expected that when additional data are obtained for systems similar to those described in this paper, these factors will become more evident.

Heteropolyvanadomanganates(IV) with Mn:V = 1:11 and 1:4

BY C. M. FLYNN, JR., AND MICHAEL T. POPE

Two new vanadomanganate(IV) heteropoly complexes have been prepared by reaction of manganese(II), peroxydisulfate, and isopolyvanadate(V) ions. One complex, isolated as $K_5MnV_{11}O_{32} \cdot 10H_2O$, $Cs_{4.5}H_{0.5}MnV_{11}O_{32} \cdot 7H_2O$, and $(NH_4)_{4.5}H_{0.5}MnV_{11}O_{32} \cdot 12H_2O$ (all red to dark red crystals) is moderately stable in solutions of pH 2–3. In the pH range 4–6 it reacts to give high yields of 13-vanadomanganate(IV), accompanied by some amorphous precipitate and at least one other complex in low yields. The second complex, isolated as $K_5HMn_3V_{12}O_{39} \cdot 10H_2O$ and $(NH_4)_5HMn_3V_{12}O_{39} \cdot 15H_2O$ (black crystals), is also obtained in the pH range 2–3 and apparently exists up to a pH near 6. It is formulated as a trimeric species on the basis of the chemical analyses and single-crystal X-ray data. The 3:12 complex is unexpectedly inert to reaction with excess vanadium(V) to give 1:11 or 1:13 complexes. No visual evidence for heteropoly "blue" species was observed on reduction of the complexes. The 1:13 complex was found to be slightly photosensitive, the decomposition products apparently including the green reduced species. The acid decomposition of vanadomanganates(IV) leads to formation of small quantities of permanganate; similar behavior was noted for 12-niobomanganate(IV).

Introduction

We have recently reported the synthesis and characterization of 13-vanadomanganate(IV) heteropoly complexes, *e.g.*, $K_7MnV_{13}O_{38} \cdot (16–18)H_2O$.[1] During that investigation it was found that a species with Mn:V = 1:11 is formed on suitable adjustment of the reaction stoichiometry and that this species can be isolated in good yield. It could also be obtained by acidification of solutions of the 1:13 complex, in which vanadium(V) oxide forms as a by-product. A second complex with Mn:V = 1:4 is also obtained along with the 1:11 species. We report here the synthesis and characterization of these complexes. Photosensitivity of the 1:13 complex is also described.

Experimental Section

Reagents.—The preparation of reagents not obtained commercially (potassium metavanadate, sodium pyrovanadate) has been described.[1]

Potassium 11-Vanadomanganate(IV), $K_5MnV_{11}O_{32} \cdot (10-12)H_2O$.—A hot solution of 7.6 g (55 mmol) of KVO_3 in *ca.* 200 ml of water was treated with 5 ml of 1 *F* HNO_3 followed by 5.0 ml of 1.0 *F* $MnSO_4$ and 2.7 g (10 mmol) of $K_2S_2O_8$. The mixture was stirred and kept at 70–90°. A brown precipitate which formed during the first 10 min (probably $MnV_2O_6 \cdot 4H_2O$) redissolved in 0.5–1 hr. The deep red solution was heated for a further 4–6 hr and allowed to evaporate to a final volume of 30–50 ml. During the final 2-hr period some red-brown precipitate, mainly V_2O_5, separated. The solution was filtered and allowed to cool. After 1 day, dark red crystals mixed with oxide precipitate were obtained. The crude product was recrystallized from a solution 0.3 *F* in K_2SO_4 and 0.2 *F* in $KHSO_4$ to give dark red parallelepiped crystals. The crystals were washed with ethanol–water

(1) C. M. Flynn, Jr., and M. T. Pope, *J. Amer. Chem. Soc.*, **92**, 85 (1970).

followed by 95% ethanol and were then air dried. The yield was about 50%. The compound is not efflorescent at moderate humidity. Room-temperature evaporation of the recrystallization solution gave more dark red crystals accompanied by black parallelepiped crystals of a second compound which proved to be the 3:12 compound described below.

The potassium 1:11 salt could also be obtained by treatment of the 1:13 compound with acids. Two grams (*ca.* 1 mmol) of $K_7MnV_{13}O_{38} \cdot 18H_2O$ was dissolved in a mixture of 10 ml of water and 10 ml of 0.3 *F* K_2SO_4–0.2 *F* $KHSO_4$ by heating the mixture nearly to boiling. When the solution was allowed to cool, much starting material recrystallized, indicating that insufficient acid was added. Addition of 0.7 g (5 mmol) of $KHSO_4$ and reheating of the solution led to further reaction. After filtration, the solution was allowed to stand for a few days so that large (3-mm) crystals could be obtained. Since more vanadium(V) oxide also precipitated at this stage, the mixture was reheated and filtered. Pure product subsequently crystallized. The yield was 1.6 g, nearly quantitative based on the reaction

$$MnV_{13}O_{38}^{7-} + 2H^+ \longrightarrow MnV_{11}O_{32}^{5-} + V_2O_5 + H_2O$$
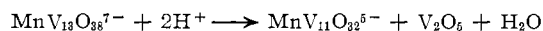
In another experiment (3.708 g of potassium 13-vanadomanganate, 5 mmol of K_2SO_4, 10 mmol of $KHSO_4$, 40 ml of water, heated for 1 hr) the yield of 1:11 compound was 2.160 g, corresponding to 76% of the manganese taken. The solution was still orange red. Further evaporation led to crystallization of K_2SO_4 and decomposition to insoluble orange brown solids. Analytical data for this and most of the following compounds are given in Table I.

Ammonium 11-Vanadomanganate(IV), $(NH_4)_{4.5}H_{0.5}MnV_{11}O_{32} \cdot 12H_2O$.—Synthesis was carried out as above, but with the substitution of the corresponding ammonium compounds for potassium compounds. The product was recrystallized from a solution 0.6 *F* in ammonium sulfate and 0.4 *F* in ammonium bisulfate. Dark red prismatic crystals (up to 1 cm long) were obtained when the solution was evaporated at room temperature. The crystals were washed with ethanol–water containing not more than *ca.*

Table I
ANALYSES OF COMPOUNDS[a]

Compound		% cation	% Mn	% V	% H₂O[b]	M/Mn	V/Mn
$K_5MnV_{11}O_{32} \cdot 11H_2O$	Calcd	12.8	3.61	36.9	13.0		
FW 1521.0	Found	12.4 (1)	3.64 (2)	37.1 (2)	13.3 (3)	4.79	11.01
$(NH_4)_{4.5}H_{0.5}MnV_{11}O_{32} \cdot 12H_2O$	Calcd	5.70	3.86	39.3	15.5		
FW 1425.2	Found	5.61 (5)	3.88 (2)	39.3 (2)	15.7[c]	4.42	10.92
$Cs_{4.5}H_{0.5}MnV_{11}O_{32} \cdot 7H_2O$	Calcd	32.3	2.96	30.3	7.1		
FW 1852.0	Found	32.1[c]	2.99 (2)	30.4 (2)	7.1 (2)	4.4	10.96
$Cs_6NaMnV_{13}O_{38} \cdot 8H_2O$	Calcd	. . .[d]	2.40	28.9	6.3		
FW 2289.7	Found	. . .[d]	2.43 (2)	28.8 (2)	6.5 (2)	. . .	12.80
$K_5HMn_3V_{12}O_{39} \cdot 10H_2O$	Calcd	11.0	9.26	34.4	10.6		
FW 1776.8	Found	11.1 (1)	9.31 (2)	34.6 (2)	9.9 (2)	5.05/3	12.02/3
$(NH_4)_5HMn_3V_{12}O_{39} \cdot 14H_2O$	Calcd	5.17	9.45	35.1	15.0		
FW 1743.5	Found	5.23 (3)	9.56 (2)	34.6 (2)	15.5[c]	5.00/3	11.72/3
$(NH_4)_5HMn_3V_{12}O_{39} \cdot 15H_2O$	Calcd	5.12	9.36	34.7	15.8		

[a] Experimental results are averages of two or more determinations. The number in parentheses is the probable maximum error in units of the last significant figure. [b] Corrected assuming reduction of Mn(IV) to Mn(II) during ignition. [c] By difference. [d] Total alkali as $Cs_2O + Na_2O$: calcd, 38.3; found (difference), 38.2. Sodium: calcd, 1.0; found, 0.6.

50% ethanol by volume and were then blotted dry. The efflorescent crystals, which crumble on washing with 95% ethanol, were stored over sodium sulfate decahydrate. During several months they decomposed, possibly under the influence of light. Further evaporation of the recrystallization solution gave more dark red prisms, accompanied by black rhombic dodecahedra of what proved to be the 3:12 compound described below.

Cesium 11-Vanadomanganate(IV), $Cs_{4.5}H_{0.5}MnV_{11}O_{32} \cdot 7H_2O$. —Potassium 11-vanadomanganate (1.5 g, ca. 1 mmol) was dissolved in a mixture of 10 ml of hot water and 1 ml of 0.3 F K_2SO_4–0.2 F KHSO₄. Cesium chloride (1.3 g, ca. 7.5 mmol, 50% excess) was added; an orange solid precipitated immediately. After the mixture cooled, the solid was isolated and recrystallized as follows. The crude solid was dissolved in ca. 200 ml of hot water containing 0.8 g (5 mmol) of CsCl and 2 ml of 0.3 F K_2SO_4–0.2 F KHSO₄ and was adjusted to pH 2–3 with sulfuric acid. Small crystals formed on slow evaporation of the solution at room temperature. After about 1 week, two crops of the red-orange product were obtained, totaling 1.4 g. Microscopy showed the product to consist of small elongated parallelogram-shaped orange plates. A small third crop of solids isolated a few days later was inhomogeneous and consisted of orange plate crystals and brownish red to nearly black plates and laths.

Cesium Sodium 13-Vanadomanganate, $Cs_6NaMnV_{13}O_{38} \cdot 8H_2O$. —This compound was prepared for comparison by microscopy with the 1:11 compound. Two grams of sodium 13-vanadomanganate(IV)–29-water were dissolved in 10 ml of hot water mixed with 1 ml of 1 F sodium acetate–1 F acetic acid. A solution of 1.7 g (10 mmol, ca. 50% excess) of CsCl in 5 ml of water was added; an orange precipitate formed immediately. After the solution cooled, the solid was isolated. The solid was recrystallized from ca. 150 ml of hot water containing 0.8 g (5 mmol) of CsCl + 5 ml of 1 F sodium acetate–1 F acetic acid. An orange crystalline powder (irregular masses of small plates under the microscope) separated after 2 days. The yield was 1.5 g. The solution was evaporated on the hot plate in an attempt to get more product. A dull light yellow precipitate formed during the evaporation. The appearance (like KV_3O_6) and chemical tests on the isolated material suggested it was $Cs-V_3O_8$. Further evaporation (with addition of 1 mmol of acetic acid) gave more orange product, but it was contaminated with brown material. This decomposition was unexpected and is unexplained; the solution was also redder than expected for the quantity of heteropoly complex present.

Potassium 12-Vanado-3-manganate(IV), $K_5HMn_3V_{12}O_{39} \cdot 10H_2O$. —The black crystals obtained in the recrystallization of the 1:11 compound were separated mechanically and recrystallized from 0.4 F K_2SO_4–0.1 F KHSO₄. Attempts to synthesize the compound directly gave yields not exceeding 15–20%. Typically, a mixture of 40 mmol of KVO_3, 100 mmol of acetic acid, 10 mmol of $MnSO_4$, and 20 mmol of $K_2S_2O_8$ in 80 ml of water

was heated at 70–90° for about 4 hr, and the volume was maintained at 30–50 ml. The mixture was then filtered to remove much red-brown precipitate. The product mixture which separated during 2 days of slow evaporation (to ca. 20 ml) was recrystallized twice from 0.4 F K_2SO_4–0.1 F KHSO₄ to give crystals of the 1:11 and 3:12 compounds. The 3:12 compound was separated mechanically and recrystallized as described above. The black crystals were washed with ethanol–water followed by 95% ethanol and were then air dried.

An attempt to obtain the 3:12 compound from the 1:13 complex, manganese(II) sulfate, and potassium peroxydisulfate gave no better yield of the product. An attempt to obtain the complex in accordance with the reaction

$$6MnV_{13}O_{38}{}^{7-} + 32H^+ \longrightarrow 2HMn_3V_{12}O_{39}{}^{5-} + 27V_2O_5 + 15H_2O$$

by using potassium 13-vanadomanganate(IV) and sulfuric acid, led to a deep brownish red solution from which only oxide precipitates were obtained, even when the solution was evaporated at room temperature. Chemical tests showed that these precipitates contained much manganese as well as vanadium.

Ammonium 12-Vanado-3-manganate(IV), $(NH_4)_5HMn_3V_{12}O_{39} \cdot (14–15)H_2O$. —The black dodecahedra obtained in the recrystallization of the 1:11 complex were separated mechanically and recrystallized from 0.8 F ammonium sulfate–0.2 F ammonium bisulfate. The product was washed with ethanol–water followed by 95% ethanol and was then air dried.

Attempts to Obtain Sodium 11-Vanadomanganate(IV). —Reactions were carried out as for the potassium compound, except that the vanadate used was $Na_4V_2O_7 \cdot 18H_2O$, and correspondingly more acid was added. The sodium persulfate was prepared by ion exchange from the ammonium salt.[1] The reaction products were mainly the 1:13 salt and the oxide precipitate. Treatment of sodium 13-vanadomanganate(IV) with sodium sulfate–sodium bisulfate mixtures also failed to give the desired compound but instead gave oxide precipitates and unchanged starting material.

Precipitation of Cesium and Guanidinium Salts. —Both of these cations give slightly soluble products with the 1:13 and 1:11 complexes. To examine behavior of the complexes at the ends of their pH stability ranges, reaction products of the complexes with each of these cations were obtained at various acidities and examined under the microscope. Reaction products with the 1:13 complex in the pH range 5–8 were the same as those obtained at pH 4–5, when sodium 13-vanadomanganate was used, with sodium acetate and acetic acid for buffering. Products with the 1:11 complex (as the potassium salt in sodium sulfate–bisulfate buffers) were apparently amorphous orange to brown materials at pH values below about 2.0, with no crystalline phases observed.

Attempts to Obtain Other Vanadomanganate(IV) Complexes. —Reactions at Mn:V ratios of 1:6 and 1:8, with potassium salts,

gave mixtures of the 1:11 and 3:12 complexes. A reaction with $KVO_3:MnSO_4:HNO_3:K_2S_2O_8 = 4:2:1:4$ gave mostly oxide precipitates and no new crystalline products.

Attempts to Obtain Manganese(III) Complexes.—No evidence for formation of vanadomanganate(III) complexes was obtained, even in reactions with lower ratios of peroxydisulfate to manganese(II), in mixtures of vanadomanganate(IV) complexes with manganese(II), or in reduction of the manganese(IV) complexes by other reagents. The bright red color of some solutions which remained after isolation of manganese(IV) compounds described above was due to formation of permanganate, identified by the characteristic visible absorption peaks at 545, 525, and 505 nm in one such solution.

Photosensitivity of 13-Vanadomanganate(IV) Salts.—Samples of sodium and potassium 13-vanadomanganates(IV) stored over sodium sulfate decahydrate which were daily exposed to bright sunlight darkened to brown on the exposed surface over a few months. The color was like that of partially reduced preparations of the potassium salt obtained in the presence of iodide[1] or from monochloroacetate or formate buffer solutions, in which the organic species cause slow reduction.

Analyses.—Elemental analyses and oxidation state determinations were carried out as described.[1] Sodium in the 13-vanadomanganate(IV) double cesium salt was estimated by flame emission. Potassium was not found in the cesium 11-vanadomanganate(IV) by flame emission.

Some of the compounds were heated at *ca.* 120° to determine water loss. Potassium 11-vanadomanganate(IV) lost 11.0 ± 0.4% weight; the calculated amount for conversion to the dihydrate was 10.7%. The cesium salt lost 6.0 ± 0.1%; the calculated amount for conversion to the monohydrate was 5.8%. Potassium 12-vanado-3-manganate(IV) lost 6.0 ± 0.1%; the calculated amount for conversion to the tetrahydrate was 6.1%. Cesium sodium 13-vanadomanganate(IV) lost 4.9%; the calculated amount for conversion to the dihydrate was 4.7%. The two potassium salts dissolved completely in water after dehydration. When the 1:11 complex was recrystallized from pH 2 buffers, it formed crystals similar to those of the original compound.

Chemical Properties of the Complexes.—Experiments were performed on a 0.1–1-mmol scale. Solid products were examined under the microscope.

(a) Potassium 11-vanadomanganate(IV) is recrystallizable from solutions with pH 2–3. When a warm solution of the 1:11 complex in water was treated with potassium acetate–acetic acid solution, crystals soon formed. Microscopy showed them to be a mixture of orange octahedral crystals (1:13 complex) and red-orange parallelepipeds which appeared to be unchanged 1:11 complex. When an acetate–buffer solution of the 1:11 complex was heated for up to 0.5 hr, the solution was still red, but much 1:13 complex separated when the solution was cooled. During continued evaporation at room temperature some brown-orange, apparently amorphous, material also precipitated. Later a low yield of brown-red to black blades or rods also crystallized; this compound may be the same as the product of recrystallization of the 3:12 compound from acetate buffer solutions. Some of this latter product on recrystallization from bisulfate buffer gave dark brown-red parallelepipeds like those of the 3:12 compound (similar-size crystals of the 1:11 compound are orange-red). In one such experiment (1.463 g of potassium 11-vanadomanganate, 10 mmol of potassium acetate, 5 mmol of acetic acid, 30 ml of H_2O) the total yield of 1:13 complex was 1.370 g, corresponding to 74% of the manganese taken. Recrystallization at a pH of *ca.* 3.0 (monochloroacetate buffer) gave a mixture of 1:11 and 1:13 complexes.

(b) Reaction of the 1:11 compound in acetate buffer in the presence of additional vanadium(V) gave solutions similar in color to those obtained without the excess vanadate. Crystals of the 1:13 compound were obtained on cooling and evaporation of the solution.

(c) Recrystallization of the 3:12 compound from solutions of pH 4–6 (potassium acetate–acetic acid) gave dark brown-red

to black blades or rods. *Anal.* Calcd for $K_2MnV_4O_{13}\cdot 4H_2O$: K, 12.7; Mn, 8.90; V, 33.0; H_2O, 11.7; ignition loss (including the conversion $MnO_2 \rightarrow MnO + 0.5O_2$), 14.3. Found: K, 13.7; Mn, 9.7 (1); V, 30.8 (2); H_2O, 13.1 (difference); loss on ignition to 400–450°, 15.1 (1); K/Mn, 1.98; V/Mn, 3.42; H_2O/Mn, 4.1.

(d) Potassium 12-vanado-3-manganate(IV) (0.12 g, 0.2 mmol of Mn) in 5 ml of water was treated with 1.8 mmol of KVO_3, 0.8 mmol of HNO_3, and 5 ml of 1 F potassium acetate–1 F acetic acid. The solution was brown red with no immediate reaction evident. When the solution was heated at 80–100° for about 1 hr, a flaky dirty yellow precipitate formed. This appeared to be KV_3O_8 mixed with a little manganese oxide on the basis of chemical tests. The filtered solution was still brown-red. Room-temperature evaporation gave the 1:13 complex (orange octahedral crystals) and later red-brown to black crystals like the product in (c) above.

(e) Reaction was carried out as in (d) but with 3 mmol of KVO_3, 0.4 mmol of HNO_3, and the 5 ml of acetate solution. No precipitate formed during the heating. The crystalline products isolated were the same as those in (d), with relatively less 1:13 complex.

(f) Reaction was carried out as in (d) but with 1.4 mmol of KVO_3, 0.8 mmol of HNO_3, and 5 ml of 0.3 F K_2SO_4–0.2 F $KHSO_4$. The brown red solution showed no evidence of immediate reaction. During heating, much brown-red precipitate formed; this was found to be mainly vanadium(V) oxide. Evaporation of the filtered solution gave black crystals of unchanged 3:12 complex.

Acid Decomposition of Vanadomanganates(IV), 12-Niobomanganate(IV), and 9-Molybdomanganate(IV).—When a dilute aqueous solution of the 1:13, 1:11, or 3:12 vanadomanganates(IV) was made 0.5–1 F in sulfuric acid, the orange to yellow solution turned a lighter yellow-brown. When it was heated, the solution turned bright orange; then much brownish red flocculent precipitate formed. The supernatant solution was light pink or yellow-pink like the color of very dilute permanganate. An absorption spectrum of one such product showed peaks at 546, 525, and 506 nm, their positions and relative intensities agreeing very well with the permanganate spectrum. The quantity of permanganate corresponded to roughly 1% of the total manganese in the sample. A portion of the supernatant became deeper pink on treatment with sodium bismuthate, showing the presence of manganese(II) and/or -(III) in addition.

A similar experiment in which a 12-niobomanganate(IV) salt[2] was used at first gave the orange precipitate previously noted; when the solution was heated to boiling, the precipitate became denser and darker brown, and a light pink supernatant was left.

Treatment of ammonium 9-molybdomanganate(IV) (prepared according to literature methods[3]) with sulfuric acid as above led to dark mixtures in which the presence of permanganate could not be ascertained.

Reduction of the Complexes.—Reaction of the 1:11 or 3:12 complexes with iodide, hexacyanoferrate(II), or oxovanadium(IV) ions at various acidities gave no visual evidence for heteropoly "blues" or other new heteropoly species but led to reductive decomposition.

Base Titrations.—Solutions of the potassium 1:11 and 3:12 complexes were titrated with sodium hydroxide. At about 5°, both complexes consumed base, but no breaks were identified in the curves below pH 7. At about 80°, both complexes were completely degraded to manganese oxide and vanadate(V). The 1:11 complex gave breaks at pH values near 7 and 9–10 corresponding to *ca.* 6 and 17–18 mol of OH^-/mol of complex. The 3:12 complex gave similar breaks at about 7 and 19–20 mol of OH^-/mol of complex. There was an additional small break at pH 5–5.5 and about 1.8 mol of OH^-/mol of complex. In both

(2) (a) C. M. Flynn, Jr., and G. D. Stucky, *Inorg. Chem.,* **8**, 332, 335 (1969); (b) B. W. Dale, J. M. Buckley, and M. T. Pope, *J. Chem. Soc. A,* 301 (1969).

(3) L. C. W. Baker and T. J. R. Weakley, *J. Inorg. Nucl. Chem.,* **28**, 447 (1966).

cases, dark brown manganese oxide precipitated and left a nearly colorless solution in the vicinity of the pH 7 break.

Spectra.—Visible–ultraviolet spectra were recorded on a Cary Model 14 instrument from 200 to 1000 nm.

Solutions of potassium 11-vanadomanganate(IV) at a pH near 2 (0.06 F in K_2SO_4 and 0.04 F in $KHSO_4$) showed intense absorption below 500 nm with no maxima. Over the concentration range 10^{-3}–10^{-5} F in complex, Beer's law is not obeyed. The color of these solutions was about the same or lighter than that of solutions of the 1:13 complex at equivalent concentrations, while more concentrated solutions were noticeably darker than corresponding solutions of the 1:13 complex. The dilute solutions showed extensive decomposition during 1 month (orange-brown precipitates).

Potassium 12-vanado-3-manganate(IV) solutions in 0.03 F K_2SO_4–0.02 F $KHSO_4$ (pH near 2) and in 0.1 F potassium acetate– 0.1 F acetic acid (pH near 5) were examined over the concentration range 10^{-2}–10^{-4} F in manganese. All solutions were unstable, the decomposition time ranging from hours for the more dilute pH 2 solutions to several days for the pH 5 solutions. The spectra at the two acidities were substantially the same qualitatively and consisted of a plateau or slight maximum near 560 nm and a steeply increasing absorption below about 520 nm. At pH 2, Beer's law was not obeyed. At pH 5 the spectra conformed to Beer's law at concentrations 10^{-3}–10^{-2} F. In these latter solutions the feature near 560 nm was a slight maximum, ϵ_{max} 214 $\pm$ 2 at 563 $\pm$ 2 nm (17.8 kK).

Crystallography.—Precession photographs were taken with Cu Kα radiation (λ 1.5418 Å). Densities were determined by flotation in carbon tetrachloride–1,1,2,2-tetrabromoethane at 22–25°.

$K_5MnV_{11}O_{32}\cdot11H_2O$ is triclinic; $a = 15.75$ (2) Å; $b = 12.75$ (2) Å; $c = 10.19$ (2) Å; $\alpha = 113.0$ (2)°; $\beta = 92.8$ (2)°; $\gamma = 100.5$ (2)°; $V = 1836$ Å^3; $\rho_{calcd} = 2.75$ g cm^{-3}; $\rho_{exptl} = 2.68$ (1) g cm^{-3}; $Z = 2$.

$(NH_4)_5HMn_3V_{12}O_{39}\cdot15H_2O$ is cubic; $a = 13.52$ (1) Å; $V = 2471$ Å^3; $\rho_{calcd} = 2.37$ g cm^{-3}; $\rho_{exptl} = 2.29$ (1) g cm^{-3}; $Z = 2$. Extinctions are $h + k + l \neq 2n$; Laue class is m3m; space group is Im3m, I$\bar{4}$3m, or I432. No reflections due to a larger true cell were found on a long-exposure first-level photograph or on a cone-axis photograph.
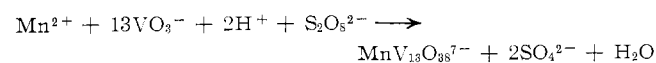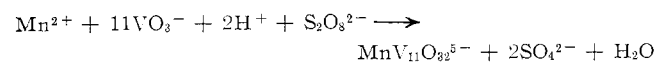
$K_5HMn_3V_{12}O_{39}\cdot10H_2O$ is triclinic; $a = 11.82$ (2) Å; $b = 16.56$ (2) Å; $c = 11.26$ (2) Å; $\alpha = 103.0$ (2)°; $\beta = 109.4$ (2)°; $\gamma = 87.0$ (2)°; $V = 2026$ Å^3; $\rho_{calcd} = 2.91$ g cm^{-3}; $\rho_{exptl} = 2.85$ (1) g cm^{-3}; $Z = 2$.

Other Characterization.—Microscopy and X-ray powder diffraction were employed to check identity and purity of products.

The 1:11 and 1:13 complexes gave no esr signals (as frozen aqueous solutions) at liquid nitrogen temperature.

Results and Discussion

Preparation of the Complexes.—The synthesis of the 11-vanadomanganate(IV) complex can be carried out in a manner like that for the 13-vanadomanganate-(IV),[1] except for the use of less vanadate, as shown by

$$Mn^{2+} + 11VO_3^- + 2H^+ + S_2O_8^{2-} \longrightarrow$$
$$MnV_{11}O_{32}^{5-} + 2SO_4^{2-} + H_2O$$

$$Mn^{2+} + 13VO_3^- + 2H^+ + S_2O_8^{2-} \longrightarrow$$
$$MnV_{13}O_{38}^{7-} + 2SO_4^{2-} + H_2O$$

The synthesis appears to proceed at first by formation of the 1:13 complex which is subsequently converted to the 1:11 complex (reaction equation given in Experimental Section), because the former separates along with the other products if insufficient time is allowed for complete reaction. Pure products can be isolated only if mechanically separable crystals are produced.

The failure to isolate a sodium salt is attributed to its high solubility, the narrow pH range of stability (see below), and instability in concentrated sodium sulfate–bisulfate solutions.

Possible reasons for the low yield of the 1:4 complex (considered to be trimeric) are indicated by the reaction for formation

$$3Mn^{2+} + 12VO_3^- + 3S_2O_8^{2-} + 3H_2O \longrightarrow$$
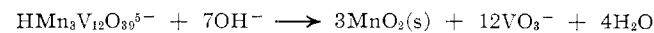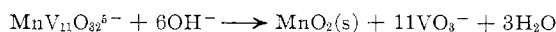$$HMn_3V_{12}O_{39}^{5-} + SO_4^{2-} + 5HSO_4^-$$
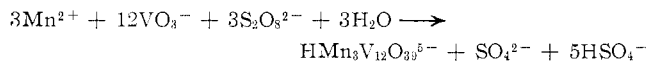
which liberates hydrogen ion, in contrast to the reactions for formation of the other complexes. A composition written as $MnV_4O_{13}^{2-}$ or $Mn(VO_3)_2(V_2O_7)^{2-}$ suggests a complex formed from manganese(IV) and basic vanadate species and is unlikely because the complex is obtained under relatively acid conditions where $V_{10}O_{28}^{6-}$ and protonated species presumably exist;[4] further, manganese(II) does not react with peroxydisulfate and metavanadate at pH 6–8 to form heteropoly complexes.[1] If the complex is in fact polymeric, there is also the thermodynamically unfavorable process of oxidizing and uniting three manganese atoms with vanadate species without merely forming insoluble oxides.

Analyses.—Analytical results for pure compounds are listed in Table I. The material balances for potassium 11-vanadomanganate(IV) and potassium and 12-vanado-3-manganate(IV) are 100.4 and 99.7%, respectively. The formulation of potassium 11-vanadomanganate depends heavily on the manganese analysis, as illustrated by calculations for a plausible 1:10 composition, $K_{4.5}H_{0.5}MnV_{10}O_{29.5}\cdot10H_2O$: FW 1393.0; K, 12.6; Mn, 3.94; V, 36.5; H_2O, 13.3. Consistent results for three salts combined with checking of the analytical procedures[1] give us confidence in the proposed formulation. The oxidation state of the manganese was found to be 4.04 $\pm$ 0.04 in potassium 11-vanadomanganate(IV) and 3.98 $\pm$ 0.02 in potassium 12-vanado-3-manganate(IV), establishing the +4 oxidation state in both complexes and agreeing with the 1:11 stoichiometry of the former. The crystallographic data also support the 1:11 composition; with the 1:10 formula above, the calculated density is 2.52 g/ml, in worse agreement with experiment than that calculated for the 1:11 formula (see Experimental Section).

Chemical Properties of the Complexes.—Most of the salts isolated appear to be stable indefinitely with respect to decomposition of the heteropoly anion. In solution, the 1:11 complex is moderately stable in the pH range 2–3, and the 3:12 complex exists in the pH range 2–6.

Both complexes are degraded by hydroxide ion in hot solution in accordance with the reactions

$$MnV_{11}O_{32}^{5-} + 6OH^- \longrightarrow MnO_2(s) + 11VO_3^- + 3H_2O$$

$$HMn_3V_{12}O_{39}^{5-} + 7OH^- \longrightarrow 3MnO_2(s) + 12VO_3^- + 4H_2O$$

Further addition of base converts VO_3^- to HVO_4^{2-}. With the 3:12 complex, a small break at pH 5–5.5 and

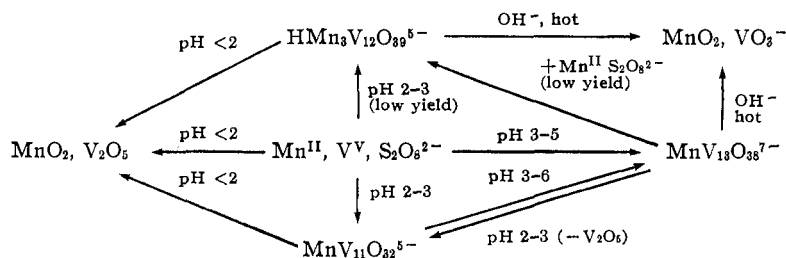(4) M. T. Pope and B. W. Dale, *Quart. Rev., Chem. Soc.*, **22**, 527 (1968).

Figure 1.—Scheme showing preparations and reactions of the heteropoly complexes of manganese(IV) and vanadium.

ca. 1.8 mol of OH^-/mol of trimeric complex could involve deprotonation of the complex.

The interconversions among the complexes and related species are illustrated in Figure 1. No evidence was found for intermediate species in the decompositions at pH 2 and 6–8. Whether the 1:11 complex reacts with isopolyvanadate in the pH range 3–5 to give the 1:13 complex or whether the 3:12 complex is formed as an intermediate in the acid decomposition of the 1:11 complex was not ascertained. The 3:12 complex was found to be unexpectedly inert to reaction with isopolyvanadate to give either the 1:11 complex (pH 2–3) or the 1:13 complex (pH 3–6); competing reactions of the isopolyvanadates occurred faster.

The failure to obtain heteropoly "blue" species or manganese(III) complexes on reduction of the 1:11 or 3:12 complexes is consistent with the instablilty of the reduced 1:13 complex[1] to acid.

Decomposition of Manganate Complexes with Excess Acid.—Unexpectedly, on treatment with excess acid, all three vanadomanganate(IV) complexes as well as 12-niobomanganate(IV)[2] produce small quantities of permanganate, corresponding to about 1% of the total manganese. Manganese(II) is also produced in relatively larger quantities. These results suggest the formation of an unstable manganese(IV) or -(III) species which can disproportionate to manganese(II) and -(VII). Relevant redox potential data for acid solutions are:[5] $Mn(III) + e^- = Mn(II)$, $+1.5$ V; $Mn(IV) + 2e^- = Mn(II)$, $+1.23$ V; $Mn(VII) + 3e^- = Mn(IV)$, $+1.70$ V; $Mn(VII) + 4e^- = Mn(III)$, $+1.5$ V; $Mn(VII) + 5e^- = Mn(II)$, $+1.51$ V. Mn(II) through Mn(VII) refer to Mn^{2+}, Mn^{3+}, MnO_2, and MnO_4^-, respectively. Manganese(III) is barely capable of disproportionation to Mn(II) and Mn(VII). Disproportionation of Mn(IV) to Mn(II) and Mn(VII) would require $E^\circ(Mn^{IV}/Mn^{II})$ of about $+1.5$ V or greater. This could be achieved, according to a Nernst equation calculation, by formation of a Mn(IV) species with a log K of *ca.* -10 with respect to MnO_2.

Constitution of the Complexes.—From the easy interconversion of the 1:11 and 1:13 complexes it would appear that the 1:11 complex is structurally related to the 1:13 complex. The visible–ultraviolet spectrum showed no absorption peaks due to d–d transitions of manganese(IV) (oxidation state based on chemical analysis); the presumed transitions are masked by

vanadate charge-transfer absorption. The manganese coordination is probably octahedral. The possibility exists that the complex is dimeric.[6] This is suggested by the composition of the ammonium and cesium salts (Table I). It is certainly allowed by the crystallographic data for the potassium salt, which preclude any state of polymerization higher than two. Attempts to settle the matter by cryoscopy were prevented by decomposition of the complex in concentrated sodium sulfate–bisulfate solutions.

A number of considerations point strongly to a polymeric structure for the complex with stoichiometry $Mn:V = 1:4$. From experiments with models involving face as well as edge sharing of octahedra, a monomeric structure $MnV_4O_{13}(H_2O)_x{}^{2-}$ would require x to be at least 5 in order to allow octahedral coordinations of all metal atoms. The potassium salt contains insufficient water to satisfy this requirement. Formulation in terms of presumed tetrahedral meta- or pyrovanadate species is unreasonable because of the synthesis conditions and chemical properties of the complex. The relative stability and inertness of the complex suggests that the manganese atoms are well enclosed by vanadate polyhedra, an arrangement which cannot be achieved with a monomeric formulation.

Lack of sufficient material prevented cryoscopic determination of the degree of polymerization of the 1:4 complex. However, the analyses and crystallographic data strongly suggest a trimeric structure. The alkali:manganese ratios are closer to 5:3 than to 3:2 or 7:4. Triclinic or cubic unit cells with a content of six formula units are rare. The fact that the ammonium salt is body-centered cubic eliminates the possibility that the complex is a hexamer. In any of the three possible space groups for the ammonium salt, there is a sixfold position $(^{1}/_{2}, 0, 0; 0, ^{1}/_{2}, 0; 0, 0, ^{1}/_{2};$ etc.). Manganese atoms in these positions would be inconsistent with a finite polynuclear complex. A finite complex would require a disordered structure. For example the manganese atoms could occupy the positions $(x, x, x,$ etc.) so as to give compact triangular groups in a complex which is rotationally disordered with respect to alignment along eight possible directions of threefold axial symmetry.

In conclusion, three vanadomanganate(IV) com-

(5) T. A. Zordan and L. G. Hepler, *Chem. Rev.*, **68**, 737 (1968).

(6) A possible structure of a dimeric complex involves removal of the odd vanadium and one other vanadium atom (with some oxygen atoms) from the proposed structure of the 1:13 complex,[1] giving an $MnV_{11}O_{36}$ group. Two of these could condense by sharing vertices to give a complex $Mn_2V_{22}O_{64}{}^{10-}$.

plexes have now been characterized, mainly by chemical analysis, chemical properties, and unit-cell data for a few salts. The three complexes with stoichiometry 1:13, 1:11, and 1:4 appear to be the major species in the system. We plan to carry out magnetochemical investigations of the complexes. X-Ray structure determinations have been initiated on the 1:13 and 3:12 compounds.

Fluorine-19 Nuclear Magnetic Resonance and Raman Spectral Studies of Tantalum(V)-Fluoride Ion Complexes in Anhydrous Hydrogen Fluoride Solutions

By N. A. MATWIYOFF, L. B. ASPREY, and W. E. WAGEMAN

In the 56.45-MHz ^{19}F nuclear magnetic resonance (nmr) spectra of anhydrous HF solutions of KTaF$_6$ and K$_2$TaF$_7$, the only ^{19}F signals that could be distinguished are those of HF and the TaF$_6^-$ ion, the latter occurring 12.8 kHz downfield from the HF resonance. The relative areas and chemical shifts of these signals over a wide range of temperature and solution compositions show that the predominant Ta(V)-F$^-$ ion complex present in these solutions is the TaF$_6^-$ ion. In the Raman spectra of the solutions, the only Ta–F vibrations that could be detected are those of the TaF$_6^-$ ion (ν_1 711 cm^{-1}, ν_2 595 cm^{-1}, and ν_5 282 cm^{-1}). The TaF$_7^{2-}$ ion must be a minor species in these solutions, if it is present at all. The ^{19}F nmr signals of anhydrous HF solutions of KTaF$_6$ and KF–KTaF$_6$ mixtures are broadened by chemical exchange of ^{19}F between HF and the TaF$_6^-$ ion *via* two paths: one is independent of the concentration of added F$^-$ ion (k_1 path); the other depends to the first order upon the F$^-$ ion concentration (k_2 path). The chemical exchange parameters derived from the temperature and solution composition dependence of the line broadening are: $k_1(25°) = 4.9 \times 10^2$ sec^{-1}, $\Delta H_1^{\ddagger} = 1.8 \pm 0.3$ kcal, $\Delta S_1^{\ddagger} = -40 \pm 4$ eu; $k_2(25°) = 2.9 \times 10^4$ m^{-1} sec^{-1}, $\Delta H_2^{\ddagger} = 2.4 \pm 0.5$ kcal, $\Delta S_2^{\ddagger} = -31 \pm 4$ eu. The mechanisms for the exchange of ^{19}F are discussed.

Introduction

Tantalum(V) exhibits coordination numbers of 6, 7, and 8 in the simple isolated fluoride ion complexes which have been characterized in the solid compounds CsTaF$_6$,[1] K$_2$TaF$_7$,[2] and Na$_3$TaF$_8$.[3] One interesting question which arises regarding the solution chemistry of these compounds is whether Ta(V) is present in the form of a single complex or whether there exist in solution several F$^-$ ion complexes in which Ta(V) exhibits different coordination numbers. Viewed from another perspective, the question is concerned with the extent to which the occurrence of the unusual ions TaF$_7^{2-}$ and TaF$_8^{3-}$ in solid compounds can be attributed to favorable crystal forces in K$_2$TaF$_7$(s) and Na$_3$TaF$_8$(s) or whether the occurrence of these ions reflects an inherently small difference in energy among the isolated TaF$_6^-$, TaF$_7^{2-}$, and TaF$_8^{3-}$ coordination polyhedra. If the latter is true, stabilization of each of the ions in solution should be possible through control of the F$^-$ ion activity.

Two studies of Ta(V)-F$^-$ ion complexes in solution have been reported. On the basis of potentiometric studies of the F$^-$ ion activity in Ta(V)-aqueous F$^-$ ion

systems, it has been suggested[4,5] that all of the species TaF$_{5+n}^{n-}$ ($n = 1$–3) do exist in solution. However, since activity measurements are sensitive to relatively weak interactions, it is, in general, not possible to distinguish whether a TaF$_8^{3-}$ "ion" detected in an activity measurement contains eight F$^-$ ions in the first coordination sphere of Ta(V) or contains six F$^-$ ions in the first sphere, the remaining two being weakly associated in the second coordination sphere. Keller and Chetham-Strode[6] used Raman spectroscopy (generally sensitive only to strong first-coordination-sphere interactions) to show the TaF$_6^-$ and TaF$_7^{2-}$ ions are present in aqueous HF solutions and aqueous NH$_4$F solutions of CsTaF$_6$ and K$_2$TaF$_7$.

Although not discussed by Keller and Chetham-Strode, the solvent dependence of the equilibria between TaF$_6^-$ and TaF$_7^{2-}$ observed by them is qualitatively consistent with control of the equilibria by the solvent F$^-$ ion activity. The TaF$_7^{2-}$ ion was found to be the predominant species in aqueous 5.42 M NH$_4$F solutions which should exhibit relatively large F$^-$ ion activities. However in 24 M aqueous HF, which is a

(1) B. Cox, *J. Chem. Soc.*, 876 (1956).

(2) J. L. Hoard, *J. Amer. Chem. Soc.*, **61**, 1252 (1939).

(3) J. L. Hoard, W. J. Martin, M. E. Smith, and J. F. Whitney, *ibid.*, **76**, 3820 (1954).

(4) L. P. Varga and H. Freund, *J. Phys. Chem.*, **66**, 21, 187 (1962).

(5) M. N. Buksh and A. G. Maddock, private communication to F. Fairbrother quoted in F. Fairbrother, "The Chemistry of Niobium and Tantalum," Elsevier, New York, N. Y., 1967, p 83.

(6) O. L. Keller, Jr., and A. Chetham-Strode, Jr., *Inorg. Chem.*, **5**, 367 (1966).