of the chloride bromide with the dichloride is only slightly favored over exchange with the dibromide. This indicates that in $(CH_3)_3SbClBr$ that Cl is only slightly more labile than Br.

In conclusion, it appears that in exchanges involving the mixed halides $(CH_3)_3SbClNO_3$, $(CH_3)_3SbClF$, and $(CH_3)_3SbClBr$, the more electronegative moiety is the more labile and the difference in activity is greater when the electronegative difference is larger.

Acknowledgment.—We are most grateful to Dr. G. G. Long of this department for his many helpful suggestions and to the North Carolina Board of Science and Technology for its financial support of this research.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
U. S. NAVAL ACADEMY, ANNAPOLIS, MARYLAND 21402

Derivatives of the Undecatungstogallate(III) Anion. I. Cobalto(II)undecatungstogallate(III). Preparation, Properties, Structure, and Salts

BY ORVILLE W. ROLLINS

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In 1966 Baker and others[1] reported an investigation in depth, centered on five complexes, which established unequivocally a large, new, and general structural category of heteropoly anions, formulated $[H_hM^{m+}O_6X^{x+}O_4W_{11}O_{30}]^{(14-m-x-h)-}$. It was indicated that a wide variety of metal ions might function as octahedrally coordinated M^{m+}, and a wide variety of nonmetals and transition metals, as well as $H_2{}^{2+}$, could function as X^{x+}.

The structure of this new series of undecatungsto complexes was shown[1-3] to be a modification of the well-known "Keggin" structure. As indicated in the general formula above, octahedrally coordinated M^{m+} replaces just one of the 12 octahedral W atoms of the conventional Keggin structure, and X^{x+} occupies the central tetrahedral cavity.

Subsequently, various authors[4-7] have reported preparation of a large number of undecatungsto and undecamolybdo complexes, with various M's and X's, which they formulated according to the above.

When the undecatungstogallate(III) anion, which is one of the five complexes mentioned above, was reported[1,3] we were not certain of the Ga(III) coordination within it. The results of some recent nuclear magnetic resonance (nmr) studies by us and others[8] suggests that there may be two forms or modifications of this anion, one with the Ga(III) ions in octahedral coordination and the other with them in tetrahedral coordination with oxygen atoms. A recent and extensive single crystal X-ray study[9] supports the latter and thus the following formulation for the undecatungstogallate(III) double salt which was used in that study, $(NH_4)_7Na_2[H_2GaO_4W_{11}O_{36}]\cdot 15H_2O$.

The undecatungstogallate(III) anion reacts in solution, at room temperature, with certain hydrated cations, for example, Co(II), Cu(II), Ni(II), and Mn(II), to form very stable derivatives. The Co(II) derivative was prepared in order to determine the coordination geometry for both the Co(II) and Ga(III) ions in that anion.

By comparison of spectra, we have shown that the Co(II) ions are octahedrally coordinated in the new heteropoly anion, and since the other 11 octahedral positions of the Keggin-type structure are surely occupied by W(VI) atoms, this places the Ga(III) ions in the center of the anion.

Also, to be reported in this article are other studies which were performed with the sodium and ammonium–sodium salts of this new heteropoly anion. These include cryoscopy in saturated sodium sulfate solution, potentiometric titrations, X-ray crystallography, and optical microscopy.

Studies with the Cu(II), Mn(II),[10] and Ni(II) derivatives mentioned above, and others, will serve as the basis for future articles.

Experimental Section

Preparation of Sodium Cobalto(II)undecatungstogallate(III).—A sample of $Na_2WO_4\cdot 2H_2O$ (J. T. Baker's Analyzed Reagent) weighing 52.00 g was dissolved in approximately 75 ml of water. To this solution, at room temperature, 10.00 ml of a gallium nitrate solution (prepared by dissolving 25.02110 g of the metal, 99.999% pure, obtained from AIAG, in a minimum of concentrated nitric acid and diluting to 250 ml) was added and the pH of the solution was brought to a value of 6.5 with 6 *M* nitric acid. These amounts of reagents correspond to an atomic W/Ga ratio of 11.0:1.0. The resulting solution was heated on a steam bath until all of the precipitated gallium hydroxide had dissolved, indicating that the undecatungstogallate(III) complex had completely formed. The solution was allowed to cool to 65° and then 15 ml of solution containing 4.175 g of $Co(NO_3)_2\cdot 6H_2O$ (Mallinchrodt's AR Grade) was added dropwise with constant stirring. This gave an atomic Ga/Co ratio of 1.0:1.0. After this solution was allowed to cool to room temperature it was treated with approximately its volume of acetone whereupon the product separated as a heavy oil. The acetone–water solution was decanted and the oil layer was washed several times with acetone until it became very viscous and tacky. The product was taken up with water and then the acetone treatments were repeated until the product was free of nitrates (brown ring test). The product was dried in a vacuum oven at 75° for 3 hr, ground to a powder, allowed to equilibrate (hydrate) with the ambient atmosphere, and then sealed in a vial. The product (Preparation A) weighed 36.1 g for a yield of 79% based on the W taken.[11]

Another sample of this new substance was prepared by the procedure given above with the exception that a different amount of $Na_2WO_4\cdot 2H_2O$, 47.25 g, was used. This caused the atomic W/Ga and W/Co ratios to be 10.0:1.0, and it was done in order to test the preparative method. The product (preparation B) weighed 37.9 g for a yield of 80% based on the W taken.

Analysis of $Na_{6.8}[H_{0.2}(H_2O)Co^{2+}O_5GaO_4W_{11}O_{30}]\cdot xH_2O$.[12,13]—

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[1] L. C. W. Baker, *et al.*, *J. Amer Chem. Soc.*, **88**, 2329 (1966).

[2] L. C. W. Baker, *et al.*, *Proc. Int. Conf. Coord. Chem.*, **9**, 421 (1966).

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[4] T. J. R. Weakley and S. A. Malik, *J. Inorg. Nucl. Chem.*, **29**, 2935 (1967).

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[6] C. Tourné, *C. R. Acad. Sci., Ser. C*, **266**, 702 (1968).

[7] C. Tourné and G. Tourné, *ibid.*, **266**, 1363 (1968); *Bull. Soc. Chim. Fr.*, 1124 (1969).

[8] L. C. W. Baker, Private Communication.

[9] H. T. Evans, *Perspect. Struct. Chem.*, **4**, 20 (1971).

[10] O. W. Rollins and C. R. Skolds, paper in preparation.

[11] O. W. Rollins, *J. Inorg. Nucl. Chem.*, **33**, 75 (1971).

[12] This formula is in accord with a more general formulation for the undecatungsto (or molybdo) heteropoly complexes recently proposed by Baker and Figgis,[13] namely, $[(Y^{y-})M^{m+}O_5X^{x+}O_4(\text{W or Mo})_{11}O_{30}]^{(12-m-x+y)-}$ wherein Y^{y-} is a monodentate ligand which occupies the one unshared coordination position of the octahedral heteroatom M^{m+}. The authors report that Y may be a constitutional water molecule, an oxide ion, or some other monofunctional ligand.

[13] L. C. W. Baker and J. S. Figgis, *J. Amer. Chem. Soc.*, **92**, 3794 (1970).

Both of the preparations described above were analyzed. The sodium analysis was performed by flame photometry using a NIL flame photometer obtained from the National Instrument Laboratories, Inc. Gallium was determined with ethylenediaminetetraacetic acid (EDTA) according to the method of Rollins and Haynes.[14] The EDTA solutions were standardized against a solution of Zn(II) ions, prepared from ZnO, according to Harris and Sweet.[15] The ZnO (J. T. Baker's Analyzed Reagent) was assayed gravimetrically.[3] Cobalt was determined spectrophotometrically employing nitroso R, after first removing the tungsten for its gravimetric analysis, according to Shipmen, *et al.*[16] Identical results were obtained when the cobalt was first removed as its hydrated oxide employing sodium hydroxide and a few milliliters of 3% hydrogen peroxide. Fisher's Certified Reagent, $CoCl_2 \cdot 6H_2O$, with an assay of 99.84% was used to prepare standard solutions for the calibration curve. The assay of this reagent was verified by titration with EDTA solution according to Harris and Sweet.[15] Tungsten was determined by the gravimetric cinchonine method.[17] The tungstic acid was precipitated, at the boiling point, from a solution of the salt containing sufficient sodium hydroxide to completely break up the heteropoly complex. The dehydrations were carried out at 500° in a muffle furnace. Heating also at 700° caused no further loss in weight. *Anal.* Calcd for $Na_{6.8}[H_{0.2}(H_2O)Co^{2+}O_5GaO_4W_{11}O_{30}] \cdot 15H_2O$ (preparation A): Na, 4.84; Ga, 2.16; Co, 1.83; W, 62.8; H_2O (total), 9.00. Found: Na, 4.85; Ga, 2.06; Co, 1.77; W, 63.5; H_2O (total) 9.08. *Anal.* Calcd for $Na_{6.8}[H_{0.2}(H_2O)Co^{2+}O_5GaO_4W_{11}O_{30}] \cdot 18H_2O$ (preparation B): Na, 4.75; Ga, 2.13; Co, 1.80; W, 61.8; H_2O (total), 10.50. Found: Na, 4.74; Ga, 2.20; Co, 1.90; W, 61.9; H_2O (total), 10.8.

Preparation and Analysis of $(NH_4)_{6.8}Na_{0.9}[H_{1.4}Co_{1.1}{}^{2+}O_6Ga_{0.9}O_4W_{11}O_{30}] \cdot 18H_2O$.[18]—This double salt was prepared by addition of ammonium nitrate to a solution containing the cobalto(II)undecatungstogallate(III) which was prepared by the procedure described above. The amounts of reagents which were used (to give the atomic W/Ga and W/Co ratios of 11.0:1.0) were as follows: $Na_2WO_4 \cdot 2H_2O$, 52.15 g; $Co(NO_3)_2 \cdot 6H_2O$, 4.20 g; and 10.00 ml of a gallium nitrate solution prepared as described above and containing 25.0424 g of the metal in 250 ml. Twenty-three grams of NH_4NO_3 (100.0%) was dissolved in 77 ml of the warm solution containing the heteropoly complex. The product, which separated as well defined red cubes after the solution had cooled to room temperature, was recovered on a sintered glass filter, washed with cold water, and then recrystallized from a minimum of deionized water. It weighed 20.9 g for a yield of 44.7% based on the W taken.

The ammonia analysis was performed with a micro-Kjeldahl apparatus according to Pregl and Grant.[19] The sodium, gallium, and cobalt analyses were carried out as described above. The dehydration–deamminations were carried out at 600° in a muffle furnace. Additional heating of the samples at 800° caused no further loss in their weight. *Anal.* Calcd for $(NH_4)_{6.8}Na_{0.9}[H_{1.4}Co_{1.1}{}^{2+}O_6Ga_{0.9}O_4W_{11}O_{30}] \cdot 18H_2O$; $NH_4{}^+$, 3.76; Na, 0.635; Ga, 1.925; Co, 1.99; W, 62.0; $(H_2O + NH_3)$, 15.8. Found: $NH_4{}^+$, 3.76; Na, 0.63; Ga, 1.87; Co, 2.00; W, 62.3, $(H_2O + NH_3)$, 16.0.

Although not indicated in the formulation for this preparation it appears that about one-tenth of the cobalt(II) is in the tetrahedral site in the anion. No experimental evidence was sought to verify this.

Preparation and Analysis of $(NH_4)_{7.3}[H_{0.7}(H_2O)Co^{2+}O_5Co^{2+}O_4W_{11}O_{30}] \cdot 17H_2O$.—This substance was prepared according to Simmons.[20] The ammonia, cobalt, and tungsten analyses were performed as described above. *Anal.* Calcd for $(NH_4)_{7.3}[H_{0.7}(H_2O)Co^{2+}O_5Co^{2+}O_4W_{11}O_{30}] \cdot 17H_2O$: $NH_4{}^+$, 4.08; Co, 3.65; W, 62.7. Found: $NH_4{}^+$, 4.09; Co, 3.74; W, 62.4.

Preparation and Analysis of $Ba_3[Co^{2+}O_4W_{12}O_{36}] \cdot xH_2O$.—Two large samples of this well-known compound were prepared and analyzed. The preparative method which was developed is a modification of that used by Simmons.[20] First the dicobalt heteropoly tungstate anion shown in the previous section was prepared in solution and its Na salt was recovered in large yield employing the technique of Rollins.[11] The Na salt was dissolved in water, the pH was adjusted to 1.5 with 6 *M* HNO_3, and the resulting solution was boiled for 10 min. This causes conversion of the dicobalt anion to the monocobalt anion (containing 12 W atoms) and the latter was also recovered as its Na salt by the technique of Rollins.[11] Analysis of this preparation revealed a high cobalt content. The "excess" cobalt was removed by passing a solution of the salt through a cation-exchange resin of Dowex 50W-X8 in the H^+ form. The free acid thus produced was treated with solid $BaCO_3$, at the boiling point, until a pH of 4.6 was reached. This solution was taken down to crystallization on a steam bath. Large dark blue crystals, spikelike in appearance, were grown which were greater than 1 cm in length. These are being used in a single-crystal electron paramagnetic resonance study.[21]

The barium analysis was performed by passing solutions of the salt through a well-washed column of Dowex 50W-X8 in the H^+ form and then potentiometrically titrating the free acid solution through the first inflection with standard NaOH solution according to Samuelson.[22] The tungsten analysis was performed gravimetrically as indicated earlier. The dehydrations were carried out in a muffle furnace at 700°, in porcelain crucibles. *Anal.* Calcd for $Ba_3[Co^{2+}O_4W_{12}O_{36}] \cdot 26H_2O$ (preparation A): Ba, 10.88; Co, 1.555; W, 58.30; H_2O, 12.39. Found: Ba, 10.74; Co, 1.564; W, 58.2; H_2O, 12.41. *Anal.* Calcd for $Ba_3[Co^{2+}O_4W_{12}O_{36}] \cdot 24H_2O$ (preparation B): Ba, 11.0; Co, 1.57_1; W, 58.85; H_2O, 11.53. Found: Ba, 10.86; Co, 1.58_0; W, 58.75, H_2O, 11.72.

Preparation and Analysis of $K_6[Co^{2+}O_4W_{12}O_{36}] \cdot 14H_2O$.—A sample of this heteropoly salt was prepared by the procedure given for preparation of the Ba salt above, with the exception that K_2CO_3 was used instead of $BaCO_3$.

The potassium analysis was performed by flame photometry, and the cobalt and tungsten analyses were also carried out as described earlier in this paper. *Anal.* Calcd for $K_6[Co^{2+}O_4W_{12}O_{36}] \cdot 14H_2O$: K, 6.82; Co, 1.74; W, 65.05. Found: K, 6.83; Co, 1.69; W, 65.0.

Potentiometric Titrations.—A 0.5030 g sample of $Na_{6.8}[H_{0.2}(H_2O)Co^{2+}O_5GaO_4W_{11}O_{30}] \cdot 18H_2O$ was dissolved in approximately 100 ml of deionized water, and it was converted to its free acid by passing the solution quantitatively through a high capacity and well-washed ion-exchange column containing the H^+ form of Dowex 50W-X8. The effluent, which was water white and contained no cobalt, was titrated potentiometrically with 0.1073 *M* NaOH solution. The titration was performed at room temperature until the end point was reached; and, from there on, after an addition of NaOH, the solution was boiled for 10–15 min to ensure complete reaction, before measuring the pH at room temperature. Volume of the free acid solution was approximately 300 ml. The titration is depicted as Figure 1, in which the end point is shown to be at 4.8_2 mol of NaOH per mole of heteropoly complex.

A 0.81155 g sample of $Na_{6.8}[H_{0.2}(H_2O)Co^{2+}O_5GaO_4W_{11}O_{30}] \cdot 15H_2O$ (preparation A above) and a 0.80736 g sample of the slightly more hydrated form of this new substance (preparation B) were each dissolved in deionized water, treated with 20.00 ml of 0.0962 *M* HCl, heated to boiling, and the resulting solutions were titrated potentiometrically to the end point, at room temperature, with 0.1073 *M* NaOH. At and beyond the end point the solutions were treated as described in the preceding paragraph. Solution volumes were approximately 100 ml. The results are displayed in Figure 2, where it is shown that 4.0_5 mol of HCl reacted with each mole of the heteropoly complex.

Other potentiometric titrations were performed in order to determine the amount of NaOH required to completely degrade the cobalto(II)undecatungstogallate(III) anion. The procedure has been described by Agarwala.[23] It consists of boiling a sample of the heteropoly complex with an excess of standard NaOH and then back-titrating with standard acid to the phenol-

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(14) O. W. Rollins and B. J. Haynes, *Chemist-Analyst*, **56**, 98 (1967).

(15) W. F. Harris and T. R. Sweet, *Anal. Chem.*, **26**, 1649 (1954).

(16) W. H. Shipmen, S. C. Foti, and W. Simon, *ibid.*, **27**, 1240 (1955).

(17) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Macmillan, New York, N. Y., 1948, p 729.

(18) Very careful analysis of this double salt does not permit the assignment of one constitutional water molecule in the anion, as was done for the pure Na salt. We have encountered the same, seemingly anomalous, phenomenon in formulating the Na and NH_4–Na salts of the undecatungstogallate(III) derivatives which contain Cu(II) and Mn(II) as the second heteroatom.

(19) F. Pregl and J. Grant, "Quantitative Organic Microanalysis," 4th English Translation, J. and A. Churchill, Ltd., London, 1945, pp 79–85.

(20) V. E. Simmons, Doctoral Dissertation, Boston University, 1963; No. 63-5910, University Microfilms, Ann Arbor, Mich.

(21) O. W. Rollins and C. W. Rector, paper in preparation.

(22) O. Samuelson, "Ion Exchange Separations in Analytical Chemistry," Wiley, New York, N. Y., 1963, p 234.

(23) U. C. Agarwala, Doctoral Dissertation, Boston University, 1960.

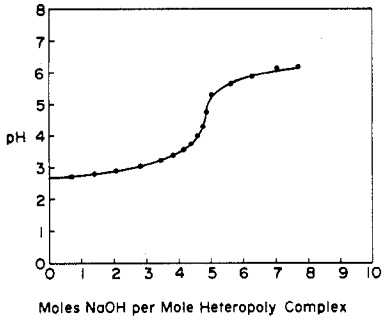

Figure 1.—Potentiometric titration, with 0.1073 *M* NaOH, of free acid solution prepared from 0.5030_5 g of $Na_{6.8}[H_{0.2}(H_2O)Co^{2+}O_5GaO_4W_{11}O_{30}]\cdot18H_2O$.

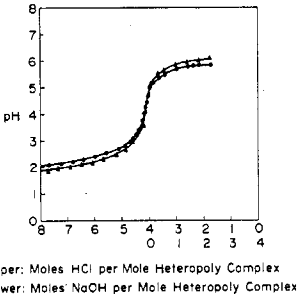

Figure 2.—Potentiometric titrations, with 0.1073 *M* NaOH, of solutions containing 0.81155 g of $Na_{6.8}[H_{0.2}(H_2O)Co^{2+}O_5GaO_4W_{11}O_{30}]\cdot15H_2O$ and 0.80736 g of $Na_{6.8}[H_{0.2}(H_2O)Co^{2+}O_5GaO_4W_{11}O_{30}]\cdot18H_2O$, each treated with 20.00 ml of 0.0962 *M* HCl.

phthalein end point. The 250-ml erlenmeyer flasks which were used were conditioned by submerging them in an alkaline solution of EDTA on a steam bath for several days.[3] The method was tested using accurately weighed samples (approximately 0.48 g) of $K_6[Co^{2+}O_4W_{12}O_{36}]\cdot14H_2O$ and $Ba_3[Co^{2+}O_4W_{12}O_{36}]\cdot26H_2O$. The number of moles of NaOH to completely degrade 1 mol of this heteropoly anion as calculated is 18, and the experimental values were 18.1, 17.9, and 18.2. With the Ba salt, the $BaWO_4$ which precipitated did not interfere with the end point determination.

Samples of the pure Na salt and the NH_4–Na salt of cobalto(II)undecatungstogallate(III) were treated as described in the preceding paragraph. The number of moles of NaOH to completely degrade 1 mol of salt, as calculated, is 16.2 for the Na salt and it is 22.0 for the NH_4–Na salt. The experimental values were 16.1, 16.0, 16.2, and 21.8, respectively.

Determination of Oxidation State for Cobalt.—Small samples (~0.2 g) from each of the three preparations containing the cobalto(II)undecatungstogallate(III) anion were dissolved in approximately 1 *M* H_2SO_4 solution containing a few crystals of dissolved KI and a few milliliters of freshly prepared starch solution. No color was developed. As a check on this method, the experiment was repeated using a heteropoly tungstate complex known to contain cobalt in the 3+ oxidation state. This compound $(NH_4)_{4.2}Na_{1.8}[GaCo^{3+}W_{10}O_{36+n}H_{2n}]\cdot(11-n)H_2O$, which was prepared and fully analyzed in our laboratory, and heretofore unreported, produced a blue color immediately with the acidified starch–KI solution. This compound has the characteristic green color of a heteropoly tungstate complex containing tervalent cobalt.

Preparation of Cobalto(III)undecatungstogallate(III).—This heteropoly anion was prepared by oxidation of the corresponding cobalt(II) anion which was prepared in solution as described earlier in this paper. Hydrogen peroxide (3%) and ammonium persulfate were used as oxidizing agents, and the pH was maintained at 6 or above. Large green cubes of the NH_4–Na salt of cobalto(III)undecatungstogallate(III) were obtained, from a red solution, however, always in small yields. Even though these preparations were not analyzed there is little doubt that they contained the new heteropoly anion.

Cryoscopy.—Analyzed samples of sodium and ammonium sodium cobalto(II)undecatungstogallate(III) were studied cryoscopically, using sodium sulfate decahydrate as the solvent. The theory, apparatus, technique, and determination of the cryoscopic constant have been described.[3] The data are shown in Table I and a plot of K_0 *vs.* molality is furnished as Figure 3.

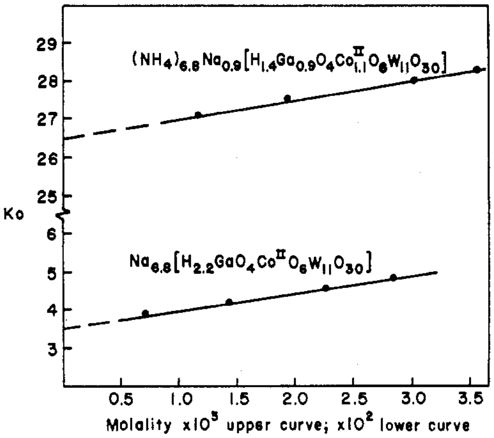

Figure 3.—Results of cryoscopy in $Na_2SO_4\cdot10H_2O$, molal freezing point depression, K_0, for the compounds indicated *vs.* molality of their solutions.

TABLE I

RESULTS OF CRYOSCOPY IN SODIUM SULFATE DECAHYDRATE[a]

Solute	Molality	ΔT, °C	K_0
$Na_{6.8}[H_{0.2}(H_2O)Co^{2+}O_5GaO_4W_{11}O_{30}]$	0.00716	0.028	3.91
	0.01430	0.060	4.20
	0.02265	0.104	4.59
	0.02845	0.138	4.85
$(NH_4)_{6.8}Na_{0.9}[H_{1.4}Co_{1.1}{}^{2+}O_6Ga_{0.9}O_4W_{11}O_{30}]$	0.001000	0.027	27.0
	0.001923	0.053	27.5
	0.00300	0.084	28.0
	0.00356	0.101	28.4

[a] In this article molalities for the cryoscopy are in terms of moles of solute per 1000 g of $Na_2SO_4\cdot10H_2O$ (as solvent) potentially present. Alternatively, the molalities could have been expressed in terms of moles of solute per 1000 g of H_2O present (an equally correct form). To convert the molalities given in the text to the latter basis, multiply each of them by 1.79, and divide each K_0 by the same factor. On that basis the K_0 per v^* at infinite dilution, for known compounds in the procedure used, becomes 3.38/1.79 = 1.89°/*m*. The v^* values, of course, come out identically on either basis.

Spectra.—The visible and near-infrared spectra of solutions containing the cobalto(II)undecatungstogallate(III) anion were compared to those of the cobalto(II)undecatungstocobaltate(II) anion (the dicobalt anion) and the dodecatungstocobaltate(II) anion (the monocobalt anion). A Beckman spectrophotometer, Model DK-2A, was used employing 1-cm quartz cells for the visible region and 1-mm quartz cells for the near-infrared region. The spectra are reproduced as Figures 4 and 5. The 1-mm cells were found to be slightly unmatched only in the 1400–1500-nm region and this was accounted for in the spectra shown in Figure 5.

X-Ray Studies.—An analyzed sample of ammonium sodium cobalto(II)undecatungstogallate(III), which had been ground to a fine powder and passed through a 200-mesh screen, was subjected to a line focus X-ray diffraction study at 26.5°, using Ni-filtered Cu Kα radiation in a GE XRD-6D diffractometer. Twenty-seven lines in the pattern were indexed for an *F* space group in the cubic system. The crystallographic unit cell edge is 22.42 Å, the pycnometer density, measured at 25.0 ± 0.05°, is 3.854 g/ml, and these taken with the formula weight correspond to 8.01 formula weights per unit cell.

Microscopy.—Crystals of ammonium sodium cobalto(II)undecatungstogallate(III) were examined with a polarizing microscope. Complete extinction was observed when the planes of polarized light were at right angles. This is, of course, characteristic of an isometric cubic crystal system. No birefringence was observed.

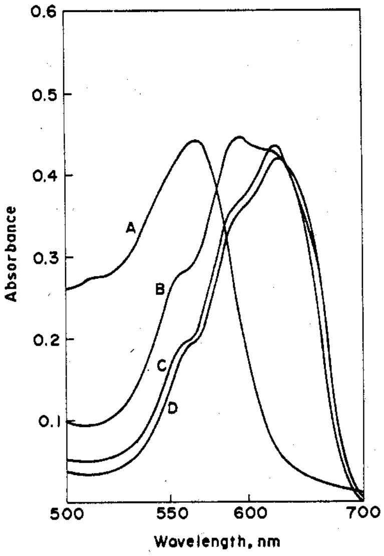

Figure 4.—Absorption spectra of solutions: curve A, 7.20 × 10^{-3} *M* solution of $Na_{6.8}[H_{0.2}(H_2O)Co^{2+}O_5GaO_4W_{11}O_{30}]$, pH 7.2; curve B, 2.00 × 10^{-3} *M* solution of $(NH_4)_{7.3}[H_{0.7}(H_2O)Co^{2+}O_5Co^{2+}O_4W_{11}O_{30}]$, pH 6.6; curve C, solution used for curve B adjusted to pH 2.1 with 6 *M* HNO_3; curve D, 1.96 × 10^{-3} *M* solution of $K_6[Co^{2+}O_4W_{12}O_{36}]$, pH 6.1.

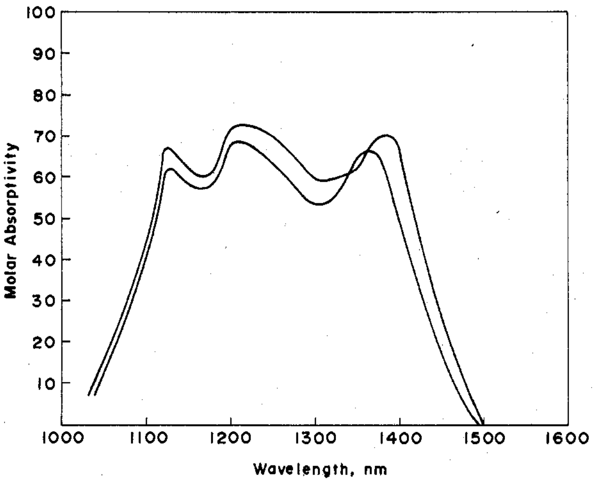

Figure 5.—Absorption spectra of solutions: upper curve, 1.00 × 10^{-2} *M* solution of $Ba_3[Co^{2+}O_4W_{12}O_{36}]$, pH 5.1; lower curve, 1.00 × 10^{-2} *M* solution of $K_6[Co^{2+}O_4W_{12}O_{36}]$, pH 6.3.

Discussion

In our studies with the $[H_2GaO_4W_{11}O_{36}]^{9-}$ anion we learned that it reacts with 4 mol of protons, in solutions of its free acid or by direct reaction of its NH_4–Na salt with mineral acid.[3] The reaction produces two polyanionic species which are degraded at different pH values in a potentiometric titration with NaOH. The two dicobalt heteropoly tungstate and Keggin-type anions $[H_{0.7}(H_2O)Co^{2+}O_5Co^{2+}O_4W_{11}O_{30}]^{7.3-}$ and $[H_{0.7}(H_2O)Co^{2+}O_5Co^{3+}O_4W_{11}O_{30}]^{6.3-}$ react with almost exactly 4 mol of protons also.[3,20] It should be noted that the anionic charges on these two heteropoly anions and the new heteropoly anions being reported in this paper are averages, just as the number of gram atomic weights in the formulations are averages.

The cobalto(II)undecatungstogallate(III) anion was shown to behave in a manner analogous to the above in the potentiometric titrations. In the free acid solution, the anion reacted with its own protons to produce cationic cobalt which was retained in the resin and thus produced two additional protons. This added to the 6.8 protons from the Na^+ ions gives a total of 8.8 protons. Subtracting 4.0 protons for the reaction leaves 4.8 protons to be titrated in the effluent solution. This is verified by the plot in Figure 1. The reaction also produces two polyanionic species which degrade at different pH values. The titration is shown beyond the H^+ ion end point and part way through the first plateau only, because any end points beyond the one shown in a titration of this type are not well defined.[3] The products for the reaction of this heteropoly anion with protons are, at present, unknown.

The potentiometric titrations with acidified solutions of sodium cobalto(II)undecatungstogallate(III) corroborate the above. The anion reacted with 4 mol of protons, as depicted in Figure 2. The first plateau beyond the H^+ ion end point corresponds to reaction of the cationic cobalt to produce insoluble $Co(OH)_2$. Beyond this point the polyanionic species are degraded.

The potentiometric titrations in which the new substances were completely degraded by NaOH are in accord with our formulations, and thus they verify the analyses and the anionic charges. These reactions are

$$(NH_4)_{6.8}Na_{0.9}[H_{1.4}Co_{1.1}{}^{2+}O_6Ga_{0.9}O_4W_{11}O_{30}] + 22NaOH \longrightarrow 6.8NH_3 + 11Na_2WO_4 + 1.1Co(OH)_2 + 0.9NaGa(OH)_4 + 12.2H_2O$$

$$Na_{6.8}[H_{0.2}(H_2O)Co^{2+}O_5GaO_4W_{11}O_{30}] + 16.2NaOH \longrightarrow 11Na_2WO_4 + NaGa(OH)_4 + Co(OH)_2 + 6.2H_2O$$

Results of the cryoscopic studies in sodium sulfate decahydrate for both the NH_4–Na and the pure Na salt of the cobalto(II)undecatungstogallate(III) anion, as shown in Figure 3, are in excellent agreement with our formulations. The values of K_0 at infinite dilution are 26.5 and 3.52, and when these are divided by the cryoscopic constant of 3.38 (which was determined experimentally by the author using several known and pure electrolytes), they give values of 7.84 and 1.04 for the number of noncommon ions (v^*) in this solvent for the NH_4–Na and the pure Na salt, respectively.[24] Since the expected values for v^* are 7.80 and 1.00, the study shows that this new heteropoly anion is very stable in saturated sodium sulfate solution at 33°. It also reveals that the preparations are free of low molecular weight impurities. Further, the purity of the Na salt attests to the value of our recently reported method for the preparation of pure Na salts of heteropoly tungstates and molybdates.[11]

The absorption spectra in the visible region, as shown in Figure 4, supports our assignment of the cobalt(II) ions to an octahedral site in the cobalto(II)-undecatungstogallate(III) anion. Curve A, which was obtained with a solution of the pure Na salt, is almost identical with the visible spectrum of hydrated Co(II) ions, $Co(H_2O)_6{}^{2+}$.

Curve B, obtained with a solution of $(NH_4)_{7.3}[H_{0.7}(H_2O)Co^{2+}O_5Co^{2+}O_4W_{11}O_{30}]$, is characteristic for cobalt(II) ions in both tetrahedral and octahedral coordination with oxygen atoms in the same anion, and this spectrum has been reported and discussed

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(24) See Table I, footnote *a*.

by Simmons.[20,25] This dicobalt(II) heteropoly anion reacts in solution with acid, quantitatively with respect to the W atoms, to produce the $[Co^{2+}O_4W_{12}O_{36}]^{6-}$ ion and hydrated cobalt(II) ions.[20] The spectrum of such a solution was first reported by Simmons[20] and it is shown as curve C in Figure 4. As expected curve C is almost identical with that obtained with a solution of $K_6[Co^{2+}O_4W_{12}O_{36}]$ which is reproduced as curve D. When solutions of $Na_{6.8}[H_{0.2}(H_2O)Co^{2+}O_5GaO_4W_{11}O_{30}]$ are acidified at room temperature (to pH of 0.8) the absorbance in the 500–700-nm region begins to decrease rapidly. The curves are identical with curve A in Figure 4, except for a shift to shorter wavelengths of approximately 25 nm. And, at no time, is there evidence for formation of the $[Co^{2+}O_4W_{12}O_{36}]^{6-}$ ion, by either spectra or color. This ion is therefore not one of the products when cobalto(II)undecatungstogallate(III) reacts with acid.

The near-infrared spectra for 1.00×10^{-2} *M* solutions of $Ba_3[Co^{2+}O_4W_{12}O_{36}]$ and $K_6[Co^{2+}O_4W_{12}O_{36}]$ are shown as Figure 5. The curves are essentially the same and they correspond to the spectrum of this heteropoly anion, and of Co(II) ions in a weak tetrahedral field, as reported by Simmons.[20,25] There was no appreciable absorption by solutions of $Na_{6.8}[H_{0.2}(H_2O)Co^{2+}O_5GaO_4W_{11}O_{30}]$ in the 1000–2000-nm range, even for solutions as concentrated as 6.0×10^{-2} *M*. This study therefore supports the visible spectral study.

Additional information relative to the octahedral coordination of cobalt(II) in the cobalto(II)undecatungstogallate(III) complex is afforded by the red (pink) color of the heteropoly anion since this is a characteristic color for cobalt(II) in octahedral coordination.[20] The blue color of the $[Co^{2+}O_4W_{12}O_{36}]^{6-}$ ion is characteristic for cobalt(II) in tetrahedral coordination.

The X-ray powder pattern of ammonium sodium cobalto(II)undecatungstogallate(III) was compared to a pattern of ammonium sodium undecatungstogallate(III), $(NH_4)_7Na_2[H_2GaO_4W_{11}O_{36}]\cdot 15H_2O$, which was taken on the same instrument at 26.0°.[26] Although the crystallographic unit cell edges are slightly different, being 22.42 and 21.12 Å, respectively, there was excellent agreement between both line positions and intensities. There were no lines corresponding to those impossible combinations of $h^2 + k^2 + l^2$ for the cubic system. Ammonium sodium cobalto(II)undecatungstogallate(III) is thus a new isomorph of that series of heteropoly tunstates possessing Keggin-type anions.[1,2,7]

Single-crystal X-ray structural work with ammonium sodium undecatungstogallate(III)[3] and other of its isomorphs[1,2] have shown that the possible space groups are $Fm3m$, $F\bar{4}3m$, $F432$, or $F23$. Each of these requires 8 ions, with the characteristic four three-fold axes of symmetry of a Keggin-type anion, in its crystallographic unit cell. Our experimental value of 8.01, for the number of formula weights of ammonium sodium cobalto(II)undecatungstogallate(III) in its crystallographic unit cell, is thus in excellent accord with the aforementioned requirement.

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(26) The temperature of the measurement is given because Baker and we discovered and reported that ammonium sodium undecatungstogallate(III) displays continuous, rapid, reversible, and appreciable *shrinkage* of its crystallographic unit cell on being heated through the temperature range 25–40°. See L. C. W. Baker, *et al.*, *J. Amer. Chem. Soc.*, **88**, 2329 (1966), and also *Chem. Eng. News*, **44**, 44 (1966).

Contribution from the Department of Chemistry,
University of Wyoming, Laramie, Wyoming 82070

The 5° Crystal Spectra of Nickel(II) Chloride and Nickel(II) Bromide[1]

By J. Ackerman, C. Fouassier,[2] E. M. Holt, and S. L. Holt*

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The optical properties of magnetically concentrated systems have generated much interest in recent times. Principally, investigations have centered around the observation of magnon side bands.[3–5] The most common type of system on which these investigations have been carried out is that in which antiferromagnetic coupling occurs. $NiCl_2$ and $NiBr_2$ are examples of a somewhat different magnetic system; both are metamagnets. In these compounds layers of ferromagnetically coupled ions are coupled together antiferromagnetically. $NiCl_2$ has a $T_n = 50°K$[6] while $NiBr_2$ has a $T_n = 60°K$.[7] Since these temperatures are within range of normal cryogenic techniques, both systems provide us an opportunity to investigate the possible optical manifestation of cooperative effects in metamagnetic compounds.

Experimental Section

Crystals of $NiCl_2$ and $NiBr_2$ were grown by vapor transport using H_2O as the transporting agent. While this technique provided crystals of excellent optical quality, the only growth habit which was found was that with the (001) face prominent. This allowed the measurement of the axial spectrum only. Typical crystal dimensions were 5 × 5 × 0.15 mm.

Crystals of Ni^{2+} in $CdCl_2$ and $CdBr_2$ were prepared by the Bridgman technique. The spectra of these materials were also measured with the incident radiation parallel to the *c*-axis crystal directions and faces were identified using precession and Weissenberg techniques.

Optical measurements were made using a Cary 14R spectrophotometer. Sample temperatures of 298, 80, and 5°K were obtained by previously reported techniques.[8–10] For temperatures of 113 and 195°K, isopentane and Dry Ice–acetone slushes were used.

Crystal Structures

$NiCl_2$ and $NiBr_2$ have the $CdCl_2$ and $CdBr_2$ struc-

(1) Supported by NSF Grants GP15432 and GP15432 A1, the Research Corp., and the Office of Naval Research.

(2) On leave from the University of Bordeaux.

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