

1:13 Heteropolyvanadates of Manganese(IV) and Nickel(IV)<sup>1</sup>C. M. Flynn, Jr., and Michael T. Pope<sup>2</sup>*Contribution from the Department of Chemistry, Georgetown University, Washington, D. C. 20007. Received July 14, 1969*

**Abstract:** The preparation and properties of the first heteropolyvanadates with transition metal central atoms and the first heteropoly anions with a 1:13 stoichiometry are reported. The complexes have been characterized by complete analysis of several salts, cryoscopy, magnetic susceptibility determination, and preliminary X-ray crystallographic examination. The salts  $K_7[Mn^{IV}V_{13}O_{38}] \cdot 18H_2O$  and  $K_7[Ni^{IV}V_{13}O_{38}] \cdot 16H_2O$  are isomorphous. Reduction of the manganate complex leads to an apparently isostructural mixed-valence anion  $[Mn^{IV}V_{12}V^{IV}O_{38}]^{8-}$ . Although unstable in solution, the reduced species has been characterized by analysis and optical and esr spectroscopy. A proposed structure for the anion in  $K_7[MnV_{13}O_{38}] \cdot 18H_2O$ , consistent with the observed unit cell symmetry, requires 39 oxygen atoms (one constitutional water molecule). Two new Mn(II) double salts,  $K_2Mn_2[V_{10}O_{28}] \cdot 12H_2O$  and  $K_4Mn[V_{10}O_{28}] \cdot 10H_2O$ , have been prepared.

There are currently between 100 and 200 reasonably well-established heteropoly anions of molybdenum and tungsten. With the possible exceptions of the 12-vanadophosphate anion<sup>3</sup> and some vanadium-substituted polytungstates and molybdates,<sup>4</sup> there are no confirmed examples of heteropoly anions with other addenda. In order to examine the factors contributing to the structures and stabilities of isopoly and heteropoly anions, we are making a systematic investigation of heteropoly anions of the group V transition elements. Recently, heteropolyniobates of manganese(IV) and nickel(IV),<sup>5-7</sup> a manganese(IV) heteropoly compound with both niobium and tantalum,<sup>7</sup> and chromium and cobalt(III) complexes with ethylenediamine and hexaniobate<sup>8</sup> have been characterized. We now report the preparation and characterization of vanadomanganate(IV) and -nickelate(IV) heteropoly anions with the unexpected stoichiometry  $M(IV):V = 1:13$ , together with a mixed-valence reduction product of the manganate(IV) complex.

**Experimental Section**

**Reagents.** Potassium metavanadate was prepared by reaction of vanadium(V) oxide (1 mole) with potassium carbonate (1 mole) in aqueous solution. Hydrogen peroxide was added to assist dissolution of the  $V_2O_5$ . After removal of a small amount of dark residue, the product was precipitated by evaporating the solution to about 300 ml. It was isolated, washed with cold water followed by 95% ethanol, and air dried at room temperature or at 100–120°. Further evaporation of the reaction solution yielded more product. *Anal.* Calcd for  $KVO_3$ : V, 36.9. Found: V, 36.8, 37.1.

Sodium pyrovanadate ( $Na_4V_2O_7 \cdot 18H_2O$ )<sup>9</sup> was prepared in the same way as  $KVO_3$ , substituting 4 moles of NaOH for the  $K_2CO_3$ . Final evaporation to about 600 ml and cooling in the refrigerator yielded the product, which was isolated, washed with ethanol-water followed by 95% ethanol, and air dried at room temperature.

(1) C. M. Flynn, Jr., D. A. Langs, and M. T. Pope, presented at the Fourth Middle Atlantic Regional Meeting of the American Chemical Society, Washington, D. C., Feb 12–15, 1969, Paper D-21.

(2) To whom correspondence should be addressed.

(3) A. Rosenheim and M. Pieck, *Z. Anorg. Chem.*, **98**, 223 (1916); G. Jander and K. F. Jahr, *Kolloid-Beihfte*, **41**, 332 (1935); P. Souchay and S. Dupois, *Ann. Chim.* (Paris), **3**, 88 (1948); R. Ripan, A. Duca, and V. Cordis, *Rev. Roumaine Chim.*, **12**, 375 (1967).

(4) See, for example, G. A. Tsigdinos and C. J. Hallada, *Inorg. Chem.*, **7**, 437 (1968); M. P. Courtin, *Bull. Soc. Chim. France*, 4799 (1968).

(5) B. W. Dale and M. T. Pope, *Chem. Commun.*, 792 (1967).

(6) C. M. Flynn, Jr., and G. D. Stucky, *Inorg. Chem.*, **8**, 332, 335 (1969).

(7) B. W. Dale, J. M. Buckley, and M. T. Pope, *J. Chem. Soc., A*, 301 (1969).

(8) C. M. Flynn, Jr., and G. D. Stucky, *Inorg. Chem.*, **8**, 178 (1969).

(9) H. Menzel and G. Müller, *Z. Anorg. Allg. Chem.*, **272**, 81 (1953).

Additional product was obtained by evaporating the reaction solution. The compound forms colorless leaflets. *Anal.* Calcd for  $Na_4V_2O_7 \cdot 18H_2O$ : V, 16.17. Found: V, 16.19, 16.21.

Buffer solutions covering the pH range 2–6 were prepared by neutralizing the appropriate acid (sulfuric, dichloroacetic, monochloroacetic, formic, or acetic) with potassium or sodium carbonate.

Solutions of sodium or ammonium hexacyanoferrate(II) were prepared by neutralizing a solution of the free acid prepared from the potassium salt by ion exchange on Dowex 50W-X8. All other reagents used were commercial products.

**Potassium Trivanadate ( $KV_3O_8$ ).** The light yellow-orange insoluble compound was prepared by heating a suitably acidified  $KVO_3$  solution.<sup>10</sup> Its X-ray powder pattern agreed with that given by Kelmers.<sup>11</sup>

**Potassium Zinc Decavanadate.** A solution of  $KVO_3$  acidified with acetic acid to a pH near 5 was treated with a zinc nitrate solution<sup>10</sup> ( $Zn:V = 1:5$ ); the product precipitated quickly. *Anal.* Calcd for  $K_2Zn_2V_{10}O_{28} \cdot 16H_2O$ : V, 36.0. Found: V, 35.0, 34.9.

**Potassium Manganese(II) Vanadates.** Solutions of  $KVO_3$  in acetic acid–potassium acetate solutions ( $KVO_3:HOAc:KOAc = 3:5:5$  and  $3:10:2$ ) were treated with manganese(II) sulfate solution and the products allowed to crystallize. For a particular Mn:V ratio, the products at the two acidities were the same. At Mn:V = 1:12, orange crystals (crusts or chunky individuals) were obtained. *Anal.* Calcd for  $K_4MnV_{10}O_{28} \cdot 10H_2O$ : K, 11.6; Mn, 4.07; V, 37.8. Found: K, 11.8, 12.4; Mn, 4.10, 4.10; V, 37.6, 37.7. At Mn:V = 1:4, golden yellow rods or needles were obtained. *Anal.* Calcd for  $K_2Mn_2V_{10}O_{28} \cdot 12H_2O$ : K, 5.73; Mn, 8.08; V, 37.4. Found: K, 6.2, 6.6; Mn, 7.96, 8.00; V, 37.6, 37.6. A mixture of these products was obtained at Mn:V = 1:6 (identified by microscopy and X-ray powder pattern).

**Potassium Nickel(II) Vanadates.** Substitution of  $NiSO_4$  for  $MnSO_4$  in the above experiment gave only one compound as orangish yellow powder or greenish-tinged yellow-orange crystals. *Anal.* Calcd for  $K_2Ni_2V_{10}O_{28} \cdot 16H_2O$ : Ni, 8.37; V, 36.3. Found: Ni, 7.69, 7.71; V, 35.2, 35.4. The X-ray powder pattern and crystal habit are very similar to those of the corresponding zinc compound.

**Potassium 13-Vanadomanganate(IV).** A solution of 35.9 g (0.26 mole) of  $KVO_3$  in 900–1000 ml of hot water was treated with 20 ml of 1 F nitric acid, 20 ml of 1.0 F manganese(II) sulfate, and 10.8 g (40 mmoles) of potassium peroxydisulfate, in that order. The mixture was kept near 80° and stirred while reaction proceeded and the solution evaporated. Sometimes a brown-red precipitate formed initially; it later redissolved giving an orange-red to brownish red solution. Later a brown-red to brown precipitate formed again; this appeared to be a mixture of  $V_2O_5$ , Mn oxide, and  $KV_3O_8$ . After 5–7 hr the volume of the reaction mixture was about 300 ml; at this point the mixture was filtered and treated with 40 ml of 1 F potassium acetate. After standing overnight, the bright red-orange crystalline product was collected and washed with a little 0.5 F potassium acetate–0.5 F acetic acid. It was recrystallized once or twice from 0.5 F potassium acetate–0.5 F acetic acid to give char-

(10) H. T. Evans, Jr., *Inorg. Chem.*, **5**, 967 (1966).

(11) A. D. Kelmers, *J. Inorg. Nucl. Chem.*, **21**, 45 (1961).

acteristic bright red-orange octahedral crystals, often in columnar growths. These were washed with ethanol-water followed by 95% ethanol and air dried.

The brown-red precipitate formed in the early stage of the above reaction could also be produced by heating manganese(II) and vanadate (e.g., 40 mmoles of  $KVO_3$ , 10 mmoles of acetic acid, and 10 mmoles of  $MnSO_4$  in 400 ml of water; the precipitate formed within 10–20 min, leaving a yellow solution, and no further reaction occurred in 1 hr). The product was filtered, washed with water, and air dried. *Anal.* Calcd for  $MnV_3O_8 \cdot 4H_2O$ : Mn, 16.91; V, 31.4;  $H_2O$ , 22.2. Found: Mn, 16.85, 16.89; V, 30.9, 31.2;  $H_2O$ , 22.4.

**Sodium 13-Vanadomanganate(IV).** A solution of peroxydisulfuric acid was prepared from a solution of 9.2 g (40 mmoles) of ammonium peroxydisulfate in 40 ml of water by ion exchange on Dowex 50W-X8. A solution of 0.26 mole of  $NaVO_3$  (prepared from  $NaHCO_3$  and  $V_2O_5$ ) in ca. 700 ml of hot water was treated with 20 ml of 1 *F*  $HNO_3$  and 20 ml of 1.0 *F*  $MnSO_4$ , followed by a solution of 40 mmoles of  $Na_2S_2O_8$  (prepared by neutralizing the acid with  $NaHCO_3$ ). The reaction was carried out as for the potassium compound. The final filtered solution (ca. 200 ml) was treated with 3.2 g (40 mmoles) of  $NaHCO_3$ , followed by a solution of 0.10 mole each of sodium acetate and acetic acid in 40 ml of water. After standing for a day, the product was separated and recrystallized twice from 1 *F* sodium acetate–1 *F* acetic acid. In the isolation of the compound, final washing with 4:1 v/v ethanol-water preserved the bright red-orange crystals; thorough washing with 95% ethanol caused the crystals to crumble to an orange powder. The crystals were stored over sodium sulfate decahydrate.

If  $Na_4V_2O_7 \cdot 18H_2O$  was used as the starting material, 0.20 mole of  $HNO_3$  was added, and the persulfate was added as the acid.

**Ammonium 13-Vanadomanganate(IV).** Reaction of  $NH_4VO_3$ ,  $HNO_3$ ,  $MnSO_4$ , and  $(NH_4)_2S_2O_8$  was carried out as in the preparation of the potassium salt. At the end of the reaction (volume of mixture ca. 200 ml), 3 g (40 mmoles) of ammonium acetate was added and the solution was filtered. It was further evaporated to about 100 ml, then allowed to stand. After a few days it had evaporated to about 50 ml and much solid had crystallized. The crude product was recrystallized from 0.5 *F* ammonium acetate–0.5 *F* acetic acid. Slow evaporation of the solution at room temperature gave large bright red-orange rhomb-based pyramidal crystals. Washing with ethanol-water mixture (more than 50% ethanol) caused the crystals to crumble; the solid was ground under portions of 95% ethanol before air drying. The large crystals could be preserved by washing with ice-cold 50% v/v ethanol-water, blotting dry, and storing in the refrigerator in a tightly closed container.

**Attempted Preparation of Lithium 13-Vanadomanganate(IV).** Two grams of potassium 13-vanadomanganate(IV) was dissolved in 30 ml of water containing one drop of 5 *F* acetic acid. The solution was converted to the lithium salt by ion exchange with Dowex 50W-X8. The eluted solution was treated with a solution made from 0.7 g (10 mmoles) of lithium carbonate and 8 ml of 5 *F* acetic acid. Evaporation to about 5 ml and storage in the refrigerator for 2 months failed to yield crystals, although no decomposition appeared to occur.

**Potassium 13-Vanadonickelate(IV).** The preparation was carried out as for the manganese compound, substituting nickel(II) sulfate for the  $MnSO_4$ . The reaction mixture gradually became very dark red-brown over a ca. 5-hr period, during which it evaporated to about 300 ml. The mixture was filtered, and isolation and recrystallization of the product were performed in the same way as for the manganese compound, except that acetone was substituted for ethanol in washing. The compound has the same crystal habit as the manganese compound, but is colored black (small crystals under the microscope are deep cherry red).

#### Reduction of 13-Vanadomanganate(IV) by Hexacyanoferrate(II).

a. **Potassium Salt.** A solution containing 5.8 g (3 mmoles) of potassium 13-vanadomanganate(IV), 60 mmoles of potassium acetate, and 60 mmoles of acetic acid in 300 ml water was treated with 30 ml of 0.1 *F* potassium hexacyanoferrate(II). The orange solution immediately turned dark yellowish green, and in a few seconds a lustrous dark yellowish green precipitate began to form. After stirring the mixture for about 5 min, the precipitate was isolated (yellow filtrate) and washed successively with 0.2 *F* potassium acetate–0.2 *F* acetic acid, ethanol-water, and 95% ethanol, then air dried. The product is an olive-tinged green to lustrous dark green powder.

b. **Ammonium Salt.** A solution of 5.3 g (3 mmoles) of ammonium 13-vanadomanganate(IV)–18-water, 40 mmoles of ammonium acetate, and 20 mmoles of acetic acid in 100 ml of water was cooled

to ca. 5° and treated with 30 ml of cold ammonium hexacyanoferrate(II). Reaction occurred as for the potassium compound. After about 10 min the product was isolated and washed with ethanol-water, followed by 95% ethanol, and air dried. The dark brownish green powder was contaminated by some light colored flocculent precipitate. Because of instability in solution, the compound cannot be purified.

**Reduction of 13-Vanadomanganate(IV) by Vanadyl(IV).** Potassium and ammonium 13-vanadomanganates(IV) were treated with 0.2 *F* vanadyl(IV) sulfate solution in procedures like those with hexacyanoferrate(II), giving products similar in appearance, except that the ammonium salt was brighter green with olive tinge. The filtrate from the potassium salt was green-brown.

**Analytical. General.** Determinations were nearly always done at least twice. Analytical procedures for manganese, nickel, and vanadium were found to be reliable by testing known mixtures, e.g., 10 V/Mn.

a. **Vanadium.** The aqueous solution of the sample was treated with sulfuric acid and reduced to V(IV) with sodium sulfite. The vanadium was then determined with permanganate. Alternatively, the sample solution was treated with Dry Ice to exclude oxygen, and potassium iodide and sulfuric acid were added. The iodine released was titrated with sodium thiosulfate.

b. **Manganese Compounds.** The aqueous solution of the sample was decomposed by heating with sodium hydroxide and hydrogen peroxide. The manganese oxide precipitate was then filtered, washed, and dissolved with hydrogen peroxide and nitric acid. The manganese was determined with EDTA at pH 10 using Eriochrome Black T indicator. The filtrate from the alkali decomposition was acidified, heated to decompose peroxides, and reduced to V(IV). The vanadium was then determined by permanganate. As a check, manganese was also determined spectrophotometrically<sup>12</sup> for potassium 13-vanadomanganate(IV).

c. **Nickel Compounds.** Dissolution of the nickel(II) compound was speeded by addition of a little sulfuric acid. For the nickel(IV) compound, addition of a little sulfuric acid caused reduction to nickel(II). The solution was then buffered to pH 10 and the nickel determined with EDTA, using murexide as indicator. The solution was subsequently acidified and the vanadium determined idiometrically.

d. **Cations.** For salts of stable anions, the aqueous solution was passed through a column of Dowex 1-X2 in the chloride form. The eluted solution was then titrated potentiometrically with silver nitrate. Potassium was determined as the tetraphenyl borate. Ammonium was determined by distillation of ammonia from sodium hydroxide solution into excess boric acid followed by titration with perchloric acid using methyl red as indicator.

e. **Water.** Weight loss on heating to ca. 120–150° and to 400–450° was determined for several compounds. At 400–450° all the compounds were decomposed, usually with fusion. Correction of these weight losses for oxygen lost on reduction of the heteroatom to the 2+ state<sup>13</sup> gave the water contents.

f. **Oxidation State.** The following procedure was found to give reliable results: an aqueous solution of the sample was placed into a semimicro distillation apparatus. About 20 ml of carbon tetrachloride followed by 10 ml of a solution 0.5 *F* in sulfuric acid and 0.2 *F* in potassium bromide were added. The bromine formed through reduction of Mn or Ni to the 2+ state was distilled with the carbon tetrachloride into a potassium iodide solution, and the liberated iodine titrated with 0.02 *F* sodium thiosulfate. Vanadium(V) is not reduced under these conditions. The reliability of the procedure was confirmed by reduction of aliquots of potassium permanganate solution.

**Acid-Base Titrations.** Samples of the salts were titrated with sodium hydroxide or perchloric acid at 0–5, 20–25, or ca. 80°, using a Corning Model 7 pH meter and a glass electrode.

**Reduction of 13-Vanadomanganate(IV).** Solutions of the potassium salt were titrated potentiometrically with potassium hexacyanoferrate(II) solution or with vanadyl sulfate solution. A platinum wire indicator electrode was used against a saturated calomel electrode.

**Identification of Products.** Qualitative identity and purity of compounds were determined by microscopy and by X-ray powder diffraction. In syntheses, attempts were always made to get well-crystallized specimens so as to check their purity more reliably.

(12) I. M. Kolthoff and P. J. Elving, Ed., "Treatise on Analytical Chemistry," Vol. 7, Part II, Interscience Publishers, New York, N. Y., 1961, pp 480–483.

(13) C. Brisi, *Ann. Chim. (Rome)*, 47, 806 (1957); 48, 270 (1958).

Table I. Analyses of Heteropoly Complexes

Compound (formula wt)		M' <sup>a</sup>	M <sup>b</sup>	V	H <sub>2</sub> O <sup>c</sup>	Oxidation <sup>d</sup> state	M'/M	V/M	Material balance
K <sub>7</sub> MnV <sub>13</sub> O <sub>35</sub> ·18H <sub>2</sub> O (1923.1)	Found	14.2 (1) <sup>e</sup>	2.88 (2) <sup>f</sup>	34.8 (2)	16.9 (1)	3.99 (2)	6.95	13.06	100.8
	Calcd	14.2	2.86	34.4	16.9	4.00			
Na <sub>7</sub> MnV <sub>13</sub> O <sub>35</sub> ·24H <sub>2</sub> O (1918.4)	Found <sup>g</sup>	8.35 (4)	2.86 (2)	34.9 (2)	22.0 (3)		6.98	13.17	100.1
	Calcd	8.39	2.86	34.5	22.5	4.00			
(NH <sub>4</sub> ) <sub>7</sub> MnV <sub>13</sub> O <sub>35</sub> ·5H <sub>2</sub> O (1541.5)	Found <sup>g</sup>	8.29 (4)	3.60 (2)	42.7 (2)	(6.1) <sup>i</sup>		7.01	12.78	
	Calcd	8.19	3.56	42.9	5.8	4.00			
K <sub>7</sub> NiV <sub>13</sub> O <sub>35</sub> ·16H <sub>2</sub> O (1896.9)	Found	14.6 (1)	3.10 (2)	34.8 (1)	14.8 (4)	3.99 (2)	7.07	12.94	99.3
	Calcd	14.5	3.10	35.0	15.2	4.00			
(NH <sub>4</sub> ) <sub>7.5</sub> H <sub>0.5</sub> MnV <sub>13</sub> O <sub>35</sub> ·7H <sub>2</sub> O <sup>o</sup> (1587.1)	Found	8.49 (3)	3.44 (2)	42.1 (3)	(7.7) <sup>i</sup>		7.54	13.24	
	Calcd	8.05	3.46	41.7	7.9	3.00			
K <sub>7.5</sub> H <sub>0.5</sub> MnV <sub>13</sub> O <sub>35</sub> ·17H <sub>2</sub> O <sup>h</sup> (1925.2)	Found	15.0 (1)	2.82 (1)	34.5 (1)	15.9 (1)	3.10 (5)	7.47	13.26	99.8
	Calcd	15.2	2.85	34.4	16.1	3.00			
K <sub>7.5</sub> H <sub>0.5</sub> MnV <sub>13.5</sub> O <sub>39</sub> ·16H <sub>2</sub> O <sup>o</sup> (1948.6)	Found	15.2 (1)	2.83 (1)	35.4 (1)	14.8) <sup>i</sup>	2.61 (2)	7.57	13.48	
	Calcd	15.0	2.82	35.3	15.0	2.50			

<sup>a</sup> M' = K, Na, or NH<sub>4</sub>. <sup>b</sup> M = Mn or Ni. <sup>c</sup> Corrected for loss of oxygen, MO<sub>2</sub> to MO. <sup>d</sup> Referred to Mn (or Ni). <sup>e</sup> Error of experimental results in units of last significant figure. <sup>f</sup> 2.85% by spectrophotometry. <sup>g</sup> Reduced by VOSO<sub>4</sub>. <sup>h</sup> Reduced by K<sub>4</sub>Fe(CN)<sub>6</sub>. <sup>i</sup> Calculated by difference. <sup>j</sup> Product washed with 95% ethanol.

X-Ray powder data were recorded with a Picker powder diffractometer with Cu K $\alpha$  radiation at 2°/min with a 3-sec time constant.

**Optical Spectra.** Spectra of solutions and of solids pressed in KBr pellets were recorded on a Cary 14 spectrophotometer over the range 200–1200 nm.

**Cryoscopy in Saturated Sodium Sulfate Solution.** The molecular weight of the vanadomanganate(IV) species (as the sodium salt) was determined by depression of the transition point of the system Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O–Na<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O. The apparatus has been described.<sup>14</sup> The molal depression constant was determined with sodium chloride as 1.8 ± 0.1° per 1000 g of water in solution. This compares with 1.89° found by Rollins and Baker<sup>15</sup> and with the thermodynamically derived value, 1.771°, given by Fernandez-Prini and Prue.<sup>16</sup> Results were (Na<sub>7</sub>MnV<sub>13</sub>O<sub>35</sub>·24H<sub>2</sub>O concentration in g/kg water, temperature depression): 29.34, 0.022; 40.54, 0.038; 61.56, 0.059.

**Chromatography.** A column of Sephadex G-25 (fine), 2.5 × 45 cm, was employed. A solution 0.1 *F* in acetic acid and 0.1 *F* in potassium or sodium acetate was used as the eluting agent.

**Magnetic Susceptibility.** Measurements were made at room temperature on a Faraday-type apparatus by Professor A. N. Thorpe and coworkers, Physics Department, Howard University.

**Electron Spin Resonance.** Aqueous solutions frozen in liquid nitrogen were examined on a Varian V-4500 spectrometer by Dr. Hideo Kon, of the National Institute of Arthritis and Metabolic Diseases, National Institutes of Health. Solids were examined on a Strand Labs spectrometer by Joseph Killiany, Physics Department, Georgetown University.

## Results and Discussion

**Manganese(II) and Nickel(II) Compounds.** No evidence was obtained for stable heteropoly complexes of manganese(II) or nickel(II) with vanadate. With potassium ion, nickel(II) gives the double salt K<sub>2</sub>Ni<sub>2</sub>V<sub>10</sub>O<sub>28</sub>·16H<sub>2</sub>O, found by morphology and powder diffraction to be isomorphous with K<sub>2</sub>Zn<sub>2</sub>V<sub>10</sub>O<sub>28</sub>·16H<sub>2</sub>O. From the crystal structure of the latter,<sup>10</sup> the constitution is K<sub>2</sub>[Ni(OH<sub>2</sub>)<sub>6</sub>]<sub>2</sub>[V<sub>10</sub>O<sub>28</sub>]·4H<sub>2</sub>O. Radau<sup>17</sup> and Fock<sup>18</sup> obtained a manganese compound K<sub>2</sub>Mn<sub>2</sub>V<sub>10</sub>O<sub>28</sub>·16H<sub>2</sub>O, described as red crystals. A compound satisfying both this composition and description was not obtained here. Two compounds were obtained here, K<sub>2</sub>Mn<sub>2</sub>V<sub>10</sub>O<sub>28</sub>·12H<sub>2</sub>O (yellow rods or needles) and K<sub>2</sub>MnV<sub>10</sub>O<sub>28</sub>·10H<sub>2</sub>O (orange crystals in crusts). The powder patterns of these differed considerably from those of K<sub>2</sub>Ni<sub>2</sub>V<sub>10</sub>O<sub>28</sub>·16H<sub>2</sub>O or the zinc compound.

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

(15) O. W. Rollins and L. C. W. Baker, *Inorg. Chem.*, **8**, 397 (1969).

(16) R. Fernandez-Prini and J. E. Prue, *J. Chem. Soc., A*, 1974 (1967).

(17) C. Radau, *Ann. Chem.*, **251**, 114 (1889).

(18) A. Fock, *Z. Kristallogr.*, **17**, 1 (1897).

**Preparation of Manganese(IV) and Nickel(IV) Complexes.** The slow reaction of manganese(II) ion, isopolyvanadate, and a moderate excess of peroxydisulfate ion is an efficient synthetic route to the new 13-vanadomanganate(IV) complexes. Starting with vanadium: heteroatom ratios of 12:1 or 13:1 leads to yields of up to 70% for the manganate and around 60% for the nickelate. The 13-vanadomanganate(IV) complex is also formed starting with V:Mn as low as 10:1 or as high as 20:1, but in reduced yield. The synthesis reaction appears to proceed efficiently in the pH range 3–5. At a pH near 6, manganese(II) metavanadate precipitates and does not react further, while at a pH near 2, lower heteropoly species (see below) are formed. Attempts to prepare the manganate by other methods, e.g., with chlorine, hypochlorite, or hydrogen peroxide as oxidizing agent, through reduction of permanganate, or with manganese(II)–permanganate mixtures, all led to formation of much brown colloid and precipitate of manganese oxides.

**Stoichiometry and Constitution.** The unexpected 13:1 stoichiometry for these heteropoly complexes is based primarily on the analytical data for three vanadomanganate salts and one vanadonickelate salt, shown in Table I. The closest 12:1 formulation gives a distinctly poorer fit to the data, as the following comparison shows. *Anal.* Calcd for K<sub>6</sub>MnV<sub>12</sub>O<sub>35</sub>·16H<sub>2</sub>O: K, 13.4; Mn, 3.14; V, 34.9; H<sub>2</sub>O, 16.5. Found: K, 14.2; Mn, 2.88; V, 34.8; H<sub>2</sub>O, 16.9. The possibility of contamination by isopolyvanadates is unlikely in view of the satisfactory preparations using different V:Mn ratios. The average results for two preparations of the potassium salt starting with a 20:1 ratio were (after two recrystallizations) Mn, 2.88 ± 0.01; V, 34.6 ± 0.1; V/Mn, 12.99.

The manganese and nickel are shown by the analytical data to possess the 4+ oxidation state (Table I). The equivalent weight calculations in Table II also support the 13:1 stoichiometry.

The electronic absorption spectra of the 13-vanadomanganate(IV) and -nickelate(IV) show no maxima and consist of absorption continuously increasing with energy through the visible and ultraviolet. There is no evidence for a manganese(IV) d–d transition expected near 450 nm, as appears in the 9-molybdomanganate(IV)<sup>19</sup> and 12-niobomanganate(IV),<sup>5–7</sup> in aqueous

Table II. Equivalent Weights<sup>a</sup> of Heteropolyvanadate Salts

Composition	Equivalent weights	
	M = Mn	M = Ni
K <sub>5</sub> M <sup>IV</sup> V <sub>12</sub> O <sub>35</sub> · 16H <sub>2</sub> O, calcd	875	877
K <sub>7</sub> M <sup>IV</sup> V <sub>13</sub> O <sub>38</sub> · 18H <sub>2</sub> O, calcd	962	964
K <sub>7</sub> HM <sup>III</sup> V <sub>13</sub> O <sub>38</sub> · 18H <sub>2</sub> O, calcd	1924	1928
Experimental (mean of three detns)	963 ± 10	952 ± 7

<sup>a</sup> With respect to reduction of the heteroatom to the 2+ oxidation state.

or glycerin-ethanol solutions or in KBr disks. This is attributed to masking by the relatively intense absorption due to the vanadate ( $\epsilon$  ca. 3000 at 450 nm).

The room-temperature magnetic susceptibility of K<sub>7</sub>[MnV<sub>13</sub>O<sub>38</sub>] · 18H<sub>2</sub>O was  $(3.31 \pm 0.03) \times 10^{-6}$  emu/g. That of the corresponding nickelate was  $(0.00 \pm 0.02) \times 10^{-6}$  emu/g. Taking the susceptibility of the nickel compound as the diamagnetic correction to the susceptibility of the manganate,<sup>20</sup> the derived molar susceptibility is  $6360 \times 10^{-6}$  emu/mole. The effective magnetic moment is then 3.91 BM, in agreement with the value 3.88 BM calculated for a high-spin d<sup>3</sup>(Mn(IV)) configuration.

No esr signals were obtained from the 13-vanadomanganate in solution or solid state at room temperature. At liquid nitrogen temperature, a broad asymmetric signal at  $g$  roughly 4.0 was obtained. Frozen solutions of both 12-niobomanganate(IV) and 9-molybdomanganate(IV) were previously found to give broad asymmetric signals at  $g$  values of 3.8.<sup>5</sup>

The constitution of these compounds as salts containing monomeric 13:1 heteropoly anions is based upon the following evidence. (1) Four salts were obtained as pure well-crystallized substances, and all analyzed as 13:1 V:M(IV) compositions. (2) The manganese in K<sub>7</sub>[MnV<sub>13</sub>O<sub>38</sub>] · 18H<sub>2</sub>O is anionic to better than 99.5% by ion exchange. (3) Cryoscopy of Na<sub>7</sub>[MnV<sub>13</sub>O<sub>38</sub>] · 24H<sub>2</sub>O in the sodium sulfate-water system gave an average molecular weight of  $2000 \pm 200$ . This agrees well with the presence of 1 mole of cryoscopically active ions per mole of salt, and in particular discounts the presence of low molecular weight species to which this procedure is very sensitive. (4) While chromatography on Sephadex led to partial separation of species, this is attributed to reduction and decomposition of the complex by the column material. The forward fractions containing the orange complex gave the characteristic octahedral crystals on evaporation with potassium nitrate. (5) Preliminary unit cell data for K<sub>7</sub>[MnV<sub>13</sub>O<sub>38</sub>] · 18H<sub>2</sub>O show the crystals to be body-centered tetragonal,  $a = 11.38 \pm 0.01$  Å,  $c = 19.65 \pm 0.02$  Å,  $Z = 2$ ,  $d_{\text{exptl}} = 2.37$  g/cm<sup>3</sup>,  $d_{\text{calcd}} = 2.51$  g/cm<sup>3</sup>. (6) Potassium 13-vanadonickelate(IV) is isomorphous with the manganate by crystal morphology and X-ray powder diffraction.

**Chemical Properties.** The solid salts appear stable indefinitely, although the higher hydrates of the sodium and ammonium salts are very efflorescent, and the

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

(20) An estimation of the diamagnetism was made by combining the magnetic susceptibilities of the component oxides. The result was positive (paramagnetic) due to the high-temperature-independent paramagnetism of vanadium(V) oxide. The effectively zero susceptibility of the nickel compound indicates the magnitude of TIP in the heteropoly compound.

potassium salts seem to be slightly efflorescent. In solution, both the manganate and nickelate are most stable in the approximate pH range 3-6. Mean analytical results for material recrystallized from buffers of pH 3, 4, 5, and 6 were Mn,  $2.88 \pm 0.02$ ; V,  $34.8 \pm 0.3$ ; V/Mn, 13.07. The manganate is stable indefinitely, and the nickelate decomposes slowly, within this pH range. The 13-vanadonickelate is perhaps more stable than the 9-molybdonickelate(IV) and definitely more stable than 12-niobonickelate(IV), decomposition being incomplete in 6 months at a pH near 5. At a pH near 2, 13-vanadomanganate(IV) is converted to a dark red complex (V:Mn = 11:1), which has been isolated and is under investigation. Vanadium(V) hydrous oxide is also a product of the decomposition. Decomposition of the nickelate at pH 2 apparently does not give an 11:1 species; vanadium(V) oxide is formed and part of the original complex is recovered. At a pH  $\geq 6$ , solutions of both complexes darken in color and ultimately decompose to isopolyvanadates with precipitation of the manganese or nickel as dark brown or black precipitates, respectively. The alkaline decomposition is slow at room temperature and fast in boiling solutions, analogous to the situation with isopolyvanadates.<sup>21</sup>

The solubility of potassium 13-vanadomanganate(IV) at room temperature appears to be 0.03-0.04  $M$  in water and 0.005-0.01  $M$  in 0.5  $M$  potassium acetate-0.5  $M$  acetic acid. The solubility of the nickelate salt is comparable. The manganate complex is precipitated by cesium, barium, guanidinium, and silver ions, but not by mono-, di-, tri-, or tetramethylammonium ions. The silver salt is not very insoluble; no inflection occurred in a potentiometric titration of the potassium salt with silver nitrate. The order of solubility of alkali salts appears to be Cs < K < Na < NH<sub>4</sub> < Li.

The results of dehydration of the 13-vanadomanganate(IV) salts are given in Table III. With the possible

Table III. Dehydration of 13-Vanadomanganate(IV) Salts at ca. 140°

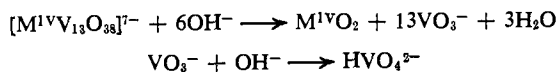
Reaction	Wt loss calcd	Wt loss found
K <sub>7</sub> MnV <sub>13</sub> O <sub>38</sub> · 18H <sub>2</sub> O to dihydrate	15.0	15.3 ± 0.2
Na <sub>7</sub> MnV <sub>13</sub> O <sub>38</sub> · 29H <sub>2</sub> O <sup>a</sup> to dihydrate	24.2	24.2 ± 0.1
Na <sub>7</sub> MnV <sub>13</sub> O <sub>38</sub> · 24H <sub>2</sub> O to dihydrate	20.7	20.5 ± 0.1
(NH <sub>4</sub> ) <sub>7</sub> MnV <sub>13</sub> O <sub>38</sub> · 18H <sub>2</sub> O <sup>b</sup> to dihydrate	18.26 <sup>c</sup>	18.0 ± 0.2
(NH <sub>4</sub> ) <sub>7</sub> MnV <sub>13</sub> O <sub>38</sub> · 5H <sub>2</sub> O to anhydrous	5.84 <sup>d</sup>	6.1 ± 0.1

<sup>a</sup> Orange crystals stored over sodium sulfate decahydrate. Total water content: found,  $25.8 \pm 0.1$ ; calcd, 26.0. <sup>b</sup> Large crystals stored in refrigerator. <sup>c</sup> Calcd for loss of 16H<sub>2</sub>O + 2NH<sub>3</sub>, 18.15. <sup>d</sup> Calcd for loss of 3H<sub>2</sub>O + 2NH<sub>3</sub>, 5.72.

exception of the ammonium salts, some water remains at ca. 140°. However the ammonium salts could lose ammonia as well as water; the data do not distinguish this possibility (see footnotes to Table III). These results suggest the presence of constitutional water in the complexes.

(21) M. T. Pope and B. W. Dale, *Quart. Revs.* (London), **22**, 527 (1968).

Titration of solutions of 13-vanadomanganate(IV) or -nickelate(IV) with perchloric acid at room temperature show no evidence for protonation reactions. Decomposition sets in at a pH near 2. Titrations of hot solutions of either complex with sodium hydroxide show only two breaks in the curves at pH values near 7 and 9.5, corresponding to the respective reactions



The breaks were not sharp, so that confirmation or denial of the 13:1 stoichiometry could not be obtained from the base titrations.

Since the dehydration results suggest the existence of constitutional water in the complexes, one might expect deprotonation of the presumed species (e.g.,  $[H_2MnV_{13}O_{38}]^{7-}$ ) to be observed in titrations with base. However, automated titrations with 0.05 *N* sodium hydroxide at 0–5° failed to show evidence of deprotonation reactions; the curves appeared no different from those given by addition of the sodium hydroxide to the same volume of water.

The 13-vanadomanganate(IV) anion is not reduced by bromide ion, but is reduced slowly by iodide ion and quickly by vanadyl(IV) or hexacyanoferrate(II) ions. Excess hydrogen peroxide decomposes the complex. Although reaction with iodide is too slow to note color changes in solution, recrystallization of potassium 13-vanadomanganate(IV) from iodide-containing solutions in the pH range 4–5 gives brown to black to dark green octahedral crystals, brown to brownish green square plates, and yellow prismatic crystals (microscopic observations). The yellow prisms are evidently an isopolyvanadate product. However, green products are obtained rapidly and in high yield when vanadyl(IV) or hexacyanoferrate(II) is employed as reductant, especially when potassium salts are used. The green species is unstable in solution and is apparently in equilibrium with the reactants, judging from spectra taken at various concentrations. With potassium salts, the solubility of the product is low, and the reaction is driven to completion. Potentiometric titrations of potassium 13-vanadomanganate(IV) were done with vanadyl(IV) sulfate or potassium hexacyanoferrate(II) in acetic acid–potassium acetate buffer solutions. With vanadyl(IV) sulfate, endpoints were not reproducible, and the solutions at the endpoint were green. With hexacyanoferrate(II), fairly reproducible end points were obtained in the more concentrated solutions; the solutions at the end point were yellow. The average consumption of cyanoferrate(II) in these titrations was  $0.99 \pm 0.06$  mole of  $[Fe(CN)_6]^{4-}$  per mole of 13-vanadomanganate(IV), showing that a one-electron reduction occurs to produce the green species. Addition of more reductant to a mole ratio of 3:1 gave no further reactions.

The 13-vanadonickelate(IV) is reduced by iodide and by hydrogen peroxide, although the reactions are not immediate at room temperature. Vanadyl(IV) and hexacyanoferrate(II) ions reduce the nickel(IV) complex quickly to Ni(II), with no evidence of formation of species analogous to the green reduced manganate.

**Properties of the Reduced 13-Vanadomanganate Species.** The green complex is formed only transiently on reduction at a pH near 3, but is sufficiently stable

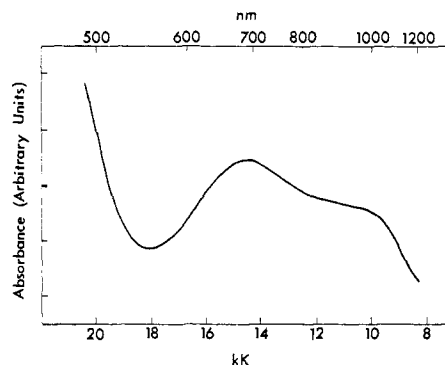


Figure 1. Solid-state spectrum (in KBr disk) of the reduced form of potassium 13-vanadomanganate(IV).

in the pH range 5.0–5.5 to permit recording spectra. The potassium and ammonium salts of the green complex were isolated; analytical data are given in Table I. The results indicate that the 13:1 stoichiometry is preserved on reduction. The somewhat high V:Mn ratios found could be due to formation of a 14:1 complex or to contamination with excess vanadium(IV) or - (V), especially in the products from vanadyl(IV) reduction. The products of both reductions gave yellowish green aqueous solutions, but the solution of the cyanoferrate(II)-reduced product turned yellow in a few minutes, while that of the vanadyl(IV)-reduced product remained green much longer. The potassium salt is nearly insoluble in potassium acetate–acetic acid solutions at room temperature; heating the mixture gave an orange solution which on cooling and evaporation yielded potassium 13-vanadomanganate(IV) as well as other crystalline material, apparently either or both of the two manganese(II) double isopoly salts described above. The powder diffractograms of the reduced and unreduced potassium salts are virtually identical, indicating that the compounds are isomorphous. These results, as well as the apparent solid solution formation of the reduced species in the crystals of the unreduced potassium salt, and the results of the reduction titration, indicate that the green complex is a one-electron reduction product of 13-vanadomanganate(IV).

The optical spectra of a solution of the reduced 13-vanadomanganate complex and of the potassium salt in a KBr disk are essentially identical. Figure 1 shows the solid-state spectrum. A maximum occurs at  $685 \pm 5$  nm ( $14,600$   $cm^{-1}$ ) and a shoulder at *ca.* 1000 nm ( $10,000$   $cm^{-1}$ ). Because of instability, the absorptivity in solution could not be determined, but it appears to be at least 500 at the 685 nm maximum.

Solid reduced potassium 13-vanadomanganate gave a symmetrical broad esr signal,  $g = 1.98$ . Frozen solutions (77°K) gave very similar spectra for both the cyanoferrate(II) and vanadyl(IV)-reduced products. Some indication of hyperfine structure was detectable in the frozen solution spectra.

**Structural Considerations.** The diamagnetism of the nickelate(IV), coupled with the isomorphism of the potassium salts, shows that the M(IV) atoms are in octahedral sites in these complexes. Dehydration of the potassium and sodium 13-vanadomanganate(IV) salts at 140° (Table III) suggests the presence of no more than two molecules of constitutional water in the anions. A possible structure, based upon edge-shared

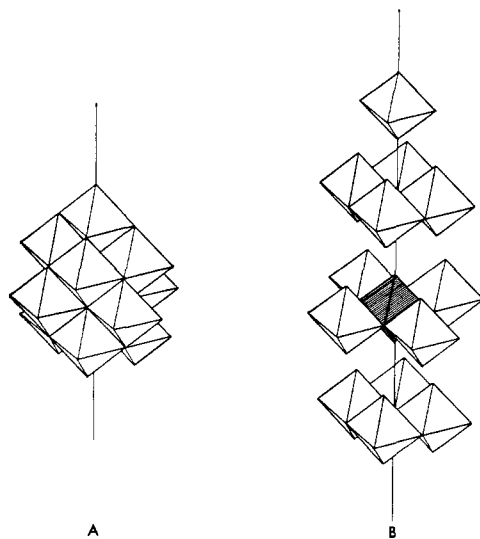


Figure 2. (A) Arrangement of VO<sub>6</sub> octahedra in the proposed structure for MV<sub>13</sub>O<sub>39</sub><sup>9-</sup>. (B) Same structure, "exploded" along the C<sub>4</sub> axis, showing the location of the octahedron containing the central atom (shaded).

VO<sub>6</sub> octahedra, as found in the isopoly decavanadate ion, requires 39 oxygen atoms (one constitutional water molecule). An arrangement of a central MnO<sub>6</sub> octahedron sharing each of its edges with a different VO<sub>6</sub> octahedron has O<sub>h</sub> point symmetry and a formula [MnV<sub>12</sub>O<sub>38</sub>]<sup>12-</sup>. By placing a 13th VO<sub>6</sub> octahedron on one of the fourfold axes of this group<sup>22</sup> a structure with the formula [MnV<sub>13</sub>O<sub>39</sub>]<sup>9-</sup> results (see Figure 2). This structure has the tetragonal symmetry indicated by the X-ray investigation of potassium 13-vanadomanganate(IV) in progress. The formation of [MnV<sub>13</sub>O<sub>39</sub>]<sup>9-</sup> as opposed to [MnV<sub>12</sub>O<sub>38</sub>]<sup>12-</sup> is reasonable on electrostatic grounds, particularly in view of the pH range of stability of the anion.

Adoption of the [MnV<sub>13</sub>O<sub>39</sub>]<sup>9-</sup> structure means that the salts prepared here must have two hydrogen atoms. As mentioned above, careful base titrations of the salts did not reveal acidic hydrogens. However, in this connection it may be noted that the six-electron reduction product of [P<sub>2</sub>Mo<sub>18</sub>O<sub>62</sub>]<sup>6-</sup>, isolated as the acid salt, (NH<sub>4</sub>)<sub>6</sub>H<sub>6</sub>[P<sub>2</sub>Mo<sub>18</sub>O<sub>62</sub>]·aq, contained only four titratable protons per molecule.<sup>23</sup> Furthermore, polarographic studies confirmed that the anion underwent hydrolytic degradation prior to the removal of the last two hydrogens, in contrast to the corresponding reduced hetero-

(22) Removal of three octahedra from this cluster gives the arrangement of octahedra found for [MnMo<sub>9</sub>O<sub>32</sub>]<sup>6-</sup> (J. L. T. Waugh, D. P. Shoemaker, and L. C. Pauling, *Acta Cryst.*, **7**, 438 (1954)); removal of six octahedra yields the "Anderson-Evans" structure found for many 1:6 heteropolymolybdates and -tungstates (H. T. Evans, Jr., *J. Amer. Chem. Soc.*, **90**, 3275 (1968)).

(23) E. Papaconstantinou and M. T. Pope, *Inorg. Chem.*, **6**, 1152 (1967).

polytungstate.<sup>24</sup> Failure to detect acidic protons in the present case, therefore, is not necessarily significant.

**Electronic Structure of the Reduced Species.** The optical and esr spectra of the reduced 13-vanadomanganates clearly show that they are not manganese(III) species. The reduced complex is therefore a mixed-valence species similar to the heteropoly blues of molybdenum and tungsten. The esr *g* value is within the range of those observed for tetragonal oxovanadium(IV) complexes;<sup>25</sup> and this fact, together with the observed traces of hyperfine structure in the low-temperature spectrum, suggests that the extra electron is fairly well trapped on a specific vanadium atom.<sup>26</sup> Little can be said about the optical spectrum except to note that similar broad absorptions have been found in the spectra of other mixed-valence vanadates.<sup>27-29</sup> Possible assignments include intervalence transitions or intensity-enhanced d-d transitions.

That an esr spectrum is observed at all indicates that the spin-spin interaction between the Mn(IV) and V(IV) centers is quite weak (although strong enough to affect the relaxation time of the "vanadium electron"). Such a weak interaction may be rationalized in terms of the proposed structure for the 13-vanadometallate framework. In this structure 12 of the vanadium atoms occupy VO<sub>6</sub> octahedra which share edges with the central MnO<sub>6</sub> octahedron (resulting in quite short Mn-V distances), whereas the unique 13th vanadium atom shares only one oxygen with the central atom. This oxygen atom participates in bonding to four other vanadium atoms and it may, therefore, be expected that the V-O-Mn bonds will be unusually long in view of their low formal bond order. The two structurally analogous "six-coordinate" oxygens which are found in [V<sub>10</sub>O<sub>28</sub>]<sup>6-</sup> have V-O distances of 2.03-2.36 Å.<sup>10</sup> If it is presumed that it is the unique vanadium atom which is reduced, spin-spin interaction between V(IV) and Mn(IV) should be weak, as observed.<sup>30</sup>

**Acknowledgments.** Grateful acknowledgment is made to Professor A. N. Thorpe, Dr. Hideo Kon, and Joseph Killiany for their assistance and advice. Thanks are also due to Dr. D. A. Langs for single crystal X-ray examination of K<sub>7</sub>MnV<sub>13</sub>O<sub>38</sub>·18H<sub>2</sub>O, and to the Air Force Office of Scientific Research for support of this work through Grant No. AF-AFOSR-1066-66.

(24) M. T. Pope and E. Papaconstantinou, *ibid.*, **6**, 1147 (1967).

(25) E. König in Landolt-Börnstein, "Zahlenwerte und Funktionen," Vol. II/2, K. H. Hellwege and A. M. Hellwege, Ed., Springer-Verlag, New York, N. Y., 1966 pp 4-7 ff.

(26) The reduced complex is thus a class II mixed-valence species in terms of Robin and Day's classification: M. B. Robin and P. Day, *Advan. Inorg. Chem. Radio-chem.*, **10**, 247 (1967).

(27) S. Ostrowetsky, *Bull. Soc. Chim. France*, 1018 (1964).

(28) C. Heitner-Wirguin and J. Selbin, *J. Inorg. Nucl. Chem.*, **30**, 3181 (1968).

(29) D. P. Smith, Ph.D. Dissertation, Georgetown University, 1970.

(30) Similar weak (according to esr) interactions are found in reduced heteropolytungstates where Fe<sup>11</sup>O<sub>4</sub> tetrahedra and WVO<sub>6</sub> octahedra share a common oxygen: G. M. Varga, Jr., E. Papaconstantinou, and M. T. Pope, *Inorg. Chem.*, in press.