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Hexamolybdogallate(III): The Free Acid Solution, the Ammonium and the Aquopentamminecobalt(III) Salt[1]

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A method is described for the preparation of ammonium hexamolybdogallate(III), an aqueous solution of the free acid of this heteropoly salt, and the corresponding aquopentamminecobalt(III) salt. The simplest formula for the anion is shown to be $[GaO_6Mo_6O_{15}]^{-3}$.

Baker[2,3] and co-workers, using a cation-exchange resin, prepared free acid solutions of 6-molybdate anions containing the tervalent metals, aluminum, chromium, iron and cobalt as central atoms. Subsequent study of solutions of these free acids and their salts showed that earlier formulations for these salts were inaccurate. Early authors[4,5] and even recent investigators[6] have postulated that these compounds are acid salts with anions of high basicity, *e.g.*, $K_3H_6[M^{+3}(MoO_4)_6]\cdot 7H_2O$. By potentiometric titration of the free acid solutions Baker[3] has demonstrated the presence of three and only three replaceable hydrogen atoms per central atom. Further, by careful dehydration studies of the salts, he has shown that all of the water in the anion is hydrate water and should therefore not be considered as a constitutional part of the anion. Baker suggested the following formula for these complex anions, $(XO_6Mo_6O_{15})_n{}^{-3n}$, which he later verified by X-ray studies. Quite recently Baker[7] determined ionic weights of these 6-molybdate anions in sodium sulfate decahydrate. The results of this cryoscopic investigation support a monomeric formula wherein $n = 1$.

This work was undertaken to investigate the possibility of preparing a 6-molybdate anion containing tervalent gallium as the central atom and to study and compare the salts and the free acid solution of this anion to the corresponding tervalent aluminum, chromium, iron and cobalt compounds.

Very recently Ivanov–Emin[8] has reported the preparation of ammonium and potassium hexamolybdogallate(III). The ammonium salt was prepared by essentially the same procedure reported in this paper. This investigator reports that the two salts lose seven molecules of water at 110–120° and begin to lose three additional water molecules at 250°, becoming apparently anhydrous at 400°. Thus Ivanov–Emin assumes that three molecules of water are present as constitutional water in the anion. He also states that hydrogen ions apparently detach themselves from the anion, yielding mildly acidic solutions of *p*H 3.5–3.8 in solutions 5×10^{-4} to 2×10^{-2} molar. He formulates these salts according to Rosenheim and Schwer,[5] *e.g.*, $(NH_4)_3[Ga(HMoO_4)_6]\cdot 7H_2O$.

Experimental

Preparation of Ammonium Salt and Free Acid Solution.—The ammonium salt was prepared by adding dropwise a solution of gallium nitrate (5 g. of the metal dissolved in 125 ml. of 6 *M* nitric acid) to a nearly boiling solution of 40 g. of ammonium paramolybdate in 125 to 150 ml. of water. The gallium metal of 99.95% purity was obtained from the Aluminum Company of America. The hot solution was stirred well and the *p*H kept at 4 to 6 by addition of ammonia solution. When the solution became cloudy, the white crystalline salt separated on slight cooling. Seeding the hot solution markedly aided crystallization. A second crop of crystals, recovered after the solution had stood for an extended period, was found to be impure. The moderately soluble salt was recrystallized from a minimum of hot water. The product was washed with alcohol and air dried. *Anal.* Calcd. for $(NH_4)_3[GaO_6Mo_6O_{15}]\cdot 8H_2O$: NH_4, 4.59; Ga, 5.91; Mo, 48.8. Found: NH_4, 4.56; Ga, 5.95; Mo, 49.1. Ammonia was determined using a semi-micro Kjeldahl apparatus. Molybdenum was determined using a Jones reductor.[9] The sulfuric acid solution of the salt was allowed to flow from the reductor into excess ferric alum solution, followed by titration of the ferrous ions with standard potassium permanganate solution. Gallium was determined gravimetrically by difference by precipitating with molybdenum using 8-quinolinol. This method is a modification of the procedure used by Geilmann.[10] The water of hydration was determined from these analyses.

The colorless free acid solution of the above mentioned salt was prepared by ion-exchange technique. A glass column (4 cm. in diameter and 1 m. in length) was filled with the acid form of Amberlite IR-120 (Rohm and Haas Company) to a height of 78.5 cm. A solution of 9.1 g. of the salt in about 250 ml. of water was passed slowly through the column. The effluent acid solution had a *p*H of 1.0. This solution gave no reaction with Nessler's reagent. The resin was regenerated with 2.9 *M* hydrochloric acid using upflow technique. The effluent from the regeneration contained much ammonium, some gallium and no molybdenum. Analysis of aliquots of the free acid solution showed an atomic Mo:Ga ratio of 6.2:1.0. The free acid solution seems quite stable and shows no apparent decomposition on standing for over two years.

Preparation of the Aquopentamminecobalt(III) Hexamolybdogallate(III) Salt.—Carbonatopentamminecobalt(III) nitrate was prepared according to Lamb and Mysels.[11] A solution of 1.9 g. of this salt in 75 ml. of water was added slowly with stirring to an excess of the hot free acid solution. The pink salt separated immediately with evolution of carbon dioxide according to the equation

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[1] Taken from a portion of a dissertation to be submitted by Orville W. Rollins to the Graduate School of Georgetown University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[9] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Co., New York, N. Y., 1948, pp. 597–599.

[10] W. Geilmann and F. W. Wrigge, *Z. anorg. allgem. Chem.*, **209**, 129 (1932).

[11] A. B. Lamb and K. J. Mysels, THIS JOURNAL, **67**, 468 (1945).

$$[Co(NH_3)_5CO_3]NO_3 + H_3[GaO_6Mo_6O_{15}] \longrightarrow [Co(NH_3)_5H_2O][GaO_6Mo_6O_{15}] + CO_2 + HNO_3$$

The solution was heated to the boiling point and allowed to stand. The salt was separated onto a sintered glass filter and air dried for many days on a watch glass. A sample consisting of well-defined crystals, which was of deeper pink color, was obtained from a very dilute solution of the free acid. *Anal.* Calcd. for $[Co(NH_3)_5H_2O][GaO_6Mo_6O_{15}] \cdot 8H_2O$: Co, 4.575; NH_3, 6.61; Ga, 5.42; Mo, 44.75. Found: Co, 4.57; NH_3, 6.59; Ga, 5.43; Mo, 44.70. The cobalt was determined colorimetrically with nitroso R salt[12] using a Beckman spectrophotometer Model DU. The cobalt solutions for the calibration curve were standardized with EDTA using Eriochrome Black T as indicator according to the method of Harris and Sweet.[13] The ammonia was determined with a semi-micro Kjeldahl apparatus. The molybdenum was determined gravimetrically with α-benzoin oxime using platinum crucibles according to the method of Knowles.[14] The gallium was determined gravimetrically by difference by precipitating with the molybdenum with 8-quinolinol. The gallium was also determined volumetrically in the combined oxinate precipitates by the method of Rollins and Deischer.[15] The water of hydration was determined from these analyses.

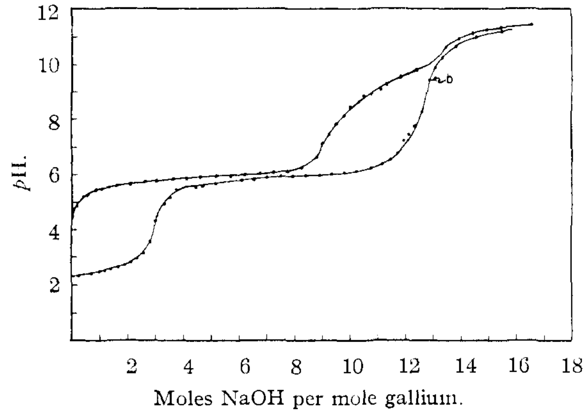

Fig. 1.—Upper curve, titration of 100 ml. of 0.001942 *M* $(NH_4)_3$ $GaO_6Mo_6O_{15}$ solution with 0.1000 *M* NaOH, lower curve, titration of 100 ml. of 0.00215 *M* $H_3GaO_6Mo_6O_{15}$ solution with 0.1000 *M* NaOH.

Potentiometric Titrations.—Solutions of the ammonium salt and the free acid solution were titrated potentiometrically with standard sodium hydroxide solution, using a Beckman *p*H meter, Model G. Precautions were taken to exclude carbon dioxide from the titration vessel. Potentiometer readings were taken when mechanical stirring for 4-5 minutes caused no change.

X-Ray Studies.—The ionic radii of tripositive gallium and chromium are very close, *viz.*, 0.62 and 0.65 Å.,[16] respectively. It was expected that the hexamolybdogallate(III) ion would be isomorphic with the hexamolybdo anions of tripositive Cr, Fe, Al and Co, which form an isomorphic series.[7] The ammonium salts of both the hexamolybdogallate(III) and the hexamolybdochromate(III) were subjected to X-ray study using a GE powder camera (143.2 mm.) with a GE XRD-1 diffraction unit. The diffraction patterns show the salts to be isomorphic. Attempts to get single crystal patterns for the gallium salt were unsuccessful.

Results and Discussion

The results of the potentiometric titrations, shown in Fig. 1, indicate the presence of three moles of hydrogen ion per mole of gallium in the free acid solution and the requirement of nine moles of hydroxide ion per mole of gallium for decomposition of the heteropoly anion. The latter may be represented by the equation

$$[GaO_6Mo_6O_{15}]^{-3} + 9OH^- \longrightarrow 6MoO_4^{=} + Ga(OH)_3 + 3H_2O$$

The form of the potentiometric titration curve for the free acid shows that the acid is moderately strong and that the three dissociation constants differ very little in magnitude. Point "b" corresponds to the disappearance of gallium hydroxide, the over-all equation for the second plateau being

$$[GaO_6Mo_6O_{15}]^{-3} + 10O\overset{-}{H} \longrightarrow [Ga(OH)_4]^- + 6Mo\overset{-}{O}_4 + 3H_2O$$

The curve for the ammonium salt shows no evidence for acidic hydrogen. Nine moles of sodium hydroxide were required for decomposition of one mole of the anion. The second small inflection corresponds to the disappearance of gallium hydroxide after titration of the ammonium ions. In each case gallium hydroxide precipitated as the long plateau was crossed.

These studies of the ammonium salt and the free acid solution show that these compounds are quite similar to the corresponding heteropoly molybdates of tervalent aluminum, chromium, iron and cobalt, and this anion conforms to the formulation of Baker.[3] The X-ray studies show that ammonium hexamolybdogallate(III) is isomorphic with ammonium hexamolybdochromate(III).

The results of our work cause us to disagree with the formulation of Ivanov-Emin[8] on two points. First, we have shown that the anion does not contain acidic hydrogen. The initial acidity of the salt solution is shown by the form of the potentiometric curve to be merely the result of a small amount of hydrolysis and not the result of acid–salt character as proposed by Ivanov-Emin. Secondly, our empirical formula for the ammonium salt differs by four hydrogen atoms and two oxygen atoms, the equivalent of two water molecules. The aquopentamminecobalt(III) cation was chosen for preparation of the new salt because McCutcheon[17] has shown that salts of this cation with three different complex anions are all anhydrous. Had the new salt also been anhydrous, the result would have resolved the issue regarding the possibility that the anion contains constitutional water. However, since the new salt is an octahydrate, any conclusion in this regard is ruled out.

In general, salts prepared from free acid solutions obtained from cation-exchange columns are of high purity. The higher degree of purity of the aquopentamminecobalt(III) salt in relation to the ammonium salt, as shown by the analyses, supports this generalization.

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