Tungstovanadate heteropoly complexes. II. Products of acidification of V2W4O194-

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Then, assuming that the difference is also reflected in T_{2e}, much broader epr lines are expected for the monochloro species, which would be difficult to detect in the presence of the sharper spectrum of $VO(H_2O)_2Cl_2$.

The liquid solution epr spectra for a number of HCl concentrations were also observed in this laboratory. The intensity of the spectrum attributed to $VO(H_2O)_4{}^{2+}$ appeared to follow qualitatively the relative concentrations indicated in Tables II and III and Figure 4. However, no attempt was made to do an absolute spin count. In 12 M HCl solution the $\langle g \rangle$ and $\langle A \rangle$ values obtained corresponded well with those reported by Kon and Sharpless and the observed

line widths were somewhat broader than those of the $VO(H_2O)_4{}^{2+}$ spectrum. That observation is compatible with a decreased τ_e relative to that of the aquo complex, but a much more detailed investigation of the relaxation processes would be necessary for quantitative comparison.

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Tungstovanadate Heteropoly Complexes. II.
Products of Acidification of $V_2W_4O_{19}{}^{4-}$ [1]

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Acidification of solutions of $V_2W_4O_{19}{}^{4-}$ is an efficient means of preparing the red complex $V_4W_9O_{40}{}^{6-}$, isolated as K, NH$_4$, Na, N(CH$_3$)$_4$, C(NH$_2$)$_3$, and C$_2$H$_4$(NH$_3$)$_2$ salts. This complex is the same as that previously formulated as $V_3W_7O_{31}{}^{5-}$. This complex is most stable at pH near 3. At pH 5 it is converted to $V_2W_4O_{19}{}^{4-}$ and isopolytungstate. On acidification it does not give an oxide precipitate; the free acid can be extracted with ether. Infrared data, elemental analyses, chemical behavior, and comparisons with metatungstate lead to proposal of a Keggin structure $V(W_9V_3)O_{40}{}^{6-}$ for the complex. At least three other complexes are formed on acidification of $V_2W_4O_{19}{}^{4-}$; one of these has been isolated as orange-red K$_5$V$_3$W$_{10}$O$_{40}$·20H$_2$O. It appears to have a Keggin structure $V(W_{10}V_2)O_{40}{}^{5-}$.

Introduction

As part of our investigations on tungstovanadate heteropoly complexes,[2] we have obtained at least four products on acidification of salts of $V_2W_4O_{19}{}^{4-}$ in the pH range 0–3. One of these products has been isolated as potassium, ammonium, sodium, and organic cation salts; their analyses all agree with the composition $M'_6V_4W_9O_{40}·nH_2O$. These salts evidently contain the same anion as some prepared, *e.g.*, by Rosenheim and Pieck[3] which, however, they formulated as (modern notation) $M'_5V_3W_7O_{31}·nH_2O$. Our characterization of these compounds, presented here, leads to a structure proposal based on a 12-tungstometalate (Keggin) constitution. Only one of the other products has been successfully purified. It has been isolated as $K_5V_3W_{10}O_{40}·20H_2O$ and appears also to possess a Keggin structure.

Experimental Section

Ammonium paratungstate was prepared by reaction of WO$_3$·H$_2$O with excess NH$_4$OH in aqueous solution. After all the solid had reacted and dissolved, the solution was evaporated at 80–90°. Ammonium hydroxide was added at intervals to keep the pH in the range 5–7. The white slightly soluble product which separated was collected on a Büchner funnel, washed with small portions of hot water, and air dried. *Anal.* Calcd for (NH$_4$)$_{10}$-(H$_2$W$_{12}$O$_{42}$)·4H$_2$O: NH$_4$, 5.76; W, 70.43. Found: NH$_4$, 5.72, 5.74; W (by ignition to 600°), 70.67, 70.74.

Sodium metatungstate was prepared by Pope and Varga[4] according to Freedman's method.[5]

The preparation of other reagents not obtained commercially has been described.[2]

Guanidinium Metatungstate.—A solution of 0.5 mmol of sodium metatungstate in 20 ml of hot water was treated with a solution of 3 mmol of guanidinium chloride in 3 ml of water. The mixture was reheated and allowed to cool. A nearly white powder separated on cooling. It was filtered off, washed with water followed by 95% ethanol, and air dried. *Anal.* Calcd for (CN$_3$H$_6$)$_6$(H$_2$W$_{12}$O$_{40}$)·3H$_2$O: C, 2.08; H, 1.28. Found: C, 2.30; H, 1.40.

Tetramethylammonium Metatungstate.—A solution of 0.5 mmol of the sodium salt in 5 ml of water was treated with a solution of 6 mmol (0.7 g) of tetramethylammonium chloride in 3 ml of water. The resulting white precipitate was isolated and recrystallized from water containing 1 mmol of tetramethylammonium chloride by room-temperature evaporation. Colorless (very pale yellow in bulk) six-sided tablets or blocks (parallel extinction, optically biaxial) were obtained. They were isolated by washing with water–ethanol and 95% ethanol and air drying. The crystals were stored over sodium sulfate decahydrate, since they are efflorescent in a dry atmosphere. *Anal.* Calcd for [N(CH$_3$)$_4$]$_6$[H$_2$W$_{12}$O$_{40}$]·10H$_2$O: C, 8.30; H, 2.73; W, 63.4. Found: C, 8.41; H, 2.70; W (by ignition to 600°), 63.4.

Salts of the 9-Tungsto-4-vanadate(V) Anion, $M'_6V_4W_9O_{40}·n$-H$_2$O (M' = Univalent Cation). (a) Potassium Salt.—A solution of 50 mmol of K$_4$V$_2$W$_4$O$_{19}$ was prepared from stoichiometric quantities of K$_2$CO$_3$, V$_2$O$_5$, and WO$_3$·H$_2$O.[2] The solution was diluted to about 200 ml and treated with a solution of 70 mmol (9.5 g) of KHSO$_4$ in 50 ml of water. There was little or no immediate visible change. The mixture was heated and stirred at about 80° for 4 hr, during which time it became red and

(1) Presented as part of Paper IN-10 at the Sixth Middle Atlantic Regional Meeting of the American Chemical Society, Baltimore, Md., Feb 3–5, 1971.

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TABLE I
ANALYSES OF TUNGSTOVANADATES

Compound		V	W	Cation	H	W/V	Cation/W
		\%—————————————					
$K_5V_3W_7O_{31} \cdot 19H_2O$	Calcd	6.18	52.0	7.90^d	1.54		
$K_6V_4W_9O_{40} \cdot 24H_2O$	Calcd	6.44	52.3	7.41^d	1.52		
FW 3165.4	Found^a	6.43 (2)	51.9 (2)	7.40 (2)^d	1.49 (1)	2.24	0.670
$(NH_4)_5V_3W_7O_{31} \cdot 18.5H_2O$	Calcd	6.48	54.6	3.87^e	2.45		
$(NH_4)_6V_4W_9O_{40} \cdot 22H_2O$	Calcd	6.79	55.1	3.60^e	2.29		
FW 3003.0	Found	6.64	55.1 (1)	3.56 (2)^e	2.30^b	2.29	0.660
$Na_6V_4W_9O_{40} \cdot 15H_2O$	Calcd	6.87	55.8		1.02		
FW 2966.5	Found	6.96	56.7		1.04 (1)	2.26	
$[N(CH_3)_4]_6V_4W_9O_{40} \cdot 3H_2O$	Calcd	6.80	55.2	9.62^f	2.62		
FW 2997.3	Found	6.85 (1)	55.2 (1)	8.68^f	2.50	2.24	0.603
$[C(NH_2)_3]_6V_4W_9O_{40} \cdot 4H_2O$	Calcd	6.96	56.5	2.46^f	1.51		
FW 2930.9	Found	6.88	56.3	2.49^f	1.50	2.27	0.677
$[C_2H_4(NH_3)_2]_3V_4W_9O_{40} \cdot 12H_2O$	Calcd	7.03	57.0	2.49^f	1.87		
FW 2900.9	Found	6.95	57.3	2.60^f	1.88	2.28	0.695
$K_5V_3W_{10}O_{40} \cdot 20H_2O$	Calcd	4.79	57.7	6.13^d	1.26		
FW 3187.1	Found	4.80	57.8	6.54^d	1.17^e	3.33	0.532

^{a} Material balance 99.1%. ^{b} By ignition to 600°, allowing for $(NH_4)_2O$. ^{c} By difference, ^{d} K. ^{e} NH_4. ^{f} C.

deposited a red-brown precipitate (V_2O_5). The mixture was finally filtered to remove the V_2O_5, giving an orange-red solution. (The V_2O_5 was isolated and dissolved in dilute sodium hydroxide, and an aliquot was taken for analysis. The amount of vanadium recovered as oxide was thus found to be 12 mmol.)

The filtrate was evaporated at room temperature or with heating to crystallize the products fractionally. The principal products were leaflets with brass luster and large scarlet to cherry red cuboctahedral crystals. Other products, obtained in the later crops of crystals, were red rhombohedra and sometimes bright reddish orange rods and potassium sulfate. The desired cuboctahedral crystals of $K_6V_4W_9O_{40} \cdot 24H_2O$ were separated mechanically from the other phases and recrystallized by room-temperature evaporation from about 200 ml of water containing 2 mmol of potassium sulfate and 1 mmol of potassium bisulfate. Some brassy leaflets formed again in the recrystallization; they were removed by filtration. If the red crystals of the product could not be separated from the leaflets, they were redissolved in the solution by heating. The pure crystals of the product were washed with ethanol–water mixtures containing not over about 40% ethanol by volume, blotted dry with tissue, and stored over sodium sulfate decahydrate. The final yield was 46 g, 66% based on tungsten. The crystals are very efflorescent; washing with 95% ethanol causes them to turn opaque and crumble. They were found to be optically anisotropic but not pleochroic. Analyses for this and other tungstovanadates are given in Table I. The by-products obtained here are the same as those obtained in the preparation of a V:W = 3:10 complex described below.

(b) **Ammonium Salt.**—(1) The preparation based on that of Rosenheim and Pieck[3] was carried out by using 2.6 g of ammonium paratungstate and 0.4–0.5 g of vanadium(V) oxide in 50 ml of water. After 2 hr at 90–100° the volume was reduced to about 10 ml. Filtration gave a clear red-orange solution. On evaporation deep red cuboctahedral crystals mixed with irregular bright orange crystals were deposited. Because of their high solubility these products were not further investigated. The former is evidently the V:W = 3:7 compound obtained by Rosenheim and Pieck,[3] and the latter appears to be the ammonium salt of $V_2W_4O_{19}^{4-}$.

(2) A solution of 20 mmol of $(NH_4)_4V_2W_4O_{19}$ in 40 ml of water (prepared by reaction of 40 mmol of NH_4VO_3, 80 mmol of $WO_3 \cdot H_2O$, and a moderate excess (up to 60 mmol) of NH_4OH by heating 3–4 hr in aqueous solution and finally filtering) was treated with a solution of 14 mmol of NH_4HSO_4 in 10 ml of water (prepared from ammonium sulfate and sulfuric acid). Reaction was carried out as for the potassium compound. The desired product, $(NH_4)_6V_4W_9O_{40} \cdot 22H_2O$, crystallized as large red cuboctahedral crystals and was separated mechanically from the other products (mainly red-orange crystalline powder consisting of tiny prisms). The product was recrystallized by room-temperature evaporation from 40 ml of water containing 5 mmol of ammonium sulfate and 0.5 mmol of sulfuric acid. The crystals were isolated in the same way as the potassium salt, except that the ethanol–water mixtures were ice cold. The very efflorescent product (7.0 g, 53% based on tungsten) was stored over sodium sulfate decahydrate. The crystals were optically anisotropic and not pleochroic.

(c) **Sodium Salt.**—Potassium 9-tungsto-4-vanadate(V) hydrate (16 g, 5.0 mmol) was dissolved in 50 ml of warm water. The solution was passed through a 20×400 cm column of Dowex 50W-X8 (Na^+). A spot test on the eluted solution with sodium tetraphenylborate showed complete removal of potassium. The solution was evaporated to dryness over calcium chloride, giving 14.1 g of rust-colored powder.

(d) **Other Salts.**—These were prepared by metathesis with the potassium salt. A solution of 1 mmol (3.2 g) of potassium 9-tungsto-4-vanadate(V) in 10 ml of 0.1 F HO_2CCH_2Cl–0.1 F KO_2CCH_2Cl was treated with 12 mmol of MCl in 6 ml of water (M = guanidinium, tetramethylammonium, or $^1/_2$(ethylenediammonium)). Much precipitate (initially oil with the ethylenediammonium salt) formed in each case. After several minutes the solid was separated by filtration. The product was recrystallized by room-temperature evaporation from water containing 1 mmol each of HO_2CCH_2Cl and KO_2CCH_2Cl and 1–2 mmol of MCl. The approximate amounts of water used were 400, 200, and 800 ml, respectively. The guanidinium salt was thus obtained as 1.9 g of orange-red (brassy luster) parallelogram-shaped leaflets often grown together in foliated masses. The tetramethylammonium salt consisted of 1.9 g of bright orange-red crystalline powder. The crystals were platy to tabular and six sided and were optically biaxial with parallel extinction. They were indistinguishable morphologically from tetramethylammonium metatungstate but differed in that they were not visibly efflorescent. Vanadium and carbon analyses were variable and low for different crops of crystals. *Anal.* Found: V, 6.25–6.68; C, 8.35–8.47; W, 55.8–56.6. The ethylenediammonium salt consisted of 2.1 g of platy to lath-like brownish red crystals which effloresced in a dry atmosphere.

The tetraethylammonium and tetrabutylammonium ions gave precipitates with the anion but they were too insoluble to be recrystallized, even from methanol, ethanol, or acetone.

The tetramethylammonium salt was also prepared by interdiffusion of solutions of the potassium salt (1 mmol dissolved in *ca*. 100 ml of water containing 1 mmol each of HO_2CCH_2Cl and KO_2CCH_2Cl) and tetramethylammonium chloride (20 mmol in about 5 ml of water placed in a vial). The vial containing the $N(CH_3)_4Cl$ was placed in a 150-ml beaker containing the heteropoly salt. Water was added carefully until the vial was immersed, and the beaker was covered and allowed to stand. Crystals of the product began forming within 2 days. About 15 days later the product was isolated. Partial separation of crystals formed earlier from those formed later was obtained. Vanadium contents were variable. *Anal.* Found: V, 6.54–6.83 (higher values for product which separated first).

The salt was prepared again by metathesis as described above first, but the recrystallization was done rapidly as follows. The crude material was dissolved in 40–50 ml of water containing 1 mmol each of HO_2CCH_2Cl and KO_2CCH_2Cl by heating to boiling. The solution was filtered and allowed to cool, during which much product separated. Then a solution of tetramethylammonium chloride (2 F, 15 ml) was added dropwise as the solution was swirled. The product was then isolated on a Büchner funnel, washed successively with small portions of 2 F $(CH_3)_4NCl$, water–ethanol, and 95% ethanol, and then air dried. The resulting

orange powder (tiny leaflet crystals) weighed 2.6 g and was not efflorescent. The analytical data for the tetramethylammonium salt in Table I are for this product.

Preparation and Analysis of Metatungstic Acid–Ether Extract.—Sodium metatungstate (5.0 g, 1.54 mmol) was dissolved in 10 ml of water and transferred to a 60-ml separatory funnel. Diethyl ether (20 ml) and 20–25 ml of 10 F sulfuric acid were added, the latter in small portions with swirling. The mixture was then shaken and the three layers were allowed to separate. The two upper layers were drawn off by pipet and the oily metatungstic acid–ether layer was washed with ether twice. Portions were drawn off and weighed quickly for the analyses. The total weight of extract obtained was about 6.4 g. Content of volatile material was estimated by weight loss at room temperature when the ether odor was slight or nil and also by drying at 110°. An infrared spectrum of the product after drying at room temperature showed no bands due to ether. Ignition at 600° gave total volatile material and tungsten content. Other portions were dissolved in water and titrated with sodium hydroxide at 0–5° to determined acid content. Results are given in Table II.

TABLE II

ANALYSIS OF COMPLEX ACID–ETHER EXTRACTS

Acid	$H_6(H_2W_{12}O_{40})$ (FW 2854.3)	$H_6(V_4W_9O_{40})$ (FW 2504.5)
mmol of W/g	2.78 (1)	2.16 (1)
mmol of V/g	...	0.962 (5)
mmol of H⁺/g	1.87 (1)	2.06 (2)
$(C_2H_5)_2O$, %^{a}	13	14
Total volatile matter, %	35.5 (2)^b	...
Complex acid, %	66.1 (2)	60.1 (3)
H_2SO_4, %^{c}	2.4	3.1
Free water, %^{d}	19	23
Total H⁺:complex acid	8.06	8.58
W:V	...	2.24
Complex acid:H_2SO_4:$(C_2H_5)_2O$:H_2O	1:1.0:7.6:46	1:1.3:7.9:53
Mol of complex acid/kg of water	1.1	1.0
Prep yield, %	Ca. 97	Ca. 89

^{a} Weight loss at room temperature in air. ^{b} By ignition to 600°. ^{c} From excess of H⁺ over that required by complex acid. ^{d} By difference: total volatile matter minus ether and sulfuric acid, corrected for constitutional water in complex acid.

Preparation and Analysis of the Ether Extract of 9-Tungsto-4-vanadic(V) Acid.—Potassium 9-tungsto-4-vanadate(V) (5.0 g, 1.57 mmol) was dissolved in 10 ml of water. Ether and sulfuric acid were added as for the metatungstate and the mixture was shaken. Three layers were obtained: excess ether, a yellow turbid aqueous layer, and an oily red layer consisting of the etherate of the complex acid. After the product layer was washed, portions were drawn off and weighed quickly for analyses. The total weight of extract was about 5.8 g. Ether content was estimated by weight loss at room temperature until ether odor was slight or nil. Tungsten and vanadium were determined in the same way as for the heteropoly salts. The acid content was determined in the same way as for the metatungstate etherate. The results are given in Table II. The material turned brown and opaque and then green-brown in 1–2 days.

Preparation of Potassium 10-Tungsto-3-vanadate(V), $K_5V_3W_{10}O_{40} \cdot 20H_2O$.—In a typical preparation, a solution of 100 mmol of $K_4V_2W_4O_{19}$ in 800 ml of water was treated with 200 ml of 1.0 F H_2SO_4. The mixture was heated near 80° and stirred 4 hr, during which red-brown V_2O_5 precipitated and the solution became red. The solution (now about 600 ml) was filtered and evaporated at 70–80° to about 500 ml. No more precipitate formed. It was then allowed to cool and evaporate slowly at room temperature. The products were isolated daily as they separated from the solution. The initial products were brass-colored to orange-red leaflets. Later the bright orange-red crystals of the 3:10 complex began to form. These were usually hexagonal prisms but sometimes appeared as stubby hexagonal bipyramids. If the 3:10 salt was a minor phase in any crop, it was mechanically separated from the other products and redissolved in the solution by warming. When the 3:10 compound separated as a major phase, the crystals were picked out and washed with ice-cold ethanol–water mixtures containing not over about 50% v/v ethanol. The washing removed the remaining leaflets and some yellow amorphous precipitate (probably $WO_3 \cdot xH_2O$). The crystals were then blotted dry with tissue. At least a fraction

of these crystals could be freed mechanically from the remaining impurities (mostly red rhombohedra and colorless potassium sulfate crystals). This operation was performed rapidly, and the efflorescent crystals were stored in a closed container over sodium sulfate decahydrate. Yields were 5–10% based on tungsten.

Other Complexes.—The red rhombohedral crystals obtained in the preceding preparation gave a mixture of both the starting material and leaflet crystals on recrystallization from potassium sulfate–bisulfate solutions. Recrystallization from potassium bisulfate solutions did give optically pure rhombohedra, but the vanadium contents of successive crops of crystals varied over a range of about 10%.

The leaflet crystals from the preceding preparation could be recrystallized over the pH range 2–5 with little or no visual changes indicative of decomposition or the presence of mixtures. However, constant vanadium content was not obtained. Metathesis tests with other cations suggested that the material was a mixture, but no convenient separation was obtained.

Variation of the ratio of acid to 2:4 complex in the preparation did not lead to production of any one complex as the major product, but always required fractional crystallizations and mechanical separations. Reactions using ammonium salts also gave mixtures of three or more products in addition to the 4:9 complex. With sodium salts the products were too soluble to isolate readily.

Various attempts to obtain complexes with high W:V ratios (e.g., 11:2, 11:1, 12:1) all failed. These included reactions starting with VO_3^- and WO_4^{2-} in these ratios as well as decompositions of, e.g., $VW_5O_{19}^{3-}$, all done in very acidic solutions (pH below 2). The main products were generally salts of $VW_5O_{19}^{3-}$.

Analyses of Salts.—Vanadium, tungsten, and water were determined as described previously.[2] Potassium was determined as the tetraphenylborate. Ammonia was determined by distillation from sodium hydroxide solution into excess boric acid solution followed by titration with perchloric acid. Bromocresol green was used as indicator. Carbon and hydrogen were determined by Galbraith Laboratories, Inc., Knoxville, Tenn.

Chemical Reactions of the 4:9 Complex.—Titrations with sodium hydroxide were carried out as described previously.[2]

Potassium 9-tungsto-4-vanadate(V) did not consume sodium hydroxide at 0–5°. At ca. 80° the reaction did occur, with breaks in the pH curve at 15.5 ± 0.8 and 19.7 ± 0.8 mol of OH⁻/mol of anion (pH 7.5–8.0 and 9.2–10.0, respectively). A small break was also noted at 2.4 ± 0.6 mol of OH⁻/mol of anion at pH 6.0–6.2.

A solution of 0.1821 g of potassium 9-tungsto-4-vanadate(V) hydrate in 20 ml of water was passed through a 15 × 170 mm column of Dowex 50W-X2 (H⁺). The eluted solution of the acid was cooled to 0–5° and titrated with sodium hydroxide. A pH curve typical of titration of a strong acid was obtained, with a sharp break centered at pH near 7 and 0.344 mmol of NaOH, giving 6.02 mol of H⁺/mol of anion for the acid.

Potassium 9-tungsto-4-vanadate(V) was recrystallized from various buffer solutions. These buffer solutions included K_2SO_4–$KHSO_4$ mixtures in ratios from 1:4 to 4:1, KO_2CCH_2Cl–HO_2CCH_2Cl mixtures in ratios from 1:1 to 5:1, 1:1 KO_2CH–HO_2CH, and 1:1 KO_2CCH_3–HO_2CCH_3. The compound recrystallized substantially unchanged from solutions with K_2SO_4:$KHSO_4$ = 1:1 or greater. More acid bisulfate buffers gave much conversion to products which were visually the same as the by-products in the synthesis of the 4:9 complex. The carboxylic acid buffers (pH above 3) caused decomposition to isopolytungstate and $V_2W_4O_{19}^{4-}$ (colorless leaflets and large orange chunky crystals, respectively). This decomposition was partial in the mono-chloroacetate and formate buffers examined and complete in the acetate buffer. The crystals of the unchanged 4:9 complex were separated mechanically from the other products and analyzed for vanadium. The vanadium content was found to be 6.35–6.45%, with no trend vs. pH. The crystals from the mono-chloroacetate and formate buffers were darker than from the bisulfate buffers due probably to slight reduction to heteropoly blue type species by the buffer reagents.

Recrystallization of guanidinium 9-tungsto-4-vanadate(V) from acetate buffer gave a fine-grained white precipitate and orange-yellow rods (isopolytungstate and $V_2W_4O_{19}^{4-}$ salt, respectively).

Solid Solution of Tetramethylammonium Salts of $H_2W_{12}O_{40}{}^{6-}$ and $V_4W_9O_{40}{}^{6-}$.—It was found that recrystallization of tetramethylammonium metatungstate from solutions containing small quantities of the 9-tungsto-4-vanadate(V) complex gave yellow

crystals morphologically like the pure metatungstate. Solutions of the respective sodium salts (each 0.010 F) were mixed in various ratios. A moderate excess of tetramethylammonium chloride was added to each sample and the solutions were allowed to evaporate. All the samples gave six-sided platy to tabular crystals which were visually indistinguishable. When the crystals were washed and allowed to dry, the metatungstate-rich crystals turned opaque (effloresced), but the tungstovanadate-richer crystals remained clear. At a metatungstate:tungstovanadate ratio of 4:1 both phases were obtained. At a 9:1 ratio, only the efflorescent phase was obtained. At ratios 2:1 or richer in tungstovanadate, only the air-stable clear crystals appeared.

Chemical Reactions of the 3:10 Complex.—Recrystallization of the very soluble potassium salt from various potassium sulfate–bisulfate mixtures ($HSO_4^-:SO_4^{2-} = 1:2$ to $2:1$) gave the unchanged compound if small samples were used, so that the time required was not more than 1 day. With larger batches and consequently longer time required for evaporation, relative yields were lower, with considerable conversion to leaflet and rhombohedral crystals and yellow precipitate.

A solution of the complex ($\sim 3 \times 10^{-3}\ F$) had a pH of 3–3.5 at 0–5°. It consumed <1 mol of OH^-/mol of complex in a titration up to pH 10. The solution was heated to about 50° and the titration continued. No well-defined end point breaks were obtained.

Treatment of a small amount of the compound in concentrated aqueous solution with 10 F H_2SO_4 and diethyl ether led to extraction of a heteropoly acid as a dense, red, oily layer. It was not further characterized.

Solid Solution of the 3:10 Complex with 12-Tungstoferrate-(III).—Potassium 12-tungstoferrate(III), $K_5[FeW_{12}O_{40}] \cdot nH_2O$, prepared by the method of Pope and Varga,[4] was recrystallized from dilute 1:1 potassium sulfate–bisulfate buffer solution. The product consisted of efflorescent light yellow hexagonal prisms. A similar solution containing a small quantity of potassium 10-tungsto-3-vanadate(V) gave efflorescent crystals of the same habit but deep yellow in color.

Physical Characterization.—Ultraviolet–visible spectra, infrared spectra (in KBr disk), and X-ray powder diffraction patterns were obtained as described.[2] Powder X-ray data were obtained for tetramethylammonium and guanidinium salts. They contained few strong or sharp peaks. The corresponding metatungstates and tungstovanadates were not isomorphous. Infrared data are given in Table III.

TABLE III
INFRARED DATA (FREQUENCIES DUE TO ANION)

Compound	Freq, cm^{-1} [b]					
Metatungstates						
Na	960 sh	933	886	760 br	580 br	400 br
N(CH₃)₄	949	925	874	765 br	600 br	400 br
C(NH₂)₃	950 sh	930	876	768 br	570 br	400 br
9-Tungsto-4-vanadates						
Na	965		892	760	500 br	
K	965		882	755	500 br	
NH₄	974, 965		890	760	500 br	
N(CH₃)₄	951		884	758	510 br	
4-Tungsto-2-vanadates and 5-tungstovanadates[a]	984–936		797–781	589–578	440–420 br	
10-Tungsto-3-vanadates	968		885 br	750 br	505 br	

[a] Reference 2. [b] sh, shoulder; br, broad.

Solutions of potassium 9-tungsto-4-vanadate(V) were examined spectrophotometrically in various buffer solutions. They appeared to be most stable at pH 2.5–3. Features were a shoulder at about 350 nm (ϵ 6.5×10^3) and a shoulder at about 240 nm (ϵ 4.0×10^4). Fresh solutions in the pH range 2–3 (potassium sulfate–bisulfate buffers) obeyed Beer's law to 4% or better in the concentration range 10^{-2}–10^{-4} F in complex. These solutions underwent some change in spectra during 16 days' standing, but gross features remained the same. Solutions of the complex in 0.5 F hydrochloric acid decomposed significantly in 1–2 hr. Solutions in acetate buffer (0.1 F each in acetic acid and potassium acetate) decomposed slowly over 60 days; the final spectrum corresponded to that of $V_2W_4O_{19}^{4-}$. From these data, 2.10 ± 0.04 mol of $V_2W_4O_{19}^{4-}$ was produced per mol of $V_4W_9O_{40}^{6-}$.

A saturated D_2O solution of the sodium 4:9 complex salt was examined on a Varian A-60 nmr spectrometer, under conditions similar to those used by Pope and Varga[6] in their nmr investigation of metatungstate. The nmr signal from the protons inside the metatungstate ion (saturated D_2O solution of sodium salt) was also reobserved here as a check. A signal due to H_2O from the hydrated 4:9 complex salt was observed in both cases. No signal indicative of protons inside the 9-tungsto-4-vanadate-(V) ion was obtained.

Potassium 10-tungsto-3-vanadate(V) appeared to decompose considerably in solution on the basis of recrystallization experiments. The significance of the spectra obtained for solutions of this salt is therefore uncertain.

Discussion

Identity of the 4:9 Complex.—About 80 years ago, Friedheim[7] prepared compounds which he formulated as (modern notation) $M'_4HV_3W_6O_{28} \cdot nH_2O$ (M', n: NH_4, $^{29}/_2$; K, $^{29}/_2$; Ba/2, $^{29}/_2$), referred to as the "purple-red" series of tungstovanadate compounds. Later, Rosenheim and Pieck[3] also prepared salts of this complex and revised the composition to $M'_5V_3W_7O_{31} \cdot nH_2O$ (M', n: NH_4, $^{37}/_2$; $C(NH_2)_3$, 6; Cs, $^7/_2$). The physical descriptions and solubilities of the potassium, ammonium, and guanidinium salts obtained by those authors agree with those of the compounds which we formulate as $M'_6V_4W_9O_{40} \cdot nH_2O$. The analytical data are presented in Table I. The derived stoichiometries depend critically on purity; for example about 3% of metatungstate impurity would raise the W/V ratio from 2.25 ($= 9:4$) to 2.33 ($= 7:3$). The vanadium and cation analyses are seen to be the most critical in this regard, as shown by calculations for the Rosenheim formulation in Table I. That our products are not mixtures is supported by optical homogeneity of the crystals and by constant vanadium content of the potassium salt when recrystallized from various buffer solutions. Difficulty was encountered in obtaining good analyses for the tetramethylammonium salt. The low vanadium and cation contents for samples recrystallized slowly, despite optical homogeneity, suggest solid solution impurities such as metatungstate or the ion $V_3W_{10}O_{10}^{5-}$ (see below). Presence of the latter impurity is somewhat more consistent with the analyses. That good analyses were obtained for rapidly recrystallized product suggests that the impurity forms during slow partial decomposition. That this difficulty was not observed for the ethylenediammonium or guanidinium salts (both recrystallized slowly) indicates reluctance of the presumed impurity to form solid solutions with these salts. This suggests that the impurity has a different charge than the 4:9 complex, thus favoring $V_3W_{10}O_{40}^{5-}$, for example, over metatungstate.

Formation and Preparation of the 4:9 Complex.—The previously reported preparations[3] involved boiling alkali paratungstate solutions with vanadium(V) oxide. The main product of this procedure is usually $V_2W_4O_{19}^{4-}$, with the red 3:7 (4:9) salts isolated in low yields. We found that preparations starting from tungstate, metavanadate, and strong acid (W:V > 2) also gave low yields of the 4:9 complex. However high yields are readily obtained by acidification of concentrated $V_2W_4O_{19}^{4-}$ solutions, in which vanadium(V) oxide is also formed. The assumed reaction is

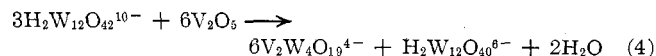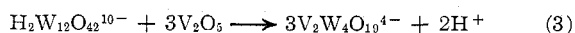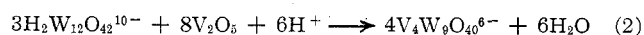$$9V_2W_4O_{19}^{4-} + 12H^+ \longrightarrow 4V_4W_9O_{40}^{6-} + V_2O_5 + 6H_2O \quad (1)$$
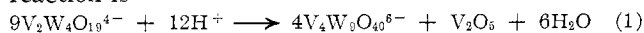
(6) M. T. Pope and G. M. Varga, Jr., *Chem. Commun.*, 653 (1966).
(7) C. Friedheim, *Chem. Ber.*, **23**, 1505 (1890).

The proportion of vanadium experimentally recovered as pentoxide, 12%, agrees well with 11% calculated from eq 1.
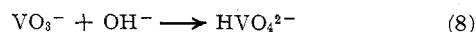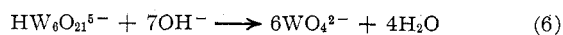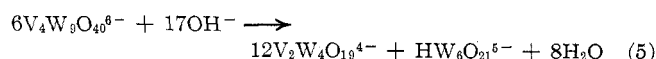
The reactions of vanadium(V) oxide with para-tungstate ion may be

$$3H_2W_{12}O_{42}{}^{10-} + 8V_2O_5 + 6H^+ \longrightarrow 4V_4W_9O_{40}{}^{6-} + 6H_2O \quad (2)$$

$$H_2W_{12}O_{42}{}^{10-} + 3V_2O_5 \longrightarrow 3V_2W_4O_{19}{}^{4-} + 2H^+ \quad (3)$$

$$3H_2W_{12}O_{42}{}^{10-} + 6V_2O_5 \longrightarrow$$
$$6V_2W_4O_{19}{}^{4-} + H_2W_{12}O_{40}{}^{6-} + 2H_2O \quad (4)$$

Our characterization of the 4:9 complex leads to the strong possibility that it is a Keggin-type complex (see below). This complex, having the same size and charge as metatungstate, would be expected to form solid solutions with the latter. Such mixtures, if obtained, might not give purer product on recrystallization. Since our preparation starts with a stable tungstovanadate, we feel that formation of metatungstate is unlikely, whereas in the previous preparations formation of metatungstate is a possibility not readily eliminated.

Chauveau[8] did not obtain a 3:7 or 4:9 complex in her investigation of dilute tungstovanadate solutions. She obtained the ammonium salt by the method of Rosenheim and Pieck[3] and retained the 3:7 formulation on the basis of incomplete analyses. From all the evidence available[2,8,9] reaction of dilute solutions of tungstate and vanadate (W:V = 2–5, pH 1–7) produces only the ions $V_2W_4O_{19}{}^{4-}$, $HV_2W_4O_{19}{}^{3-}$, and/or $VW_5O_{19}{}^{3-}$. The 4:9 and other red complexes are obtained only at higher concentrations; however, once formed, some of them are fairly stable in dilute solutions.

Chemical Properties of the 4:9 Complex.—Salts of the complex can be recrystallized at pH near 3, though very dilute solutions show some decomposition as indicated by ultraviolet spectra and analyses of the recrystallized tetramethylammonium salt. At pH near 5, the complex decomposes to $V_2W_4O_{19}{}^{4-}$ and isopolytungstate, as shown by ultraviolet spectra and recrystallization experiments. Reaction with sodium hydroxide is very slow at 0–5° but reasonably fast at 70–80°. Titrations in hot solutions give results consistent with the successive reactions

$$6V_4W_9O_{40}{}^{6-} + 17OH^- \longrightarrow$$
$$12V_2W_4O_{19}{}^{4-} + HW_6O_{21}{}^{5-} + 8H_2O \quad (5)$$

$$HW_6O_{21}{}^{5-} + 7OH^- \longrightarrow 6WO_4{}^{2-} + 4H_2O \quad (6)$$

$$V_2W_4O_{19}{}^{4-} + 6OH^- \longrightarrow 2VO_3{}^- + 4WO_4{}^{2-} + 3H_2O \quad (7)$$

$$VO_3{}^- + OH^- \longrightarrow HVO_4{}^{2-} \quad (8)$$

Reaction 5 is also consistent with the spectrophotometric results obtained[8] by Chauveau, who described the reaction in terms of a 3:7 complex. Reactions 6 and 7 occur concurrently. These reactions thus lead to successive end points at 2.83, 16, and 20 mol of OH^-/mol of 4:9 complex.

At pH below 3, the complex is slowly converted to at least three other species, their yields depending on the acidity. These are discussed below. If a solution of the 4:9 complex is made strongly acid, no tungsten oxide precipitate is formed, in agreement with the observations of Rosenheim and Pieck.[3]

(8) F. Chauveau, *Bull. Soc. Chim. Fr.*, 834 (1960).
(9) F. Chauveau and P. Souchay, *ibid.*, 561 (1963).

Ether Extraction of 9-Tungsto-4-vanadic(V) Acid. —The ether extraction of the free acid of the 4:9 complex (also noted by Chauveau[8]) proceeds similarly to that for other 12-tungstoheteropoly complexes. The results of analyses of the vanadate together with data for the metatungstic acid–ether extract are listed in Table II. It is seen that the compositions of the two systems are similar on a mole ratio basis and that the 4:9 metal ratio is preserved in the case of the vanadate. It would be of interest to obtain similar data for other systems with different charge type, *e.g.*, $H_3PW_{12}O_{40}$. The excess of acid over that required by the anion is attributed to sulfuric acid extracted with the complex. (This was confirmed for the vanadate complex by qualitative detection of sulfate.)

Constitution of the 4:9 Complex.—We propose that the 4:9 complex is $V_4W_9O_{40}{}^{6-}$ with a structure based on the unknown Keggin-type 12-tungstovanadate(V) anion $VW_{12}O_{40}{}^{3-}$. The 4:9 complex would be derived therefrom by substitution of three tungsten atoms by vanadium atoms, giving $V(W_9V_3)O_{40}{}^{6-}$. Considerations in support of this formulation follow. (1) The formulation is derived readily from the 4:9 stoichiometry. (2) The formation of the complex acid etherate parallels that observed for other 12-tungstoheteropoly (Keggin structure) complexes. (3) A solution of the acid prepared by ion exchange consumed sodium hydroxide in agreement with 6 mol of OH^-/mol of anion, with all protons strongly acidic. The same behavior is observed for metatungstate.[10] (4) The potassium salt did not react with sodium hydroxide rapidly at 0–5° up to pH 11. This is consistent with the absence of constitutional water (hence ionizable protons) in the complex. (5) The infrared spectra (Table III) are similar to those of metatungstates but not to the spectra[2] of salts of $V_2W_4O_{19}{}^{-4}$ or $VW_5O_{19}{}^{3-}$. (6) The failure to detect protons inside the anion by nmr in nearly saturated solutions of the very soluble sodium salt opposes a formulation such as $H_2(W_{12-n}V_n)O_{40}{}^{(6+n)-}$ or $H_2(W_{12-n}V_n)O_{40}H_n{}^{6-}$. Such a formulation is also inconsistent with the cation analyses and/or with the base titration results. An integral value of n also does not even nearly satisfy the experimental W:V ratios. (The cases $n = 2$ and 4 are analytically equivalent to $VW_5O_{19}{}^{3-}$ and $V_2W_4O_{19}{}^{4-}$, which were shown to have the $M_6O_{19}{}^{n-}$ constitution.[2]) (7) The extensive solid–solution formation between the tetramethylammonium salts of the 4:9 complex and metatungstate implies that the two ions have similar structures.

There exists the possibility that the anion may contain a tungsten atom in the presumed central tetrahedral position instead of a vanadium atom. Our data do not eliminate this possibility. However, we consider it unlikely for two reasons: (1) isopoly or heteropoly complexes with tungsten in tetrahedral coordination have not been reported; (2) recent crystal structure determinations show vanadium(V) to be smaller than tungsten(VI) in both tetrahedral and octahedral coordination in oxides (radii: $V(V)_{tet}$, 0.355 Å; $W(VI)_{tet}$, 0.42 Å; $V(V)_{oct}$, 0.54 Å; $W(VI)_{oct}$, 0.60 Å).[11]

(10) O. Glemser, W. Holznagel, and E. Schwarzmann, *Z. Naturforsch. B*, **20**, 725 (1965).
(11) R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969); *Sect. B*, **26**, 1046 (1970).

Another possible formulation retains the old 3:7 metal atom ratio and is based on the unknown 2:18 tungstovanadate, $V_2W_{18}O_{62}{}^{6-}$, by substitution of four tungsten atoms by vanadium, giving $V_2(W_{14}V_4)O_{62}{}^{10-}$. While considerations (2), (3), (4), and (6) could be taken in support of this structure, items (5) and (7) oppose it.

The proposed Keggin formulation $V(W_9V_3)O_{40}{}^{6-}$ implies the existence of several isomers. No evidence of isomer formation or separation has been noted by us here. Such isomers would presumably form solid solutions and not be separable by recrystallization. We contemplate nmr (^{51}V and/or ^{183}W) studies to learn more about the structure of this complex, including isomerism. Since Keggin complexes are liable to crystallize in disordered structures,[12] X-ray studies may not succeed in determining isomerism.

Other Complexes.—Treatment of the 4:9 complex at pH 1–2 or syntheses starting from the 2:4 complex and acidification to pH 1–2 give at least three more complexes. One of these has been isolated fairly pure as the potassium salt $K_5V_3W_{10}O_{40}\cdot20H_2O$. Analyses are given in Table I. This 3:10 complex is itself unstable in solution and appears to be involved in equilibria with other complexes. Crystals of the potassium salt appear to possess hexagonal symmetry, but efflorescence precluded X-ray studies. The similarity of its infrared spectrum (Table III) to those of the 4:9 complex salts, its high solubility like that of potassium 12-tungstoferrate(III), its solid solution formation with the morphologically similar crystals of potassium 12-tungstoferrate(III), and its extraction by ether from strongly acidified solutions, combined with the stoichiometry, indicate a structure $V(W_{10}V_2)O_{40}{}^{5-}$ related to the 4:9 complex.

The other complexes which were not successfully purified are also orange to red. One of these (potassium salt as red rhombohedra) is stable in very acid solutions. Another complex (or possibly a mixture of two complexes, giving leaflet crystals as the potassium salt) appears to be stable in the pH range 1.5–5. Analyses of some of these materials gave V:W ratios near 1:4. No evidence was obtained, despite various attempts, for species with W:V ratios greater than 5.

Summary of Tungstovanadate(V) Species.—On the basis of the structural evidence obtained, the complexes may be systematized according to the structural types of known related complexes, as outlined in Table IV. The substituted metatungstate formulations with

(12) 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).

TABLE IV
SUMMARY OF TUNGSTOVANADATE(V) COMPLEXES

Structure type	Stability	Ref
$W_{6-n}V_nO_{19}{}^{(2+n)-}$		
$n = 0$	Decomposes in aq soln	a
$n = 1$	pH 1–4	2
$n = 2$	pH 4–7	2
$n = 3$	See ref 2	3
$n = 4, 5$	Unknown; see ref 2	
$H_2W_{12-n}V_nO_{40}H_m{}^{(6+n-m)-}$		
$n = 0$	pH 1–8	10
$n = 1, 3$	Unknown	. . .
$n = 2, 4$	See text	. . .
$VW_{12-n}V_nO_{40}{}^{(3+n)-}$		
$n = 0, 1$	Unknown	. . .
$n = 2$	3:10 complex, pH 1–2	This work
$n = 3$	4:9 complex, pH near 3	This work
$n > 3$	Unknown	b
$V_2W_{18-n}V_nO_{62}{}^{(6+n)-}$	See text	. . .

^{a} K. F. Jahr, J. Fuchs, and R. Oberhauser, *Chem. Ber.* **101**, 477 (1968). ^{b} We have recently obtained the species with $n = 4$ and will describe it in a separate publication.

$n = 2$ and 4 (with $m = 2$ in both cases) correspond analytically to the 1:5 and 2:4 complexes, which have the $M_6O_{19}{}^{n-}$ structure instead. Attempts to obtain $VW_{12}O_{40}{}^{3-}$ or its monosubstituted derivative $V_2W_{11}O_{40}{}^{4-}$ have failed. The ion $PW_{12}O_{40}{}^{3-}$ is stable at pH below 1–2, but $AsW_{12}O_{40}{}^{3-}$ is much less stable and has been isolated only in poor yield.[13] The E–O distances (E = P, As, V) in the tetrahedral anions in the isomorphous salts $Ca_2(EO_4)Cl$ are[14] 1.54 (P), 1.69 (As), and 1.71 Å (V). Assuming formation of the 1:12 complex is determined largely by the size of the heteroatom, $VW_{12}O_{40}{}^{3-}$ is expected to be less stable than the arsenate analog.

Possibly one or more of the complexes which we failed to purify have structures based on substitution of $V_2W_{18}O_{62}{}^{6-}$, whose P and As analogs are well known and stable. We obtained no evidence for the parent divanadate ion. Vanadium(V) in acid solutions prefers octahedral coordination over tetrahedral.[15] The hypothetical 1:12 and 2:18 complexes may just be unstable with respect to $VW_5O_{19}{}^{3-}$, which type of complex phosphorus(V) and arsenic(V) would hardly be expected to form.

(13) A. Rosenheim and J. Jaenicke, *Z. Anorg. Allg. Chem.*, **101**, 235 (1917).
(14) E. Banks, M. Greenblatt, and B. Post, *Inorg. Chem.*, **9**, 2259 (1970).
(15) M. T. Pope and B. W. Dale, *Quart. Rev., Chem. Soc.*, **22**, 527 (1968).