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Tungstovanadate Heteropoly Complexes. I. Vanadium(V) Complexes with the Constitution $M_6O_{19}^{n-}$ and $V:W \leq 1:2$[1]

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Orange-yellow salts $M'_4V_2W_4O_{19} \cdot nH_2O$ and yellow salts $M'_3VW_5O_{19} \cdot nH_2O$ (M′ = univalent cation) have been obtained from stoichiometric mixtures of V(V) and W(VI) with appropriate pH adjustment. The $V_2W_4O_{19}^{4-}$ ion is stable in the pH range *ca.* 4–7. Above pH 7 it is degraded into VO_3^- and WO_4^{2-}. At pH 1–3 it is converted into other heteropoly complexes, including $VW_5O_{19}^{3-}$. At pH 2–3 suitable cations give products which are evidently solid solutions of $M'_3HV_2W_4O_{19}$ and $M'_3VW_5O_{19}$. The $VW_5O_{19}^{3-}$ ion is stable in the pH range *ca.* 1–4. Above pH 4 it is converted to $V_2W_4O_{19}^{4-}$ and isopolytungstate. Solutions of either ion give tungsten(VI) oxide precipitates when made strongly acid. Data from cryoscopy, thermal dehydration, X-ray powder diffraction, infrared spectroscopy, and visible–ultraviolet spectroscopy lead to the proposal that these ions are $V_2W_4O_{19}^{4-}$ and $VW_5O_{19}^{3-}$ with the $M_6O_{19}^{n-}$ structure exhibited by isopoly anions of niobium, tantalum, molybdenum, and tungsten.

Introduction

As part of our investigation on heteropoly complexes containing group V transition metals, we have begun studies of complexes of vanadium with tungsten and with molybdenum. Each of these systems offers the possibility of formation of new Keggin-type complexes (parallel to $PVW_{11}O_{40}^{4-}$, $PV_3Mo_9O_{40}^{6-}$, etc.[2,3]) and also species of the type $M_6O_{19}^{n-}$. The latter type is so far represented by isopoly anions with M = Nb, Ta, Mo, or W in their highest oxidation states.[4-6] The reduction chemistry of $M_6O_{19}^{n-}$ species may prove fruitful. There is also the potential for complex formation, as demonstrated by $Nb_6O_{19}^{8-}$ in complexes with Mn(IV), Ni(IV), Cr(III), and Co(III).[7-9]

The older literature[10] contains descriptions of a variety of vanadium–molybdenum and vanadium–tungsten heteropoly (or mixed isopoly) complexes. The synthetic procedures used were generally not very systematic, *e.g.*, the preparation of compounds $M'_4V_2W_4O_{19} \cdot nH_2O$ (M′ = univalent cation) by boiling a paratungstate solution with vanadium(V) oxide. Our investigations reveal the existence of at least six complexes in the vanadate(V)–tungstate(VI) system, some of which we have isolated and characterized.[1] Among these complexes are the ions $V_2W_4O_{19}^{4-}$ and $VW_5O_{19}^{3-}$. Some V:W = 2:4 salts were previously prepared by Rosenheim and coworkers.[10] Chauveau[11] has studied the 2:4 complex in dilute aqueous solution. Chauveau and Souchay[12] have reported the $VW_5O_{19}^{3-}$ ion in dilute aqueous solution but did not isolate solid compounds. We report here an efficient preparation of the 2:4 salts and isolation of the 1:5 complex, with characterization which leads us to propose the $M_6O_{19}^{n-}$ structure for both of these ions. We have also obtained products which are evidently solid solutions of $M'_3HV_2W_4O_{19} \cdot nH_2O$ and $M'_3VW_5O_{19} \cdot nH_2O$.

Experimental Section

Potassium metavanadate and sodium pyrovanadate were obtained as described.[13] Solutions of K_2WO_4 were prepared from $WO_3 \cdot H_2O$ and potassium hydroxide in hot water; complete and stoichiometric reaction was determined by absence of precipitate and a final pH of about 8 (by test paper). Solutions of salts of some organic cations were prepared from the bases (aqueous solutions of methylamines, 98% ethylenediamine, or guanidinium carbonate) by treatment with the desired acid. Buffer solutions with formate or mono- or dichloroacetate were prepared from the acids and alkali carbonate.

Salts of the 4-Tungsto-2-vanadate(V) Anion. a. Potassium Salt (I).—Quantities of KVO_3, K_2WO_4, and acetic acid in 1:2:6 ratio were mixed in *ca.* 1 *F* aqueous solution. The mixture was heated to about 80° to complete the reaction and to evaporate the resulting clear yellow-orange solution. Then it was allowed to cool. Room-temperature evaporation over several days led to formation of large (1-cm) bright yellowish orange tabular to chunky crystals of the product. These were recrystallized from a potassium acetate–acetic acid (1:1) solution. The yield was 89% in one preparation.

The compound could also be made directly by using metal oxides as starting materials. Potassium carbonate (5.5 g, 40 mmol) was added in small portions to a stirred mixture of V_2O_5 (3.6 g, 20 mmol) and $WO_3 \cdot H_2O$ (20.0 g, 80 mmol) in about 100 ml of hot water. Hydrogen peroxide (*ca.* 5 mmol) was added to assist dissolution of the V_2O_5. The solution evaporated while the reaction proceeded during 2–3 hr; the volume was finally maintained at about 50 ml by additions of water. After 3 hr some solid was still present in the mixture. The mixture was filtered, giving an orange solution. Potassium acetate and acetic acid (20 mmol each) were added to the solution. During several days the large crystals of the product formed. These were accompanied by small quantities of tiny white leaflets (probably potassium paratungstate) and tiny dark orange square plates or blocks (unidentified). The product was separated mechanically and recrystallized by room-temperature evaporation from 40 ml of water containing 20 mmol each of potassium acetate and acetic acid. The large crystals obtained were washed with ethanol–water mixtures (not over about 50% v/v ethanol) and blotted with tissue. Since they effloresce rapidly except at high relative humidity, they were stored over sodium sulfate decahydrate in a closed container. The yield was near 90%.

Analyses for this and most of the compounds described below are given in Table I.

b. Sodium Salt (II).—A solution of 8.4 g (6 mmol) of the potassium salt in about 20 ml of water was treated with 1 mmol each of sodium acetate and acetic acid. It was passed through a

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

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TABLE I

ANALYSES OF PURE HETEROPOLY COMPOUNDS

		V		W		Organic cation		Inorganic cation		H			Cation/
No.		Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	W/V	anion
I	$K_4V_2W_4O_{19}\cdot 8H_2O$	7.07	7.11	51.0	50.8			10.8	11.2[b]	1.11	1.09	1.98	4.12
II	$Na_4V_2W_4O_{19}\cdot 14H_2O$	6.86	6.86 (1)[a]							1.89	1.90 (1)		
III	$[C(NH_2)_3]_4V_2W_4O_{19}$	7.38	7.56 (4)	53.2	52.6 (1)	3.47	3.66			1.75	1.81	1.92	4.20
IV	$(CH_3NH_3)_2Na_2V_2W_4O_{19}\cdot 6H_2O$	7.49	7.60 (2)	54.1	53.7	1.77	1.83	3.4	3.4 (1)	1.78	1.82	1.96	1.99[c] 2.06[d]
V	$[(CH_3)_2NH_2]_2Na_2V_2W_4O_{19}\cdot 7H_2O$	7.25	7.48	52.3	52.3	3.42	3.37	3.3	3.3 (1)	2.15	2.09	1.95	1.97[c] 1.87[d]
VI	$[(CH_3)_4N]_{2.5}Na_{1.5}V_2W_4O_{19}\cdot 4H_2O$	7.02	6.94	50.7	50.4	8.38	8.10	2.4	2.4 (1)	2.67	2.72	2.01	1.52[c] 2.48[d]
VII	$[C_2H_4(NH_3)_2]_2V_2W_4O_{19}\cdot 2H_2O$	7.83	6.12	56.5	55.9	3.69	3.79			1.86	1.88	1.91	2.03
VIII	$[(C_4H_9)_4N]_3VW_5O_{19}$	2.54	2.49 (1)	45.9	45.8	28.80	28.65			5.44	5.56	5.11	3.00
IX	$[(C_2H_5)_4N]_3VW_5O_{19}$	3.06	2.98	55.2	54.8	17.32	17.53			3.64	3.78	5.08	3.07
X	$[(CH_3)_4N]_3VW_5O_{19}$	3.40	3.36 (1)	61.4	61.4	9.64	9.69			2.42	2.43	5.07	3.02
XI	$[C(NH_2)_3]_3VW_5O_{19}$	3.50	3.71 (1)[e]	63.2	62.8	2.47	2.33			1.24	1.20	4.69	2.80

[a] Maximum deviation from average of duplicate determinations, in units of last significant figure. [b] Calculated by difference. [c] Ratio Na/anion. [d] Ratio organic cation/anion. [e] A later crop from one preparation gave 4.48% V. A sample recrystallized from 0.1 *F* sulfuric acid–0.2 *F* guanidinium chloride gave 3.52% V.

20 × 400 mm column of Dowex 50W-X8 in the Na^+ form. Complete removal of potassium was shown by lack of a precipitate with sodium tetraphenylborate in a test on a small sample of the eluted solution. The solution was evaporated to about 20 ml, cooled, and treated with 40 ml of 95% ethanol. The oil which separated was converted to crystalline solid by vigorous stirring. The solid was washed by decantation with 95% ethanol, transferred to a Büchner funnel, washed with more ethanol, and sucked dry. The yield was 8.2 g (92%) of orange-yellow crystalline powder.

c. **Guanidinium Salt (III).**—A solution of the sodium salt was prepared from $Na_2WO_4\cdot 2H_2O$ (13.2 g, 40 mmol) and $Na_4V_2O_7\cdot 18H_2O$ (6.3 g, 10 mmol) dissolved in 40 ml of hot water by adding 30 ml of 5 *F* acetic acid. A solution of guanidinium acetate (prepared from 25 mmol (4.5 g) of guanidinium carbonate and 20 ml of 5 *F* acetic acid) was added. Much orange-yellow precipitate formed. The mixture was heated nearly to boiling with addition of enough water to dissolve most of the solid. After filtration, orange-yellow needles separated as the solution cooled. These were washed with ethanol–water and then with ethanol and air-dried. The solution was evaporated to about 50 ml to obtain a second crop of crystals. Both crops were combined and recrystallized from about 80 ml of a solution 0.1 *F* each in guanidinium acetate and acetic acid. The hot slightly turbid solution was filtered and allowed to cool. The needle crystals obtained were washed with ethanol–water followed by ethanol and air-dried. A second crop was obtained on evaporating the solution. The total yield was about 12 g (*ca.* 87%) of air-stable orange-yellow needles. Analyses given in Table I are for products recrystallized a second time.

d. **Other Salts.**—These were prepared in the same way as the guanidinium salt. Their compositions and analyses are given in Table I. Details of individual preparations (millimoles of $V_2W_4O_{19}^{4-}$, reagents added, isolation of product, and recrystallization medium) follow: methylammonium sodium salt (IV), 10 mmol of anion, 50 mmol each of methylammonium acetate and acetic acid, octahedral or tabular trigonal crystals isolated after cooling, recrystallization from 100 ml of water with 10 mmol each of methylammonium acetate and acetic acid; dimethylammonium sodium salt (V), 5 mmol of anion, 30 mmol of $(CH_3)_2NH_2Cl$, chunky crystals after cooling and evaporation to 5–10 ml, recrystallization from 20 ml of water containing 20 mmol of $(CH_3)_2NH_2Cl$ and 1 mmol each of sodium acetate and acetic acid; tetramethylammonium sodium salt (VI), 2.5 mmol of anion, 20 mmol of $(CH_3)_4NCl$, flat prismatic crystals after cooling and evaporation to 5–10 ml, recrystallization from 10 ml of water containing 20 mmol of $(CH_3)_4NCl$ and 1 mmol each of sodium acetate and acetic acid; ethylenediammonium salt (VII), 2.5 mmol of anion, 5 mmol of $C_2H_4(NH_3)_2Cl_2$, needles on cooling and evaporation to 5–10 ml, recrystallization from 100 ml of water containing 5 mmol of $C_2H_4(NH_3)_2Cl_2$ and 1 mmol each of sodium acetate and acetic acid.

Guanidinium Decavanadate.—This slightly soluble compound was prepared for optical comparison with the tungstovanadate compound. A report on it was not found in the literature. An acidified vanadate solution (50 mmol of NH_4VO_3 in 120 ml of boiling water, 10 mmol of nitric acid, 20 mmol of acetic acid) was treated with a solution of 40 mmol of guanidinium nitrate in 40 ml of water. An orange-yellow precipitate formed immediately. The mixture was cooled to room temperature and the solid was isolated. It was recrystallized from about 1200 ml of boiling water containing 10 mmol each of guanidinium acetate and acetic acid. The solution was refiltered when it had cooled to about 50°. After reheating, it was allowed to cool to room temperature, giving fine yellow-orange needles. The next day the product was isolated by washing with ethanol–water followed by ethanol and air-dried. *Anal.* Calcd for $[C(NH_2)_3]_6V_{10}O_{28}\cdot 6H_2O$: V, 35.7; C, 5.05; H, 3.39. Found: V, 35.8 (1); C, 5.15; H, 3.36.

Salts of the 5-Tungstovanadate(V) Anion.—Following Chauveau and Souchay,[12] a solution of 6.6 g (20 mmol) of sodium tungstate dihydrate and 4 mmol of $NaVO_3$ (from a stock solution prepared from Na_2CO_3 and V_2O_5) in about 900 ml of hot water was treated with 35–40 ml of 0.5 *F* H_2SO_4. (The excess of acid over that required for the reaction $VO_3^- + 5WO_4^{2-} + 8H^+ \rightarrow VW_5O_{19}^{3-} + 4H_2O$ was added to provide buffering.) The clear yellow solution was cooled after about 20 min of heating at about 80°.

a. **Tetrabutylammonium Salt (VIII).**—A solution of the anion prepared as above (4 mmol of V) was treated with a hot solution of 5.9 g (16 mmol) of tetrabutylammonium iodide in 100–120 ml of water. A yellow precipitate formed immediately. The mixture was warmed and stirred a few minutes to coagulate the precipitate. The solid was then isolated by filtering and washing with water. The air-dried product weighed 7.7 g. The solid was recrystallized from boiling methanol (about 250 ml) by slow cooling in a large beaker filled with water initially at 50–60°. Bright lemon yellow rectangular blocks and prisms separated during cooling. These were washed with ethanol, ethanol–ether, and ether and air-dried. The yield was 5.2 g. Evaporation of the solution on the hot plate and subsequent cooling gave additional product.

b. **Tetraethylammonium Salt (IX).**—A solution of the anion (2 mmol of V) was treated with 20 mmol of tetraethylammonium chloride in 20 ml of water. Some yellow precipitate formed during several seconds. The mixture was heated nearly to boiling, during which time most of the precipitate dissolved. The solution was filtered, diluted to about 1000 ml with water, and let stand to evaporate. During 2–3 weeks small polyhedral yellow crystals mixed with some yellow rods formed. They were washed with ethanol–water and ethanol and air dried. The two kinds of crystals were separated mechanically. The yield of polyhedral crystals (lemon yellow in bulk) was 2.0 g. The yield of rod crystals was much smaller; the C and H analyses, infrared spectrum, and X-ray powder pattern were the same as for the polyhedral crystals.

c. **Tetramethylammonium Salt (X).**—Tetramethylammonium chloride was substituted for the tetraethylammonium salt in procedure b. No precipitate formed. Room-temperature evaporation during several days gave 2.3 g of chunky (roughly octahedral) gold yellow crystals. Visually these resembled one of the products isolated from acidified $V_2W_4O_{19}^{4-}$ solutions (see below).

d. **Guanidinium Salt (XI).**—The preparation of the anion solution was done with half as much water as first described

TABLE II

ANALYSES OF SOLID SOLUTIONS $M_3(HV_2W_4O_{19})_{1-x}(VW_5O_{19})_x \cdot nH_2O$

				V		W		C		Acid proton		H			
No.	M	*n*	*x*	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	W/V	Cation/anion
XIIa	$C(NH_2)_3$	0	0.186	6.86	6.84	57.2	57.0	2.68	2.59	0.061	0.061	1.41	1.39	2.308	2.92
XIIb	$C(NH_2)_3$	0	0.471	5.62	5.63 (2)	59.4	59.4	2.60	2.46	0.039	0.043	1.35	1.35	2.924	2.76
XIIIa	$(CH_3)_4N$	1	0.063	7.09	6.90 (2)	53.7	52.2 (1)	10.36	9.96	0.068	0.062	2.83	2.70	2.097	2.97
XIIIb	$(CH_3)_4N$	1	0.248	6.30	6.15 (2)	55.1	53.8 (1)	10.18	10.00	0.064	0.058	2.77	2.68	2.425	3.02

above. For 2 mmol of vanadium, 20 mmol of guanidinium chloride in 20 ml of water was added. Room-temperature evaporation during several days gave polyhedral orange-yellow crystals which visually resembled the products isolated from acidified $V_2W_4O_{19}{}^{4-}$ solutions (see below), except that the latter are more orange. The crystals were washed with ethanol-water and ethanol and air-dried. The yield was 2.6 g.

e. Attempt to Obtain a Potassium Salt.—A solution of the complex prepared from potassium salts as starting materials (4 mmol of V) was evaporated on the hot plate to about 50 ml. (Spectra taken on samples withdrawn at intervals showed little change indicative of decomposition.) Room-temperature evaporation led to formation of some pale yellow or white precipitate, small orange-red plates or leaflets, and much light yellow material as masses of long fine needles. The needles were isolated and found to have a high content of sulfate from chemical tests and ir spectrum. The material was apparently a potassium acid sulfate.

Reaction of 4-Tungsto-2-vanadate(V) Salts with Acids. a. Guanidinium Salt (XII).—Recrystallization of guanidinium 4-tungsto-2-vanadate(V) from acid solutions (typically 2–3 g of the compound, 2 mmol of guanidinium chloride, 2 mmol of total Na_2SO_4 + $NaHSO_4$, 40 ml of water, room-temperature evaporation) gave yellow-orange polyhedral crystals as the main product. With a $HSO_4{}^-:SO_4{}^{2-}$ ratio of <0.5, rod crystals of the starting materials also separated. With ratios >1, orange-red plate crystals accompanied the polyhedral crystals. The desired polyhedral crystals were separated mechanically. It was found that the vanadium analyses varied considerably with the $HSO_4{}^-$: $SO_4{}^{2-}$ ratio of the recrystallization solution and even with successive crops of crystals from the same solution. Complete analyses for two preparations are given in Table II.

b. Tetramethylammonium Salt (XIII).—(1). A solution of sodium 4-tungsto-2-vanadate(V) was prepared by heating a stoichiometric mixture of $WO_3 \cdot H_2O$ and $Na_4V_2O_7 \cdot 18H_2O$ in water until reaction appeared complete; the solution was then filtered and adjusted to the desired concentration. A quantity of this solution, containing 10 mmol of complex, was treated with 20 mmol of $NaHSO_4$ in 20 ml of water and 20 mmol of tetramethylammonium chloride in 20 ml of water. Much yellow precipitate formed. The solid was isolated after about 3 hr (water–ethanol and ethanol wash, air-dried). Portions (2–3 g) were recrystallized in the same manner as the guanidinium salt. Mixtures of blades or needles with chunky crystals were obtained. Mechanical separation of the chunky crystals was often possible. Variable vanadium analyses were found as for the guanidinium salt. Another preparation in which sufficient water was added to prevent immediate precipitation gave a mixture of the same kinds of crystals on room-temperature evaporation. Complete analyses for one preparation of chunky (roughly octahedral) golden yellow crystals (XIIIa) are given in Table II.

(2) A sample of optically pure needle-crystal material (XIIIb) was obtained as follows. A mixture of 4 mmol of $Na_4V_2W_4O_{19}$ (from stock solution), 16 mmol of $NaHSO_4$, and 32 mmol of tetramethylammonium chloride in about 130 ml of water was allowed to cool slowly in a refrigerator by placing the flask with the mixture in a large beaker of water. The golden yellow needles or blades of the product were isolated the next day by collection on a Büchner funnel. The product was washed with ethanol–water mixtures followed by ethanol and air-drying. Analyses are given in Table II.

Analyses.—For vanadium determination, the sample (0.2–0.3 g) was dissolved with heating in 5–10 ml of water and 5 ml of 1 *F* NaOH. (The tetrabutylammonium salt was dissolved in methanol and then treated with the base.) The solution was kept hot until it was colorless. It was then transferred to a polyethylene beaker. Sodium fluoride (1 g) was added, followed by 10 ml of 6 *F* HCl and 5 ml of 5 *F* H_3PO_4. The solution was then titrated with 0.02 *F* standard iron(II) solution (0.5 *F* in H_2SO_4). Barium diphenylaminesulfonate was used a indicator.[14]

For tungsten determination, the sample (0.2–0.4 g) was dissolved in the minimum amount of water. (If the compound was not very soluble, it was dissolved in 1 *F* NaOH instead. The tetrabutylammonium salt required methanol or acetonitrile to assist dissolution.) Concentrated hydrochloric acid (15–20 ml) was added; the precipitate which formed redissolved to give a brownish red solution. If sodium was present, a white crystalline residue remained. The solution was treated with sodium sulfite and warmed to reduce vanadium to the IV state (color change to light blue). About 100 ml of water was then added to precipitate tungsten(VI) oxide. Five milliliters of a solution 1.5 *F* in HCl and 0.3 *F* in cinchonine was then added. The mixture was digested and the tungsten(VI) oxide isolated, ignited, and weighed according to standard methods.

Sodium was estimated by flame emission on a Jarrell-Ash "Dial-Atom" instrument.

Water in the inorganic salts was determined by ignition to 500° in a muffle furnace. Other dehydrations were performed at various temperatures in a drying oven or muffle furnace. Potassium 4-tungsto-2-vanadate(V) lost all its water below 200°, with no weight change on further heating to 500°. The product heated to 200° was completely water soluble and could be crystallized to give the starting material. Guanidinium 4-tungsto-2-vanadate(V) underwent a weight loss of about 0.1% on heating to 200° and decomposed (turned black) when heated to 300°. The tetraalkylammonium salts of $VW_5O_{19}{}^{3-}$ lost no more than 0.2% in weight on heating at 200° for 3 hr with no change in appearance. The guanidinium salt lost 1.2% of its weight in 3 hr at 200° but had turned red-brown. (The weight loss was not over 0.2% on heating at 110–120°.) The dehydrated (200°) guanidinium salt redissolved completely in bisulfate buffer solution and gave crystals like those of the original compound, along with a little yellow precipitate.

Carbon and hydrogen were determined by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y., or by Galbraith Laboratories, Inc., Knoxville, Tenn.

Cryoscopy.—The molecular weight of sodium 4-tungsto-2-vanadate(V) was determined by cryoscopy in the $Na_2SO_4 \cdot 10H_2O$–Na_2SO_4–H_2O system. The apparatus has been described.[15] The cryoscopic constant was taken[13] as 1.8 ± 0.1 kg of water/mol. The solvent employed was an aqueous solution 0.05 *F* each in sodium acetate, acetic acid, and potassium nitrate. Results are given as grams of salt per kilogram of solvent, transition point depression, derived molecular weight: 55.5, 0.07 ± 0.02, 1430 ± 410; 101.0, 0.12 ± 0.02, 1520 ± 250.

Spectra.—Infrared spectra (samples in pressed KBr pellets) were recorded from 4000 to 400 cm^{-1} on a Perkin-Elmer Model 337 or 225 instrument. The spectra of guanidinium carbonate and some tetraalkylammonium halides were recorded for comparison with the heteropoly salts. Results are listed in Table III.

Visible–ultraviolet spectra of solutions were recorded from 700 to 200 nm on a Cary Model 14 spectrophotometer. Data for the pure complexes are given in Table IV.

X-Ray Diffraction.—Powdered samples of some compounds were scanned on a Picker powder diffractometer by use of Cu Kα radiation (λ 1.5418 Å) from $2\theta = 6$ to 60° at 0.5°/min and a time constant of 3 sec. Potassium chloride ($a = 6.2931$ Å at room temperature) was used as a calibrant. The data are listed in Table V.

Titrations.—Solutions of the compounds were titrated with standard sodium hydroxide or perchloric acid by use of a Corning Model 7 pH meter and a glass electrode.

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(14) I. M. Kolthoff and P. J. Elving, Ed., "Treatise on Analytical Chemistry," Part II, Vol. 8, Interscience, New York, N. Y., 1963, p 227.

(15) G. A. Tsigdinos, Ph.D. Dissertation, Boston University, 1961.

TABLE III

INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF ANIONS

Compd	Anion	Absorption bands						
I	$V_2W_4O_{19}^{4-}$	984	964	950	936	781	589	435 b[c]
III	$V_2W_4O_{19}^{4-}$	991	963	951	939	784	578	425 b
IV	$V_2W_4O_{19}^{4-}$	984	970			784	580 b	425 b
VIII	$VW_5O_{19}^{3-}$	984	959		947	795 b	581	440
IX	$VW_5O_{19}^{3-}$	989	966	952		797	582	442
X	$VW_5O_{19}^{3-}$	987		954	947	796	580	439
XI	$VW_5O_{19}^{3-}$	997	972	951		785	579	420 b
XIIIa	$HV_2W_4O_{19}^{3-}$	995		954	946	795	580 b	430 b
$[(C_4H_9)_4N]_2Mo_6O_{19}$[a]			961			805	605	440
$[(C_4H_9)_4N]_2W_6O_{19}$[a]			978			815	588	447
$K_8Nb_6O_{19}\cdot 16H_2O$[b]			856			685	523	414
$K_8Ta_6O_{19}\cdot 16H_2O$[b]			845			710	543	406

[a] Reference 5. [b] F. J. Farrell, T. A. Maroni,and T. G. Spiro, *Inorg. Chem.*, **8**, 2638 (1969). [c] b = broad.

TABLE IV

ULTRAVIOLET ABSORPTION SPECTRA[a]

	$V_2W_4O_{19}^{4-}$ [b]	$HV_2W_4O_{19}^{3-}$ [c]	$VW_5O_{19}^{3-}$ [c]	$VW_5O_{19}^{3-}$ [d]
λ_{max}	395	374	385	390
$10^3\epsilon_{max}$	2.8_8		2.5_0	2.5_8
λ_{min}	327	328	333	336
$10^3\epsilon_{min}$	1.9_2		0.84	0.80
λ'_{max}	250 sh		267	267
$10^3\epsilon'_{max}$	14		11	11
$\lambda_{1/2}$[e]	454	436	424	428

[a] Units: λ, nm; ε, $(\text{mol}/\text{l.})^{-1}\ \text{cm}^{-1}$. [b] In 0.1 *F* KO_2CCH_3–0.1 *F* HO_2CCH_3. [c] In 0.1 *F* K_2SO_4–0.02 *F* $KHSO_4$. [d] In methanol (tetrabutylammonium salt). [e] Half-height wavelength of near-uv band.

TABLE V

X-RAY POWDER DIFFRACTION DATA

Guanidinium salts				Tetramethylammonium salts					
XI		XIIa		X		XIIIa		XIIIb	
d, Å	Rel intens	*d*, Å	Rel intens	*d*, Å	Rel intens	*d*, Å	Rel intens	*d*, Å	Rel intens
11.1	62	11.1	59	8.4	100	9.3	78	9.3	100
10.4	39	10.3	54	7.3	45	8.7	59	8.8	22
7.6	100	7.5	100	7.2	26	8.4	100	8.4	85
6.12	23	6.08	22	5.17	5	7.9	70	7.9	46
		5.95	12	4.25	5	6.34	19	6.38	14
5.55	17	5.53	18	4.20	5			4.64	6
5.19	18	5.16	15	3.37	6			3.64	12
3.79	27	3.76	16	3.34	6	3.47	16	3.49	11
3.70	24	3.68	18	2.988	5	3.43	15	3.46	11
3.48	80	3.46	46	2.834	4	3.41	10	3.41	9
3.45	57	3.44	20	2.807	3			3.26	5
3.19	19	3.18	9	2.451	3			3.18	5
3.12	12	3.11	10	2.061	3			3.08	5
3.06	14	3.04	7			3.05	11	3.05	6
2.883	21	2.870	16			2.981	7	2.943	11
2.777	11	2.766	8			2.908	9	2.916	9
2.549	15	2.538	4			2.457	8	2.463	5
2.513	20	2.509	20						
		2.433	9						
		2.341	7						
2.319	22	2.313	7						
2.179	16	2.173	13						

a. 4-Tungsto-2-vanadates(V).—The potassium salt consumed no NaOH at 0–5°. The guanidinium salt reacted with NaOH at *ca.* 80°, giving a poorly defined end point at a pH near 8 and 5.7 ± 0.6 mol of OH^-/mol of anion. The change from yellow to colorless occurred gradually over the pH range 7–9. Titration of the potassium salt at 0–5° with $HClO_4$ (about 1 *N*) gave no breaks in the titration curve indicating formation of protonated species.

b. 5-Tungstovanadates(V).—The tetramethylammonium salt at 0–5° reacted very slowly with NaOH. A fast titration gave no evidence for any rapid reactions such as deprotonation. In a titration at *ca.* 70° base was consumed, with breaks in the curve at 5.5 ± 0.4 (pH 6.6–7.0), 7.8 ± 0.3 (pH 7.6–8.4), and 8.9 ± 0.4 (pH 9–10) mol of OH^-/mol of anion.

c. Products from Acidified $V_2W_4O_{19}^{4-}$ Solutions.—Samples (0.1–0.2 g) were titrated with NaOH at 0–5°. Breaks in the curves occurred at pH 5–8. Acid contents so determined are given in Table I. The pK_a of $HV_2W_4O_{19}^{3-}$ was found to be about 4 from these titrations (0–5°; ionic strength estimated at ~0.03). Because of sample size and limited stability of $VW_5O_{19}^{3-}$ to base, the accuracy of these results is considered not better than 5–10%.

Chemical Properties.—Samples were treated with various reagents or recrystallized under various conditions on a semimicro scale. Products were examined under the microscope. Solutions were also examined spectrophotometrically.

The $V_2W_4O_{19}^{4-}$ complex is stable in the pH range 4–7. Solutions in 1:1 acetic acid–acetate buffer obeyed Beer's law over the concentration range 10^{-2} to 3×10^{-5} *F* in complex. The anion coexists with its basic degradation products in the pH range 7–9. (The guanidinium salt can be recrystallized unchanged at pH 7–9 but in reduced yields.) When solutions of KVO_3 and K_2WO are mixed, a deeper yellow color appears rapidly. Spectra indicated formation of some $V_2W_4O_{19}^{4-}$, and evaporation with guanidinium chloride gave the orange-yellow rods of the complex. At pH near 2, suitable cations give products evidently containing the acid anion $HV_2W_4O_{19}^{3-}$ as well as $VW_5O_{19}^{3-}$ (see above). These solutions are unstable, being slowly converted to red complexes. When a solution of the anion is made about 2 *F* in sulfuric acid, its color lightens, and much light yellow precipitate forms rapidly. Attempts to extract a complex with diethyl ether failed.

The $VW_5O_{19}^{3-}$ ion is stable at low concentrations in the pH range 1–4. Solutions in 1:5 bisulfate–sulfate buffer obeyed Beer's law in the concentration range 10^{-2} to 3×10^{-5} *F* in anion. At concentrations much higher than 10^{-2} *F*, the complex undergoes slow reactions to form red species. In the pH range 4–5 the complex is converted to $V_2W_4O_{19}^{4-}$ and isopolytungstate.

Recrystallization of the guanidinium salt from formate or acetate buffers gave some polyhedra of the starting material, along with orange-yellow rods of the 2:4 complex and fine white precipitate which is probably a guanidinium paratungstate. A solution of the complex is decolorized on addition of a moderate excess of NaOH faster than a similar solution of the 2:4 complex. When a solution of the anion is made about 2 *F* in sulfuric acid, little color change occurs, and several minutes elapses before the solution becomes turbid and deposits a light yellow precipitate.

Discussion

Formation and Preparation of the complexes.—Rosenheim, *et al.*,[10] prepared salts formulated as $2M'_2O \cdot V_2O_5 \cdot 4WO_3 \cdot nH_2O$ (the "red-yellow" series of tungstovanadate salts) by boiling alkali paratungstate solutions with vanadium(V) oxide. This procedure also gave low yields of red compounds formulated with V:W = 3:7, with which we deal in a later publication.[16] The "red-yellow" series salts are evidently identical with the compounds $M'_4V_2W_4O_{19} \cdot nH_2O$ prepared by us. We have prepared the 2:4 complex by either of the reactions

$$2VO_3^- + 4WO_4^{2-} + 6H^+ \longrightarrow V_2W_4O_{19}^{4-} + 3H_2O \qquad (1)$$

$$V_2O_5 + 4WO_3 + 2CO_3^{2-} \longrightarrow V_2W_4O_{19}^{4-} + 2CO_2 \qquad (2)$$

The potassium salt gives large crystals in high yield which are readily separated from the relatively small amount of impurities. Other salts are easily prepared by metathesis from this salt or from a solution of the sodium salt. The successful synthesis starting from metal oxides and alkali carbonate, as well as the high yield, attest to the stability of the $V_2W_4O_{19}^{4-}$ complex.

We found no reports of preparation of solid $VW_5O_{19}^{3-}$ compounds until our investigation was under way. Our preparation proceeds readily starting with a solution of the anion prepared according to Chauveau and Souchay[12] (eq 3), by addition of large cations. Tkach

$$VO_3^- + 5WO_4^{2-} + 8H^+ \longrightarrow VW_5O_{19}^{3-} + 4H_2O \qquad (3)$$

and Polotebnova[17] have recently claimed isolation of V:W = 1:5 compounds with some organic bases. Their procedure involved the use of tungstovanadate acid solutions (V:W = 1:5 or 1:6) prepared by an ether-extraction method; solids were obtained by precipitation with organic amines. The complete details were not available.

Analyses.—The results for the pure compounds are presented in Table I. Our results for the sodium and potassium salts of the 2:4 complex agree with those of Rosenheim, *et al.*[10] They formulated the guanidinium salt as a monohydrate, but they gave no water determination. Our analyses, including the lack of weight loss on heating to 200°, indicate that the guanidinium salt is anhydrous. The effect of impurities on analyses is illustrated by the guanidinium salt: a 1% contamination by an isopolyvanadate would account for the high vanadium content obtained (Table I). The second recrystallization did not lower the vanadium content significantly; this suggests that a low concentration of isopolyvanadate exists in equilibrium with the 2:4 complex in solution.

Our results for the 1:5 compounds confirm the solution results of Chauveau and Souchay.[12] Tkach and Polotebnova[17] did not recrystallize their products. Their preparation of the guanidinium salt implies a solubility *ca.* 10^{-3} *F;* this is inconsistent with our observations, which imply a solubility of at least 10^{-2} *F* for this salt. The complexity of the system tungstate(VI)–vanadate(V) makes it very possible, perhaps probable, that they obtained mixtures in their procedure, and the approximately 1:5 ratios of V to W obtained may be fortuitous.

The Species $HV_2W_4O_{19}^{3-}$.—Chauveau[11] obtained evidence for formation of $HV_2W_4O_{19}^{3-}$ on acidification of $V_2W_4O_{19}^{4-}$. This was confirmed by our isolation of products from acidified solutions of the 2:4 complex. However our results indicate that our products are actually solid solutions of $HV_2W_4O_{19}^{3-}$ with $VW_5O_{19}^{3-}$, implying that the latter is also formed at a moderate rate in such solutions. The successful isolation of these products depends on the low solubility obtained with the guanidinium and tetramethylammonium salts. On standing a few days, these acidified solutions undergo reactions to form other species.

Analyses for some of these products are presented in Table II. That these products are solid solutions is supported by the variable vanadium content of various preparations despite optical homogeneity and by isomorphism with pure salts of the 1:5 complex (see below). The mole fraction *x* in the composition $M'_3(HV_2W_4O_{19})_{1-x}(VW_5O_{19})_x$ was determined from the experimental W/V ratio. The formula obtained from the derived mole fraction was used for the theoretical composition. The results for the tetramethylammonium salts indicate a monohydrate (from the experimental H/C ratio), but the low absolute contents of V, W, and C suggest a trihydrate or 2–3% of inert impurity such as sodium sulfate. However this amount of impurity should have been visible under the microscope. The acid hydrogen content required by the proposed formulas was confirmed within experimental error by titration with sodium hydroxide at 0–5°.

Vanadium analyses for several preparations of the guanidinium acid salt ranged from 5.63 to 7.35%, corresponding to *x* ranging from 0.47 to 0.07. Analogous data for tetramethylammonium products are 3.90–6.90%, implying *x* = 0.82–0.06. (The needle and chunky crystal forms of this product appear to be isomorphous, so the two forms are probably different crystal habits of the same compound. They could also be different hydrates, but if so, their water contents would not differ by more than 1–2 mol per formula. The precision of the analyses does not allow assigning the water content to better than about 1 mol.)

Chemical Properties.—The ultraviolet spectral data on solutions prepared from the solid compounds (Table IV) agree with those of Chauveau and Souchay[11,12] in the near-ultraviolet region for solutions prepared from sodium vanadate and tungstate by acidification (they did not report data below 320 nm). This indicates that the solid compounds contain the same respective species as the solutions prepared by Chauveau and Souchay. Our data for the pH stability of the complexes, obtained by spectroscopy and by recrystallization experiments, agree well with the results of Chauveau and Souchay,[11,12] obtained by spectroscopy and titrimetry. Additional data obtained here are discussed in the following paragraphs.

The degradation of $V_2W_4O_{19}^{4-}$ by base in hot solution

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[16] C. M. Flynn, Jr., and M. T. Pope, *Inorg. Chem.*, in press.

[17] E. F. Tkach and N. A. Polotebnova, *Zh. Neorg. Khim.*, **14**, 3354 (1969).

is in accordance with the reactions

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

$$VO_3^- + OH^- \longrightarrow HVO_4^{2-} \quad (5)$$

The behavior at the alkaline end of the stability range suggests an equilibrium such as

$$V_2W_4O_{19}^{4-} + 6HVO_4^- \rightleftharpoons 4WO_4^{2-} + 8VO_3^- + 3H_2O \quad (6)$$

From the results of Chauveau and Souchay[12] and from the compositions of our acid salt products, the 1:5 complex is one product of the acidification of the 2:4 complex. The protonated 2:4 complex is unstable, at least in concentrated solutions, and undergoes reactions to give red complexes with the loss of vanadium(V) oxide. The formation of tungsten(VI) oxide on treatment with strong acids and the failure to obtain an ether-extractable species in acid solutions are in accord with the paratungstate-like behavior noted by Rosenheim, *et al.*[10]

The 1:5 complex is degraded by base in hot solution in accordance with the reaction

$$2VW_5O_{19}^{3-} + 10OH^- \longrightarrow V_2W_4O_{19}^{3-} + 6WO_4^{2-} + 5H_2O \quad (7)$$

followed by reactions 4 and 5.

Constitution of the Complexes.—Several considerations support the proposal that both of these ions have the $M_6O_{19}^{n-}$ structure exhibited by various isopoly complexes.[4-6] (1) The compositions of all the salts obtained show that each of the anions must contain some multiple of three metal atoms. (2) Cryoscopy of $Na_4V_2W_4O_{19}$ shows that the 2:4 complex in fact has two vanadium and four tungsten atoms, eliminating a possible Keggin structure $H_2(W_8V_4)O_{40}H_2^{8-}$. (3) Titrations of either complex with sodium hydroxide do not show the presence of any acidic hydrogen in the complexes. This combined with the dehydration data (some of the salts appear to be anhydrous) indicates that neither complex contains constitutional water; *i.e.*, each anion contains 19 oxygen atoms. (4) The infrared spectra of the complexes are very similar to each other and to the spectra of $Mo_6O_{19}^{2-}$ and $W_6O_{19}^{2-}$ reported by Fuchs and Jahr[5] (see Table III). The ion $W_6O_{19}^{2-}$ has been shown to possess the $M_6O_{19}^{2-}$ structure in a partial structure determination of the tetrabutylammonium salt.[6] Following the vibrational analysis of Farrell, *et al.*,[18] for $Nb_6O_{19}^{8-}$ and $Ta_6O_{19}^{8-}$, the 978-cm^{-1} band in the spectrum[5] of $W_6O_{19}^{2-}$ can be assigned as a nearly pure asymmetric stretching mode for the terminal W–O groups. It is this band which has split into three or four components in the spectra of $VW_5O_{19}^{3-}$ and $V_2W_4O_{19}^{4-}$. The remaining three bands involve the bridging oxygen atoms and are expected to be less sensitive to substitution of tungsten by vanadium. (5) That the ions $HV_2W_4O_{19}^{4-}$ and $VW_5O_{19}^{3-}$ have the same structure is supported by the observed solid-solution formation. The guanidinium solid-solution product is isomorphous with the pure 1:5 salt by X-ray powder diffraction (Table V) and by morphology. However, this does not appear to be the case for the tetramethylammonium salts. The foregoing thus renders very unlikely a structure such as $H_2(W_{10}V_2)O_{40}H_2^{6-}$ for the 1:5 complex.

Further Investigations.—Assuming the $M_6O_{19}^{n-}$ structure for the 2:4 complex, the vanadium atoms may occupy cis or trans positions in the octahedral structure. We contemplate ^{51}V and/or ^{183}W nmr studies on the complexes in attempts to shed more light on their structures.

The complexes described here are members of a series $W_{6-n}V_nO_{19}^{(2+n)-}$ with $n = 1$ and 2. The case $n = 3$ is possibly represented by the compounds $5M_2O \cdot 3V_2O_5 \cdot 6WO_3 \cdot 2xH_2O$ (or $M_5V_3W_3O_{19} \cdot xH_2O$) reported in the old literature (the "dichromate-colored" series).[10] Members with $n = 4$ or 5 have not been isolated and may not be stable in aqueous solutions; *e.g.*

$$V_5WO_{19}^{7-} \longrightarrow 5VO_3^- + WO_4^{2-} \quad (8)$$

The isopolyvanadate ($n = 6$) is unstable with respect to VO_3^- and $V_2O_7^{4-}$.[4]

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(18) F. J. Farrell, V. A. Maroni, and T. G. Spiro, *Inorg. Chem.*, **8**, 2638 (1969).