JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

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VOLUME 78 SEPTEMBER 22, 1956 NUMBER 18

PHYSICAL AND INORGANIC CHEMISTRY

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

Heteropoly Salts Containing Cobalt and Hexavalent Tungsten in the Anion[1]

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RECEIVED APRIL 17, 1956

The preparations and properties of four new heteropoly anions are described. Their chemical interrelationships are summarized by the reaction chart given in the third paragraph of the text. Two of the anions are binuclear, containing two cobalt and twelve tungsten atoms apiece. The two cobalt atoms are in oxidation states +2 and +3, respectively, in one of the binuclear complexes. In the other, both cobalts are in oxidation state +2. The binuclear complexes form isomorphous cubic salts with alkali cations. A structural interpretation is deduced from a combination of the chemical evidence with the results of a crystallographic symmetry argument. The latter is based on X-ray measurements and other crystallographic data. It serves to indicate the main features of the probable structures of the binuclear complexes. Each of these structures probably involves a cobaltous atom coördinated to the exterior of a basket of 12 WO_6 octahedra which surround the other cobalt atom. The mononuclear 12-tungsto complexes are isomorphous. In one of them the central atom is cobaltous; in the other it is cobaltic. Free acids are described which are insoluble in ether but extraordinarily soluble in water.

This paper reports preparations, properties and structural considerations concerning heteropoly electrolytes which contain both cobalt and hexavalent tungsten in the anion. Some years ago one of the present authors conducted an investigation[3] during which a green ammonium salt of such an anion was prepared and qualitatively examined. The fact that there is no other reference to such compounds in the literature is surprising because (1) heteropoly tungstate anions containing most of the other transition elements have been reported, (2) the 6-*molybdo*cobaltiate ion is well-known,[4,5] and (3) the coördination complexes of cobalt were very thoroughly investigated during the period when heteropoly tungstates were thought to be coördination compounds of a conventional type.

A system of four closely-related heteropoly anions has been discovered which exhibits a number of unique features, especially with respect to valence interrelationships of the "central" atoms, but also with respect to structure and chemical behavior. The ions are entirely different in these respects from the molybdocobaltiate complex[4,5] or other known heteropoly complexes.

The four new anions and their chemical interrelationships may be summarized by means of the following reaction chart

$$\begin{tikzcd}
Co^{++} \arrow[d, "\begin{array}{l}\text{hot neutral}\\ \text{tungstate soln.}\end{array}"] & & \\
\begin{array}{l}[Co^{+2}Co^{+2}W_{12}O_{42}]^{-8}\\ \text{I (emerald green)}\\ \text{12-tungstodicobaltoate}\end{array} \arrow[rr, shift left, "H^+"] \arrow[d, shift right, "\text{oxidation}"'] & & \begin{array}{l}[Co^{+2}(W_2O_7)_6]^{-10}\\ \text{III (emerald green)}\\ \text{12-tungstocobaltoate}\end{array} \arrow[ll, shift left, "\begin{array}{c}(NH_4)_2CO_3\\ \text{(with dec.)}\end{array}"] \arrow[d, shift right, "\text{oxidation}"'] \\
\begin{array}{l}[Co^{+2}Co^{+3}W_{12}O_{42}]^{-7}\\ \text{II (dark brown—almost black)}\\ \text{12-tungstocobaltocobaltiate}\end{array} \arrow[u, shift right, "\text{reduction}"'] \arrow[rr, "H^+"] & & \begin{array}{l}[Co^{+3}(W_2O_7)_6]^{-9}\\ \text{IV (light yellow)}\\ \text{12-tungstocobaltiate}\end{array} \arrow[u, shift right, "\text{reduction}"']
\end{tikzcd}$$

Hydrated normal ammonium salts and potassium salts of anions I and II have been prepared. A normal rubidium salt and a cesium acid-salt,[6,7] $Cs_6H[Co^{+2}Co^{+3}W_{12}O_{42}]\cdot 13H_2O$, have also been prepared for anion II. All of these salts form cubic crystals, concerning which structural X-ray

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[1] Presented at the Symposium on Heteropoly Anions, National Meeting, American Chemical Society, September, 1956. Portions presented at the Meeting-in-Miniature of the Philadelphia Section, American Chemical Society, January, 1951.

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[3] H. A. Alsentzer, Jr., Dissertaton, University of Pennsylvania, Philadelphia, 1926, pp. 22–24.

[4] L. C. W. Baker, G. Foster, W. Tan, F. Scholnick and T. P. McCutcheon, THIS JOURNAL, **77**, 2136 (1955).

[5] C. W. Wolfe, M. L. Block and L. C. W. Baker, *ibid.*, **77**, 2200 (1955).

[6] A. F. Wells, "Structural Inorganic Chemistry," Second Edition, Oxford University Press, New York, N. Y., 1950, p. 353. See also First Edition, p. 343.

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

work is reported below. Anions I and II may replace each other isomorphously in any of these crystals, with appropriate adjustments in proportions of cations as necessitated by the difference in valence. Ammonium, potassium and rubidium ions may replace each other isomorphously in all of these salts. Cesium ions may replace the other alkali ions isomorphously within limits.

Potassium salts of anions III and IV have been prepared. Both salts exist as needle-like prismatic crystals. They are isomorphous. In the absence of a better system of representation, Miolati—Rosenheim formulas have been tentatively assigned, *i.e.*, $K_5H_5[Co^{+2}(W_2O_7)_6]\cdot 16H_2O$ and $K_4H_5[Co^{+3}(W_2O_7)_6]\cdot 18H_2O$. The Miolati—Rosenheim formulas happen to require forty-two oxygen atoms per anion, the same number which exists in each of the closely-related dicobalt anions. Moreover, there is some evidence that these crystals are in fact acid-salts. However, the assignment of forty-two oxygen atoms to the monocobalt anions must be regarded as tentative.

Numerous other salts of the four new anions have been prepared and examined qualitatively. None of the anions is decomposed by boiling or by low temperatures. However, the cobaltic compounds are very easily reduced; and acid causes the immediate irreversible expulsion of one cobaltous ion from either of the dicobalt anions.

The parent of the series, anion I, is most readily formed in hot, *neutral* solution—an interesting circumstance which may account in part for the fact that the compounds were not discovered earlier. The normal salts of anions I and II form solutions which are nearly neutral.

A powerful oxidizing agent, such as lead dioxide or a hot persulfate, is required to effect the oxidations indicated. Hydrogen peroxide solutions, up to 10% in concentration, will not bring about either of these oxidations, even when heated to effervescence. Exactly half of the cobalt in anion I is susceptible to oxidation. Anion II may also be prepared, in the presence of certain surface-active catalysts, from a cobaltic coördination complex: carbonatotetramminecobalt(III) ion. In the latter reaction exactly half of the cobalt entering the heteropoly ion is reduced to the bivalent state.

The free acids of anions I and II do not exist. Attempts to prepare them lead to formation of anions III and IV, respectively. The free acids of III and IV are not soluble in diethyl ether, unlike the heteropoly tungstic acids of most other transition elements. The free acid of III has been prepared in an impure condition by the ion-exchange method.[8,9] The solution, apparently because it contained excess tungstate ions, deposited WO_3 very slowly. The acid of anion III exhibits an extraordinary solubility in water. Over 100 g. of solid will dissolve in one ml. of water, producing a solution with a density of over 4 g./ml. The hydrated solid free acid exists as cubic crystals. The impure free acid of anion IV was prepared, in solution, by oxidizing the acid of anion III. The sodium and lithium salts of anions I and II also have very great solubilities. Their crystal forms differ from the salts of the other alkalies.

In the following sections a structural interpretation is deduced from a combination of the chemical evidence with the results of a crystallographic symmetry argument. The symmetry argument is based on X-ray data, other crystallographic data, and elimination of possibilities on chemical grounds. It serves to indicate the main features of the probable structures for anions I and II.

It is concluded that in neither of the dicobalt complexes are the two cobalt atoms structurally equivalent.

According to the structural interpretation, it appears that anion I in solution contains one oxidizable cobaltous atom at the center of a CoO_6 octahedron which in turn is enclosed in a basket of twelve WO_6 octahedra. Each WO_6 group is sharing one corner with the central CoO_6 while sharing corners and an edge with other WO_6 octahedra. The other cobaltous atom is at the center of a CoO_6 octahedron which is *exterior* to the basket of WO_6 octahedra but which is attached to the basket by sharing of (probably three) corners with (probably three) WO_6 groups. It is this exterior cobaltous atom which cannot be oxidized and which may be stripped from the rest of the complex by the action of acid. The exterior cobalt, unlike the interior one, can also be easily and completely removed by a cation-exchange resin operating in either the hydrogen or the potassium cycle. Anion II has the same structure as I except that the interior cobalt is tervalent.

In the solid potassium and ammonium salts of anion II there is one complex per simple cubic cell. The structural argument places a $Co^{+3}O_6$ octahedron at the center of each cell. The cell also has a one-eighth interest in the cobalt atom within each of eight $Co^{+2}O_6$ octahedra located at the corners of the cell. Crystallographically, the choice is arbitrary as to which type of CoO_6 octahedron is considered to be at the center and which at the vertices of the cell. Thus, there are two simple cubic translation lattices, any given cobalt atom being surrounded by eight nearest cobalt atoms which are of different oxidation state. Each CoO_6 octahedron is surrounded by an atmosphere of twelve WO_6 octahedra which are sharing corners and edges. However, the arrangement of WO_6 groups about the tervalent cobalt is not the same as the arrangement about the bivalent cobalt. The cations and water molecules fill remaining spaces between the complexes. The structure of the corresponding salts of anion I is the same, except that all of the cobalt atoms are bivalent.

Experimental

Preparation of Compounds. A. Ammonium 12-Tungstodicobaltoate (Anion I).—One hundred and ninety-eight g. (0.6 mole) of $Na_2WO_4\cdot 2H_2O$ was dissolved in 400 ml. of water. The *p*H of the solution was adjusted to a value between 6.5 and 7.5 by the addition of 40 ml. of glacial acetic acid. A separate solution was prepared by dissolving 24.9 g. (0.1 mole) of cobaltous acetate tetrahydrate in 125 ml. of warm water to which a few drops of glacial acetic acid had

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[8] L. C. W. Baker, B. Loev and T. P. McCutcheon, THIS JOURNAL, **72**, 2374 (1950). See also: R. E. Dodd and P. L. Robinson, "Experimental Inorganic Chemistry," Elsevier Publishing Co., Amsterdam, 1954, p. 296–297.

[9] L. C. W. Baker, G. A. Gallagher and T. P. McCutcheon, THIS JOURNAL, **75**, 2493 (1953).

been added. The sodium tungstate solution was brought to a boil and the cobaltous acetate solution was added to it slowly with stirring. Small amounts of a transitory pink precipitate[10] appeared and redissolved very rapidly, forming a deep green solution. After all of the cobaltous acetate had been added, the solution was boiled for ten minutes and then filtered hot to remove traces of insoluble matter. The solution then contained the extremely soluble sodium salt of anion I.

The solution was heated to boiling again and 135 g. of ammonium acetate dissolved in a small amount of boiling water was added to it. Upon cooling, an 85% yield of dark emerald green cubic crystals separated. The yield contained traces of two rather insoluble substances: a white ammonium tungstate and a pink cobaltous tungstate.[10] The product was recrystallized from hot dilute acetic acid (0.5 ml. of glacial acetic acid per 100 ml. of water). Five recrystallizations gave a product which dissolved without leaving a solid residue. The salt showed a very considerable change of solubility with temperature and a moderate tendency to form supersaturated solutions. The final sample was air-dried at room temperature. *Anal.* Calcd. for $(NH_4)_8[Co^{+2}Co^{+2}W_{12}O_{42}]\cdot 20H_2O$: N, 3.20; Co, 3.36; W, 63.1; H_2O, 10.3. Found: N, 3.17; Co, 3.48; W, 62.9; H_2O, 10.3.

B. **Potassium 12-Tungstodicobaltoate (Anion I).**—A hot saturated solution containing 130 g. of potassium chloride was added to a boiling solution of sodium 12-tungstodicobaltoate, obtained as described above for preparation "A." An 85% yield of the green crystals of the desired potassium salt separated on cooling. These were less perfect, less pure, and showed a smaller change of solubility with temperature than was the case with the ammonium salt. The product was divided into portions which were recrystallized successively through the same 400 ml. of water, which contained 2 ml. of glacial acetic acid. The hot saturated solutions were always filtered before cooling. After this entire recrystallization procedure had been repeated five times, the salt was pure and formed well-defined cubes. These were air-dried. *Anal.* Calcd. for $K_8[Co^{+2}Co^{+2}W_{12}O_{42}]\cdot 15H_2O$: K, 8.74; Co, 3.30; W, 61.7; H_2O, 7.54. Found: K, 8.62; Co, 3.40; W, 62.1; H_2O, 7.62.

Optimum Conditions for Preparing Anion I and *p*H Effects.—In order to learn the most favorable conditions for the preparation of 12-tungstodicobaltoates and also to observe the *p*H changes which accompany the formation of the complex, the preparation of the potassium salt was repeated eleven times in each of two series of experiments. In order to avoid confusing hydrolysis effects, the anions of strong acids were substituted for all the acetates in the procedure given above. The *p*H's of the sodium tungstate solutions were adjusted, by addition of varying amounts of HCl or H_2SO_4, to values ranging from 3.5 to 8.6. The results were decisive. When the *p*H was within a few tenths of a unit of neutral, the yields were much larger and only traces of impurities appeared. However, the green complex formed to some extent over the entire *p*H range studied. The only green crystals which separated were the cubic potassium 12-tungstodicobaltoate. The formation of the complex from neutral or moderately acidic solutions was always accompanied by a drop in *p*H. The drop ranged from 0.6 to 1.6 units, despite the fact that the formal equation for the preparative reaction represents that a number of moles of base is produced. The drop reflects the fact that the heteropoly complex is the anion of a much stronger acid than the tungstic acids involved.[11] The best yields were obtained when a weak acid, such as acetic, was used to adjust the *p*H of the original sodium tungstate solution, because the resulting buffer action kept the solution nearly neutral during the later reaction.

Although traces of the complex will form over a long period at room temperature, hot solutions are necessary for a convenient reaction. If the cobaltous acetate to sodium tungstate ratio is varied widely from theoretical, the same compounds are formed, accompanied by greater amounts of impurities.

C. **Ammonium 12-Tungstocobaltocobaltiate (Anion II).**—A solution of the sodium salt of anion I was prepared exactly as described above under preparation "A." This was brought to 80°, and 15 g. of solid ammonium persulfate was added. The solution was heated to vigorous effervescence and finally to boiling. Within a few minutes the color changed from green, through olive green, to very dark brown. After boiling for five more minutes, the solution was filtered with suction and again brought to a boil. Two hundred and fifty ml. of hot saturated ammonium nitrate solution was added. The mixture was stirred and allowed to cool. Very dark brown cubic crystals of the desired product separated. The yield was 55%. The salt was recrystallized from hot water containing two drops of concentrated sulfuric acid per 100 ml.

The ammonium salt of anion II was also prepared in 40% yield by the following method. A mixture of 50 ml. of glacial acetic acid and 75 ml. of water was saturated at 100° with pure ammonium 12-tungstodicobaltoate. Forty g. of lead dioxide was stirred into this solution while boiling. It was boiled for ten minutes, filtered hot, cooled to 0°, and filtered cold. The filtrate was heated to boiling again and 125 ml. of a boiling solution which contained 190 g. of ammonium acetate was added. The resulting solution was placed in a 50° oven and allowed to stand for several hours, following which it was cooled slowly to room temperature. Dark cubic crystals of the desired salt separated and were recrystallized from very dilute acetic acid. The crystals contained no lead. *Anal.* Calcd. for $(NH_4)_7[Co^{+2}Co^{+3}W_{12}O_{42}]\cdot 19H_2O$: N, 2.82; Co(total), 3.40; Co(tervalent), 1.70; W, 63.7; H_2O, 10.1. Found: N, 2.79; Co(total), 3.54; Co(tervalent), 1.65; W, 63.5; H_2O, 10.1.

The ammonium salt of anion II was also prepared in 9% yield by a method of theoretical interest: 25 g. of $Na_2WO_4\cdot 2H_2O$ was dissolved in 75 ml. of water and the solution was made neutral by addition of nitric acid. One-half g. of PtO_2 was added to the mixture. A solution of 5 g. of $[Co(NH_3)_4CO_3]NO_3\cdot {}^1/_2H_2O$ in 40 ml. water was warmed to 40° and added extremely slowly from a dropping funnel to the boiling stirred tungstate solution. After refluxing for three hours, the solution was cooled, filtered and reheated. Excess hot concentrated ammonium nitrate solution was added. Upon cooling and standing the very dark cubic crystals of desired product separated. Numerous experiments in which the PtO_2 was omitted produced only pink precipitates, possibly tungstates of cobaltammine cations. Attempts to use silica gel as the catalyst led to the same negative results.[12] When active charcoal, freed from reducing agents, was substituted for the PtO_2, mixed crystals of the ammonium salts of anions I and II were produced. These results may be related to the probable role of ammine nitrogen as reducing agent. They may be contrasted with the preparation of 6-molybdocobaltiate ion from carbonatotetramminecobalt(III) ion.[8]

Samples of ammonium 12-tungstocobaltocobaltiate prepared by each of the three methods gave identical X-ray patterns.

D. **Potassium 12-Tungstocobaltocobaltiate (Anion II).**—The same procedure was employed as the first one given above under the preparation of the corresponding ammonium salt, except that 13 g. of potassium persulfate and 250 ml. of boiling saturated potassium nitrate solution were substituted for the ammonium persulfate and ammonium nitrate solution, respectively. A 70% yield was obtained. The well-formed dark brown cubic crystals showed a marked change of solubility with change in temperature. The product was recrystallized four times from hot water containing a few drops of sulfuric acid and a pinch of potassium persulfate per 100 ml. *Anal.* Calcd. for $K_7[Co^{+2}Co^{+3}W_{12}O_{42}]\cdot 16H_2O$: K, 7.69; Co(total), 3.32; Co(tervalent), 1.66; W, 62.1; H_2O, 8.10. Found: K, 7.74; Co(total), 3.43; Co(tervalent), 1.81; W, 61.8; H_2O, 8.17. The salt may also be prepared by a lead dioxide oxidation analogous to that described under preparation "C."

E. **Rubidium 12-Tungstocobaltocobaltiate (Anion II).**—A sodium persulfate solution was prepared by passing 200 ml. of a solution containing 15 g. of ammonium persulfate through a cation-exchange column (sodium cycle Amberlite IR-120). A solution of the sodium salt of anion I, made exactly as described in preparation "A," was oxidized by 1.5 times the theoretical quantity of this sodium persulfate. The oxidation procedure was as given in preparation "C." The resulting dark brown solution contained the extremely

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[10] A. Rosenheim, *Z. anorg. Chem.*, **96**, 164 (1916).

[11] P. C. L. Thorne and E. R. Roberts, "F. Ephraim's Inorganic Chemistry," 4th Ed., Interscience Publishers, Inc., New York, N. Y., 1947, p. 507.

[12] J. C. Bailar, Jr., and J. B. Work, THIS JOURNAL, **67**, 176 (1945).

soluble sodium salt of anion II. Nine g. of rubidium sulfate, in hot saturated solution, was added for every 150 ml. of the brown solution. Upon cooling, dark brown cubic crystals separated. The yield was 70% based on rubidium. The salt was recrystallized once from very dilute acetic acid and air-dried. *Anal.* Calcd. for $Rb_7[Co^{+2}Co^{+3}W_{12}O_{42}]\cdot 17H_2O$: Rb, 15.3; Co(total), 3.02; Co(tervalent), 1.51; W, 56.6; H_2O, 7.85. Found: Rb, 15.1; Co(total), 3.20; Co(tervalent), 1.42; W, 56.4; H_2O, 8.13.

F. **Cesium 12-Tungstocobaltocobaltiate (Anion II).**—A brown solution of the sodium salt of anion II was prepared as described in preparation "E," above. Two g. of cesium sulfate in 5 ml. of hot water was added to each 30 ml. of the brown solution. The very dark brown cubic crystals which separated represented an 85% yield based on cesium. They were recrystallized twice from very dilute acetic acid. The compound did not exhibit so great a change of solubility with temperature as did the other salts of anion II. *Anal.* Calcd. for $Cs_6H[Co^{+2}Co^{+3}W_{12}O_{42}]\cdot 13H_2O$: Cs, 19.8; Co(total), 2.93; Co(tervalent), 1.47; W, 54.8; H_2O, 6.04. Found: Cs, 19.5; Co(total), 3.23; Co(tervalent), 1.47; W, 54.9; H_2O, 6.00.

G. **Potassium 12-Tungstocobaltoate (Anion III).**—Twenty g. of recrystallized potassium 12-tungstodicobaltoate was dissolved in 100 ml. of 1 *M* hydrochloric acid. The solution was evaporated on the steam-bath until green needle-like prisms began to form. The solution was filtered hot and cooled in the ice-box. Green prisms separated and were filtered off. A second crop was obtained by evaporating off one-third of the mother liquor. A 70% yield was obtained. The green prisms were extremely soluble. They exhibited marked change of solubility with temperature. Crystals 2 cm. in length could be grown easily. The sample used for analysis was recrystallized three times from water. The crystals contained no chloride. *Anal.* Calcd. for $K_5H_5[Co^{+2}(W_2O_7)_6]\cdot 16H_2O$: K, 5.70; Co, 1.72; W, 64.4; H_2O, 9.74. Found: K, 6.07; Co, 1.90; W, 63.8; H_2O, 9.87.

H. **Potassium 12-Tungstocobaltiate (Anion IV).**—Seventy-five g. of potassium 12-tungstodicobaltoate was dissolved in 80 ml. of 2 *M* sulfuric acid. While this solution was boiling, solid potassium persulfate was added in small amounts. The green color became progressively lighter, changing through light emerald green to light brownish yellow. During the oxidation, no dark colored stage was observed.[13] Upon cooling, light yellow needle-like prisms separated. These were filtered off. A second crop, containing small amounts of impurities, was obtained from the cold mother liquor by stirring in solid potassium chloride as long as it would dissolve readily. (Chloride reduces anion IV in hot solution.) The total yield was about 90% of theoretical. The product was recrystallized once from water, washed with 95% ethanol and air-dried. The crystals contained no chloride. *Anal.* Calcd. for $K_4H_5[Co^{+3}(W_2O_7)_6]\cdot 18H_2O$: K, 4.57; Co(total), 1.72; Co(tervalent), 1.72; W, 64.5; H_2O, 10.8. Found: K, 4.60; Co(total), 1.91; Co(tervalent), 1.79; W, 64.5; H_2O, 10.5.

Analytical Procedures.—Tervalent and total cobalt determinations were made by the method of Sarver, as modified for the purpose.[14,15] Alkali metals were determined by weighing the platinum derived from their chloroplatinates.[16] The cesium analyses were also checked on separate samples by weighing cesium chloroplatinate.[17] Nitrogen was estimated by the Kjeldahl method.

Tungsten was weighed as its trioxide. Each complex was decomposed by sodium hydroxide and any ammonia present was boiled off. Tungstic acid was then precipitated by hot hydrochloric acid. Addition of cinchonine hydrochloride ensured complete precipitation.[18] When cesium was present, it was necessary to dissolve the precipitated tungstic oxide and reprecipitate it.

Water was determined directly in potassium 12-tungstodicobaltoate and in cesium 12-tungstocobaltocobaltiate. In the other salts it was determined by difference.

TABLE I

SOLUBILITIES OF SALTS IN PURE WATER AT 28° AND *p*H OF EACH SATURATED SOLUTION[19]

Salt	*p*H of satd. soln.	*M* of satd. soln.,	Solubility: g. solute per 100 ml. soln.
$(NH_4)_8[Co^{+2}Co^{+2}W_{12}O_{42}]\cdot 20H_2O$	7.00	0.0151	5.29
$K_8[Co^{+2}Co^{+2}W_{12}O_{42}]\cdot 15H_2O$	7.00	.00880	3.15
$(NH_4)_7[Co^{+2}Co^{+3}W_{12}O_{42}]\cdot 19H_2O$	6.50	.0101	3.50
$K_7[Co^{+2}Co^{+3}W_{12}O_{42}]\cdot 16H_2O$	6.78	.0101	3.60
$Rb_7[Co^{+2}Co^{+3}W_{12}O_{42}]\cdot 17H_2O$	6.68	.00154	0.601
$Cs_6H[Co^{+2}Co^{+3}W_{12}O_{42}]\cdot 13H_2O$	6.52	.00173	0.696
$K_5H_5[Co^{+2}(W_2O_7)_6]\cdot 16H_2O$	0.18[19]	1.34	460.
$K_4H_5[Co^{+3}(W_2O_7)_6]\cdot 18H_2O$	1.13[19]	0.204	70.0

Interconversions.—The powder X-ray pattern was obtained for each of the salts mentioned above. Interconversions of compounds, corresponding to every arrow in the reaction scheme given in the Introduction, were carried out. The products were identified by their powder X-ray patterns and, in several cases, by chemical analyses also.

Anions II and IV may be reduced extremely easily, to form anions I and III, respectively. Care must be exercised since even dust or, on standing, filter paper can cause partial reduction. Sulfur dioxide may be used for quantitative reduction of the cobaltic compounds.

The conversion of anion III into anion I was always accompanied by the precipitation of large amounts of insoluble tungstates. According to the reaction scheme cited in the Introduction, this conversion must proceed through the partial decomposition of anion III and elimination of the excess tungstate. The conversion was brought about by adding a hot acidic solution containing anion III to a hot solution of ammonium acetate or to a cold solution of ammonium carbonate. Much ammonium tungstate precipitated. After several recrystallizations, the ammonium salt of anion I was obtained. The presence of ammonium ion greatly facilitates this conversion.

In accordance with the reaction scheme, the other transformations, without exception, took place quantitatively and without formation of by-product tungstates.

Addition of a moderate amount of strong acid to a solution of I or II resulted in production of anions III and IV, respectively, plus cobaltous ions. However, neutralization of the resulting solutions did not bring about the reverse reactions.

Free Acids.—The free acid of anion III was obtained by passing a solution of the ammonium salt of anion I through a cation-exchange column containing Amberlite IR-120 in the hydrogen cycle.[8,9] The green, strongly acidic effluent was preserved for a year. However, some decomposition occurred while the liquid was in contact with the resin. In consequence, the effluent contained tungstate ions. Much cobalt, primarily from the anion conversion, was retained by the resin. Analysis of the liquid showed an atomic Co:W ratio of about 1:16. Addition of the effluent to potassium bicarbonate resulted in formation of the prisms of potassium 12-tungstocobaltoate, which was identified by its X-ray pattern. The solution of the free acid was evaporated in a cellophane tube placed in a current of warm air, so as to minimize decomposition. Eventually a viscous liquid remained in which green cubes appeared after some days. Some of the crystals measured 3 mm. on an edge. The material was probably the free acid, but it could not be purified because of its extraordinary solubility (see Introduction). The liquid deposited WO_3 slowly and the solid decomposed, forming WO_3. The atomic Co:W ratio in the solid was about 1:16.

Oxidation by hot persulfuric acid of a solution of the

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[13] A. F. Wells, "Structural Inorganic Chemistry," First Ed., Oxford University Press, New York, N. Y., 1945, p. 231–233. See also: Second Edition, 1950, p. 217–218.

[14] L. C. W. Baker and T. P. McCutcheon, *Anal. Chem.*, **27**, 1625 (1955).

[15] L. A. Sarver, *Ind. Eng. Chem., Anal. Ed.*, **5**, 275 (1933).

[16] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Revised Ed., the Macmillan Co., New York, N. Y., 1946, p. 411–413.

[17] W. W. Scott, "Standard Methods of Chemical Analysis," (Edited by N. H. Furman), 5th Ed., Vol. I, D. Van Nostrand Co., New York, N. Y., 1939, pp. 869–870, 897.

[18] R. B. Moore, *et al.*, "Analytical Methods for Certain Metals," Bureau of Mines Bulletin, U. S. Dept. of Interior, 1923, p. 158–159.

[19] The *p*H values were determined with a glass-electrode *p*H meter. The results for the concentrated solutions of the salts of anions III and IV indicate only that the solutions are very acidic.

green acid of anion III gave a yellow solution containing both sulfuric acid and the acid of anion IV.

Other Ion-exchange Experiments.—A solution of the ammonium salt of anion I was passed through a column of cation-exchange resin (Amberlite IR-120) in the potassium cycle. The neutral green effluent gave no ammonia test with Nessler reagent, and did not decompose on boiling. When the column was regenerated, the used regenerant contained much ammonium and cobaltous ions. Evaporation of the effluent produced in it an extremely soluble, apparently homogeneous, green solid of no detectable crystal shape. The separate particles resembled irregularly broken pieces of clear green glass. It is supposed that this was the normal potassium salt of anion III. Addition of acetic acid to a very concentrated solution of this neutral green material caused immediate formation of green prisms, which were identified, by X-ray pattern, as the potassium acid-salt of anion III already described.

The green color of anion III was not noticeably destroyed when a solution stood for a year in contact with cation-exchange resins in either the potassium or hydrogen cycles.

Other Reactions Pertinent to Formulation

A number of experiments was performed in order to show that all of the cobalt in salts of anions I and II is in the heteropoly complexes, rather than being in part cationic, as for example: $(NH_4)_8Co[CoW_{12}O_{42}]\cdot 20H_2O$. The dark color of anion II, which persists even in very dilute solution, is in itself excellent evidence for the existence of the two cobalt atoms, in differing oxidation states, within the same complex.[13]

Reactions of Anions I and II with Acid.—Cinchonine hydrosulfate precipitated anion I quantitatively from a neutral solution of its ammonium salt. The precipitate was blue. The filtrate contained ammonium sulfate and was colorless. Only a trace of cobalt could be detected in the colorless filtrate by sensitive tests. The experiment was repeated, using a solution of the ammonium salt of anion I to which a very little acetic acid had been added. The filtrate was again colorless, but tests revealed that it contained much more cobalt than had been the case in the unacidified experiment. When the experiment was repeated with the addition of more acetic acid, the color of cobaltous ion was observed in the filtrate. Substitution of concentrated hydrochloric acid for the acetic acid resulted in a filtrate which contained much cobaltous ion and the precipitate was green. The green precipitate was also produced when cinchonine hydrosulfate was added to a strongly acidified solution of the purified potassium salt of anion III; but the filtrate then contained no cobalt.

An entirely analogous set of experiments was made, using cinchonine hydrosulfate and solutions of anion II, acidified to varying extents. Cobalt was almost undetectable in the neutral filtrate. When precipitations were made at progressively lower *p*H's, the amount of cobalt in the filtrate increased markedly. The cinchonine salt of anion II was light brown. When a large amount of a weak acid or a moderate amount of a strong acid was added, the solution of anion II immediately changed from dark brown to light yellow (anion IV). Cinchonine hydrosulfate then produced a light yellow precipitate and a filtrate colored pink by cobaltous ion. Addition of cinchonine hydrosulfate to a solution of the recrystallized potassium salt of anion IV produced the light yellow precipitate, but cobaltous ion was absent from the filtrate.

Entirely analogous results were obtained when the heteropoly anions were precipitated with various other cations, such as barium. In the latter case, the crystal forms and solubilities of the various precipitated salts were also clearly different.

Electrolysis Experiments.—The stability of anion I in neutral solution and the effects of acid on that anion were confirmed by a series of electrolyses of neutral and acidified solutions of 12-tungstodicobaltoate.

In the first experiment about 4 g. of the ammonium salt of anion I was dissolved in about 30 cc. of pure hot water. This neutral solution was mixed with an equal volume of hot 5% agar-agar solution. Some of the resulting green mixture was placed in a U-tube, filling it to about one-third of its height. After chilling had jelled the agar-agar, the arms of the U-tube were almost filled with a colorless agar-agar solution containing potassium nitrate. When this had also jelled, a little potassium nitrate solution was placed above each column of gel and platinum electrodes were inserted therein. A d.c. potential of approximately 65 volts was applied. The U-tube was surrounded by ice-water. When the current acted on this neutral solution for three hours, the green anion moved to the anode, but there was no evidence of the liberation of cobaltous ion.

Other experiments were performed in exactly the same way except that the water used to dissolve the heteropoly salt was first acidified. In one experiment 0.5 cc. of glacial acetic acid was used for that purpose. After electrolysis for two hours, the green complex had all started to move toward the anode while a very small band of pink cobaltous ion was moving toward the cathode through the clear potassium nitrate–agar-agar gel. After 3.5 hours the front of the trace of cobaltous ion had encountered the front of hydroxyl ion, moving from the cathode where it had been generated. A tiny band of pink cobaltous hydroxide was precipitated in the gel.

When 1.5 cc. of glacial acetic acid was used to acidify the solution, the electrolysis produced analogous results, except that the very small band of cobaltous ion which appeared was obviously larger than in the previous experiment. As the amount of added acid was increased in successive experiments, the band of cobaltous ion became wider and more deeply colored.

The effect of acid on anions I and II, taken with the high relative solubilities of salts of anions III or IV, accounts for the fact that the analyses for bivalent cobalt were a little high. Acid was added in the recrystallization procedures for the cubic salts to prevent precipitation of traces of impurities which otherwise appeared. In consequence, cobaltous ions were released. These uncomplexed cobaltous ions apparently replaced, in trace amounts, some of the alkali ions in the crystals. The interpretation of these discrepancies in the bivalent cobalt analyses is interesting, but the discrepancies themselves are small from the standpoint of determining the atomic ratios.

The potassium salt of anion III can be precipitated from concentrated solution by addition of 12 *M* HCl. This fact supports the tentative assignment of acid-salt formulas to these salts. The high solubilities of the salt and its anion IV analog, as well as the low *p*H of the saturated solutions, also support acid-salt formulation.

The Oxidation States of Cobalt in the Complexes.—Salts of anions I and III gave only blue or pink precipitates when decomposed by sodium hydroxide. This cobaltous hydroxide dissolved in hydrochloric acid without liberating chlorine (oxygen being excluded from the system). The dark color of anion II is excellent evidence for the presence of cobalt in two oxidation states in the same complex.[13] It has been shown above that salts of anion II produce, upon acidification, simple cobaltous ions plus a complex containing only tervalent cobalt. The method of analysis employed for total and tervalent cobalt[14] is also sufficient to establish the oxidation states assigned to cobalt in anions II and IV.

Solutions containing anions I or III all reflect green light and transmit red light.

Crystallographic Data

Goniometer and Polarizing Microscope.—The angles between the non-parallel faces of a crystal of the ammonium salt of anion I were measured with a goniometer and all were found to be 90°. A little water, slightly acidulated with acetic acid, was saturated with the same salt at room temperature. The solution was heated to 100° and a small additional amount of the salt was dissolved in it. The solution was poured onto a microscope slide. A cover glass was placed on the solution as crystallization began. Under the polarizing microscope the crystals which appeared gave complete extinction when the microscope's planes of polarization were at right angles. After two hours the crystals were larger and still gave complete extinction. By this time the solution was cold and the crystals were no longer growing rapidly with decreasing temperature. They were growing slowly as solvent evaporated around the edges of the cover glass. Three hours later each crystal, still immersed in mother liquor, gave a distinct pattern, rather than extinction, when the planes of polarization were at right angles. Edges of this centrosymmetric pattern, for each square crystal face, consisted of the diagonals of the face and lines joining mid-points of opposite edges. The pattern suggests a tetragonal or orthorhombic crystal form. Apparently isometric crystals grow from hot solution; but, at lower temperatures, these either invert to a form of lower symmetry or become covered with a non-isometric overgrowth which crystallizes from solution at room temperature (see below).

X-Ray Data.—Pure samples of the ammonium and the potassium salts of anion I and of anion II were recrystallized from hot solution. The crystals were filtered off when they had been in the mother liquor for less than an hour. The four samples were finely ground and passed through a 200-mesh screen. The powder diffraction patterns were taken with a General Electric XRD-3 Geiger Counter X-Ray Spectrometer, employing a copper target and a nickel oxide filter. In each case, there were no lines between Bragg θ = 0.1° and the first, strongest line of the pattern. The first line of the ammonium salt of anion I was examined using the highest resolving power of the spectrometer, and was thereby shown to be a single line. The four salts produced typical simple cubic patterns. The first 22 lines of each, corresponding to $h^2+k^2+l^2$ values up to 25, were indexed. The lengths of the unit cell edges were: 11.1 Å. for the ammonium salt of anion I; 10.7 Å. for the potassium salt of anion I; 11.0 Å. for the ammonium salt of anion II; and 10.7 Å. for the potassium salt of anion II. The measurements justify the use of only three significant figures in reporting these values, but the relative diffraction angles for the higher lines make it clear that the cell edge for the potassium salt of anion II is longer, by a few hundredths of an Ångström unit, than is the cell edge for the potassium salt of anion I. Measurement of the pycnometer densities on the same samples revealed that each unit cell contained one formula of the salt.

An unsaturated, slightly acidulated solution of the ammonium salt of anion I was evaporated in a desiccator at room temperature. In the course of a few days moderate size crystals grew, none of which was a cube, although the angles between the faces were 90°. Rotation and Weissenberg X-ray diffraction patterns were taken of one of these crystals. These revealed a tetragonal unit cell, 11.4 × 11.4 × 10.4 Å. (see polarizing microscope expt., above). No chemical analysis of the tetragonal crystals was made. They probably represent a different hydrate or an acid-salt.

Structural Argument

Since the effect on polarized light is primarily controlled by the valence electrons in the structure, the experiment with the polarizing microscope reveals that the oxygen atoms are arranged with cubic symmetry in the crystals which grow from hot solution. These extinction experiments are much more sensitive to very slight general deviations from cubic symmetry than are the powder X-ray patterns. On the other hand, the X-ray patterns are sensitive to the positions of the atoms of high atomic number and therefore reveal, primarily, that the tungsten atoms are arranged according to the requirements of simple cubic symmetry, in cells containing twelve tungsten atoms apiece. The chemical evidence shows that two cobalt atoms are associated with the twelve tungstens. While two lone cobalt atoms would be virtually undetectable, by X-ray means, in the presence of the 1450 to 1550 atomic number units in the cell, the chemical evidence has shown clearly that these cobalts are complexed in tungstate groups; and any such complex group would, of course, be easily detectable. Therefore, it is a safe assumption that the cobalt atoms also must be placed in accordance with the requirements of cubic symmetry. Further, the ionic radius and well-known chemical properties of cobalt make it virtually certain that the cobalt atoms are at the centers of CoO_6 octahedra.[20] The results with polarized light require that each of these octahedra be arranged as a unit, compatibly with cubic symmetry. This can be done only if one CoO_6 octahedron is at the center of the cell, with its eight octahedral faces oriented toward the eight cell verticles, while the cell has a one-eighth interest in the cobalt atom within each of eight other CoO_6 octahedra which are at the cell vertices. The latter CoO_6 octahedra are so oriented that a body diagonal of the cube pierces the mid-point of a face of each of them. These stipulations follow from the fundamental requirement that each of the four body diagonals of a cubic unit cell must be an axis of threefold symmetry with respect to each atomic species present.

The arrangement of the tungsten atoms about the central cobalt must be different from the total tungsten arrangement about a cobalt at the vertex. If these arrangements were the same, a body-centered cubic cell with respect to cobalts and tungstens would result. The X-ray patterns were unambiguously simple cubic.

If, for the central CoO_6 octahedron, one set of four tetrahedrally related faces[22] be designated "Set C-1" and the other four faces of the CoO_6 be designated "Set C-2," it is evident that the arrangement of tungstens over each of the four Set C-1 faces must be identical in order to preserve threefold symmetry about the cube's body diagonal. Similarly, the arrangement of tungstens over each of the four Set C-2 faces must be identical with one another, although not necessarily the same as the arrangement over each Set C-1 face. In the same way, the two sets of tetrahedrally related faces of each vertex CoO_6 octahedron may be designated "Set V-1" and "Set V-2." By the same reasoning, the tungsten arrangement over each V-1 face must be identical. The tungsten arrangement over each V-2 face must be identical to that over any other V-2 face, but need not be the same as the arrangement over a V-1 face.

The only possibilities for dividing the twelve tungsten atoms between the various sets of faces of the central and vertex CoO_6 groups, while preserving the restrictions in the preceding paragraph, are as summarized in Table II.

TABLE II

POSSIBLE ARRANGEMENTS OF 12 TUNGSTENS OVER THE FACES OF THE CoO_6 OCTAHEDRA

Arrangement no.	Central CoO_6 octahedron		Vertex CoO_6 octahedron	
	Set C-1	Set C-2	Set V-1	Set V-2
1	4 Groups of 1 W	None	4 Groups of 2 W	None
2	4 Groups of 1 W	None	4 Groups of 1 W	4 Groups of 1 W
3	None	None	4 Groups of 1 W	4 Groups of 2 W
4	None	4 Groups of 3 W	None	None

Interchanging the headings of the main columns in Table II does not give another set of possibilities because the choice of which CoO_6 was central and which at the vertex was arbitrary. (With respect to cobalts, the structure consists of two simple cubic translation lattices. Any cobalt is at the center of a cube, the vertices of which are occupied by cobalts of a different type.) Similarly, interchanging the headings of the subcolumns does not give more possibilities because the selection of sets of tetrahedrally related faces is also arbitrary.

It will be shown below that only a subcategory of Arrangement Number 4 (Table II) is possible for the compounds under consideration.

Before examining the four possible arrangements listed in Table II, the safe assumption must be made that the tungsten atoms are at the centers of WO_6 octahedra. This octahedral packing is clearly indicated by the radius ratio and has been found in all heteropoly tungstates subjected to X-ray investigation. It has also been found in all tungstates and molybdates crystallized from neutral or acidic solutions. The WO_6 octahedra must, of course, share corners and/or edges with one another and with the CoO_6 groups, so that the correct total number of oxygen atoms will be involved.

Remembering that the arrangement over each face of each CoO_6 octahedron must preserve threefold symmetry about the cube's body diagonal, it will be seen that any group containing only one tungsten (Arrangement no. 1, 2, or 3; Table II) must be so placed that the tungsten atom lies on the cell's body diagonal, and the oxygens about it must be so arranged that the body diagonal pierces the mid-points of two parallel faces of the WO_6 octahedron. Similarly, when groups of two tungstens are considered (Arrangement

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(20) Magnetic measurements have revealed the existence of such CoO_6 groups in the 6-molybdocobaltiate ion.[4,5,21]

(21) P. Rây, A. Bhaduri and B. Sarma, *J. Indian Chem. Soc.*, **25**, 51 (1948).

(22) Two imaginary tetrahedra may be envisioned within an octahedron. One tetrahedron is formed by joining the mid-points of four of the octahedron's eight faces. This designates one "set of tetrahedrally related faces." The other interior tetrahedron is formed by joining the mid-points of the remaining four faces of the octahedron. Those four faces comprise the other set.

TABLE III

SUBDIVISIONS OF ARRANGEMENT NO. 4: TRIGONAL GROUPINGS OF THREE WO_6 OCTAHEDRA

Grouping	Arrangement of 3 WO_6 octahedra	Formula of grouping	Axis of trigonal symmetry	Remarks
a	Sharing 3 faces	W_3O_{12}	Through W's	No distortions required
b	Sharing 3 edges. 2 edges of one face of each octahedron are shared. All 3 octahedra share a common vertex which is one end of each of the shared edges. The planes of all the faces of each octahedron are parallel to planes of faces in the others	W_3O_{13}	Through the common O, equidistant from each W	No distortions required
c	Sharing 3 edges. For each octahedron 2 edges, having a common vertex but not bounding the same face, are shared. The common vertex is also common to all 3 octahedra. The shared edges lie in nearly the same plane	W_3O_{13}	Through the common O, equidistant from the outer ends of the shared edges	Moderate distortion from perfect octahedra has eliminated 3 O's and made edge sharing possible
d	Sharing 3 vertices. Each octahedron has 2 ends of one edge shared	W_3O_{12}	Through the mid-point of the triangle formed by the edges which have shared ends. Normal to the plane of that triangle	No distortion required or slight distortion from perfect octahedra, depending upon how applied

1 or 3; Table II), one must envision a W_2O_9 unit consisting of two WO_6 octahedra sharing one face. The tungsten-tungsten axis therein must coincide with the cube's body diagonal.

When the groups of 1W (WO_6) or groups of 2W (W_2O_9) are considered (lying on the cell's body diagonal between the central and vertex CoO_6 units), they may be envisioned as independent units or as sharing an octahedron's face with either or both of the CoO_6 octahedra. Space does not permit a detailed analysis of each of the possible structures which results. Suffice it to say that each may be eliminated easily as a possibility for the structure of the salts. Several of the following reasons apply in each case: (1) the length of the cube's body diagonals would be far from that observed, (2) the numbers of oxygen atoms required would be far from that possible, (3) some of the structures would be body-centered cubic, (4) many octahedra would be required to share faces. Sharing of faces between WO_6 octahedra has not been observed in any poly tungstates which have been investigated. A structure which involves many shared faces is extremely improbable. Further, the structures involving Arrangements no. 1, 2 and 3 (Table II) would, in most cases, indicate very different chemical properties from those observed.

Arrangement no. 4 involves more possibilities than any of the other arrangements listed in Table II because there are several ways for three WO_6 octahedra to form groups having an axis of threefold symmetry. However, consideration may only be given to groupings which can attach to the triangular face of a CoO_6 octahedron (by sharing edges, corners, and/or faces) in such a way that the group's axis of trigonal symmetry is normal to the midpoint of that face. These trigonally symmetric groupings containing three tungstens are all listed in Table III.

Grouping "a" is easily eliminated on the same grounds mentioned above for Arrangements no. 1, 2 and 3. No matter which of the remaining groupings is utilized, it will be seen that the placement of tungsten atoms about the central CoO_6 will be the same, in main features, as the placement of the twelve tungstens about phosphorus in the structure which Keggin,[23–25] Hoard,[26] and others[7,27–29] have elucidated for the 12-tungstophosphate anion and related complexes. The placement of the oxygen atoms, however, must be distinctly different.[9]

When grouping "b" is used, the complex assemblage can only involve 38 oxygen atoms. The symmetry of the arrangement practically prohibits distortion to allow introduction of more oxygens. To utilize this grouping one of the cobalts would have to be in cubic coördination with four tetrahedrally arranged oxide ions and four oxygens from four tetrahedrally adjacent complex ions. That is extremely improbable.

When grouping "c" is applied, the central complex involves 46 oxygen atoms. The assemblage would satisfy the requirements only if one envisions the corner cobalt as an uncoördinated simple cobaltous ion and also considers that four of the water molecules are really part of the complex. The four oxygens needed to reconcile the structure with the analysis are thus provided, but eight hydrogens are also provided which cannot be symmetrically attached to outer points on the complex. The arrangement seems unlikely. It might be expected to produce independent cobaltous ions in solution. If the cobaltous ion is coördinated to the tungstate complex in solution, it is reasonable to expect it to remain coördinated in the crystal.

Grouping "d" may be applied in three ways (**x**, **y** and **z**). Application **y** seems highly probable, but it is most easily visualized if the improbable application **x** is described first. In application **x**, the central CoO_6 is taken as being the same size as each WO_6 octahedron and trigonal grouping "d" is placed over each of the "C-2" set of faces without distortion of octahedra. A structure is obtained wherein the six oxygens of the central CoO_6 coincide with the inner vertices of six faces which are being shared between adjacent W_3O_{12} groups. The whole complex group contains 42 oxygen atoms. Therefore the cobalts at the cube's vertices would have to be simple cobaltous ions. The structure is improbable for that reason and also because of its six shared faces. Its dimensions are within acceptable limits.

Application **x** can be converted to application **y** by distorting WO_6 octahedra, thereby converting each shared face to a shared edge (the inner end of which coincides with one of the oxygens of the central CoO_6). The required distortion may be made in such a way that it is distributed over all of the WO_6 octahedra, each being distorted only slightly. The directions of the distortions are such that the perfect application of the rules of cubic symmetry is not disturbed. The central complex involves 48 oxygens and has three vertices sharply projecting over each of one set of the complex's tetrahedral faces. These three oxygens could, in each case, be shared with a vertex CoO_6. Consider a vertex CoO_6. One of its faces, say of set "V-1," is thus attached to the complex at the center of an adjacent cell. However, the vertex CoO_6 forms a corner of eight adjacent cells. The "V-1" faces are oriented toward the centers of four of these cells while the "V-2" faces are oriented toward the other four. The vertex CoO_6 must be attached in the same way to complexes over each of its "V-1" faces. If the grouping is applied as stated, this CoO_6 would be unattached to the complexes over its "V-2" faces. Since each oxygen of the vertex CoO_6 is therefore shared between two complexes, the net formula involves 42 oxygen atoms per cell. The length of the cube's diagonal would be correct. When the

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

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

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

[26] J. L. Hoard, *Z. Krist.*, **84**, 217 (1933).

[27] J. de Almeida Santos, *Rev. Faculdade Cienc., Univ. Coimbra* (*Coimbra, Portugal*), **16**, 5 (1947).

[28] O. Kraus, *Z. Krist.*, **91**, 402 (1935); **93**, 379 (1936).

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

crystal dissolved, the cobalt atom at the vertex of the cell might remain coördinated to one of the corners of the complex at three points while coördinating to water molecules at the other three. If, upon dissolving, each complex remained joined to one vertex cobalt, each complex would have to take up six oxygens during the dissolving process to replace the deficiency caused by elimination of the sharing of oxygens between complexes. These six oxygens might be supplied by water molecules. The twelve hydrogens from these waters could be symmetrically distributed over projecting oxygens over one or another of the central CoO_6's sets of faces. In one case this would imply that the exterior cobalt would become attached through a triol bridge. Strong acid might be expected to disrupt such bonds irreversibly. Oxidation of such an exterior cobalt should be exceedingly difficult.

Finally, arrangement z, based on trigonal grouping "d" may be considered. If the shared edges in the preceding structure are opened out, forming six shared vertices, the complex satisfies the symmetry requirements, with no distortions of octahedra. It involves an unreasonably big octahedral hole in the center of the complex. The complex, containing no shared edges, has 54 oxygen atoms. Possibilities involving this structure may be worked out by adding water molecules to the complex together with some sharing of oxygen between complexes. However, most of these possibilities involve more water than was found in the stable hydrate of the cesium salt of anion II. The others are relatively improbable sterically.

To return to the most acceptable arrangement, y: there are spaces, over the unit cube's faces, just adequate for the cations and waters of hydration. The differences between water molecules, ammonium ions and potassium ions in size and in diffractive power for X-rays would be very slight in these crystals. Strictly speaking, the salts are probably not simple cubic, of the indicated cell sizes, with respect to alkali cations unless perhaps these are distributed statistically throughout the six available places per cell throughout the crystal.

The reader is reminded that a symmetry argument, interesting, revealing and useful as it may be, is far from a complete X-ray proof of structure. It necessarily relies on the correctness of the chemical analyses.

Additional Discussion

According to any of the reasonable structural interpretations, anions I and II represent structures wherein *given* WO_6 octahedra are simultaneously attached to two "central atoms." These complexes are the first polynuclear heteropoly anion structures, of those elucidated on modern bases,[4,5,6,30,31] wherein such a type of linkage seems clearly required. Anion II is the first binuclear heteropoly complex discovered in which the two "central atoms" are not of the same oxidation state.

Anion I may also be considered as a dimeric 6-heteropoly tungstate complex. As such, its novel properties reinforce the contention that no single structural model represents 6-heteropoly tungstates and molybdates.[4,5] Anions III and IV represent tentative new additions to the list of complexes formulated $[X^{+n}O_6(\text{Mo or W})_{12}O_{36}]^{-(12-n)}$, to which the 12-molybdo anions of tetravalent cerium and thorium belong.[9]

The acid-salt formula of the cesium salt of anion II provides an additional interesting example of the effect previously elucidated by Santos,[6,7] who showed that steric factors force the crystallization of certain cesium derivatives of heteropoly anions in acid-salt form. In the present case the acid-salt formula is strongly supported by the solubility and *p*H data in Table I. (The solubilities of all salts of anions I and II are greater in acid solution.) The water analysis excludes the possibility that the salt contains a sodium ion.

The exterior cobaltous atom could be removed easily from anion I by a cation-exchange resin, while the interior cobaltous atom was largely unremoved when the solution stood in contact with the resin for over a year. When the 6-molybdo anions of tervalent Co, Cr, Fe or Al were passed slowly through a bed of exchange resin, little removal of "central atom" occurred[8]; but each of these complexes decomposed completely upon standing with the resin for a few days.[8] All these results are clearly consistent with the degrees of enclosure or exposure of the "central atoms" in the various structures proposed,[4,5] and the consequent equilibria expected in the solutions.

Further investigation of the complexes herein described, including preparations, magnetic measurements and single crystal X-ray work, is in progress. The formulations of anions III and IV are tentative, being based on analysis of only one derivative in each case.

Acknowledgments.—The authors are indebted to Dr. A. L. Patterson for generous aid and advice concerning the X-ray interpretations and to Dr. John F. Dowdall for preliminary preparative work on anion III.

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