4</sub> O <sub>19</sub> <sup>4-</sup> salts, range <sup>c</sup>	991-936			784-781		589-578	435-425
VVW <sub>3</sub> O <sub>19</sub> <sup>3-</sup> salts, range <sup>c</sup>	997-947			797-785		582-579	442-420
H <sub>2</sub> W <sub>11</sub> V <sup>IV</sup> O <sub>40</sub> <sup>8-</sup> salts							
Potassium	944 sh	930	875	778	~620 w, vb		~400
Ammonium	945 sh	929	882	778	~610 w, vb		~400
((CH <sub>3</sub> ) <sub>4</sub> N) <sub>3</sub> H <sub>3</sub>	944		873	787	670		~400
V <sub>4</sub> W <sub>3</sub> O <sub>40</sub> <sup>6-</sup> , V <sub>3</sub> W <sub>10</sub> O <sub>40</sub> <sup>5-</sup> , V <sub>5</sub> W <sub>4</sub> O <sub>40</sub> <sup>7-</sup> salts, range <sup>d</sup>		976-950	892-878	764-749		515-497	
H <sub>2</sub> W <sub>12</sub> O <sub>40</sub> <sup>6-</sup> salts, range <sup>d</sup>		960-925	886-874	768-760	600-570 w, vb		~400

<sup>a</sup> Key: sh, shoulder; v, very; b, broad; w, weak. <sup>b</sup> Sulfate double salt; SO<sub>4</sub><sup>2-</sup> bands at 1189, 1110, 619 cm<sup>-1</sup>. <sup>c</sup> Reference 3a. <sup>d</sup> References 3b, 3c.

The magnetic susceptibility of (CN<sub>3</sub>H<sub>6</sub>)<sub>5</sub>H(V<sup>IV</sup>W<sub>4</sub>O<sub>19</sub>)<sub>5</sub>·H<sub>2</sub>O was determined by the Faraday method to be  $2203 \times 10^{-6}$  and  $8456 \times 10^{-6}$  cgs/mol at 297 and 77°K, respectively. The susceptibility of (CN<sub>3</sub>H<sub>6</sub>)<sub>4</sub>VV<sub>2</sub>W<sub>4</sub>O<sub>19</sub>,  $(-170 \pm 10) \times 10^{-6}$  cgs/mol, was used to estimate the diamagnetic correction. The effective moments per V are 1.68 (297°K) and 1.63 BM (77°K).

The salt K<sub>8</sub>(H<sub>2</sub>W<sub>11</sub>V<sup>IV</sup>O<sub>40</sub>)<sub>13</sub>H<sub>2</sub>O (FW 3262.3) is face-centered cubic: *a* = 21.36 (3) Å; *V*<sub>cell</sub> = 9745 Å<sup>3</sup>;  $\rho_{\text{exptl}} = 4.4$  (1) g cm<sup>-3</sup> at 25° (by displacement in toluene);  $\rho_{\text{calcd}} = 4.45$  g cm<sup>-3</sup> (*Z* = 8). The Laue symmetry is *m3m*, with systematic absences *h* + *k* = 2*n*, *k* + *l* ≠ 2*n*, *h* + *l* ≠ 2*n*. The space group is therefore *Fm3m*, *F43m*, or *F432*.

The salt (NH<sub>4</sub>)<sub>7.5</sub>H<sub>0.5</sub>(H<sub>2</sub>W<sub>11</sub>V<sup>IV</sup>O<sub>40</sub>)<sub>15</sub>H<sub>2</sub>O (FW 3121.3) is face-centered cubic, *a* = 22.22 (3) Å, isomorphous with the potassium salt.

The salt (CN<sub>3</sub>H<sub>6</sub>)<sub>5</sub>H(V<sup>IV</sup>W<sub>4</sub>O<sub>19</sub>)<sub>5</sub>·H<sub>2</sub>O (FW 1460.7) is cubic: *a* = 14.27 (2) Å; *V*<sub>cell</sub> = 2906 Å<sup>3</sup>;  $\rho_{\text{exptl}} = 3.36$  (6) g cm<sup>-3</sup> at 23° (by displacement in toluene);  $\rho_{\text{calcd}} = 3.34$  g cm<sup>-3</sup> (*Z* = 4). The Laue

symmetry is *m3*, with no systematic extinctions; hence the space group is *Pm3* or *P23*.

The crystal habits of (CH<sub>3</sub>NH<sub>2</sub>)<sub>2</sub>Na<sub>2</sub>(V<sup>IV</sup>W<sub>5</sub>O<sub>19</sub>)<sub>6</sub>·H<sub>2</sub>O and its VV<sub>2</sub>W<sub>4</sub>O<sub>19</sub><sup>4-</sup> isomorph<sup>3a</sup> suggested trigonal symmetry. Difficulty was experienced in obtaining good single crystals. When a relatively large excess of methylammonium chloride was used in recrystallization of the VV<sub>2</sub>W<sub>4</sub>O<sub>19</sub><sup>4-</sup> salt, tabular crystals were obtained. These crystals were optically uniaxial with the optic axis perpendicular to the plate, as shown by extinction under crossed polarizers and by interference figures. When an excess of sodium acetate was used for recrystallization, long rhombohedra were obtained. Precession photographs of the VV<sub>2</sub>W<sub>4</sub>O<sub>19</sub><sup>4-</sup> salt showed Laue symmetry *31m* with systematic absences *-h* + *k* - *l* ≠ 3*n*, corresponding to space group *R3m*, *R3m*, or *R32*. The derived cell dimensions (hexagonal setting) were *a* = 8.52 (2) Å, *c* = 30.37 (4) Å, *V*<sub>cell</sub> = 1911 Å<sup>3</sup>,  $\rho_{\text{exptl}} = 3.43 \pm 0.03$  g cm<sup>-3</sup> at 23° (by displacement in toluene), and  $\rho_{\text{calcd}} = 3.54$  g cm<sup>-3</sup> (*Z* = 3). That this compound is a threefold twin of a structure of lower symmetry is unlikely.

**Chemical Reactions.** Various preparations and recrystallizations were carried out, and crystalline phases were identified by microscopy and vanadium analysis. Behavior of the complexes in solution was

Table IV. Optical Spectra

Complex (solvent)	Energy, <sup>a</sup> kK	$\epsilon, M^{-1} \text{ cm}^{-1}$	Ref
$V^{IV}W_5O_{19}^{4-}$ (aq, pH 5)	11.3 (4) b	15.9 (2)	This work
	15.2 (3) sh	34 (1)	
	20.0 (2)	112 (2)	
	37.5 (2)	11,400 (200)	
$H_nV^{IV}_2W_4O_{19}^{-6+n}$ (aq, pH 8) <sup>b</sup>	10.6 (5) b	38 (2)	This work
	16.0 (5) sh	48 (2)	
	24.2 (3)	320 (10)	
	40 (1) sh	12,000 (1000)	
$H_2W_{11}V^{IV}O_{40}^{8-}$ (aq, pH 5)	11.6 (5) sh, b	60 (2)	This work
	14.8 (5) sh	197 (5)	
	20.6 (1)	635 (5)	
	40 (1) sh	34,000 (1000)	
$PW_{11}V^{IV}O_{40}^{5-}$ (aq, pH 2)	12.0 sh, b	130	12, 13
	14.5 sh, b	300	
	20.0	750	
	24.5 sh	600	
$VO^{2+}$ (aq) (1 F HClO <sub>4</sub> )	13.1	16.5	11
	16.0	7.5	
	41.7	240	
$VO(C_2O_4)_2^{2-}$ (aq)	12.6	25	11
	16.5	9	
	29.2	170	
$VO(H_3CCOCHCOCH_3)_2$ (alcohols)	12.8-13.8	~35	11
	16.9-17.6	~20	
	25.0-26.0	~90	

<sup>a</sup> Key: b, broad; sh, shoulder. <sup>b</sup> Solution also 0.01 F in Na<sub>2</sub>WO<sub>4</sub>.

Table V. Electron Spin Resonance Parameters

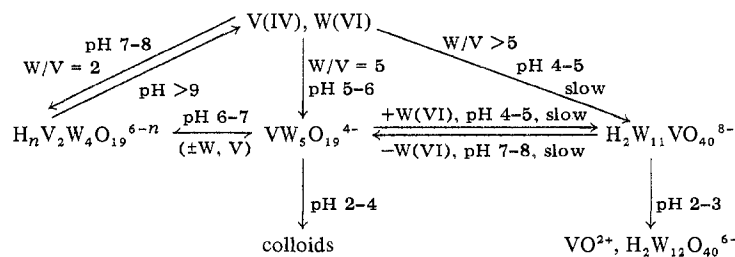
Complex (state)	$\langle g \rangle$	$10^4 A_{iso}, \text{ cm}^{-1}$
$V^{IV}W_5O_{19}^{4-}$ (aq, pH 5)	1.966	94
$HV^{IV}_2W_4O_{19}^{5-}$	<i>c</i>	
$H_2W_{11}V^{IV}O_{40}^{8-}$ (aq, pH 5)	1.953	90
$PW_{11}V^{IV}O_{40}^{5-}$ (aq, pH 2) <sup>a</sup>	1.947	96
$VO^{2+}$ (aq) <sup>b</sup>	1.961	106

<sup>a</sup> Reference 12. <sup>b</sup> K. Wuthrich, *Helv. Chim. Acta*, 48, 779 (1965).  
<sup>c</sup> See Discussion.

investigated by optical spectra and esr spectra. (Data for the pure complexes are given in Tables IV and V.) Titrations with acid or base were also performed as described previously.<sup>3</sup> Buffer solutions employed were derived from sulfate, formate, acetate, hydrazine, ammonia, or carbonate according to the desired pH value. The results of these experiments are summarized in Scheme I.

**5-Tungstovanadate(IV).** The methylammonium sodium and guanidinium salts could be recrystallized unchanged at pH 5-6 and solutions were stable for up to 30 days if protected from oxidation, e.g., by the presence of N<sub>2</sub>H<sub>5</sub>Cl. Beer's law was obeyed in the range  $5 \times 10^{-3}$  to  $5 \times 10^{-5}$  F at pH 5-6. Solutions at pH 8 or pH 4 or lower all decomposed within 1 day, although at pH 4 the decomposition was incomplete (see Figure 1).

Solutions titrated at 5° or near 70° with hydrochloric acid gave no indication of protonation reactions or definite steps in the decomposition. Solutions titrated with sodium hydroxide at 5° showed no rapid reaction (pH up to 11). At about 70°, titration with NaOH (carried out under nitrogen) resulted in degradation with change to the brown color of isopolyvanadate(IV). A poorly defined inflection in the titration curve occurred at pH near 9 and 6-7 mol of

Scheme I. Interconversions of Tungstovanadates<sup>a</sup>

<sup>a</sup> In the absence of oxalate ion, much amorphous precipitate forms at pH 5-9 with low W/V and at pH <4 at any W/V ratio.

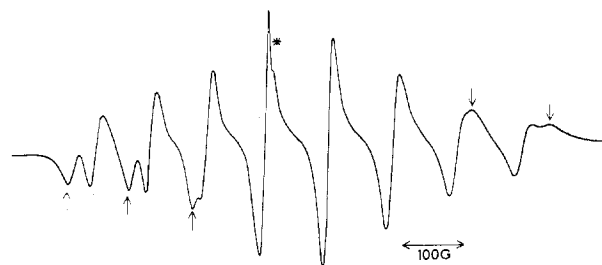


Figure 1. ESR spectrum for a solution of  $VW_5O_{19}^{4-}$  ion,  $10^{-2}$  M, stored under nitrogen at pH 4 for 6 weeks. Arrows indicate peaks due to  $VO(H_2O)_5^{2+}$  (asterisk, DPPH).

$OH^-$ /mol of complex. This is consistent with the reaction  
 $3VW_5O_{19}^{4-} + 20OH^- \rightarrow 15WO_4^{2-} + V_3O_7^{2-} + 10H_2O$

(We are also investigating isopolyvanadates(IV) and have found that the salts previously formulated as, e.g.,  $K_2V_4O_9 \cdot nH_2O$  are in fact  $M'_2V_3O_7 \cdot pH_2O$ . The results will be reported in another publication.)

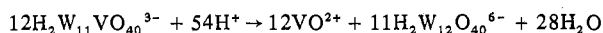
**4-Tungsto-2-vanadate(IV).** The guanidinium salt crystallizes very well despite the presence of amorphous precipitate. Because of its low solubility (about 0.01 F), slow dissolution, and instability to oxidation in solution, it was not recrystallized. Solutions in the pH range 8-9 were prepared for spectral measurements; all operations were carried out with rigorous exclusion of air. They were made 0.01 F in sodium tungstate to prevent development of turbidity. Fresh solutions at pH 9 gave the same spectra as solutions at pH 8. On standing for 1 day, the pH 9 solutions became nearly colorless and deposited a dark brown to black granular precipitate which did not contain tungsten. A pH 8 solution underwent no change in visible spectrum during 22 hr. (Spectra of solutions at pH 8 but 0.1 F in

sodium tungstate indicated partial conversion to 5-tungstovanadate(IV).

**11-Tungstovanadate(IV).** The potassium salt can be recrystallized unchanged in the pH range 4–8. The solubility increases with decreasing pH. With tetramethylammonium ion, two phases were obtained, depending on the pH at which the compound was recrystallized. This salt forms solid solutions with tetramethylammonium metatungstate. In solution the complex appears to resist oxidation by air, but solutions for spectral studies were made 0.01 *F* in  $N_2H_5Cl$  as a precaution.

Thermal dehydration of the potassium salt gave the following results (temperature (°C), % weight loss): 120, 1.7 (1); 150, 2.5 (1); 200, 6.8 (1); 320, 7.2 (1); 550, 7.4 (1); 700, 7.4 (1). Weight losses calculated for removal of water from the tridecahydrate are as follows (mol of water/mol of complex, % weight loss): 3, 1.66; 5, 2.76; 12, 6.63; 13, 7.18. The total water content, corrected for oxidation of vanadium to the V state, is given in Table I. Qualitative behavior of heated samples is shown by the following data (temperature (°C), appearance, behavior with acetate buffer solution): 200, unchanged, recrystallized unchanged; 320, little change, recrystallized to give starting material and yellow and white decomposition products; 550, light gray powder, partially soluble giving light yellow solution.

Optical spectra were obtained for solutions  $2 \times 10^{-3}$  to  $2 \times 10^{-5}$  *F* in complex. At pH 5 solutions conformed to Beer's law and were stable for up to 40 days. Solutions at pH 4 or lower decomposed (incomplete in 40 days at pH 4 and  $2 \times 10^{-3}$  *F*, to complete decomposition in less than 8 hr at pH 2 and  $2 \times 10^{-5}$  *F*), turning very pale blue or colorless. At pH 8 or 9, decomposition occurred during several days, the pH 9 solution becoming colorless. From absorbance measurements on the decomposed acid solutions,  $1.07 \pm 0.03$  mol of  $VO^{2+}$ /mol of complex was obtained (pH 2,  $2 \times 10^{-3}$  *F*). The ultraviolet spectra of the decomposed acid solutions were characteristic of metatungstate;  $0.91 \pm 0.01$  mol of metatungstate/mol of complex was obtained (pH 2, 3). These results are in good accord with the reaction



Reactions of this type have been previously demonstrated for substituted Keggin-type ions such as  $Co^{III}W_{11}Co^{II}O_{40}H_2^{7-}$ .<sup>14</sup> At pH 7–8, there is slow decomposition leading to formation of some 5-tungstovanadate(IV), by a reaction such as



The visible absorption maximum varied with pH as follows (pH,  $\lambda_{max}$  (nm),  $\epsilon_{max}$ ): 9, 472 (2), . . . ; 8.0, 473 (2), 620 (10); 5.0, 486 (2), 635 (5); 3.9, 488 (2), 620 (5); 2.9, 489 (2), . . . ; 2.4, 490 (2), . . . This variation was found to be reversible, aside from the decomposition of the complex in the more acid solutions, and indicates the existence of the protonated species  $H(H_2W_{11}VO_{40})^{7-}$  with a  $pK_a$  of about 5. This correlates well with the increased solubility of the potassium and ammonium salts in more acid solutions.

Titration of the potassium salt with sodium hydroxide at 3–5° revealed no rapid reaction (pH up to 11). Decomposition requires several minutes in boiling 0.1 *F* NaOH, with a color change to brown (isopolyvanadates(IV)). A violet-blue intermediate was observed in the decomposition of the more soluble ammonium salt in 2–10 *F* NaOH; the solutions were finally colorless or pale brown.

A solution of potassium 11-tungstovanadate(IV), at pH near 8, was flushed with nitrogen and stored in a stoppered flask for up to 6 weeks. At that time a mixture of chunky dark purple-red and lath-shaped colorless crystals had formed. ESR spectra of the supernatant pink solution and of an aqueous solution of some of the colored crystals indicated  $V^{IV}W_5O_{19}^{4-}$  as the only V(IV) species present. The colored crystals had infrared absorptions at 984 (sh), 971, 800, 637, 580, and 564  $cm^{-1}$ , also corresponding to those of 5-tungstovanadate(IV) (see Table III).

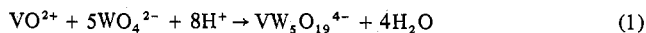
**Other Reactions.** Metatungstate and oxovanadium(IV) ions were mixed in 1:1 ratio in buffer solutions, covering the pH range 2–5. Heating the solution at about 90° for 1 hr resulted in a color change to pink- or orange-tinged brown, the color being faint for pH 2 and increasing with pH. If the vanadium(IV) was introduced as  $VO(C_2O_4)_2^{2-}$ , no reaction was evident on heating near 90° for 3 hr at pH 2 or 3. Solutions at pH 4 treated in the same way became gray-pink, and pH solutions became dull purple-pink. A spectrum of a pH 5 solution showed a broad maximum near 490 nm indicating about 20% conversion to 11-tungstovanadate(IV).

(14) L. C. W. Baker, V. S. Baker, K. Eriks, M. T. Pope, M. Shibata, O. W. Rollins, J. H. Fang, and L. L. Koh, *J. Amer. Chem. Soc.*, **88**, 2329 (1966).

A solution of tetramethylammonium metatungstate in pH 5 buffer was mixed with a similar quantity of 5-tungstovanadate(V). Evaporation led to recovery of colorless crystals of the metatungstate, indicating no solid solution formation.

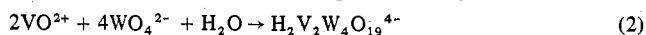
## Discussion

**Syntheses.** We obtained 5-tungstovanadate(IV) in high yield by heating the reaction mixture up to 1 hr near 90°, while Souchay, *et al.*,<sup>4</sup> reported quantitative formation on boiling for several hours. The net reaction is

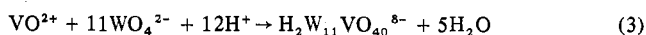


The salts of  $V^{IV}W_5O_{19}^{4-}$  were expected to have solubilities comparable to corresponding salts<sup>3a</sup> of  $V^{V}_2W_4O_{19}^{4-}$  and this was confirmed by the isolation of five well-crystallized salts. The formation of  $V^{V}_2W_4O_{19}^{4-}$  through oxidation must be avoided, since it forms solid solutions with the 5-tungstovanadate(IV) salts. Hydrazine is a convenient oxidation inhibitor and permits conducting the preparations in air. That this complex is somewhat labile was indicated by the failure to obtain a pure potassium salt.

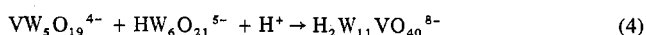
The 4-tungsto-2-vanadate(IV) complex is apparently more labile than the 1:5 complex, in agreement with the observations of Souchay, *et al.*<sup>4</sup> In the preparation, use of an oxalate complex of vanadium(IV) and a slight excess of tungstate minimizes the formation of amorphous precipitates. Hydrazine serves both to buffer the reaction mixture (pH near 8) and to inhibit oxidation. (The complex is oxidized nearly as readily as isopolyvanadates(IV), and solutions must therefore be handled in an inert atmosphere.) Allowing for uncertainty in the degree of protonation of the complex (see below), its formation can be represented by the reaction



Souchay, *et al.*,<sup>4</sup> did not report the formation of any 11-tungstovanadate(IV); its low rate of formation may have prevented their detection of it. Tourne and Tourne reported an ammonium salt but they did not give details of preparation.<sup>5</sup> The formation of the 1:1 complex proceeds more efficiently if the vanadium(IV) is introduced as an oxalate complex, which minimizes the formation of brown amorphous precipitate. The net reaction is



The 5-tungstovanadate complex appears to form initially and may be an intermediate which could react further as



The formation of the 1:1 complex appears to be incomplete at equilibrium; the low solubility of the potassium salt allows one to obtain a fairly high yield. While paratungstates were a troublesome impurity in the preparation of the potassium or ammonium salts, any metatungstate which formed caused no interference because of its much higher solubility. However, metatungstate does interfere in the preparation of the tetramethylammonium salt, since the two slightly soluble compounds form solid solutions. This fact required preparation of that salt by metathesis from the solid potassium or ammonium salts. (The successful recrystallization of the ammonium salt requires the presence of sodium ion. The direct preparation (no sodium ion present) evidently gives  $(NH_4)_{10}(H_2W_{12}O_{42}) \cdot nH_2O$  as the impurity. The salt with  $n = 10$  has been demonstrated to contain the ion  $H_2W_{12}O_{42}^{10-}$ .<sup>15</sup> On the other hand, when sodium ion is present, as in the metathesis procedure, the impurity is evidently  $Na(NH_4)_4HW_6O_{21} \cdot 6.5H_2O$ ,<sup>8,9</sup> for which there is evi-

(15) R. Allmann, *Acta Crystallogr., Sect. B*, **27**, 1393 (1971).

dence pointing to the anion  $\text{HW}_6\text{O}_{21}(\text{H}_2\text{O})_n^{5-}$  in the solid.<sup>9</sup>

**Analyses.** Data for the pure compounds are presented in Table I. The compositions of most of the 5-tungstovanadates(IV) parallel those of corresponding 4-tungsto-2-vanadates(V).<sup>3a</sup> The pure (optically homogeneous) tetramethylammonium sodium salt was found to contain sulfate (derived from oxovanadium(IV) sulfate) on the basis of chemical tests and the infrared spectrum (Table III); the cation analyses were in accord with 1 mol of sulfate/mol of complex. The water contents, estimated from the hydrogen analyses and from the formula weights implied by the metal analyses, are probably reliable to  $\pm 1$  mol of water/mol of salt. Whether the guanidinium salt was really hydrated could not be judged from infrared spectra, since the guanidinium ion absorbs in the same regions (1600–1700 and 3300–3500  $\text{cm}^{-1}$ ) as does water.

The composition of the guanidinium salt of the 4-tungsto-2-vanadate(IV) implies a singly protonated anion, at variance with the composition equivalent to  $\text{H}_3\text{V}^{\text{IV}}\text{V}_2\text{W}_4\text{O}_{19}^{3-}$  deduced by Souchay, *et al.*,<sup>4</sup> for the species in solution. However, the species that exists in this solid salt may not be the principal species in solution. This salt may be anhydrous; we are uncertain of the water content for the same reasons as for the 5-tungstovanadate(IV) salt.

The composition of the 11-tungstovanadates is established by the reproducible analyses for different preparations and for successive crops of crystals in a single preparation. Tourne and Tourne<sup>5</sup> reported the ammonium salt  $(\text{NH}_4)_8(\text{H}_2\text{W}_{11}\text{V}^{\text{IV}}\text{O}_{40}) \cdot 13\text{H}_2\text{O}$  but gave no analytical data. However variation and even nonstoichiometry in cation and water contents of salts of this type are frequently encountered.<sup>16</sup> (Note data for two different tetramethylammonium salts in Table I.) The lower water contents implied by the hydrogen analyses of the tetramethylammonium salts are attributed to efflorescence.

**Structures.** The 5-tungstovanadate(IV) and 4-tungsto-2-vanadate(IV) complexes are believed to possess the  $\text{Nb}_6\text{O}_{19}^{8-}$ -type structure, which may be referred to as the Lindqvist-Aronsson structure<sup>17</sup> in analogy with nomenclature for other prominent heteropoly structure types. This structure is illustrated in Figure 2 and is supported by the following evidence. (1) The lack of rapid reaction of the 1:5 complex with hydroxide ion at 5° indicates the absence of acidic protons ( $\text{p}K_a < 10$ ). This suggests that the anion contains no constitutional water. (2) The infrared spectra of these salts (Table III) parallel those of the salts of  $\text{V}^{\text{V}}_2\text{W}_4\text{O}_{19}^{4-}$  and  $\text{V}^{\text{V}}\text{W}_5\text{O}_{19}^{3-}$ . They correlate less well with the spectra of related Keggin-type compounds. (3) The optimum pH ranges for stability of both of the vanadate(IV) complexes and of  $\text{V}^{\text{V}}_2\text{W}_4\text{O}_{19}^{4-}$  overlap, and crystals isolated from mixtures of any of these have vanadium analyses indicative of solid solution formation among these complexes. Data for a typical product are given in Table I. The solid solution formation implies that all three of these complexes have similar structures. (4) The methylammonium sodium salts of  $\text{V}^{\text{IV}}\text{W}_5\text{O}_{19}^{4-}$  and  $\text{V}^{\text{V}}_2\text{W}_4\text{O}_{19}^{4-}$  are isomorphous by X-ray powder diffraction (Table II), and the pairs of dimethylammonium sodium and ethylenediammonium salts have similar powder patterns. In the rhombohedral methylammonium sodium salts the anion is required to possess a threefold symmetry axis, consistent with an orientationally disordered  $\text{M}_6\text{O}_{19}$ -type anion. (5) The single-crystal data for guanidini-

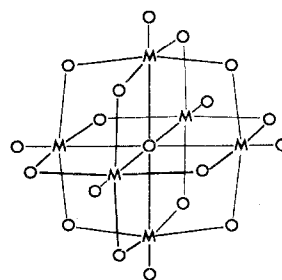


Figure 2. The Lindqvist-Aronsson structure,  $\text{M}_6\text{O}_{19}^{n-}$ .

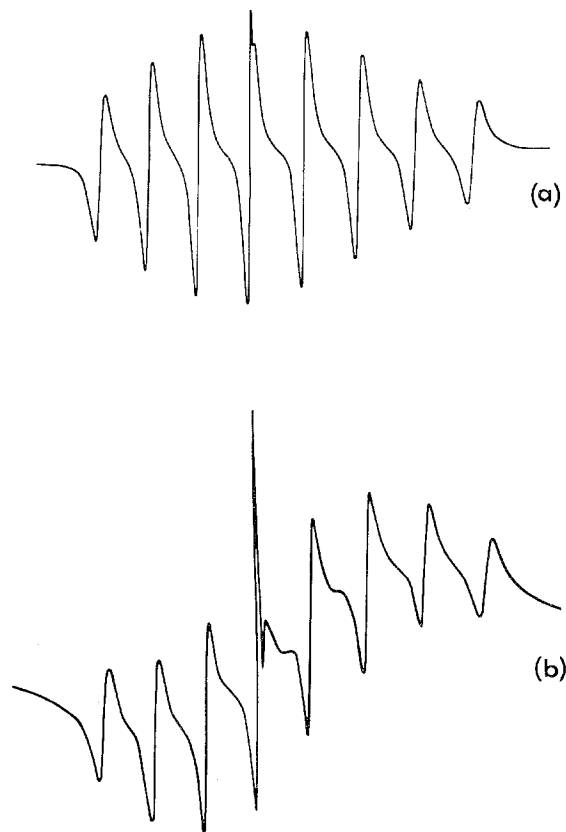


Figure 3. ESR solution spectra of 1:5 and 2:4 complexes: (a)  $\text{VW}_5\text{O}_{19}^{4-}$  ( $10^{-2} M$ ), pH 5; (b)  $\text{H}_n\text{V}_2\text{W}_4\text{O}_{19}^{-6+n}$  ( $10^{-2} M$ ), pH 8. The lower spectrum was recorded at a gain 2.5 times that used for (a).

um-4-tungsto-2-vanadate(IV) are consistent with the Lindqvist-Aronsson structure. While space groups  $P23$  and  $Pm3$  each have two onefold and two threefold positions, only  $P23$  has a fourfold position. Only the  $P23$  space group is commensurate with crystallographic equivalence of all four anions in the unit cell. While a mixture of cis and trans isomers may be present (see below), the site symmetry of most of the likely sets of positions requires that the anions be orientationally disordered. (6) The far-ultraviolet spectra of the two complexes (Table IV) differ little from the spectra of the respective vanadium(V) complexes<sup>3a</sup> ( $\text{V}^{\text{V}}_2\text{W}_4\text{O}_{19}^{4-}$ ,  $E = 40 \pm 1$  kK (shoulder),  $\epsilon = 14,000 \pm 1000$ ;  $\text{V}^{\text{V}}\text{W}_5\text{O}_{19}^{3-}$ ,  $E = 37.5$  kK (maximum),  $\epsilon = 11,000 \pm 1000$ ). (7) The ESR spectrum of  $\text{V}^{\text{IV}}\text{W}_5\text{O}_{19}^{4-}$  doped into rhombohedral  $(\text{CH}_3\text{NH}_3)_2\text{Na}_2(\text{V}^{\text{V}}_2\text{W}_4\text{O}_{19}) \cdot 6\text{H}_2\text{O}$  is consistent with vanadium(IV) distributed statistically over the metal atom sites of a structure containing orientationally disordered  $\text{M}_6\text{O}_{19}$ -type anions.<sup>18</sup>

The vanadium(IV) atoms in the 2:4 complex can occupy

(16) See, for example, H. T. Evans, Jr., *Perspect. Struct. Chem.*, 4, 1 (1971).

(17) I. Lindqvist, *Ark. Kemi*, 5, 247 (1953); I. Lindqvist and B. Aronsson, *ibid.*, 7, 49 (1954).

(18) H. So, C. M. Flynn, Jr., and M. T. Pope, submitted for publication in *J. Inorg. Nucl. Chem.*



sites that are mutually cis or trans in the Lindqvist-Aronsson structure. A similar possibility for isomerism occurs with  $V^V_2W_4O_{19}^{4-}$ .<sup>3a</sup> According to  $^{51}V$  nmr,<sup>19</sup> only one isomer is present in solutions of the 4-tungsto-2-vanadate(V) ion, and a convincing argument can be made that this is the cis form. The argument considers recent studies of the kinetics of isopolytungstate formation.<sup>20</sup> According to the mechanism proposed by Tytko and Glemser, a tetratungstate intermediate can lead only to the *cis*-divanadate complex.<sup>21</sup> In the absence of further information we presume the divanadate(IV) complex has the cis structure also. In this structure the symmetry axes, and hence the  $d_{xy}$  orbitals, of the vanadium(IV) ions are mutually orthogonal. It might be expected therefore that intramolecular antiferromagnetic interactions would be small in spite of a short (*ca.* 3.3 Å) V-V distance. The high magnetic moment at 77°K supports this view. In other binuclear oxovanadium(IV) complexes where the metal atoms share common oxygen atoms (as here) the moments range from 1.3 to 1.5 BM at 77°K ( $J = 90$ –218  $cm^{-1}$ ).<sup>22</sup> The binuclear tartrato<sup>23</sup> and oxalato<sup>24</sup> complexes of vanadium have room-temperature moments that are close to 1.7 BM, but in these complexes it is known<sup>25</sup> or presumed<sup>24</sup> that the metal atoms are well separated by bridging ligand molecules. Further low-temperature magnetic studies on the heteropoly complex are planned.

The following evidence supports the substituted Keggin structure  $H_2(W_{11}V^{IV})O_{40}^{8-}$  for 11-tungstovanadate(IV). (1) The infrared spectra (Table II) parallel the spectra of other Keggin complexes. (2) The crystallographic data for the potassium and ammonium salts show both are face-centered cubic with  $Z = 8$ . Tourne and Tourne<sup>5</sup> reported the same symmetry for the ammonium salt, with  $a = 22.20$  Å, in agreement with our result  $a = 22.22$  (3) Å. Various other salts of the type  $M'_{7-8}(XW_{11}MO_{39}H_n) \cdot xH_2O$  ( $M' =$  alkali ion or ammonium,  $X = H_2, Si,$  etc.;  $M, n = V^{IV}, 0; Co^{III}, 2;$  etc.) have the same symmetry.<sup>5,14</sup> (3) The infrared spectra in the range 400–800  $cm^{-1}$  when compared with the data for metatungstates and for  $V_4W_9O_{40}^{6-}$  and related complexes<sup>3b</sup> (summarized in Table III) suggest the existence of internal protons as in metatungstate rather than tetrahedral vanadium or tungsten. More convincing is the observation of a proton nmr signal in the corresponding vanadate(V) derivative prepared by direct oxidation of the vanadate(IV) complex. Details on this new tungstovanadate(V) will be given elsewhere.<sup>26</sup> (4) Tetramethylammonium metatungstate forms solid solutions with 11-tungstovanadate(IV) but not with 5-tungstovanadate(IV). (5) Decomposition at pH 2–3 gives metatungstate quantitatively, as do some related Keggin-type complexes.<sup>14</sup>

**Spectra.** A single-crystal esr spectral investigation of  $V^{IV}W_5O_{19}^{4-}$  is reported elsewhere<sup>18</sup> and the relationships between the esr and optical spectra are discussed there. The room-temperature solution esr spectra of the 1:5 and 2:4 complexes are shown on Figure 3. Instead of a fifteen-line

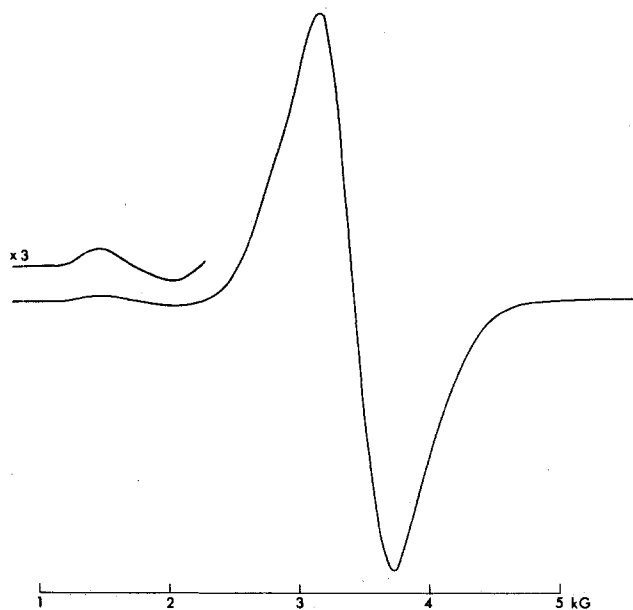


Figure 4. Polycrystalline esr spectrum of  $(C(NH_2)_3)_5H(V_2W_4O_{19}) \cdot H_2O$ .

spectrum expected for the 2:4 complex, only a weak eight-line spectrum is observed, superimposed upon a broad absorption. The hyperfine splitting parameter and  $g$  value in this spectrum are identical with those for  $V^{IV}W_5O_{19}^{4-}$  and probably merely indicate partial formation of this ion on dissolution of the 2:4 complex. The guanidinium salt of the latter complex dissolves very slowly. No half-field ( $\Delta m_s = 2$ ) transition could be observed in these solution spectra, and the alternative explanation for an eight-line spectrum, that the magnetic exchange parameter  $J$  is  $\ll 10^{-2}$   $cm^{-1}$ , is considered to be unlikely in view of the fact that there is a detectable reduction in the magnetic moment per vanadium at 77°K. Both  $g \approx 2$  and  $g \approx 4$  transitions are observed in the powder esr spectrum (Figure 4); unfortunately no isomorphous host crystal is available and both powder and single-crystal spectra are broad and structureless.

The optical spectra of the three tungstovanadates(IV) together with that of  $PW_{11}V^{IV}O_{40}^{5-}$ <sup>12</sup> are shown in Figure 5.<sup>27</sup> The d-d transitions of V(IV) at *ca.* 12 and 15 kK which show as poorly defined shoulders in the spectra of the substituted Keggin anions are better resolved in the 1:5 and 2:4 complexes. The more intense bands at 20 and 25 kK are presumed to be  $V^{IV} \rightarrow W^{VI}$  intervalence charge-transfer transitions.<sup>28</sup> While there are clearly two of these for  $PW_{11}VO_{40}^{5-}$ , the spectrum of  $H_2W_{11}VO_{40}^{8-}$  shows only a single asymmetric band. We have noted similar differences in the spectra of the heteropoly blues; bands II and III in the spectrum of  $PW_{11}W^{VI}O_{40}^{4-}$  are replaced by an asymmetric band in the spectrum of  $H_2W_{11}W^{VI}O_{40}^{7-}$ . It was suggested that the presence of two or three bands in the spectra of the 12-tungstate heteropoly blues arose through the possibility of charge transfer to structurally different metal atoms in the Keggin structure,<sup>7</sup> *i.e.*, to those  $W^{VI}O_6$  octahedra sharing corners or edges with the  $W^{VO}_6$  octahedron. In  $VW_5O_{19}^{4-}$  the four nearest neighbor tungsten atoms are equivalent, and only one intervalence band is observed. The

(27) The spectra of the 1:5 and 2:4 complexes reported by Souchay, *et al.*,<sup>4</sup> cover the region from 330 to 600 nm only. Our data for the 2:4 complex differ significantly from those of Souchay ( $\lambda_{max} \sim 360$  nm,  $\epsilon \sim 680$ ). The difference can be attributed to partial oxidation of the French workers' solution since tungstovanadates(V) absorb very strongly below 450 nm.

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(23) R. E. Tapscott and R. L. Belford, *Inorg. Chem.*, 6, 735 (1967).

(24) D. N. Sathyanarayana and C. C. Patel, *J. Inorg. Nucl. Chem.*, 28, 2277 (1966).

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(26) C. M. Flynn, Jr., M. T. Pope, and S. O'Donnell, in preparation.



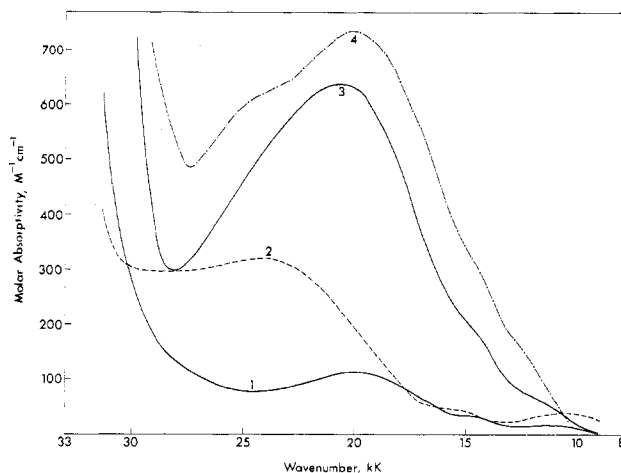


Figure 5. Absorption spectra of tungstovanadate(IV) complexes: 1,  $\text{VW}_5\text{O}_{19}^{4-}$ , pH 5; 2,  $\text{H}_n\text{V}_2\text{W}_4\text{O}_{19}^{-6+n}$ , pH 8; 3,  $\text{H}_2\text{W}_{11}\text{VO}_{40}^{8-}$ , pH 5; 4,  $\text{PW}_{11}\text{VO}_{40}^{5-}$ , pH 2.<sup>12</sup>

six metal atoms in the Lindqvist-Aronsson structure occupy sites of  $C_{4v}$  symmetry with mutually orthogonal  $C_4$  axes. If it is assumed that the observed charge transfer is from  $d_{xy}(\text{V})$  to  $d_{xy}(\text{W})$ , then the orthogonality of these orbitals might account for the low intensity of this transition compared with the corresponding one in the Keggin anions.

The charge-transfer band in the 2:4 complex occurs at a higher energy than in the 1:5 complex. Again, this behavior parallels that of the heteropolytungstate blues in which addi-

tion of a second electron, e.g.,  $\text{PW}_{11}\text{WVO}_{40}^{4-}$  to  $\text{PW}_{10}\text{WV}_2\text{O}_{40}^{5-}$ , causes a hypsochromic shift of the visible spectral bands.

The tungstovanadate(IV) complexes are therefore electronic analogs of heteropoly blues, differing only in the extent to which the "optical" electron is trapped on a specific metal atom. The present studies indicate that poly anions with the Lindqvist-Aronsson structure should be reducible to heteropoly blue species, and we have noted elsewhere<sup>29</sup> a rationalization for this behavior.

**Registry No.**  $(\text{CH}_3\text{NH}_3)_2\text{Na}_2(\text{VW}_5\text{O}_{19})$ , 37340-33-3;  $(\text{CH}_3)_2\text{NH}_2\text{Na}_2(\text{VW}_5\text{O}_{19})$ , 37340-35-5;  $(\text{CH}_3)_4\text{N}_2\text{Na}_4(\text{SO}_4)(\text{VW}_5\text{O}_{19})$ , 37341-43-8;  $(\text{C}(\text{NH}_2)_3)_4(\text{VW}_5\text{O}_{19})$ , 37341-42-7;  $(\text{C}_2\text{H}_4(\text{NH}_3)_2)_2(\text{VW}_5\text{O}_{19})$ , 37340-36-6;  $(\text{C}(\text{NH}_2)_3)_5\text{H}(\text{V}_2\text{W}_4\text{O}_{19})$ , 37340-34-4;  $\text{K}_8(\text{H}_2\text{W}_{11}\text{VO}_{40})$ , 37340-41-3;  $(\text{NH}_4)_{7.5}\text{H}_{0.5}(\text{H}_2\text{W}_{11}\text{VO}_{40})$ , 37340-40-2;  $(\text{CH}_3)_4\text{N}_7\text{H}(\text{H}_2\text{W}_{11}\text{VO}_{40})$ , 37340-39-9;  $(\text{CH}_3)_4\text{N}_5\text{H}_3(\text{H}_2\text{W}_{11}\text{VO}_{40})$ , 37340-38-8.

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(29) M. T. Pope, *Inorg. Chem.*, **11**, 1973 (1972).

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## Electron Paramagnetic Resonance and Optical Studies of Pentavalent Uranium<sup>1</sup>

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Epr and optical spectra are reported for uranium-doped  $\text{LiNbO}_3$ ,  $\text{LiTaO}_3$ , and  $\text{BiNbO}_4$ . The  $\text{U}^{5+}$  ion gives rise to an epr signal at  $|g| \sim 0.7$  and appears to be a site of almost regular octahedral symmetry in every case. An analysis of the data yields crystal field splittings and orbital reduction factors similar to those involved in the previously studied octahedral fluorides. Attempts to prepare magnetically dilute  $\text{U}^{5+}$  in oxides with the perovskite structure were unsuccessful. An epr absorption was found at approximately  $|g| = 1.2$  in  $\text{Na}_3\text{UF}_8$  at 7°K which is attributed to  $\text{U}^{5+}$  in eightfold cubic coordination.

### Introduction

The actinide elements have been studied by magnetic resonance techniques to a lesser extent than the other metals, and consequently less is known about the nature of their bonding. Several factors have deterred a thorough study of the bonding in actinides. Experimentally one must frequently deal with highly radioactive materials whose chemistry is greatly complicated by the occurrence of multiple stable oxidation states. Theoretically the problem is encumbered by intermediate coupling, so that the usual perturbation-type calculations are of limited applicability. Also, for more

than a single f electron, consideration must be given to electron-electron interactions.

Many of these difficulties can be minimized if one's attention is confined to pentavalent uranium compounds. The  $f^1$  configuration is of comparative theoretical simplicity, and the radiation hazards are minor so that numerous preparative techniques can be readily attempted.

We have previously discussed the problem of covalency in actinide series compounds and have reported on the  $^{17}\text{O}$  nmr studies of  $^{17}\text{O}$ -enriched  $\text{K}_2\text{UO}_6$ ,  $\text{Bi}_2\text{UO}_7$ , and  $\text{UO}_2$ .<sup>3</sup> The purpose of this paper is to report the results of epr and optical studies of a number of compounds containing pentavalent uranium.

In the present work particular attention was given to com-

(1) Work done at the Los Alamos Scientific Laboratory, supported by the U. S. Atomic Energy Commission.

(2) (a) Los Alamos Scientific Laboratory; (b) University of Texas at El Paso; Los Alamos Scientific Laboratory Postdoctoral Fellow, 1968-1970, and Associated Western Universities Faculty Participant, summer 1971.

(3) M. P. Eastman, H. G. Hecht, and W. B. Lewis, *J. Chem. Phys.*, **54**, 4141 (1971).