verted to HCl by this point in the experiment. A weighed amount of water was used for a hydrolysis and 98.6% of its theoretical equivalent as HCl was captured and determined during the distillation. Both of these facts show that there is little hope of isolating $GeCl_3OH$ from this reaction by distillation, but they do not eliminate its existence during the earlier stages of the reaction where it may be formed and then consumed by rapid condensation.

Acknowledgment.—The authors express their appreciation to the Lincoln Laboratories at this Institute for their interest and material aid in this study.

Cambridge, Massachusetts

[Contribution from the Department of Chemistry, University of Pennsylvania]

Some Heteropoly 6-Molybdate Anions: Their Formulas, Strengths of their Free Acids, and Structural Considerations[1]

By Louis C. W. Baker,[2] George Foster, Willy Tan, Frank Scholnick and Thomas P. McCutcheon

Received October 21, 1954

A study of 6-molybdo heteropoly anions, in which tervalent aluminum, chromium, iron or cobalt functions as central atom, indicates that $[(XO_6Mo_6O_{15})_n]^{-3n}$ is a reasonable formula for these anions, rather than $[X^{+3}(MoO_4)_6]^{-9}$, as given in an older notation. XO_6 is an octahedral group containing the central atom and n is an undetermined integer which is probably small but probably not unity. Structural considerations, which are included, suggest that the compounds may be bimolecular. A method is given for the preparation of ammonium 6-molybdoferrate(III) in a pure state. The free acid of the aluminum complex is described. It is made evident that there is neither a general formula nor a single structural model which can represent 6-heteropoly anions as a class.

Recent work[3] on the determination of the valence of a heteropoly anion of the 12-molybdo class suggested a restudy of 6-molybdo heteropoly anions containing tervalent aluminum, chromium, iron and cobalt as central atoms.

These 6-molybdo compounds, discovered a century ago,[4] were the subject of several early investigations,[5-7] in whch dualistic "oxide" formulas were used. Miolati-Rosenheim[8-11] formulas, modifications thereof, and formulas implying the same anionic composition have been widely used by recent workers[12-17] to represent these and other 6-heteropoly compounds. Examples of such formulas are: $(NH_4)_3H_6[X(MoO_4)_6]\cdot 10H_2O$ or $(NH_4)_3H_6[XMo_6O_{24}]\cdot 10H_2O$, where X represents one of the tervalent elements listed above.

In 1929, Pauling[18] accepted Rosenheim's formulas and structure for the 6-heteropoly anions considered herein. In the same paper he rejected the Miolati–Rosenheim formulas for 12-heteropoly compounds and made the fundamental suggestions concerning the considerations governing their structures which, after certain important modifications, led to the "Keggin Type" formula for 12-heteropoly anions.[3,19-23]

In 1937, Anderson[13,24] proposed a structure for 6-heteropoly anions based on the principles made evident by the above-mentioned studies of 12-heteropoly compounds. The central atom in the Anderson model is in octahedral coördination with oxygen, and the central octahedron is surrounded by a hexagon of MoO_6 octahedra. All of the octahedra lie in one plane. The anion, as in the Rosenheim formula, contains twenty-four oxygen atoms. This hypothetical configuration received experimental support when Evans[25] showed by X-ray analysis that it is an extremely probable structure for the 6-molybdotellurate(VI) anion in $(NH_4)_6[TeO_6Mo_6O_{18}]\cdot 7H_2O$ and $K_6[TeO_6Mo_6O_{18}]\cdot 7H_2O$. Evans has recently reported further X-ray evidence which conclusively establishes his former view.[26]

The work described in this paper, on 6-molybdo complexes of tervalent metals, is not in agreement with the views of Rosenheim and Schwer.[9] Their conclusions were based on conductivity measurements (which Rosenheim observed might also be interpreted as consistent with normal salt formulas) and, especially, on dehydration data. Their results

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[1] Presented before the Physical and Inorganic Division of the Meeting-in-Miniature of the Philadelphia Section, American Chemical Society, January 18, 1951.

[2] Department of Chemistry, Boston University, Boston 15, Mass.

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[5] J. G. Gentele, *ibid.*, **81**, 413 (1860).

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[10] A. Rosenheim in Abegg's "Handbuch der anorg. Chem.," Vol. IV, part 1, ii, Leipzig, Germany, 1921, pp. 977–1065.

[11] (a) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XI, Longmans, Green and Co., London, 1931, pp. 600–603. (b) Gmelins "Handbuch der anorg. Chem.," 8th Edition, Vol. 53, 374 (1935).

[12] A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, New York, N. Y., 1947, pp. 344–345.

[13] H. J. Emeléus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," Second Edition, D. Van Nostrand Co., Inc., New York, N. Y., 1952, pp. 225–226. See also First Edition, pp. 193–194.

[14] H. T. Hall and H. Eyring, This Journal, **72**, 782 (1950).

[15] I. Lindqvist, *Arkiv Kemi*, **2**, 325 (1950).

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[18] L. Pauling, *ibid.*, **51**, 2868 (1929).

[19] J. F. Keggin, *Nature*, **131**, 908 (1933).

[20] J. F. Keggin, *Proc. Roy. Soc (London)*, **A144**, 75 (1934).

[21] (a) J. L. Hoard, *Z. Krist.*, **84**, 217 (1933); (b) J. A. Santos, *Proc. Roy. Soc. (London)*, **A150**, 309 (1935); (c) O. Kraus, *Z. Krist.*, **91**, 402 (1935); **93**, 379 (1936).

[22] R. Signer and H. Gross, *Helv. Chim. Acta*, **17**, 1076 (1934).

[23] J. W. Illingworth and J. F. Keggin, *J. Chem. Soc.*, 575 (1935).

[24] J. S. Anderson, *Nature*, **140**, 850 (1937).

[25] H. Evans, Jr., This Journal, **70**, 1291 (1948).

[26] H. Evans, Jr., abstracts of papers presented before the spring meeting of the American Crystallographic Association, Cambridge, Mass., 1954.

indicated[9,11] that seven of the ten molecules of water in the empirical formula could be removed easily from each potassium salt at 170°, but that a red heat, which melts and decomposes the salts, was required to expel the last three molecules of water. These three molecules were considered to be a constitutional part of the salt. In consequence, the compounds were formulated as acid salts with anions at high basicity, *e.g.*, $K_3H_6[Cr(MoO_4)_6]\cdot 7H_2O$.

Potentiometric titrations of the free acids, described in detail below, yielded curves (Figs. 1–4) which indicate clearly the presence of three and only three hydrogen ions per central atom of each complex. The titration curves for the salts show that the compounds are not acid salts. Further, conditions have been found under which the salts may be completely dehydrated without decomposing the complex anions.

Structure.—For reasons presented below, it seems clear that these complex anions contain only twenty-one oxygen atoms per central atom instead of twenty-four. Any monomeric structure which utilizes only twenty-one oxygen atoms necessarily involves the sharing of so many faces between octahedra that it cannot be considered as a possibility. A dimeric structure[27] involving only edge sharing between polyhedra is proposed which is closely related to the structure recently reported by Lindqvist[15,28] for the paramolybdate ion, from which these compounds are directly prepared.

These suggestions are based on considerations developed in the discussion section below.

Experimental

Preparation of Compounds.—The potassium salt of the aluminum complex was prepared by a modification of Hall's method.[7] 0.1 molar $K_2SO_4\cdot Al_2(SO_4)_3\cdot 24H_2O$ solution was added, drop by drop, to a boiling and stirred solution of 30 g. of potassium paramolybdate in 170 ml. of water. The addition of the alum solution was stopped as soon as a permanent cloudiness was produced. On cooling, white crystals separated. The material was recrystallized from hot water. *Anal.* Calcd. for $K_{3n}[(AlO_6Mo_6O_{15})_n]\cdot 10nH_2O$: K, 9.5; Al, 2.2; Mo, 45.6. Found: K, 9.3; Al, 2.3; Mo, 46.0. The white ammonium salt of the complex was prepared[7] and recrystallized. *Anal.* Calcd. for $(NH_4)_{3n}[(AlO_6Mo_6O_{15})_n]\cdot 10nH_2O$: N. 3.58; Mo, 49.1. Found: N, 3.49; Mo, 49.1.

The colorless free acid of the aluminum complex was prepared from the recrystallized ammonium salt by the ion-exchange method,[17] using Amberlite IR-120 (Rohm and Haas Co.) which had been upflow regenerated and suitably washed.[17] This is the only method by which the free acids of these complexes have been prepared in a pure state because their very great water solubility and insolubility in organic solvents make purification by recrystallization impractical.[3] Pure samples are essential for reliable potentiometric titration of heteropoly acids.[3] The solution of this new acid showed no reaction with Nessler reagent. The very soluble white solid acid was obtained by evaporation. Analysis of aliquots gave an atomic Mo:Al ratio of 6:0.98.

The potassium salt of the very stable pink chromic complex was prepared by the method of Hall.[7] It was recrystallized twice from hot water. *Anal.* Calcd. for $K_{3n}[(CrO_6Mo_6O_{15})_n]\cdot 10nH_2O$: K, 9.3; Cr, 4.12; Mo, 45.7. Found: K, 9.5; Cr, 4.13; Mo, 45.4. The pink solution of the free acid was obtained by the ion-exchange method. Analysis of aliquots gave an atomic Mo:Cr ratio of 6:0.98.

The ammonium salt of the white ferric complex was prepared by a modification of the method of Rosenheim and Schwer.[9] The following procedure gave a product that was free from the traces of reddish brown impurity[4] that is present when the salt is prepared by older methods.[7,9] Thirty grams of recrystallized ammonium paramolybdate was dissolved in 600 ml. of water in a 2-liter beaker. (The size of the beaker influences the rate of cooling.) The solution was heated to 45° and removed from the source of heat. A one-half saturated solution of ammonium ferric alum was added immediately, drop by drop, with vigorous stirring, at such a rate that the yellow precipitate which formed when a drop was added had just redissolved before the next drop entered. After about 15 ml. of the ferric alum solution had been added, the temperature of the molybdate solution had fallen to 38°, and a white crystalline substance had just started to precipitate. The solution was then quickly filtered with the aid of suction. Upon standing overnight in the ice-box, the filtrate deposited a good yield of tiny white four-sided plates. They were removed and washed thoroughly with cold water. The product was not recrystallized because it decomposed readily when heated in solution. The substance looked white when seen in small quantities; but, when seen in depth, it had a very slight greenish cast, which was not removed by oxidizing agents. *Anal.* Calcd. for: $(NH_4)_{3n}[(FeO_6Mo_6O_{15})_n]\cdot 10nH_2O$: N, 3.49; Fe and Mo, 52.5; Mo, 47.9. Found: N, 3.54; Fe and Mo, 52.4; Mo, 47.9. The potassium salt of this complex was prepared analogously. *Anal.* Calcd. for: $K_{3n}[(FeO_6Mo_6O_{15})_n]\cdot 10nH_2O$: K, 9.3; Fe and Mo, 50.0. Found: K, 9.4; Fe and Mo, 50.1.

The light blue-green monomethylammonium salt of the cobaltic complex was prepared.[17] *Anal.* Calcd. for $(CH_3NH_3)_{3n}[(CoO_6Mo_6O_{15})_n]\cdot 9nH_2O$: N, 3.42; Co, 4.81; Mo, 47.0. Found: N, 3.53; Co, 4.80; Mo, 46.7. The atomic Mo:Co ratio was 6:0.97 for the free acid, prepared as above.

Potentiometric Titrations.—The concentration of the solution of each free acid was determined by putting aliquots through a Jones reductor. The effluents were passed into ferric alum solution and then titrated with standard potassium permanganate solution. The concentrations of solutions of the salts were determined by the same method.

Suitable volumes of the solutions, after dilution to the concentrations indicated in the captions to Figs. 1–4, were potentiometrically titrated with standard sodium hydroxide solution. Potentiometer readings were taken when stirring for 5 minutes failed to cause a change of 0.01 *p*H unit. Precautions were taken to avoid the presence of carbon dioxide or carbonates.

The results of the titrations, shown graphically in Figs. 1–4, indicate the presence of only three replaceable hydrogen ions per central atom of the acids. In each case these are shown to be moderately strong (pK's of about 2 to 3). For each acid, the several dissociation constants are of very nearly the same value. The titration curve for each acid shows only two points of inflection: at the points where three and where twelve moles of base per mole of central atom have been added. The first plateau corresponds to the neutralization of the three replaceable hydrogen ions per central atom, and the second plateau corresponds to the decomposition of the complex according to the equation

$$[(XO_6Mo_6O_{15})_n]^{-3n} + 9nOH^- \longrightarrow 6nMoO_4^{=} + nX(OH)_3 + 3nH_2O$$

The color of each complex was unaffected until the first point of inflection was reached. Thereafter, the amount of precipitated $X(OH)_3$ progressively increased as the second plateau was crossed. The precipitations of $X(OH)_3$ from the iron, cobalt and chromium compounds were accompanied by gradual destructions of the characteristic colors of the complexes. The titration curves for the salts, corresponding in every way to the second plateaux of the acid curves, demonstrate that the compounds are not acid salts.

Dehydration Experiments.—Samples of the potassium salts of the chromic, ferric and aluminum complexes were spread on large watch glasses and heated at 110° in an electric oven. The salts were analyzed periodically.

In order to minimize errors caused by absorption of water from the air, the following technique was used to remove samples for analysis: The sample was transferred to an

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[27] Results of a subsequent X-ray investigation of the ammonium salts of these complexes are reported elsewhere in this issue: C. W. Wolfe, M. L. Block and L. C. W. Baker, THIS JOURNAL, **77**, 2200 (1955). The crystals contain two empirical formulas per simplest unit cell, and therefore the anions are not larger entities than dimers.

[28] I. Lindqvist, *Acta Cryst.*, **3**, 159 (1950).

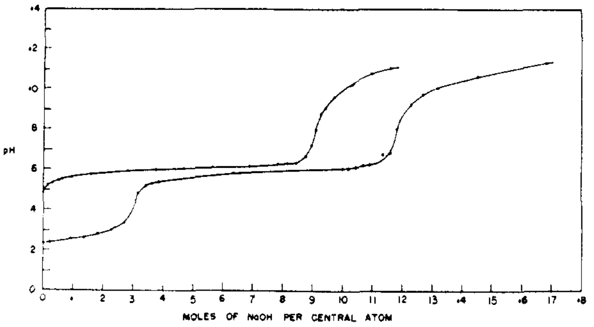

Fig. 1.—Upper curve: titration of 120 ml. of $K_{3n}[(AlO_6Mo_6O_{15})_n]\cdot 10nH_2O$ soln., 0.00297 molar with respect to the central atom, with 0.1116 *M* NaOH. Lower curve: titration of 130 ml. of $H_{3n}[(AlO_6Mo_6O_{15})_n]$ soln., 0.00189 molar with respect to the central atom, with 0.1116 *M* NaOH.

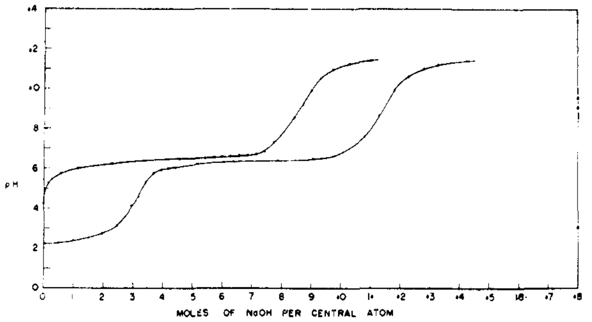

Fig. 2.—Upper curve: titration of 131 ml. of $K_{3n}[(CrO_6Mo_6O_{15})_n]\cdot 10nH_2O$ soln., 0.00298 molar with respect to the central atom, with 0.1116 *M* NaOH. Lower curve: titration of 71.5 ml. of $H_{3n}[(CrO_6Mo_6O_{15})_n]$ soln., 0.00317 molar with respect to the central atom, with 0.1116 *M* NaOH.

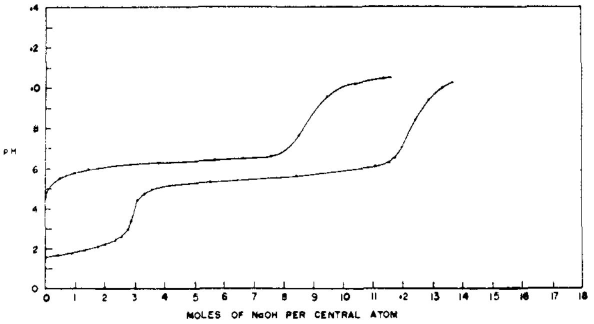

Fig. 3.—Upper curve: titration of 100 ml. of $(CH_3NH_3)_{3n}[(CoO_6Mo_6O_{15})_n]\cdot 9nH_2O$ soln., 0.00240 molar with respect to the central atom, with 0.1135 *M* NaOH. Lower curve: titration of 100 ml. of $H_{3n}[(CoO_6Mo_6O_{15})_n]$ soln., 0.0102 molar with respect to the central atom, with 0.1135 *M* NaOH.

oven-dried weighing bottle, the transfer being made within the oven. The stoppered bottle was cooled, while unenclosed, to room temperature, weighed, and about one gram of the salt was transferred quickly to a volumetric flask and dissolved. The bottle was weighed again. Aliquots of the solution were passed through a Jones reductor and titrated with standard potassium permanganate solution. Since the relative proportion of each reducible constituent was known, the results could be used to calculate the empirical formula weight of each salt. Hence the number of water molecules associated with each such formula was obtained. In every case, when there was no further loss of water, the results of the analysis checked those calculated for anhydrous material within 1.5 parts per 1000. For

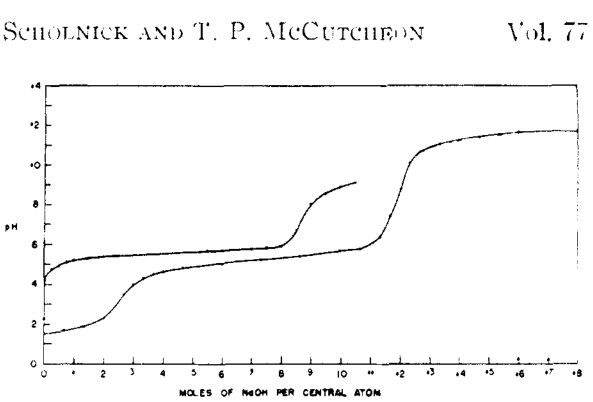

Fig. 4.—Upper curve: titration of 77.6 ml. of $(NH_4)_{3n}[(FeO_6Mo_6O_{15})_n]\cdot 10nH_2O$ soln., 0.00287 molar with respect to the central atom, with 0.1135 *M* NaOH. Lower curve: titration of 70 ml. of $H_{3n}[(FeO_6Mo_6O_{15})_n]$ soln., 0.00284 molar with respect to the central atom, with 0.1323 *M* NaOH.

these salts one water molecule per empirical formula would account for a change of about 18 parts per 1000 in these analyses. Prolonged heating at temperatures well over 200° failed to produce any further change in the analyses.

When the salts were first placed in the oven, they were not finely ground. After heating at 110° for over a week, each still retained 2–3 molecules of water per central atom. The samples were removed and reground. After they were replaced in the oven, the temperature was raised. The ferric compound became anhydrous after 12 hours at 140°. Calcd. anhydrous empirical formula weight, 1085; found 1086, 1085. The chromic salt was anhydrous after 24 hours at 155°. Calcd. anhydrous empirical formula weight, 1081; found 1080. The aluminum salt was the most difficult to dehydrate. It was anhydrous after being heated for 36 hours at 200°. Calcd. anhydrous empirical formula weight, 1056; found 1057.5.

While the salts were in the oven, the color of the chromic compound changed gradually from pink to light brown, and the ferric compound acquired a faint brownish tint. There was no reason to believe, however, that the anions had decomposed, because the fully dehydrated salts dissolved immediately and completely in cold water, forming solutions which showed the characteristic colors of the original compounds.

Samples of the anhydrous potassium salts, weighing 1–2 grams, were heated for two hours at 650° in an electric muffle furnace. The salts melted and decomposed, but the loss in weight was not more than a few tenths of a milligram in any case. When each of the fused materials was treated with water, it proved to be a mixture of partly soluble, but mainly insoluble, substances. The fused materials did not exhibit the characteristic colors of the complexes before or after water was added.

It seems clear that the complete dehydration of these compounds, without decomposition, depends upon the use of very finely divided material. It is essential to employ an analytical technique which avoids the absorption of significant amounts of atmospheric moisture. Although the results differ from those reported by Rosenheim and Schwer,[9,11] they are in accord with the earlier observation of Hall,[7] who noted that all of the water was lost by the ammonium salt of the ferric complex at 150° before any appreciable amount of ammonia was expelled.

Magnetic Measurements.—The magnetic susceptibilities of the isomorphous[27,29] ammonium salts of the aluminum and ferric complexes were measured by the Gouy method.[30] The aluminum salt was diamagnetic, but the technique used was not sufficiently accurate to warrant reporting the results. The measurement was made on the aluminum salt for the purpose of evaluating the very small diamagnetic correction, caused by atoms other than iron, which was to be applied in the calculation of the paramagnetic moment of the iron atom. All measurements were made at 22°. The Gouy magnetic balance was calibrated with recrystal-

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(29) G. A. Barbieri, *Atti Acad. Lincei*, [5] **23I**, 338 (1914).

(30) P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York, N. Y., 1943, pp. 2–6, 98–99, 142 ff.

lized Mohr salt at five field strengths up to 6000 gauss. The susceptibility of the solid ammonium salt of the ferric complex was measured at the same strengths. Our results, differing very slightly from those previously reported by Rây, *et al.*,[16] were: magnetic susceptibility per gram (χ_g) = 11.5×10^{-6}; magnetic susceptibility per mole (χ_m), based on a dimeric formula = 276×10^{-4}; effective magnetic moment of iron atom ($\mu_{\text{eff.}}$) = 5.71 Bohr magnetons.

Attempts at Optical Resolution.—Efforts to resolve the chromium complex by the use of strychnine, cinchonine and brucine, under a variety of conditions, gave negative results. This confirms the observations of Rosenheim and Schwer,[9] who attempted to resolve the aluminum and chromium complexes by use of strychnine.

Discussion

The Anions Are Based on $X^{+3}O_6$ Octahedra.—Rây, *et al.*,[16] have shown that the cobaltic complex is diamagnetic. Therefore the central atom has no unpaired electrons and is involved in coördination through six octahedrally directed d^{2}sp^3 bonds.[30] These must be Co–O bonds since hexavalent Mo lacks appropriate electrons to coördinate to Co. This interpretation is conclusive in view of the very great experimental difference between the observed diamagnetism and the paramagnetic susceptibility indicated for any other possibility.

Barbieri showed by studies of mixed crystals that the ammonium salts of the complexes under consideration are isomorphous.[27,29]

The magnetic measurements alone do not unequivocally establish the existence of $X^{+3}O_6$ groups for the central atoms other than cobalt, but there can be little doubt of the existence of these groups in the other cases. For all of the compounds, the magnetic data are as would be expected if such groups exist. The case is strongly supported for each complex by the isomorphism of its ammonium salt with the corresponding cobalt compound, by the expected Werner coördination number and configuration, and by ionic radius ratio data.

Our magnetic measurements, reported in the experimental section above, support the opinion of Rây, *et al.*,[16] that each iron atom in the ferric complex has five unpaired electrons. The iron atoms are therefore at the centers of ionic associated ("outer orbital") complexes wherein sp^{3}d^2 octahedral Fe–O bonds may resonate with purely ionic bonds. The whiteness of the complex in the hydrated solid, the lack of any color in its solutions, its stability in the presence of an ion-exchange resin,[17] and the constant composition of the salts precipitated by Hall[7] leave no doubt that very little uncomplexed ferric ion exists in the solid or in cold solutions.

The diamagnetic aluminum complex must be of the ionic associated type also.

The results reported by Rây, *et al.*,[16] show that each chromium central atom possesses three unpaired electrons. This would be the case whether the chromium atoms are at the centers of octahedral penetration complexes with d^{2}sp^3 bonds or at the centers of octahedral ionic associated complexes.

When a solution of either the chromic or cobaltic complex was boiled for an hour or so, no decomposition was detected. In marked contrast, the aluminum complex decomposes moderately rapidly in boiling water and the ferric complex decomposes very easily when heated in solution. These differences in behavior are clearly primarily attributable to differences in lability rather than to variations in stability.[31] The series of compounds provides another striking example of the correlation between electronic structure and lability recently proposed by Taube.[31] According to his elegantly documented interpretation, the failure of the chromic and cobaltic complexes to decompose under the conditions cited would result from the non-availability of unoccupied 3d orbitals. This, considered with the colors involved, the magnetic data, and the thermal decomposition behaviors of the other compounds, justifies the rather definite assignment of the chromic complex to the category of a penetration complex with d^{2}sp^3 octahedral bonds.[32]

The considerations in the preceding paragraph reveal a striking fundamental similarity between the bonding of metallic central atoms in heteropoly anions and in coördination complexes. This similarity appeared self-evident twenty years ago because it was implicit in the assumptions upon which the Miolati–Rosenheim structures[10] were based. It has not been so self-evident in recent years. Furthermore, because Taube's conclusions[31] are correlated through the mechanisms of decomposition of coördination complexes, the above considerations very strongly imply that the same mechanisms suggested in his paper apply to the decompositions of these heteropoly anions.

The Molybdenum Atoms are at the Centers of MoO_6 Octahedra.—This conclusion is demanded by radius ratio data. The octahedral arrangement of Mo^{+6} and O^{-2} has been revealed by X-ray studies of numerous higher molybdates, including all of the heteropoly molybdates which have been investigated.[19–26,33] The complexes are formed in solutions of paramolybdates, probably by rapid reaction of the paramolybdate ion itself, as shown below. The structure of the paramolybdate ion involves only MoO_6 octahedra. The structures of other isopoly molybdates which might exist in significant proportions in the solutions in which these complexes are made also involve only MoO_6 octahedra.

The Formula of the Complexes is $[(XO_6Mo_6O_{18})_n]^{-3n}$.—The potentiometric titrations demonstrate the presence of three replaceable hydrogen ions per central atom of each free acid. Therefore the anion is seen to contain twenty-one oxygen atoms per central atom, provided the anion contains no hydrogen.

A fundamental argument against the inclusion of hydrogen in the anion is that no valid reason has been advanced to justify such a postulate. The point arises primarily because the inclusion of hydrogen in the anion was required by several now-outmoded theories.[18,34–36] It has not been

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[31] H. Taube, *Chem. Revs.*, **50**, 69ff (1952).

[32] C. H. Johnson, *Trans. Faraday Soc.*, **28**, 845 (1932).

[33] I. Lindqvist, *Arkiv Kemi*, **2**, 349 (1950).

[34] G. Jander, K. Jahr and W. Heukeshoven, *Z. anorg. Chem.*, **194**, 383 (1930).

[35] A. Rosenheim, *ibid.*, **96**, 141 (1916).

[36] H. Brintzinger and C. Ratanarat, *ibid.*, **224**, 97 (1935).

necessary to place any hydrogen atoms in any of the heteropoly or isopoly anions for which the structures have been determined by X-ray analysis[15,19–26,33] (with the possible exception of the metatungstate ion wherein hydrogen may function as central atom). The dehydration experiments reported herein indicate very strongly that all of the hydrogen in the crystals of the salts is merely a constituent of the water of hydration.

The complete absence of breaks in each long plateau of the potentiometric titration curves is also very strong evidence against inclusion of hydrogen in the anions. The only positions at which hydrogen atoms might be expected to attach themselves to a heteropoly ion are at the projecting unshared oxygens. Every poly ion has a respectable number of such oxygens. If a few of these could attach hydrogen ions so strongly that they were undetectable during potentiometric titration, it would be very unreasonable to expect exactly three other hydrogen ions per central atom to remain virtually unattached to the several remaining equivalent oxygens. The number of available unshared oxygens may not be decreased by covering them with hydrogen atoms, because valence requires that an oxygen be added to the structure for every two hydrogens added. Whenever an oxygen is added, sharing of another oxygen between two polyhedra is eliminated, and two more unshared oxygens thus become available.

It is therefore extremely unlikely that the anion contains any hydrogen atoms.

Structural Problem.—We are now in a much better position to discuss structural problems than were previous writers, who were not dealing with the correct relative number of oxygen atoms in the complex. Our problem is to conceive of a structure for the anion, based on one $X^{+3}O_6$ octahedron per six MoO_6 octahedra. The octahedra must be sharing corners, edges, and/or faces in such a way that twenty-one oxygen atoms per X atom are utilized.

A Monomeric Formula Is Unlikely.—It is evident that all monomeric possibilities must involve a great deal of face sharing, because there are not enough oxygen atoms available for structures wherein the octahedra are joined primarily by edge and corner sharing. The most reasonable of the monomeric arrangements have no fewer than nine shared faces. Such structures are extremely improbable, especially with octahedra containing hexavalent central atoms.[37] Shared faces have not been found in any of the structures of heteropoly or isopoly tungstates or molybdates which have been determined.

Severe limitations are imposed on the structural possibilities by the smallness of the relative number of oxygen atoms. All of the monomeric structures of which we have been able to conceive should be resolvable into optical isomers. The complete failure to effect any optical resolution of the complexes provides an additional argument against a monomeric formula.

If dimeric or higher formulas are contemplated, one may envisage arrangements which involve only the sharing of edges and corners between octahedra.[27]

Hall showed[7] that the anions could easily pass through a dialysis membrane. Therefore they are not highly polymeric. The rapidity of the formation of the chromic complex in cold dilute paramolybdate solution[14] provides additional indication that *n* is small.[27]

A Highly Possible Structure.—Although several structures may be devised within the above rather stringent limits, there is one in particular which has much to recommend it over the others.

The complexes form readily in paramolybdate solution. For reasons presented below, the reaction appears to be between the tervalent ion and paramolybdate ion itself. It is reasonable then to expect the structure of the heteropoly anion to be closely related to that of the paramolybdate ion. Lindqvist[15,28] has recently reported a thorough X-ray study of the paramolybdate ion, in which he concludes that its structure is based on a central MoO_6 octahedron surrounded by six other octahedra which are attached by edge sharing. In this structure, of formula $[MoO_6Mo_6O_{18}]^{-6}$, two of the molybdenum atoms do not lie in the same plane as the other five.

If, in the paramolybdate ion, that MoO_6 octahedron which has the most shared edges (*i.e.*, the most centrally located one) is replaced by an $X^{+3}O_6$ octahedron, a structure results which has the formula $[XO_6Mo_6O_{18}]^{-9}$. Joining two of these together, by the sharing of those six oxygens which lie in one plane, with the corresponding six from another such group, produces $[(XO_6Mo_6O_{15})_2]^{-6}$, a rather symmetrical structure which satisfies all of our requirements and involves only edge sharing between polyhedra.

The application of what amounts to "Pauling's Rules for linking polyhedra in complex ionic crystals"[37] has provided the key to the modern elucidation of the structures of heteropoly and isopoly anions. The internal structures of these poly anions may be treated in the same terms as those employed for complex ionic crystals. The justification for doing so is largely empirical, but is strongly supported by the observed distortions of the polyhedra. "Pauling's second rule," that which requires local neutralization of charges within the structure, is usually strained to some extent in the poly ion structures. The other three rules apply quite well to all of those structures which have been investigated, and even the "second rule" applies well through large portions of the structures.

The established structure of the paramolybdate ion strains the "second rule" most seriously at the shared corners of the MoO_6 octahedron which has the most shared edges. Replacement of that MoO_6 octahedron by an $X^{+3}O_6$ octahedron would appear most probable, not only because it provides the most centrosymmetric arrangement, but also because the substitution of a tervalent central atom for a hexavalent one would be more compatible with the "second, third and fourth rules." In part the foregoing sentence amounts to saying

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(37) A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, New York, N. Y., 1947, pp. 112–115.

that an $X^{+3}O_6$ octahedron would find it much less difficult to share six of its edges than a $Mo^{+6}O_6$ octahedron does, because of lower repulsion between the central atoms of the octahedra which share edges. Since the paramolybdate ion's central MoO_6 octahedron shares an edge with each of the other six octahedra, each of these unions would be favorably affected by the substitution of the $X^{+3}O_6$ octahedron for the MoO_6 group.

These foregoing factors predict that the new ion should be much more stable than the parent paramolybdate. This would account for the ease of formation of the complexes and for the fact that they do not undergo further changes in more acidic solutions, as do paramolybdates.

Substitution of the $X^{+3}O_6$ for any of the other MoO_6 groups of the paramolybdate structure leads to much less satisfying results from all of the foregoing standpoints.

General Principle.—It would appear that considerations of the type discussed in the preceding four paragraphs may have rather general applicability to heteropoly ion structures, including those which are known and those which remain to be elucidated. In most cases heteropoly ions are formed from isopoly ions which, because of the high charge on the central atoms of their polyhedra, necessarily involve more or less serious strains on "Pauling's second, third and fourth rules." Such isopoly ions react readily to form heteropoly ions wherein each "addendum" polyhedron becomes attached directly to one or more "central" polyhedra. These latter almost always involve central atoms of lower charge than the central atoms of the "addenda" polyhedra. The resulting structures are much more satisfying from the standpoints of the "second, third and fourth rules" than are their parents. This would account for the ease of formation of the heteropoly ions and the fact that they are generally more stable over ranges of *p*H and other conditions than are their isopoly parents. In the few cases where charge difference on central atoms is not involved, it turns out that the size differences of the groups concerned would operate in the same direction to produce a similar effect.

Conductometric Evidence.—The conductometric titration curves discussed below must be interpreted in the light of the following pieces of pertinent evidence.

The fact that paramolybdate solutions contain primarily anions with seven molybdenum atoms apiece has been shown by the works of Darmois and Périn,[38] Travers and Malaprade,[39] Byé,[40] Doucet,[41] and by Carpéni's[42] and Souchay's[43] reinterpretations of the diffusion and electrodialysis data of Jander, *et al.*,[34] and Brintzinger, *et al.*[36] Lindqvist, who recently determined completely the structure of the paramolybdate ion by X-ray analysis, has argued effectively[16] that the same ion must exist in solutions of paramolybdates. The view that there is primarily only one kind of molybdate complex in an ammonium paramolybdate solution is supported by the interpretation placed upon the conductometric titrations discussed below. Carpéni[42] has shown that, in such solutions, the equilibria involving paramolybdate ions with other isopoly molybdates are established relatively slowly.

Hall and Eyring[14] have reported conductometric titrations of ammonium paramolybdate with chromic nitrate. These titrations, having been made for another purpose, were given no detailed interpretation by those authors. Figure 3 of their paper represents the conductometric titration of 25.00 ml. of 0.1001 *M* (in Mo) ammonium paramolybdate with 0.0202 *M* "fresh" (*i.e.*, uncomplexed) chromic nitrate. The conductivity curve first falls at a moderate rate for most of the titration, then it rises steeply to a second break at the final end-point, which occurs at 20.65 ml. of $Cr(NO_3)_3$ solution, when the atomic Mo:Cr ratio is exactly 6:1. The first break occurs at a point corresponding to the addition of between 14 and 18 ml. of chromic nitrate solution.

The over-all reaction produces acid

$$6n[\mathrm{MoO_6Mo_6O_{16}}]^{-6} + 7n\mathrm{Cr}^{+3} + 3n\mathrm{H_2O} \longrightarrow 7[(\mathrm{CrO_6Mo_6O_{15}})_n]^{-3n} + 6n\mathrm{H}^+$$

Therefore the conductivity at the final end-point is much higher than at the start of the titration.

If the initial reaction involves the expulsion of a molybdenum from the paramolybdate, with a chromium atom taking the place of the expelled molybdenum, then the following equation applies

$$n[\mathrm{MoO_6Mo_6O_{16}}]^{-6} + n\mathrm{Cr}^{+3} + n\mathrm{H_2O} \longrightarrow [(\mathrm{CrO_6Mo_6O_{15}})_n]^{-3n} + \{n\mathrm{MoO_4}^{-2} + 2n\mathrm{H}^+]$$

The $MoO_4^=$ represented in this equation would not be stable as such in this solution. It would immediately react with and consume the hydrogen ion produced, forming isopoly molybdates. After all of the paramolybdate had been consumed, chromium would react with the new isopoly molybdates. These latter reactions would of necessity produce acid rapidly since the over-all reaction produces it. It is impossible to tell which isopoly molybdates would be formed as intermediates. The proportion of each would depend upon conditions. There are minor breaks just before the final end-point of the second, steeply rising portion of the titration curve. These indicate the presence, just before the end of the titration, of a mixture of isopoly molybdates. Many of the isopoly molybdates involved would probably have structures closely related to that of paramolybdate.[33]

It is possible to gain some insight by picking any one of the probable isopoly molybdates, assuming that it is formed exclusively, and writing an over-all equation for the first segment of the conductometric curve. The tetramolybdate ion may be chosen as the product for such an equation. This ion is taken as an example because its formula is definitely established[33] as $[Mo_8O_{26}]^{-4}$, its structure is closely related to that of paramolybdate ion, and it is not unreasonable to expect its formation in such a solution. Then, if all of the hydrogen ion produced is immediately consumed in the production of isopoly molybdates from the expelled fragments, the following net equation results

$$10\mathrm{Cr}^{+3} + 12[\mathrm{MoO_6Mo_6O_{16}}]^{-6} \longrightarrow 5[(\mathrm{CrO_6Mo_6O_{15}})_2]^{-6} + 3[\mathrm{Mo_8O_{26}}]^{-4}$$

If this reaction occurred exclusively until all of the paramolybdate species was used up, the first break in the conductometric curve would occur at about 14.8 ml. of chromic nitrate solution. It will also be seen that the conductivity should fall during this portion of the titration for three reasons: (1) The conductivity of the products of the above reaction should be much less than that of the $12[MoO_6Mo_6O_{16}]^{-6}$; (2) hydrogen ions other than those formed by reaction are probably being consumed in polymerization of the expelled molybdate; and (3) the solution is becoming diluted as the titration progresses.

The foregoing equation is written merely as an example of many similar ones, showing other isopoly products, which can be written. In the other cases the results with respect to conductivity change and position of the first end-point turn out practically the same.

The first end-point in these titrations is not sharp because, in that region, paramolybdate ions are scarce compared to other isopoly species, and the first and second types of reaction must therefore occur simultaneously. Furthermore a small amount of paramolybdate is probably formed or consumed by reactions with the other molybdate species present. That this amount is small is in accord with Car-

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[38] E. Darmois and J. Périn, *Compt. rend.*, **177**, 762 (1923).

[39] A. Travers and A. Malaprade, *Bull. soc. chim.*, [4] **39**, 1555 (1926).

[40] (a) J. Byé, *ibid.*, [5] **9**, 517 (1942); (b) J. Byé, Thèse, Paris, France, 1945.

[41] (a) Y. Doucet, *J. phys. radium*, **4**, 41 (1943); (b) Y. Doucet, Thèse, Paris, France, 1942.

[42] G. Carpéni, *Bull. soc. chim.*, [5] **14**, 492 (1947).

[43] P. Souchay, *ibid.*, [5] **14**, 914 (1947).

peni s[42] conclusion that equilibria between paramolybdates and other isopoly species are relatively slowly established under such conditions.

The conductometric data support the structure suggested above for these 6-heteropoly molybdates: (1) by indicating that the initial rapid formation of the complexes in the cold occurs by direct reaction between the tervalent ion and the paramolybdate ion itself and (2) by supporting the idea of the formation of mixtures of isopoly molybdates from expelled fragments.[44]

General.—The general results of this investigation make it clear that 6-heteropoly anions as a class cannot be represented by a single formula or by a single structural model, as is usually attempted. At least three fundamentally different structural types are now known for 6-heteropoly tungstates and molybdates: (1) the 6-molybdotellurate(VI) ion has the Anderson-Evans structure. (2) The anions herein described have a different empirical formula and a polymeric, probably dimeric, structure. (3) The 6-heteropoly tungstates of cobalt have an entirely different type of dimeric structure, which we have elucidated by chemical evidence and X-ray investigation.[45]

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(44) Figure 4 of the paper of Hall and Eyring is more difficult to interpret because the titration involved the addition of an unspecified amount of ammonium hydroxide. Enough ammonium hydroxide was apparently added so that the acid produced by the reaction was all consumed.

(45) L. C. W. Baker and T. P. McCutcheon, abstracts of papers presented at the Fourth Meeting-in-Miniature of the Philadelphia Section, American Chemical Society, pp. 81–83 (January 1951).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

The Equilibrium $2LiOH(s) = Li_2O(s) + H_2O(g)$

BY N. W. GREGORY AND R. H. MOHR

RECEIVED NOVEMBER 22, 1954

Equilibrium pressures of water vapor above LiOH and Li_2O have been measured between 250 and 400° using both transpiration and effusion methods. Data correlate well with third law entropies of Johnston and Bauer[1] leading to the equation $\Delta F^0 = 32359 - 4.177T \ln T + 0.0116T^2 - 12.661T$. An estimate of the accommodation coefficient (*ca.* 0.01) for the condensation of water on lithium oxide has been made from steady-state effusion pressures.

The lithium hydroxide–lithium oxide–water system has been studied recently by Johnston and coworkers.[1-3] Johnston and Bauer have calculated thermodynamic properties at 25° from low temperature heat capacity measurements and from heat of solution data of de Forcrand.[4] Ditmars and Johnston[3] have attempted to confirm these values in a study of the equilibrium

$$2LiOH(s) = Li_2O(s) + H_2O(g)$$

using the effusion method. We have observed that, although a rough check of the heat of reaction was obtained, the pressures reported are approximately one hundredth as large as those predicted from third law entropies.

Considerable deviation of effusion steady-state pressures from equilibrium values has been observed in this Laboratory in the study of decomposition reactions in halide systems. We believe this to indicate a small accommodation coefficient for the condensation process. The present study was undertaken to see if the low pressures reported by Ditmars and Johnston were associated with a similar difficulty. A transpiration method has been developed which permits the equilibrium to be studied in the same pressure range used in effusion. Two additional series of experiments have been carried out in effusion cells with larger and smaller orifices, respectively, than used by the previous investigators.

Experimental

Lithium hydroxide was prepared by adding an excess of lithium carbonate to calcium hydroxide (Baker's C.P. reagents). After boiling the solution several hours, the supernatant liquid was separated by filtration and concentrated in a nitrogen atmosphere, resulting in crystallization of the monohydrate of LiOH. A five-gram sample (prepared in several batches) was transferred to a nickel boat (under nitrogen) and the anhydrous form, partially decomposed, obtained by heating for two hours at 150° and five hours at 400° under high vacuum in the transpiration apparatus. Analysis of a portion of the material after completion of the transpiration experiments (by titration against standard HCl and gravimetric determination of lithium as the sulfate) indicated that 46.4 mole per cent. of the hydroxide had decomposed and that the original purity was 99.7%.

An independent sample of oxide was prepared by passing oxygen over lithium iodide at 300–400°. The product was found to contain 3.25% $LiIO_3$. After hydration and removal of excess water as described above, equilibrium pressures were found identical with those for the material prepared from the carbonate.

The transpiration apparatus is shown in Fig. 1. The flow of nitrogen, introduced through a P_2O_5 drying trap P, was measured with a calibrated sulfuric acid flowmeter N. Cold traps on each side of the meter were kept at −80°. The temperature of the sample (in furnace M) was measured with five calibrated chromel–alumel thermocouples spaced around the Pyrex tube, and controlled with a Micromax regulator within ±1° of the desired value. Furnaces K and L were used to preheat the carrier gas. The pressure of nitrogen was measured with a manometer attached between E and F; the gas was exhausted through a cold trap (liquid oxygen) and capillary tube at G. The water vapor carried out of the decomposition chamber was collected in H (cooled in liquid oxygen). After completion of an experiment, the system was evacuated to J, and the water collected transferred to the capillary U tube at C. The amount present was determined by observing the pressure produced on vaporization in the calibrated volume between D and B, using a cathetometer and the differential mercury manometer AB. Pressures were measured at 15 mm. or less (v.p. H_2O = 23.8 at 25°). The total volume of the calibrated section

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(1) H. L. Johnston and T. W. Bauer, THIS JOURNAL, **73**, 1119 (1951).

(2) T. W. Bauer, H. L. Johnston and E. C. Kerr, *ibid.*, **72**, 5174 (1950).

(3) W. R. Ditmars and H. L. Johnston, *ibid.*, **75**, 1830 (1953).

(4) H. R. de Forcrand, *Ann. chim. phys.*, [8] **15**, 433 (1908).