assignments for Co– and Mn–dmnapy complexes even though metal isotope studies are not possible. The Mn–dmnapy spectra are quite similar to the Zn–dmnapy spectra in that three medium-intensity bands occur below 210 cm^{-1}. By comparison with the zinc complex spectra we assign the 203- and 152-cm^{-1} bands to manganese–nitrogen stretching vibrations. The cobalt complex spectrum has one medium-strength band at 214 cm^{-1} and another broad, asymmetric band with a minimum at 165 cm^{-1}. Gaussian analysis indicates this band envelope contains two medium-strength bands at 183 and 165 cm^{-1}. We assign the 183-cm^{-1} band to the Co–N stretching vibration.

Discussion

In order to compare the M–N stretching frequencies for four- and five-member chelate ring systems, the M–N stretching bands for $(dmnapy)_3$ and $(bipy)_3$ complexes are listed in Table II. The M–N stretching frequencies are of particular interest since they provide direct information about the coordinate bond. The following factors may affect the frequency of metal–ligand stretching modes: mass of ligand and metal, symmetry of the complex, nature and size of the anion, basicity of ligand, oxidation state and coordination number of the metal, and nature of the coordinate bond.

The comparisons made in this work examine ligands of closely similar mass (a difference of 2 amu), complexes of similar symmetry (D_3), complexes containing similar anions, and metals of similar oxidation state and coordination number. The type of M–N bonding in these cases is expected to be essentially σ bonding since π back-bonding is important primarily in cases where a transition metal is in a low oxidation state.[7] The basicity of the two ligands is similar and molecular models indicate no steric hindrance due to ligand–ligand crowding.[1] The principal difference in the two types of complexes is the chelate ring size.

The data in Table II show a sizable and consistent decrease in M–N stretching vibrations when metal–bipy complex spectra are compared with metal–dmnapy complex spectra. We feel these decreases are the result of strain in the four-member chelate ring. The per cent change for each M–N stretching band is also given in Table II. The per cent decrease ranges from 24% for Ni–N stretching bands to about 16% for Mn–N. The per cent M–N stretching change as well as the M–N stretching vibrations follow the Irving–Williams order, Mn < Co < Ni > Zn, for high-spin transiton metal complexes. The 10*Dq* value of $Ni(bipy)_3^{2+}$ is 12.65 kK, while the 10*Dq* value for the $Ni(dmnapy)_3^{2+}$ is 9.56 kK.[1,8] This represents a 24.4% decrease and agrees very well with the per cent decreases found from the infrared data. A similar comparison of cobalt complexes shows a slightly smaller decrease in 10*Dq* values,[8] and this is also reflected in the infrared data. Bands due to d → d transitions for Mn^{2+} and Zn^{2+} are not observed, but infrared data reflect the absence of ligand field stabilization energy through the low frequency of the M–N stretching bands. The strain effect in these complexes should be similar to that which occurs in the non-transition-metal complexes of $(dmnapy)_3$.

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[7] R. Fitzgerald, B. B. Hutchinson, and K. Nakamoto, *Inorg. Chem.*, **9**, 2618 (1970); M. Wicholas and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 6946 (1968).

[8] R. A. Palmer and T. J. Piper, *Inorg. Chem.*, **5**, 864 (1966).

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Tungstovanadate Heteropoly Complexes. III. The Ion $V_5W_8O_{40}^{7-}$

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In a recent publication[1] we described the preparation and characterization of the ions $V_4W_9O_{40}^{6-}$ and $V_3W_{10}O_{40}^{5-}$. These were considered to be derivatives of the unknown 12-tungstovanadate(V) with partial replacement of tungsten(VI) by vanadium(V), *i.e.*, $V(W_{12-n}V_n)O_{40}^{(3+n)-}$ with $n = 2$ or 3. In this communication we describe the ion $V_5W_8O_{40}^{7-}$ which appears to be the member $n = 4$ of this series.

Experimental Section

The preparations of KVO_3, $Na_4V_2O_7 \cdot 18H_2O$, and K_2WO_4 were described previously.[2,3]

Potassium 8-Tungsto-5-vanadate(V).—Potassium metavanadate (KVO_3, 3.45 g, 25 mmol) was dissolved with heating in 12 ml of water. The solution was cooled to room temperature and added to 40 ml of 1.0 *F* K_2WO_4, giving a medium-yellow solution. Formic acid (25 ml of 10 *F* solution) was added immediately and rapidly to this solution. The resulting red-orange mixture was heated quickly almost to boiling to dissolve the solid which had precipitated. The hot, clear red solution was then poured into a large preheated crystallizing dish, covered, and set aside. The next day, the first crop of product had crystallized as a red-orange crust. After the solution was decanted, the product was washed with a little water, then with ethanol–water (1:4 by volume) until the washings were nearly colorless, and finally with 95% ethanol, and air-dried at room temperature. The decanted reaction solution was filtered and allowed to stand in a large open dish to obtain further crops of product during the next 2–3 days. The last crop isolated contained chunky orange-yellow crystals ($V_2W_4O_{19}^{4-}$ salt), which were dissolved out in the ethanol–water washing. The crops were kept separate for analyses. The total yield was 4–5 g of red-orange crystalline powder consisting of small orange to red-orange square blocks (microscope). (If the reaction solution was allowed to stand longer, more of the product separated, but the crystals were brown colored and were mixed with much $V_2W_4O_{19}^{4-}$ salt.) Attempted recrystallization led to much decomposition. *Anal.* Calcd for $K_7V_5W_8O_{40} \cdot 12H_2O$: K, 9.59; V, 8.92; W, 51.5; H_2O, 7.57. Found: K, 9.73–9.75; V, 8.91–8.95; W, 51.4–51.5; H_2O, 7.60–7.67 (for different crops of product). The mean material sum was 100.2%. Experimental mole ratios are W/V = 1.598 and K/W = 0.889. In the water determination, the weight loss was 1.92 ± 0.15% at 110° and 7.14 ± 0.03% at 200°. These data correspond to loss of 3.0 ± 0.2 and 11.2 ± 0.1 mol of H_2O/mol of salt, respectively. The salt heated at 200° was brown. Instability of the anion in solution precluded recrystallization tests. (The product of the final 500° ignition was black.)

When the preparation was carried out with less formic acid than stated above, the yield of 5:8 complex was lower. When more acid was used, the product was contaminated with a light

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[1] C. M. Flynn, Jr., and M. T. Pope, *Inorg. Chem.*, **10**, 2745 (1971).

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

[3] C. M. Flynn, Jr., and M. T. Pope, *Inorg. Chem.*, **10**, 2524 (1971).

yellow amorphous precipitate. If acetic acid was used instead of formic acid, the yield of 5:8 product was minute or nil, and only the 2:4 complex was obtained. When lower reagent concentrations were used in the preparation, the yield of 5:8 complex was lower; with higher concentrations, the yield was increased, but the vanadium content was high (9.24–9.32% V), suggesting contamination by vanadium(V) oxide. If the reactants were heated before mixing, the solution obtained was orange instead of red, and the only heteropoly product isolated was the 2:4 complex.

Other Salts.—Sodium tungstate dihydrate (13.2 g, 40 mmol) and $Na_4V_2O_7 \cdot 18H_2O$ (7.9 g, 12.5 mmol) were dissolved together with warming in 35–40 ml of water. The solution was cooled to room temperature, and 35 ml of 10 *F* formic acid was added rapidly. The resulting clear red solution failed to yield the expected 5:8 complex after evaporating at room temperature for several days. At that time, the solution was viscous and had become dark brown.

A solution made up from sodium salts, as described above, was treated with 40 ml of 2 *F* dimethylammonium chloride (from aqueous dimethylamine and hydrochloric acid), with 80 ml of 1 *F* trimethylammonium chloride (from aqueous trimethylamine and hydrochloric acid), or with 80 ml of 1 *F* tetramethylammonium chloride. The products described below were isolated by filtration, washed with ethanol–water, followed by 95% ethanol, and air-dried at room temperature.

The reaction with dimethylammonium chloride gave orangish red lath-shaped crystals during 4 hr, at which time they were isolated. On further standing, more of this phase crystallized, accompanied by a larger quantity of orange-yellow crystals ($V_2W_4O_{19}{}^{4-}$ salt). Any yellow crystals found in the isolated red product were removed mechanically. The yield was 2.7 g. *Anal.* Calcd for $((CH_3)_2NH_2)_{12}H(V_4W_9O_{40})(V_5W_8O_{40}) \cdot 3H_2O$: V, 8.38; W, 57.1; C, 5.27; H, 1.93. Found: V, 8.41; W, 57.0; C, 5.26; H, 1.75; Na, 0.046; W/V, 1.879.

In the reaction with trimethylammonium chloride, solid began to precipitate in about 5 min. After 4 hr, much solid had separated and it was isolated. The product was 3.4 g of bright orange crystalline powder which consisted of tiny, poorly formed rods (microscope). *Anal.* Calcd for $((CH_3)_3NH)_{11.5}H_{1.5}(V_4W_9O_{40})(V_5W_8O_{40}) \cdot 7H_2O$: V, 8.07; W, 55.0; C, 7.29; H, 2.32. Found: V, 8.09; W, 54.9; C, 7.34; H, 2.05; Na, 0.092; W/V, 1.879.

In the reaction with tetramethylammonium chloride, some solid formed immediately. More solid separated during 4 hr, at which time it was isolated. The product was 3.7 g of bright orange crystalline powder consisting of tiny, rhomb-shaped leaflets or plates (microscope); no yellow crystals were noted. The filtrate yielded more product on standing, but it consisted of small yellow chunky crystals (acid 2:4 salt[3]) mixed with the orange phase. *Anal.* Calcd for $((CH_3)_4N)_{10.5}H_{2.5}(V_4W_9O_{40})(V_5W_8O_{40}) \cdot 15H_2O$: V, 7.75; W, 52.8; C, 8.53; H, 2.70. Found: V, 7.78; W, 52.7; C, 8.72; H, 2.64; Na, 0.062; W/V, 1.876.

These three organic cation salts appeared optically pure under the microscope. Recrystallizations were attempted, but considerable decomposition occurred.

Reaction of 4-Tungsto-2-vanadate(V) with Formate Buffer.—A 7.2-g (5 mmol) portion of $K_4V_2W_4O_{19} \cdot 8H_2O$ was dissolved in 20 ml of water. A buffer mixture, prepared from formic acid (10 ml of 10 *F* solution) and potassium carbonate (1.7 g, 12.5 mmol), was added to this solution. No visible change occurred within several minutes. The solution was covered tightly and allowed to stand. During 40–50 days the solution turned red, and about 0.2 g of crystals (small brown to black square blocks) separated. The solution was filtered and allowed to evaporate at room temperature. More black square crystals were obtained, accompanied by chunky crystals of unchanged starting material, cuboctahedral dark red crystals ($K_6V_4W_9O_{40} \cdot 24H_2O$), and lustrous yellow leaflets similar to by-products obtained in the preparation of the 4:9 complex.[1]

Analyses.—Vanadium, tungsten, potassium, and water in the potassium salt were determined as described previously.[3] Carbon, hydrogen, and sodium were determined by Galbraith Laboratories, Inc., Knoxville, Tenn.

The filtrates from the organic salt preparations contain much $V_2W_4O_{19}{}^{4-}$. For recovery they were combined, neutralized to pH near 5 with sodium bicarbonate, treated with a small amount of sodium tungstate to obtain W/V about 2.0, and heated near boiling for 0.5 hr to convert all heteropoly species to the 2:4 complex. Addition of CH_3NH_3Cl in slight excess, and allowing to cool and stand for a day, gave an estimated 90% recovery of $(CH_3NH_3)_2Na_2V_2W_4O_{19} \cdot 6H_2O$.[3]

Characterization.—Visible–ultraviolet spectra and infrared spectra were obtained as described previously.[3]

Optical spectra of the complex (potassium salt, 10^{-3} to 10^{-4} *F*) were obtained in solutions buffered at pH near 5 (acetate), 4 (formate), 3 (formate), and 2 (bisulfate). The spectra of fresh pH 4 and 3 solutions showed a shoulder at about 350 nm with ϵ 6900–7800. (Spectra of a fresh solution of the complex in 10^{-4} *F* HCl were very similar; in addition there was an ill-defined inflection at about 240 nm with ϵ about 4×10^4.) During 30 days the pH 4 solutions decomposed; the final spectra showed a maximum at 360–375 nm and a minimum at 325–335 nm. (A synthetic mixture of $V_2W_4O_{19}{}^{4-}$ and V^V in 2:1 mole ratio at pH 4 had a nearly identical spectrum.) Solutions at pH 5 decomposed during 1 week giving spectra like those of the decomposed pH 4 solutions. Spectra of solutions at pH 3 and 2 showed decreased absorbance (above 300 nm) during 30 days; no new features appeared.

Infrared data for metal–oxygen vibrations (cm^{-1}) are as follows: potassium salt, 966, 891, 764, 497; dimethylammonium salt, 965, 878, 749, 504; trimethylammonium salt, 976 (sh), 957, 883, 757, 509; tetramethylammonium salt, 950, 880, 760, 515.

The salt $K_7V_5W_8O_{40} \cdot 12H_2O$ (formula weight 2855.4) was examined by single-crystal X-ray precession photography, using Cu Kα radiation (λ 1.5418 Å). The crystals are cubic with a = 10.61 (1) Å at 20–25°. The Laue symmetry was $m3m$, and no systematic absences were present. Neither an hhl photograph nor a cone-axis photograph (both long exposures) showed any indication that the true cell edge was a multiple of the value stated. The space group is thus $Pm3m$, $P\bar{4}3m$, or $P432$. The density (by displacement in toluene) was 4.0 ± 0.1 g cm^{-3} at 25°. The density calculated for 1 formula unit per unit cell is 3.97 g cm^{-3}.

Discussion

We have not found any report in the literature of compounds corresponding to those described here. The successful preparation of the potassium salt $K_7V_5W_8O_{40} \cdot 12H_2O$ depends on its low solubility. A similar preparation of an ammonium salt was not attempted since the appropriate starting materials are not very soluble, and a good yield would require the use of concentrated solutions. The brown color of products formed after several days is attributed to solid-solution contamination by products such as $V^V{}_3V^{IV}W_9O_{40}{}^{7-}$ formed through slow reduction by the buffer reagents.

The stoichiometry, infrared spectrum, and particularly the crystal data for the potassium salt imply a Keggin structure $V(W_8V_4)O_{40}{}^{7-}$ of the anion. The most likely alternate formulation allowed by the analytical data is $K_8V_6W_{10}O_{49} \cdot 15H_2O$ (Calcd: K, 8.91; V, 8.70; W, 52.3; H_2O, 7.70; formula weight 3511.2). However, the formula weight is inconsistent with the crystal data, implying 0.82 formula unit per unit cell. The infrared spectrum is very similar to that of the related ion $V(W_9V_3)O_{40}{}^{6-}$ (range for various salts[1] (cm^{-1}): 974–951, 892–882, 760–755, 510–500 (br)) but differs significantly from that of $V_2W_4O_{19}{}^{4-}$ (range for various salts[3] (cm^{-1}): 991–984, 970–963, 951–950, 939–936, 784–781, 589–578, 435–425 (br)). The crystal data for the potassium salt (cubic, a = 10.61 (1) Å) are most consistent with an orientationally disordered Keggin-type complex. Several potassium and ammonium salts of ions of the type $[XW_{11}MO_{39}(OH_2)]^{n-}$ (X = B, Co, etc.; M = Co, Zn, etc.; n = 7 or 8) are face centered cubic with a about 20–22 Å and eight formula units per unit cell.[4,5] (The possibility that $K_7V_5W_8O_{40}\cdot 12H_2O$ has a unit cell edge twice as large as given here is unlikely because of the failure to observe the necessary reflections on long-exposure photographs.) Formulations of the structure in terms of other known complexes (*e.g.*, as double salts) are incompatible with the crystal data and with the solution chemistry involved. Other attempts to indicate whether constitutional water was present were inconclusive or were frustrated owing to the instability of the complex in solution.

The analyses of the three organic ammonium salts all give W/V = 1.88 ± 0.01, which is close to 17/9 = 1.889 or 15/8 = 1.875. Possible formulations based on known tungstovanadates and their stability in relation to the pH are $M'_7V_5W_8O_{40}\cdot M'_6V_4W_9O_{40}\cdot nH_2O$ and $2M'_7V_5W_8O_{40}\cdot 13M'_4V_2W_4O_{19}\cdot nH_2O$ for W/V = 17/9 and $2M'_7V_5W_8O_{40}\cdot 11M'_4V_2W_4O_{19}\cdot nH_2O$ for W/V = 15/8 (M' = univalent cation). However, the infrared spectra of all three salts are very similar to the spectrum of $K_7V_5W_8O_{40}\cdot 12H_2O$ and to the spectra of the salts of $V_4W_9O_{40}{}^{6-}$, all of which differ systematically from the spectra of the salts of $V_2W_4O_{19}{}^{4-}$.[1] The formation of the 4:9 complex in these systems is confirmed by the observed crystallization of the potassium salt from solutions of potassium 4-tungsto-2-vanadate(V) in formate buffer solutions. Therefore we retain only the formulation based on a 1:1 combination of $V_5W_8O_{40}{}^{7-}$ and $V_4W_9O_{40}{}^{6-}$. With this constitution, the organic and sodium analyses require formulation as acid salts. The formation of acid salts of this type is not unprecedented; previously known acid salts include $K_5H[CoW_{12}O_{40}]\cdot 18H_2O$,[6] $Cs_3H_2[BW_{12}O_{40}]\cdot 2H_2O$, and $Cs_3H[SiW_{12}O_{40}]\cdot 2H_2O$.[7] The nonstoichiometry with respect to cation content is not attributed to partial reduction, since reduction is very slow compared to the time consumed in the preparations. The presumed Keggin-type anions may form a fairly symmetrical packing bound together electrostatically by disordered cations and solvent molecules.[4]

The ion $V_5W_8O_{40}{}^{7-}$ is unstable in solution; however, it may exist as a minor species in equilibria involving more stable complexes. (The potassium salt was probably first observed as a minor by-product in our preparation of the $V_2W_4O_{19}{}^{4-}$ salt[3] as small brownish orange square blocks. We have observed a similar phase in very low yield in ammonium salt preparations. The phase is also observed when solutions of $K_4V_2W_4O_{19}$ are acidified, as in the preparation[1] of $K_6V_4W_9O_{40}$, but are allowed to stand for several days at room temperature.) The 5:8 complex decomposes to give the 2:4 complex at pH 4–5. At pH 2–3, it decomposes evidently to condensed species including the 4:9 complex rather than to $VW_5O_{19}{}^{3-}$, even in solutions less than 10^{-3} *F* in vanadium.

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[4] L. C. W. Baker, V. S. Baker, K. Eriks, M. T. Pope, M. Shibata O. W. Rollins, J. H. Fang, and L. L. Koh, *J. Amer. Chem. Soc.*, **88**, 2329 (1966).

[5] C. Tourné and G. Tourné, *C. R. Acad. Sci., Ser. C.*, **266**, 1363 (1968); *Bull. Soc. Chim. Fr.*, 1124 (1969).

[6] L. C. W. Baker and T. P. McCutcheon, *J. Amer. Chem. Soc.*, **78**, 4503 (1956).

[7] J. A. Santos, *Proc. Roy. Soc., Ser. A*, **150**, 309 (1935).

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The Reaction of Cobalt(III) with Sodium Salicylate in Aqueous Perchloric Acid

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The instability of perchloric acid solutions of cobalt(III) complicates investigations of oxidation–reduction reactions involving $Co^{3+}(aq)$ and $CoOH^{2+}(aq)$ ions. Although many reactions have been studied,[2] in only a few of these systems has there been any spectrophotometric detection of the formation of intermediate complexes, *e.g.*, the chloride[3] and malic acid systems.[4] In order to obtain additional information on the types of reductant that readily complex cobalt(III), we chose to examine the cobalt(III)–salicylate system. In studying the reaction of cobalt(III) with sodium salicylate, we see not only the formation of a monocoordinated cobalt(III)–salicylate complex but also the formation of a dicoordinated salicylate intermediate complex. The intramolecular transfer of electrons appears to occur at a slow rate at 25°, since only after 1 hr or so do we see the formation of a pink to colorless solution due to formation of cobalt(II).

Experimental Section

Cobalt(III) solutions (0.01–0.02 *M*) were prepared by electrooxidation of stock solutions of cobalt(II) perchlorate hexahydrate (G. F. Smith Chemical Co.) in 3 *M* perchloric acid at 0° and a current density of about 20 mA cm^{-2}. The cobalt(II) and cobalt(III) solutions were standardized spectrophotometrically (ϵ_{max}(Co(III)) 35.3 at 605 nm and ϵ_{max}(Co(II)) 4.84 at 509 nm).[5]

A stock solution of sodium salicylate (0.10 *M*) (The New York Quinine and Chemical Works, Inc.) was always freshly prepared and standardized by titration with cerium(IV). When necessary, the ionic strength was adjusted with sodium perchlorate (G. F. Smith Chemical Co.). All other reagents were of analytical grade, and doubly distilled, deionized, and deoxygenated water was used throughout.

Kinetics were studied at 25° and an ionic strength of 1.5 *M* using the stopped-flow technique (Durrum-Gibson Model D-110). The reductant was present in sufficient excess to ensure pseudo-first-order conditions. The acidity was adjusted with perchloric acid (Baker and Adamson reagent).

On mixing a 10^{-4} *M* cobalt(III) solution with a 10^{-3}–10^{-2} *M* sodium salicylate solution, two distinct changes in absorbance are observed at 400 nm. The initial increase in absorbance is associated with the formation of the monosalicylate complex of cobalt(III) (absorbance ≃0.4) and the subsequent slow decrease in absorbance is attributed to the formation of a disalicylate complex (absorbance ≃0 at 400 nm).

Although the rate of formation of the dicoordinated cobalt–salicylate complex is slower than for the monocoordinated complex, the two rates overlap significantly near the end of the monocomplexation reaction. Thus a plot of our kinetic data in terms of absorbance at 400 nm *vs.* time resembles a Maxwell–Boltzmann distribution curve with the maximum occurring at ∼10 sec and ∼0.4 absorbance unit. The first-order rate constant for the formation of the monocoordinated cobalt–salicylate intermediate was therefore obtained from the first ∼70% (mea-

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[1] (a) University of Utah. (b) Adams State College.

[2] G. Davies and B. Warnquist, *Coord. Chem. Rev.*, **5**, 349 (1970).

[3] T. J. Conocchioli, G. H. Nancollas, and N. Sutin, *Inorg. Chem.*, **5**, 1 (1966).

[4] J. Hill and A. McAuley, *J. Chem. Soc. A*, 1169 (1968).

[5] G. Davies and K. O. Watkins, *J. Phys. Chem.*, **74**, 3388 (1970).