agreement with other fluorosulfates, the S=O symmetric and asymmetric and S—F stretching frequencies occurred over a narrow range.[4,11,14,18,19] Some other tentative assignments are also given.

The F^{19} nmr results are summarized in Table IV. All of the compounds showed an F^{19} resonance in the fluorosulfate region at about ϕ −50.[20] The F^{19} resonance for the fluorosulfate group was shifted downfield as successive replacement of chlorine by fluorosulfate occurred. For the thionyl fluorosulfates the S–F resonance was slightly broadened. For $SiCl_2(OSO_2F)_2$ the high-resolution nmr showed a sharp resonance with a broad resonance slightly downfield.

Acknowledgment.—The author gratefully acknowledges Professor G. H. Cady for helpful suggestions and generous use of his research facilities. The nmr spectra were taken by Mr. B. J. Mist.

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Molybdovanadophosphoric Acids and Their Salts.
I. Investigation of Methods of Preparation and Characterization

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By the use of improved procedures, the free heteropoly acids $H_4[PMo_{11}VO_{40}]\cdot 34H_2O$, $H_5[PMo_{10}V_2O_{40}]\cdot 32H_2O$, and $H_6[PMo_9V_3O_{40}]\cdot 34H_2O$ were prepared reproducibly as orange crystalline solids. Potentiometric titration measurements showed that the number of replaceable hydrogen ions in these free acids is four, five, and six, respectively. The salts $Na_4[PMo_{11}VO_{40}]\cdot 8H_2O$ and $(NH_4)_3H[PMo_{11}VO_{40}]\cdot 7.5H_2O$ were prepared for the first time. The molybdovanadophosphate anion had unusually high hydrolytic stability. Infrared, visible, and ultraviolet spectra were obtained for these salts. Thermogravimetric and differential thermal analyses were performed on $H_4[PMo_{11}VO_{40}]\cdot 32H_2O$ and $Na_4[PMo_{11}VO_{40}]\cdot 8H_2O$. Potentiometric titration measurements with methanol as the solvent and $NaOCH_3$ as the titrant showed that the $H_4[PMo_{11}VO_{40}]$ acid is tetraprotic in solvents with low dielectric constants.

Introduction

The heteropolymolybdovanadates constitute an important class of heteropoly compounds on which only limited research has been conducted. The most well known of these heteropolymolybdovanadates is the 10-molybdo-2-vanadophosphate(V) anion prepared by Kokorin.[1] In 1964, Souchay and co-workers[2–4] were able to replace molybdenum in the 12-molybdophosphate anion structure by up to three pentavalent vanadium atoms,[2] but the compounds prepared were not fully characterized and no analytical data were given.[4]

In work published in 1964, Krivy and Krtil[5] assigned a basicity of 3 to the 10-molybdo-2-vanadophosphoric acid on the basis of radiometric titration studies employing cesium-137. They gave the salt the formula $Cs_3H_4[P(Mo_2O_7)_5V_2O_6]$.

The present work elucidates the properties of the free acids and salts of the anions $[PMo_{11}VO_{40}]^{4-}$, $[PMo_{10}V_2O_{40}]^{5-}$, and $[PMo_9V_3O_{40}]^{6-}$. The desired free acids were obtained in a reproducible manner by using detailed, improved procedures. Further characterization of the properties of these anions was accomplished by physicochemical means discussed in this paper.

Experimental Section

Prepurified grade sodium metavanadate containing 2% water (Matheson Coleman and Bell) was used without further purification. All other reagents used were Baker Analyzed grade.

Preparation of Compounds. (a) 11-Molybdo-1-vanadophosphoric Acid.—Na_2HPO_4, 7.1 g, was dissolved in 100 ml of water and mixed with 6.1 g of sodium metavanadate that had been dissolved by boiling in 100 ml of water. The mixture was cooled and acidified to a red color with 5 ml of concentrated sulfuric acid. To this mixture was added a solution of 133 g of $Na_2MoO_4\cdot 2H_2O$ dissolved in 200 ml of water. Finally, 85 ml of concentrated sulfuric acid was added slowly with vigorous stirring of the solution. With this addition the dark red color changed to a lighter red. The heteropoly acid was then extracted with 400 ml of ethyl ether after the water solution was cooled. In this extraction, the heteropoly etherate was present as a middle layer; the bottom layer (water) was yellow and probably contained vanadyl species. After separation, a stream of air was passed through the heteropoly etherate layer to free it of ether. The orange solid that remained was dissolved in 50 ml of water, concentrated to the first appearance of crystals in a vacuum desiccator over concentrated sulfuric acid, and then allowed to crystallize further. The orange crystals that formed were filtered, washed with water, and air dried. The yield was 28 g. The crystalline acid effloresces slowly at room temperature; thus the amount of water of crystallization varied slightly from sample to sample. *Anal.* Calcd for $H_4[PMo_{11}VO_{40}]\cdot 32.5H_2O$: P, 1.31; Mo, 44.60; V, 2.15; H_2O, 24.71. Found: P, 1.31; Mo, 44.54; V, 2.68; H_2O (based on Mo), 24.86. The molar ratios are Mo to P, 10.97 to 1.00; and V to P, 1.24 to 1.00. Similar analyses were

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(5) I. Krivy and J. Krtil, *Collection Czech. Chem. Commun.*, **29**, 587 (1964).

obtained in duplicate preparations of compounds reported in this paper.

(b) **10-Molybdo-2-vanadophosphoric Acid.**—Sodium metavanadate, 24.4 g, was dissolved by boiling in 100 ml of water and then mixed with 7.1 g of Na_2HPO_4 in 100 ml of water. After the solution was cooled, 5 ml of concentrated sulfuric acid was added, and the solution developed a red color. An addition of 121 g of $Na_2MoO_4 \cdot 2H_2O$ dissolved in 200 ml of water was then made. While the solution was vigorously stirred, 85 ml of concentrated sulfuric acid was added slowly, and the hot solution was allowed to cool to room temperature. The 10-molybdo-2-vanadophosphoric acid was then extracted with 500 ml of ethyl ether. Air was passed through the heteropoly etherate (bottom layer) to free it of ether. The solid remaining behind was dissolved in water, concentrated to first crystal formation, as already described, and then allowed to crystallize further. The large red crystals that formed were filtered, washed with water, and air dried. The yield was 35 g. The solid effloresces slowly at room temperature. *Anal.* Calcd for $H_5[PMo_{10}V_2O_{40}] \cdot 34.5H_2O$: P, 1.31; Mo, 40.69; V, 4.32; H_2O, 26.33. Found: P, 1.34; Mo, 40.69; V, 4.77; H_2O (based on Mo), 26.32. The molar ratios are: Mo:P, 9.80:1.00; V:P, 2.16:1.00. Duplicate preparations gave similar analytical results.

As expected, this acid dissolved in ethyl ether to form an oil that is insoluble in ether. However, it dissolves in other oxygen-containing solvents (ethyl alcohol, methanol, ethyl acetate, dimethyl sulfoxide, and tetrahydrofuran) to form single phases.

10-Molybdo-2-vanadophosphoric acid was also prepared by the method used by Kokorin,[1] the only modification being the substitution of MoO_3 for the crystalline yellow $MoO_3 \cdot 2H_2O$. In this preparation, 30.0 g of sodium metavanadate, 3.4 ml of 85% H_3PO_4, and 74.0 g of molybdenum trioxide were refluxed in 800 ml of water for 8 hr. The acid was extracted with 200 ml of ether after acidification with 145 ml of concentrated hydrochloric acid and was subsequently recrystallized from water after the ether was removed. *Anal.* Calcd for $H_5[PMo_{10}V_2O_{40}] \cdot 32.5H_2O$: P, 1.33; Mo, 40.68; V, 4.32; H_2O, 26.33. Found: P, 1.34; Mo, 41.34; V, 5.15; H_2O (based on Mo), 25.14. The molar ratios are: Mo:P, 9.95:1.00; V:P, 2.33:1.00.

(c) **9-Molybdo-3-vanadophosphoric Acid.**—Na_2HPO_4, 7.1 g, was dissolved in 50 ml of water and mixed with 36.6 g of sodium metavanadate that had been dissolved by heating in 200 ml of water. After 5 ml of concentrated sulfuric acid was added to the cooled mixture, it attained a cherry red color. This solution was mixed with 54.5 g of $Na_2MoO_4 \cdot 2H_2O$ dissolved in 150 ml of water, and then, while it was being vigorously stirred, 85 ml of concentrated sulfuric acid was slowly added. The hot solution was allowed to cool to room temperature. The free acid was extracted with 400 ml of ethyl ether, the heteropoly etherate being the middle layer. The etherate was freed of ether when a stream of air was passed through the solution. The red solid remaining was dissolved in 40 ml of water and concentrated to crystal formation in a vacuum desiccator over concentrated sulfuric acid. The red crystals were filtered and washed with water. The yield was 7.2 g. The solid effloresces slowly at room temperature. *Anal.* Calcd for $H_6[PMo_9V_3O_{40}] \cdot 34H_2O$: P, 1.35; Mo, 38.76; V, 6.71; H_2O, 26.66. Found: P, 1.38; Mo, 38.78; V, 6.89; H_2O (based on Mo), 26.71. The molar ratios are: Mo:P, 9.07:1.00; V:P, 3.04:1.00. A duplicate sample preparation gave similar analytical results.

(d) **Sodium 11-Molybdo-1-vanadophosphate.**—Twenty grams of $H_4[PMo_{11}VO_{40}] \cdot 35H_2O$ was dissolved in 50 ml of water, and the resultant solution was slowly passed through an ion-exchange column containing 20–50 mesh Dowex 50-X8 ion-exchange resin in the sodium form. The resin bed was 1.25 in. in diameter and 20 in. in height. The orange effluent containing the desired sodium salt was then placed in a vacuum desiccator over concentrated sulfuric acid for removal of water. Evaporation was continued to dryness since this sodium salt is very soluble in water. *Anal.* Calcd for $Na_4[PMo_{11}VO_{40}] \cdot 8H_2O$: Na, 4.57; P, 1.54; Mo, 52.42; V, 2.53; H_2O, 7.15. Found: Na, 5.10; P, 1.51; Mo, 50.27; V, 3.08; H_2O (based on dehydration), 7.45.

(e) **Preparation of Ammonium Salts.**—Triammonium 11-molybdo-1-vanadophosphate and triammonium 10-molybdo-2-vanadophosphate were prepared by the addition of solid ammonium chloride to solutions of the corresponding free acids. The orange solids that formed were filtered and washed with water, and then dried in a vacuum desiccator over concentrated sulfuric acid. *Anal.* Calcd for $(NH_4)_3H[PMo_{11}VO_{40}] \cdot 3.5H_2O$: N, 2.21; P, 1.63; Mo, 55.68; V, 2.69; H_2O, 3.45. Found: N, 2.37; P, 1.66; Mo, 55.61; V, 2.88; H_2O (based on Mo), 3.32. *Anal.* Calcd for $(NH_4)_3H_2[PMo_{10}V_2O_{40}] \cdot 7.5H_2O$: N, 2.18; P, 1.61; Mo, 49.88; V, 5.30; H_2O, 7.02. Found: N, 2.48; P, 1.65; Mo, 49.90; V, 5.85; H_2O (based on Mo), 6.99.

Characterization of Compounds. (a) **Analytical Procedures.**—The molybdovanadophosphates were analyzed as described in the literature.[6] Vanadium was separated from molybdenum and phosphorus by ion exchange after reduction to quadrivalent vanadyl cation followed by elution with dilute sulfuric acid and subsequent titration with standard potassium permanganate. Molybdenum was determined gravimetrically by the α-benzoin oxime procedure; phosphorus was determined by precipitation as magnesium ammonium phosphate and weighing as magnesium pyrophosphate.

(b) **Potentiometric Titrations.**—All potentiometric titration measurements were performed with a Beckman Model H2 pH meter equipped with a standard calomel electrode and a glass electrode suitable for high-temperature measurements. The pH meter readings were repeated until a constant value was reached. All solutions were magnetically stirred during the titration. The normality of the NaOH used was 0.1000 *N*.

The potentiometric titration of $H_4[PMo_{11}VO_{40}]$ in methanol and in the water–dioxane mixture was conducted using a saturated calomel electrode, a glass electrode, and a Precision vacuum tube voltmeter, PRV 63 (G. Bank Elektronik, Göttingen, West Germany).

(c) **Visible and Ultraviolet Spectra.**—The absorption spectra of the acids $H_4[PMo_{11}VO_{40}]$, $H_5[PMo_{10}V_2O_{40}]$, $H_6[PMo_9V_3O_{40}]$, and $H_3[PMo_{12}O_{40}]$ in water were taken with a Beckman DB automatic recording spectrophotometer employing 1-cm silica cells.

(d) **Infrared Spectra.**—The infrared spectra of the three molybdovanadophosphoric acids and the 12-molybdophosphoric acid were obtained in Nujol mulls with a Perkin-Elmer 31 spectrophotometer. The infrared spectrum of 10-molybdo-2-vanadophosphoric acid was also obtained in a KBr disk and was found to be identical with that obtained in Nujol.

(e) **Differential Thermal Analysis (dta) and Thermogravimetric Analysis (tga).**—A Harrop Precision Furnace Co. dta and tga unit was used for the dta and tga experiments.

Results and Discussion

Preparation of the Compounds.—The free acids $H_4[PMo_{11}VO_{40}]$, $H_5[PMo_{10}V_2O_{40}]$, and $H_6[PMo_9V_3O_{40}]$ were prepared in very pure form according to the procedure described in the literature.[2] However, the acidity specified for extraction into ether (5 *N* H_2SO_4) was totally insufficient to accomplish extraction. Additional acid therefore had to be added. The analytical results could not be compared with those of Souchay and co-workers[2-4] since they failed to publish such data. However, if the procedures outlined in this paper are strictly followed, products of very good purity can be obtained.

The 10-molybdo-2-vanadophosphate and 9-molybdo-3-vanadophosphate anions are not stable in the strongly acid media afforded by ion-exchange resins, reportedly the former being partially decomposed into the 11-molybdo-1-vanadophosphate species and VO_2^+ cations.[3] The $H_6[PMo_9V_3O_{40}]$, which is difficult to prepare, is

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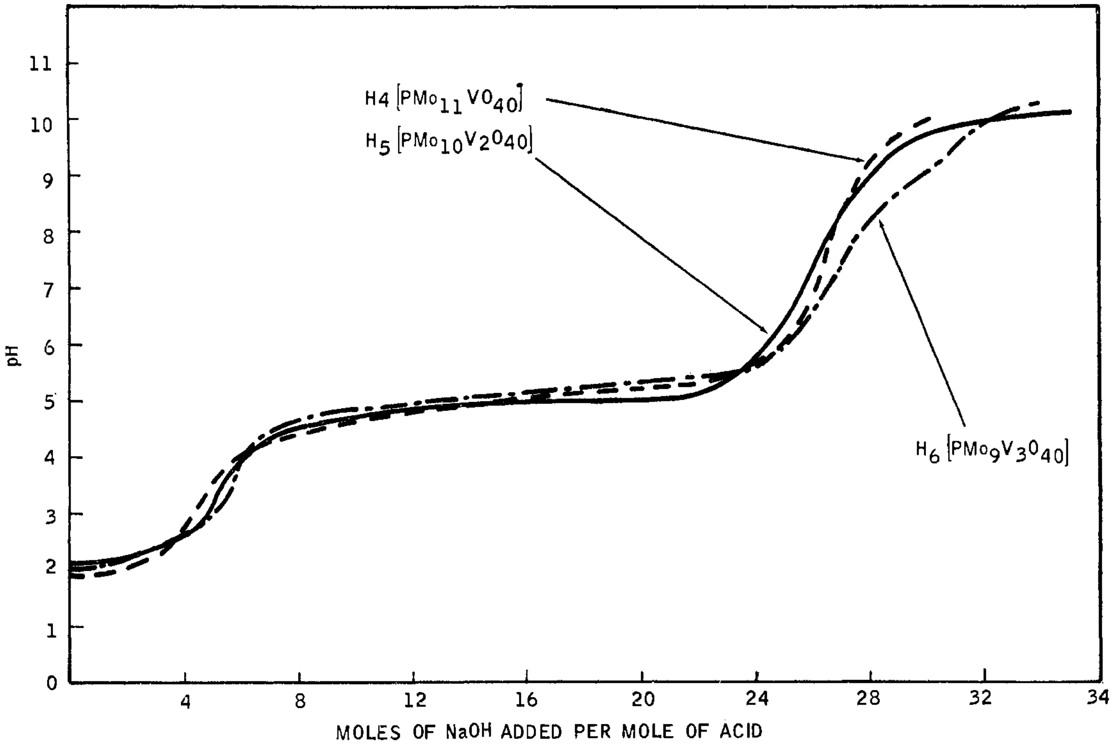

Figure 1.—Potentiometric titration of 100 ml of 2 × 10^{-3} *M* solutions of (a) $H_4[PMo_{11}VO_{40}]$, (b) $H_5[PMo_{10}V_2O_{40}]$, and (c) $H_6[PMo_9V_3O_{40}]$ with 0.1000 *N* NaOH.

decomposed by both weak and strong cation-exchange resins in the hydrogen form. The 11-molybdo-1-vanadophosphate anion is least affected by ion-exchange resins.[3] The low yield of the 9-molybdo-3-vanadophosphoric acid obtained in this work is consistent with such observations.

The method of Kokorin[1] for preparing the 10-molybdo-2-vanadophosphoric acid was reexamined, and the only modification made was the substitution of the readily available molybdenum trioxide for the yellow crystalline molybdic acid, $MoO_3 \cdot 2H_2O$. This reaction yielded the desired compound; however, the V:P ratio was higher than that obtained by the other procedure described in this paper. The predominant heteropoly species formed in preparations employing MoO_3 instead of MoO_4^{2-} appear to be the $[PMo_{10}V_2O_{40}]^{5-}$ anion as discussed previously. It is quite likely that the $[PMo_{11}VO_{40}]^{4-}$ and $[PMo_9V_3O_{40}]^{6-}$ may form in small amounts along with the $[PMo_{10}V_2O_{40}]^{5-}$ species.

The preparation of any of the three heteropoly acids in question with the proper stoichiometry depends, therefore, on the relative quantities of phosphate, molybdate, and vanadate ions initially present, as outlined in the preparative procedures given. It was necessary to purify the acids obtained in this work to obtain the correct stoichiometry.

The sodium salt of the 11-molybdo-1-vanadophosphate anion was prepared for the first time and found to be a normal salt. However, the ammonium salts of the 11-molybdo-1-vanadophosphate and 10-molybdo-2-vanadophosphate anions, namely, $(NH_4)_3H[PMo_{11}VO_{40}]$ and $(NH_4)_3H_2[PMo_{10}V_2O_{40}]$, were prepared by the addition of ammonium chloride to the free acids and were found on the basis of the analysis to be acid salts. This fact is qualitatively consistent with the values obtained by Hallada, *et al.*,[7] for the dissociation constants of the heteropoly acids in question.

Potentiometric Titrations.—The potentiometric titrations of the heteropoly acids yielded information on the number of replaceable hydrogen ions of the acid and on the charge of the anion. It was assumed here that the molybdovanadophosphate anions possess the Keggin structure, and hence the total number of oxygen atoms with the heteropoly anion is 40. Since the oxidation state of each element in the anion is known, the charges of the anions possessing one, two, and three vanadium atoms are −4, −5, and −6, respectively. The potentiometric titrations of the free acids show two points of inflection (Figure 1). The first point of inflection corresponds to the neutralization of the replaceable hydrogen ions, and the second point of inflection corresponds to the complete degradation of the heteropoly anion by base. The interpretation of the second point of inflection depends on a knowledge of the nature and degree of polymerization of the vanadium species at that pH. Figure 1 shows that the second inflection point centers around pH 8. At that pH, the molybdate and phosphate species are present as MoO_4^{2-} and HPO_4^{2-}, respectively. The vanadate species are present as HVO_4^{2-} ions.[8,9] For $H_4[PMo_{11}VO_{40}]$, the first point of inflection confirms the presence of the theoretical four replaceable hydrogen ions since it occurs at 4.1 moles of base added per mole of acid.

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[7] C. J. Hallada, G. A. Tsigdinos, and B. S. Hudson, submitted for publication in *Inorg. Chem.*

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[9] K. Schiller and E. Thilo, *Z. Anorg. Allgem. Chem.*, **310**, 262 (1961).

The second point of inflection occurs at the addition of 26 moles (pH ~8.5) of base per mole of acid. Hence, the reaction can be written

$$[PMo_{11}VO_{40}]^{4-} + 22OH^- \longrightarrow HPO_4^{2-} + 11MoO_4^{2-} + HVO_4^{2-} + 10H_2O$$

The titrations of the acids $H_5[PMo_{10}V_2O_{40}]$ and $H_6[PMo_9V_3O_{40}]$ showed that these acids are pentaprotic and hexaprotic, as expected. These data are also shown in Figure 1. Since anionic degradation is extremely slow at 25°, the titration had to be performed at 80°. The hydrolytic stability of the molybdovanadophosphate anions is remarkable in contrast to that of the $[PMo_{12}O_{40}]^{3-}$ anion, which undergoes degradation into simpler species even in acid solutions.

Further corroboration of the charge of the $[PMo_{11}VO_{40}]^{4-}$ anion was obtained from the titration of $Na_4[PMo_{11}VO_{40}]$ with base. First, the initial pH (3.6) of this solution (2×10^{-3} *M*) is the same as that found after four H^+ ions of $H_4[PMo_{11}VO_{40}]$ had been neutralized, the latter acid being of the same concentration. The single point of inflection occurs at pH ~8.5 and corresponds to 21.3 equiv of base added, the theoretical being 22. This salt, as expected, is normal rather than acid.

The titration of $H_4[PMo_{11}VO_{40}]$ with ~0.1 *N* $NaOCH_3$, in methanol, showed a single point of inflection at the addition of 4 moles of sodium methoxide per mole of acid, indicating the tetrabasicity of the acid in this medium also. Despite the lower dielectric constant of methanol, differences in acidity of these four hydrogens were not resolved.

The formulation by Krivy and Krtil[5] of the acid $H_7[P(Mo_2O_7)_5V_2O_6]\cdot 16H_2O$ as tribasic, which was based on radiometric titration studies using cesium-137, is not tenable since the basicity of salts of heteropoly anions may be governed by packing considerations.[10] For example, 12-tungstosilicic acid is tetraprotic, yet with cesium ion, only $Cs_3H[SiW_{12}O_{40}]\cdot 2H_2O$ is formed no matter what proportions of cesium salt and acid are mixed.[10] It is likely that cesium 10-molybdo-2-vanadophosphate has the formula $Cs_3H_2[PMo_{10}V_2O_{40}]\cdot xH_2O$, which is consistent with a charge of -5 as found in this research.

Spectra.—The infrared spectra of the compounds $H_3[PMo_{12}O_{40}]\cdot 15H_2O$, $H_4[PMo_{11}VO_{40}]\cdot 35H_2O$, $H_5[PMo_{10}V_2O_{40}]\cdot 32H_2O$, and $H_6[PMo_9V_3O_{40}]\cdot 33H_2O$ are shown in Table I. The peaks at the 3400–3300- and 1610–1650-cm^{-1} regions correspond to those of water. Probable assignments for other peaks are 1055–1100 cm^{-1} for P–O, 1000–900 cm^{-1} (sharp) due to Mo–O, and finally 850–700 cm^{-1} due to metal–oxygen–metal bridging. The V–O absorption may be masked by that of Mo–O. These bands are in accordance with those observed for the nearly anhydrous acids of 12-heteropolytungstate anions containing various central atoms.[11] However, the strong absorption band found at 1170 cm^{-1} by Brown[11] and attributed to W–O bonding was not found for the heteropolymolybdates examined in this work. The strong band at 1000–900 cm^{-1} may be due to the independent Mo–O bond present in heteropoly compounds consistent with a value of 985 cm^{-1} being found for an independent Mo–O bond in the infrared spectra of anhydrous simple metal molybdates.[12] Similarly, the peaks at 850–700 cm^{-1} correspond to the bridging Mo–O–Mo bonding present in the heteropoly cage. Such peaks also appear in several metal molybdate spectra.[12]

TABLE I

INFRARED SPECTRA OF MOLYBDOVANADOPHOSPHORIC ACIDS[a]

Compound	Absorption bands, cm^{-1}
$H_3[PMo_{12}O_{40}]\cdot 15H_2O$	3500 s, 1610 s, 1055 ms, 965 s, 895 s, br, 850–700
$H_4[PMo_{11}VO_{40}]\cdot 35H_2O$	3300 s, 1640 s, 1060 ms, 965 s, 890 s, br, 830–700
$H_5[PMo_{10}V_2O_{40}]\cdot 32H_2O$	3400 s, 1650 s, 1100 ms, 950 s, 860 s, br, 820–700
$H_6[PMo_9V_3O_{40}]\cdot 33H_2O$	3350 s, 1650 s, 1100 ms, 960 s, 875 s, br 830–710

[a] s = strong, m = medium, br = broad.

The visible and ultraviolet spectra of the three molybdovanadophosphoric acids show a characteristic absorption at 310 mμ (ϵ 17,000–18,100) that is absent in the corresponding 12-molybdophosphoric acid. The presence of this absorption is probably associated with the vanadium in the heteropoly cage.

Differential Thermal Analysis (dta) and Thermogravimetric Analysis (tga).—The dta and tga results on $H_4[PMo_{11}VO_{40}]\cdot 32H_2O$ and $Na_4[PMo_{11}VO_{40}]\cdot 8H_2O$ showed that the 11-molybdo-1-vanadophosphate anion is stable up to 375°. The dta of the acid showed that water molecules are given off at 25–50° and at 65–150°, which is consistent with the fact that the acid begins to effloresce even at room temperature.

Structural Considerations.—The three molybdovanadophosphate anions may have the Keggin type of structure proposed for the $[PMo_{12}O_{40}]^{3-}$ and $[PW_{12}O_{40}]^{3-}$ anions,[13,14] which have been further refined recently in the $[CoW_{12}O_{40}]^{5-}$ anion.[15] This is supported by the fact that the X-ray powder diagrams of the tricesium salts of the 12-tungstosilicate and 10-molybdo-2-vanadophosphate anions are identical.[16] In this structure, the central atom is tetrahedrally coordinated to four oxygen atoms, which in turn are surrounded by twelve MoO_6 or WO_6 octahedra. The total number of oxygen atoms within the anion is 40. The charge of the molybdovanadophosphate anions obtained by potentiometric titrations lends further support to this formulation.

An interesting case of structural isomerism could be present in $[PMo_{10}V_2O_{40}]^{5-}$ and $[PMo_9V_3O_{40}]^{6-}$ as a result of the distribution of the vanadium atoms in the heteropoly cage. For example, in the 10-molybdo-2-vanadophosphate anion, the two vanadium atoms may

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be joined to each other by an oxygen atom or they may be entirely separated. An even greater possibility of distribution of the three vanadium atoms within the heteropoly cage exists for the 9-molybdo-3-vanadophosphate anion. No evidence for such isomerism was found in this work although it may well exist.

Acknowledgment.—The authors are indebted to Thomas J. Risdon for preparing the ammonium salts of the molybdovanadophosphate anions and to the analytical staff of the Research Laboratory, Climax Molybdenum Company of Michigan, for performing the analyses.

CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY,
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Magnetic Susceptibility of Barium Molybdate(IV) and Strontium Molybdate(IV) in the Range 2–300°K[1]

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The compounds $BaMoO_3$ and $SrMoO_3$ have been prepared by hydrogen reduction of the corresponding molybdates(VI). Magnetic susceptibilities, measured by the Gouy method, are positive, moderately large, and independent of temperature over almost the entire range between liquid helium and room temperature. After correction for diamagnetic constituents, the molar magnetic susceptibilities are 215×10^{-6} cgs unit at 290°K for $BaMoO_3$ and 201×10^{-6} cgs unit at 291°K for $SrMoO_3$. These values are considerably higher than expected on the basis of a free-electron gas model that would be consistent with the high metallic conductivity and low Seebeck effect observed. A narrow d-band model with nonparabolic density-of-states filling seems to be indicated, with the Fermi energy apparently lying at a minimum in the density-of-states curve.

Introduction

The transition metal oxide bronzes have proven to be valuable sources of information on the important problem of electron transport and magnetic interaction in transition metal oxides. The tungsten bronzes, M_xWO_3, are slightly paramagnetic and metallic; the vanadium bronzes, $M_xV_2O_5$, are magnetic and semiconducting.[2] Titanium bronzes, Na_xTiO_2,[3] and niobium bronzes, Sr_xNbO_3,[4] though less well investigated, also apparently show metallic properties. Thus, there is a crude periodic correlation in that moving down a group or to the left in a period favors the appearance of metallic behavior. The molybdenum bronzes, M_xMoO_3, are particularly interesting since they appear to be close to the line of semiconductor-to-metal transition. Blue potassium molybdenum bronze, $K_{0.30}MoO_3$, for example, shows a curious mixture of metallic paramagnetism and semiconductive-to-metallic conductivity.[5] When, in connection with another investigation, we had occasion to synthesize samples of the metallic molybdates $BaMoO_3$ and $SrMoO_3$, it was thought useful to measure their magnetic susceptibility properties in the hope of gaining more insight into the nature of their electronic structure. Although they do not deviate from stoichiometry and, therefore, are perhaps not classifiable as true bronzes, they represent an important reference point in the series.

Experimental Section

Preparation of Samples.—The compounds were prepared by the hydrogen reduction method of Scholder and Brixner.[6] $BaMoO_4$ and $SrMoO_4$ were made by precipitation from pH 10 aqueous solutions of $(NH_4)_2MoO_4$ with the appropriate alkaline earth nitrate. After being dried overnight and fired in air to constant weight at 800°, the molybdates were heated under a slow stream of 85% argon–15% hydrogen in scrupulously clean platinum boats. Reduction time was about 8–12 hr, at 950° for $SrMoO_3$ and 1000° for $BaMoO_3$. Completeness of the reduction was monitored by weight loss and confirmed by weight gain on reoxidation. Agreement in each case was within 0.1% of the theoretical. X-Ray pictures taken with Cu Kα radiation gave unit-cell spacings of 4.040 Å for $BaMoO_3$ and 3.975 Å for $SrMoO_3$ in agreement with the reported values of Brixner.[7] Both materials were found to be highly conducting.

Magnetic Measurements.—The apparatus was the same Gouy balance and cryogenic setup previously described.[8] Tubes were of quartz, 4 mm in diameter, and were filled to a height of about 20 cm. Forces were measured with a Mettler H-6 microbalance over a field range from 1000 to 6000 G. Susceptibilities showed a slight field dependence (11% for $BaMoO_3$ and 13% for $SrMoO_3$) compared to $NiCl_2$ standard, so values of χ were extrapolated to zero reciprocal field. The slopes of χ *vs.* H^{-1} were about 13% greater at liquid helium temperature than at room temperature. Reproducibility of the extrapolated susceptibility at liquid

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(2) The properties and structures of the tungsten and vanadium bronzes are reviewed in: R. P. Ozerov, *Usp. Khim.*, **24**, 951 (1955); M. J. Sienko, "The Alkali Metals," Special Publication No. 22, The Chemical Society, London, 1967, p 429; M. J. Sienko, Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, p 224.

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