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Heteropolyniobate Complexes of Manganese(IV) and Nickel(IV)[1,2]

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The manganese(II)-EDTA complex reacts with sodium 6-niobate and hydrogen peroxide to give a moderate yield of $Na_{12}MnNb_{12}O_{38}\cdot(48\text{–}50)H_2O$, an orange manganese(IV) complex. Salts with some other cations were also obtained, including $K_8Na_4MnNb_{12}O_{38}\cdot 21H_2O$. Nickel(II) salts react with sodium 6-niobate and excess NaOBr to give a low yield of $Na_{12}NiNb_{12}O_{38}\cdot(48\text{–}50)H_2O$, a dark maroon nickel(IV) compound. Another product, $K_8Na_4NiNb_{12}O_{38}\cdot 21H_2O$, was obtained if potassium ion was also present; it is isomorphous with the corresponding manganese compound. These compounds were characterized by chemical and thermal analyses, visible-ultraviolet spectroscopy, and X-ray diffraction and were compared with the known 9-molybdomanganate(IV) and -nickelate(IV). The data are consistent with octahedral coordination of the Mn(IV) and Ni(IV) atoms in the niobate complexes.

Introduction

Isopoly and heteropoly complexes of molybdenum and tungsten and isopoly complexes of niobium and tantalum are well known, and several have been characterized by X-ray crystallography.[3-5] Since all of these complexes have common structural features and presumably similar bonding, one would expect niobium and tantalum to form heteropoly complexes as well. The lack of reports of such complexes motivated the present investigation. We report here the preparation and some properties of manganese(IV) and nickel(IV) heteropolyniobates; the structure of the manganese complex is presented in an accompanying paper.[6] Recently, Dale and Pope also reported a manganese(IV) heteropolyniobate complex.[7,8]

Experimental Section

Starting Materials.—All starting materials were commercially available reagents. Niobium(V) oxide was obtained from the Fairmount Chemical Co., Inc. (99.5% Nb_2O_5), and through the Gallard-Schlesinger Chemical Mfg. Co. (99.9+% Nb_2O_5). (The Fairmount product was digested with hot, concentrated HCl to remove a dark impurity, presumably iron.)

Potassium 6-Niobate.—Nb_2O_5 was fused with 85% KOH (1:8 mole ratio) in a nickel crucible. The reaction product was extracted with ethanol-water to remove excess KOH, and the niobate was recrystallized from water by precipitation with ethanol. The white product was washed with 95% ethanol and air dried. An analytical sample was obtained by a recrystallization. *Anal.* Calcd for $K_7HNb_6O_{19}\cdot 13H_2O$: Nb, 40.7; H, 1.98; H_2O, 17.1. Found: Nb, 40.2; H, 2.01; H_2O, 17.5.

Sodium 6-Niobate.—This was prepared in the same way as the potassium compound, except that the reaction product was extracted with water and the niobate was recrystallized from hot water by addition of sodium acetate and cooling. The white product was washed with ethanol and air dried. A recrystallization yielded an analytical sample. *Anal.* Calcd for $Na_7HNb_6O_{19}\cdot 15H_2O$: Nb, 43.1; H, 2.42; H_2O, 20.8; Na, 12.4. Found: Nb, 42.6; H, 2.42; H_2O, 21.6; Na, 11.9.

Reaction of Manganese Compounds with Alkali Niobates.—An orange complex is formed in low yields by the reaction of Mn^{2+} and niobate with hydrogen peroxide, potassium persulfate, or atmospheric oxygen. Treatment of permanganate with niobate and hydrogen peroxide also seems to produce some of the complex. In these reactions, much of the manganese is converted to brown oxide which is usually colloidal. However, if the manganese(II) is introduced as its EDTA complex, higher yields of the niobate complex are obtained, with formation of little or no brown oxide.

The methods used for niobium analysis have been described previously.[9]

Manganese was estimated in two ways, EDTA titration or iodometric titration. For EDTA titration, a solution of the compound was decomposed with dilute HF, and the manganese was reduced and titrated after buffering the solution to a pH near 8. For iodometric titration, the complex was treated with KI and dilute HF, and the iodine formed was titrated with thiosulfate. Comparison of results showed that the manganese was in the +4 oxidation state. Since some niobium oxide precipitation is present during the EDTA titration, the iodometric results are considered more reliable, once the oxidation state had been ascertained.

Sodium 12-Niobomanganate(IV).—A manganese(II)-EDTA solution (5 mmol of $Mn(O_2CCH_3)_2\cdot 4H_2O$, 5 mmol of disodium-EDTA dihydrate, 10 mmol of NaOH mixed in 20 ml of water) was added to a boiling solution of sodium 6-niobate (12.9 g, 60 g-atoms of Nb) in 300-350 ml of water. Hydrogen peroxide (3%) was added in 2-ml portions and the solution was kept boiling, until the orange color produced did not deepen further. Cooling the solution in an ice bath yielded a light orange product which was recrystallized from warm (50-60°) 0.2 *M* sodium acetate. Treatment of the remaining crude reaction mixture with more H_2O_2 as before yielded some more product, which was recrystallized in the same way. The crops of product were finally combined and recrystallized from warm 0.2 *M* sodium acetate. Slow recrystallization gave orange rods which were washed with cold 1:4 v/v ethanol-water and stored over saturated $Na_2SO_4\cdot 10H_2O$ solution or at 0-5° because of efflorescence in the room atmosphere. Yields up to 60% were obtained. *Anal.* Calcd for $Na_{12}MnNb_{12}O_{38}\cdot 48H_2O$ (mol wt, 2918): Na, 9.45; Mn, 1.88; Nb, 38.20; H_2O, 29.63. Found: Na, 9.45; Mn, 1.90; Nb, 38.05; H_2O, 30.10 (Na/Mn = 11.88, Nb/Mn = 11.84, H_2O/Mn = 48.31).

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[1] Taken from the Ph.D. dissertation of C. M. Flynn, Jr., University of Illinois, 1967.

[2] This work was initially presented in part at the American Crystallographic Association Meeting, University of Minnesota, Minneapolis, Minn., Aug 20-25, 1967.

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The efflorescence of this compound and the corresponding nickel complex (see below) makes the water content uncertain. A detailed X-ray analysis[6] of a single crystal of the manganese compound surrounded by the mother liquor suggests the presence of 50 water molecules. Removal of the manganese crystals from the mother liquor results in the rapid decomposition of the original crystalline form and probably some loss of solvent. Rapid recrystallization from solutions containing 0.2 *M* or higher sodium acetate concentrations yielded lustrous, light yellow-orange leaflets; these were washed and stored in the same way. The same substance was obtained by recrystallization from 0.5 *N* sodium hydroxide, chloride, or carbonate. *Anal.* Calcd for $Na_{12}MnNb_{12}O_{38} \cdot 44H_2O$ (mol wt, 2846): Na, 9.69; Mn, 1.93; Nb, 39.17; H_2O, 27.85. Found: Na, 9.65; Mn, 1.95; Nb, 38.98; H_2O, 27.95 (Na/Mn = 11.83, Nb/Mn = 11.82, H_2O/Mn = 43.71).

These two sodium salts can be readily interconverted by appropriate recrystallizations; thus the same niobomanganate complex is most likely present in both salts. The leaflet crystals could also be obtained on recrystallization from 0.5 *N* sodium hydroxide, carbonate, or chloride instead of sodium acetate. Therefore, the substance is not likely to be a double salt of the niobate complex with the other solute.

Dehydration of Sodium 12-Niobomanganate(IV).—A portion of the 48-water compound reached constant weight over $CaCl_2$ after 3–4 months. *Anal.* Calcd for $Na_{12}MnNb_{12}O_{38} \cdot 9H_2O$: H_2O, 7.3. Found: H_2O, 7.3 (micro).

The 48-water compound was also studied on the thermobalance. Weight losses of two samples were 29.7 and 30.3% on heating to 200°, corresponding to 48–50 mol of H_2O/mol of MnO_2. No further weight loss occurred up to 400°.

Potassium Sodium 12-Niobomanganate(IV).—Three grams of $Na_{12}MnNb_{12}O_{38} \cdot 50H_2O$ was dissolved in 50 ml of warm water, and a solution of 20 mmol of potassium acetate in 10 ml of water was added. The mixture was cooled and stirred, yielding a precipitate of bright orange powder. Slow recrystallization from warm 0.3 *M* KOAc–0.1 *M* NaOAc gave bright reddish orange octahedral crystals. The product was collected, washed with 1:4 v/v ethanol–water, and air dried. The compound is not efflorescent. Since the complex is sparingly soluble in cold water, it can also be made easily from the sodium compound by reaction with potassium acetate in aqueous solution. According to this latter method, 3.0 g of $Na_{12}MnNb_{12}O_{38} \cdot 50H_2O$ is dissolved in 50 ml of warm water, and a solution of 2.0 g (20 mmol) of potassium acetate in 10 ml of water is added. On cooling in ice and shaking, the product precipitates as a bright orange powder. *Anal.* Calcd for $K_8Na_4MnNb_{12}O_{38} \cdot 21H_2O$ (mol wt, 2579): K, 12.22; Na, 3.59; Mn, 2.15; Nb, 43.53; H_2O, 14.77. Found: K, 12.01; Na, 3.51; Mn, 2.14; Nb, 43.20; H_2O, 14.60 (K/Mn = 7.88, Na/Mn = 3.92, Nb/Mn = 11.94, H_2O/Mn = 20.80).

When a hot solution of the complex was titrated with 0.1 *M* $HClO_4$, turbidity developed and increased as acid addition was continued, up to an end point at which the precipitate coagulated, leaving a colorless solution. Visual acid–base indicators could not be used as they were absorbed on the precipitate. Two portions of the potassium sodium 12-niobomanganate titrated in this way consumed 4.69 and 4.66 mmol of H^+/g of compound. The mean equivalent weight was thus 214. A 12:1 ratio of alkali ion to manganese would give a formula weight of 2.57×10^3, in good agreement with the proposed formula (calcd, 2579).

The compound retains 21 mol of water/mol of manganese when stored over $CaCl_2$ (found, 14.8% H_2O). It is readily interconvertible with the sodium salts by suitable recrystallization.

Sodium Lithium 12-Niobomanganates(IV).—Two additional phases were obtained on crystallizing solutions of sodium 12-niobomanganate from solutions containing some sodium acetate and varying quantities of lithium acetate. One phase, isolated from solutions with an Li:Na mole ratio from 7:1 to 6:1, consisted of efflorescent, chunky, low-symmetry crystals. *Anal.* Calcd for $Na_5Li_7MnNb_{12}O_{38} \cdot 44H_2O$ (mol wt 2733): Na, 4.20; Mn, 2.01; Nb, 40.78; H_2O, 28.99. Found: Na, 4.07; Mn, 2.07; Nb, 40.46; H_2O, 29.0 (Na/Mn = 4.69, Nb/Mn = 11.56, H_2O/Mn = 42.72, Na/Nb = 4.87/12, H_2O/Nb = 44.35/12, Mn/Nb = 1.04/12, H_2O/Na = 45.46).

The second phase was obtained from solutions with larger excess of lithium acetate and consisted of yellow-orange efflorescent leaflets which were found by etch pits and optical properties to have trigonal symmetry. *Anal.* Calcd for $Na_2Li_{10}MnNb_{12}O_{38} \cdot 44H_2O$ (mol wt 2865): Na, 1.71; Li, 2.58; Mn, 2.05; Nb, 41.51; H_2O, 29.51. Found: Na, 1.77; Li, 2.39; Mn, 2.04; Nb, 41.33; H_2O, 29.60. (Na/Mn = 2.07, Nb/Mn = 11.98, H_2O/Mn = 44.24).

Sodium 12-Niobonickelate(IV).—A solution of 1 mmol of $NiSO_4 \cdot 7H_2O$ in 5 ml of water was added to a hot solution of 2.6 g of sodium 6-niobate (12 mmol of Nb) in 60 ml of water. A light green, flocculent precipitate formed and redissolved to give a yellow-green solution. If the solution was not clear, it was centrifuged. A solution of NaOBr (20 ml of 1 *M* NaOH treated with 10 mmol of Br_2) was added to the niobate solution, and the mixture was kept at 50–60° for 30–40 min. The resultant dark brownish red solution was allowed to cool, whereupon a mixture of dark maroon needles and a fine, black precipitate separated. The dense needles were washed free of the readily suspendible precipitate by decantation with 0.3 *M* sodium acetate and were recrystallized quickly from warm 0.3 *M* sodium acetate (during which a little decomposition occurred). The final product was washed quickly with ice-cold 1:1 v/v ethanol–water, sucked nearly dry on the filter, and stored at 0–5° or over saturated $Na_2SO_4 \cdot 10H_2O$ solution at room temperature. Yields were typically 10–15%.

For analysis, an aqueous solution of the sample was treated with sodium sulfite to reduce the nickel, then with sodium diethyldithiocarbamate to complex the nickel. The $Ni(S_2CN(C_2H_5)_2)_2$ was extracted with CCl_4 and finally the nickel was determined with EDTA. The aqueous phase from the extraction was treated with dilute acid to precipitate the niobium. Nickel could also be determined by treating the dissolved sample with dilute HF and finally by titrating with EDTA. For oxidation-state estimation, KI was added before the HF, and the iodine formed was titrated with thiosulfate. *Anal.* Calcd for $Na_{12}NiNb_{12}O_{38} \cdot 50H_2O$ (mol wt, 2958): Na, 9.33; Ni, 1.99; Nb, 37.69; H_2O, 30.45. Found: Na, 9.24; Ni, 1.94; Nb, 37.65; H_2O, 29.9; oxidation state, 3.75 (Na/Ni = 12.16, Nb/Ni = 12.24, H_2O/Ni = 50.22). The low values for the oxidation state are attributed to some decomposition of the complex in solution.

If this compound was recrystallized from 0.6 *M* sodium acetate, orange-red leaflets of another phase formed, but the small quantity of material was not investigated further. The compound is presumably analogous to the leaflet manganese compound, $Na_{12}MnNb_{12}O_{38} \cdot 44H_2O$.

Potassium Sodium 12-Niobonickelate(IV).—The unrecrystallized product from a synthesis of the sodium salt was dissolved in a potassium acetate solution (10 mmol of KOAc and 20 ml of water when starting with 1 mmol of Ni). A black product separated from the deep red solution over a 2-day period; it was filtered off, washed with water, and air dried, giving a black, crystalline powder. Recrystallization of a portion of this product on a microscope slide gave black, octahedral crystals.

Analyses of this material were not conclusive but indicated a K/Na ratio of 2:1. *Anal.* Calcd for $K_8Na_4NiNb_{12}O_{38} \cdot 21H_2O$ (mol wt, 2564): K, 12.20; Na, 3.59; Ni, 2.29; Nb, 43.47; H_2O, 14.75. Found: K, 11.42; Na, 3.68; Ni, 2.47; Nb, 42.78; H_2O, 15.3. The high result for nickel is attributed to decomposition during preparation: nickel(II) material precipitated, and some free niobate remained in solution. Since it was found that the X-ray powder pattern of a small quantity of this compound is identical with that of the potassium sodium 12-niobomanganate(IV), a similar stoichiometry was assigned.

Chemical Analyses.—Analyses were performed by J. Nemeth and coworkers of the Microanalytical Laboratory of the Chemistry Department, University of Illinois, and by V. Mossotti and coworkers of the Analysis Department of the Materials Research Laboratory, University of Illinois.

Microscopy.—Products were examined under a polarizing microscope to check their purity and characterize their crystal forms and optical properties.

Spectra.—Electronic absorption spectra of the complexes in aqueous solution were recorded on a Cary 14 spectrophotometer from 1000 to 220 mμ.

Thermal Analysis.—Dehydration of some of the compounds was studied using an instrument built according to a description given by Groot and Troutner.[10]

Results

Chemical Properties.—Aqueous solutions of the 12-niobomanganate(IV) and -nickelate(IV) give gelatinous precipitates (orange and brown-orange, respectively) on treatment with dilute noncomplexing acids; this behavior parallels that of the isopolyniobates. The color of the precipitates suggests a composition $Na_{12}M^{IV}Nb_{12}O_{32} \cdot xH_2O$. When the precipitates are digested with strong acids (plus reducing agent in case of the manganese complex), decomposition to niobium(V) hydrous oxide occurs. Reagents which complex niobium(V) decompose the heteropoly complexes as expected.

In the solid state, both 12-niobometalate complexes appear stable indefinitely. The orange solutions of the 12-niobomanganate(IV) ion appear stable indefinitely at room temperature but decompose slightly when hot, giving some brown precipitate. The complex is reduced by tin(II), hydroxylamine, or sulfite ion, and is decomposed by excess hydrogen peroxide. The complex is stable at hydroxide ion concentrations as high as 0.5 *M*. The deep cherry red solutions of the corresponding nickel complex decompose slowly on standing at room temperature. As expected, the complex is readily reduced, even by hydrogen peroxide. Hydroxide ion accelerates the decomposition of the complex. The sodium and sodium potassium salts of these complexes are all slightly soluble in cold water and can be easily interconverted.

Crystal Properties.—The sodium salts $Na_{12}M^{IV}Nb_{12}O_{38} \cdot 50H_2O$ are strongly pleochroic. X-Ray powder photographs show that they are not isomorphous. The double salts $K_8Na_4M^{IV}Nb_{12}O_{38} \cdot 21H_2O$ are isomorphous. The complex powder patterns and the optical properties indicate that the octahedral crystals are twinned.

Spectra.—Solutions of the 12-niobomanganate(IV) ion show absorption maxima at 453 mμ (22.1 kK), log $\epsilon = 2.61$, and at 293 mμ (34.1 kK), log $\epsilon = 4.20$. Dale and Pope[7,8] report bands at 20.75 and 21.9 kK for their niobomanganate complex at pH 7.[7] We observed no maximum near 20.75 kK. The nickel(IV) complex shows only one broad maximum at 361 mμ (27.7 kK), log $\epsilon = 4.2$. For comparison, $Mn^{IV}Mo_9O_{32}^{6-}$ has a split peak at 20.6 and 21.3 and $Ni^{IV}Mo_9O_{32}^{6-}$ has a peak at 17.6 kK.[11]

Discussion

Oxidation State of the Heteroatom.—Both the analytical data and the absorption spectra (by comparison with the known 9-molybdometalates(IV)) support assigning the +4 oxidation state to manganese and nickel in the 12-niobo complexes. We failed to obtain an epr signal from the manganate at room temperature, either as solid or as solution. The isomorphism of $K_8Na_4NiNb_{12}O_{38} \cdot 21H_2O$ with the corresponding manganese compound also supports assigning the +4 state to nickel in the heteropolyniobate. The existence and properties of the 12-niobomanganate(IV) and -nickelate(IV) further illustrates the similarities of d^3 and d^6 complexes. Besides the well-known parallels of chromium(III) and cobalt(III) chemistry, manganese(IV) and nickel(IV) are known to form parallel sets of compounds, for example, the 9-molybdometalates $M^{IV}Mo_9O_{32}^{6-}$, fluoro complexes $M'_2M^{IV}F_6$ (M' = heavy alkali metal), and the periodates $NaM^{IV}IO_6$ and $KM^{IV}IO_6$.[12,13]

Structure of the Complexes.—The crystal structure of $Na_{12}MnNb_{12}O_{38} \cdot 50H_2O$ has been determined and is presented in the following paper.[6] The manganese atom is coordinated to two Nb_6O_{19} groups such that the manganese is surrounded by an octahedron of oxygen atoms elongated along a threefold axis. From the isomorphism of the double potassium sodium salts of manganese and nickel, the 12-niobonickelate ion must have the same general structure as the manganate. The absorption spectra are consistent with octahedral coordination of the heteroatom. These species then represent a new type of heteropoly complex, in which the ligands do not form a cage about the heteroatom; only six edges of the MnO_6 (or NiO_6) octahedron are shared with the attached polyhedra.

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