[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Complex Sulfates Containing Tri- and Pentavalent Columbium and the Possibility of Their Use in the Purification of Columbium

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The electrolytic reduction of columbium in sulfuric acid solution has been reported by several investigators[1,2,3,4] but no well-defined compounds have been isolated from the reduced solutions. Ott[1] prepared a red compound which was given a possible formula $(NH_4)_2SO_4 \cdot Cb_2(SO_4)_3 \cdot H_2SO_4 \cdot 6H_2O$ and Kiehl, Fox and Hardt[3] observed the separation of a red crystalline compound to which they gave tentative formulas $4K_2O \cdot Cb_2O_5 \cdot 2Cb_2O_3 \cdot 12H_2SO_4 \cdot 12H_2O$ and $4K_2O \cdot Cb_2O_5 \cdot 2Cb_2O_3 \cdot 13H_2SO_4 \cdot 16H_2O$.

The work reported here concerns the reduction of columbium in sulfuric acid solution, the preparation of crystalline complex sulfates containing trivalent and pentavalent columbium, and by means of these compounds the purification of columbium, that is, its separation from small amounts of tantalum.

A solution of 75% sulfuric acid containing 2.8% columbium was used for the electrolysis. Its preparation will be described later. Solutions of greater columbium content can be prepared with more concentrated acid and an attempt to use 80% sulfuric acid was made but reduction of sulfate was found to occur.

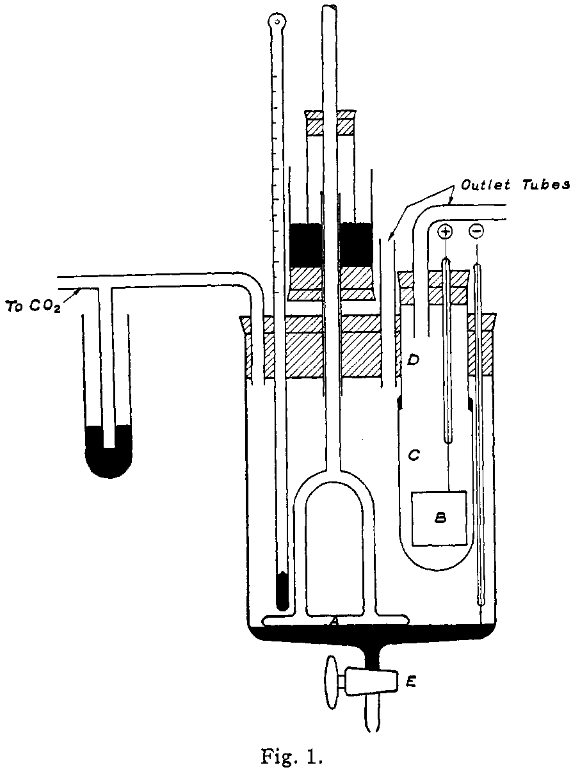

Fig. 1.

The apparatus employed for the electrolytic reduction of the columbium in the presence of carbon dioxide is shown in Fig. 1. It consisted of a 400-ml. glass cylinder, to which was fitted tightly a large rubber stopper. A mercury seal stirrer was so adjusted that a cross bar (A) 49 mm. long just touched a pool of mercury, 42 sq. cm. in area, which served as the cathode. The anode was a platinum plate B, 17 mm. sq., which was contained in a porous cup C, 25 mm. in diameter. The latter was cemented to a glass tube D, which passed through the rubber stopper. A stopcock (E) served to drain the mercury, and the mixture of solution and precipitated crystals containing lower valence columbium at such a rate that the withdrawal was complete before the anode solution had seeped through the porous cup.

Preparation of Complex Sulfates Containing Columbium in an Average Oxidation State of 3.67.—For each run about 350 g. of solution was used: adequate stirring was necessary, and the mixture was kept at 5 to 10° throughout to prevent hydrolysis. A current density of 0.017 ampere per cm.^{2} was employed. The solution first assumed a blue color which turned to red-brown after about six hours, and red-brown needle-like crystals precipitated (Fig. 2). After ten hours there appeared to be no further change in the mixture. Titration of samples of the crystals and solution with permanganate showed that the columbium had reached an average oxidation state of 3.7 and further reduction was proceeding very slowly. Determinations of the columbium content of the solution showed only about 5 to 10% of the total.

The crystals were very soluble in all solvents investigated which were miscible with 75% sulfuric acid. They could be washed, however, with 95% sulfuric acid and the latter removed with ether. From the analyses for columbium and sulfate given in Table I an empirical formula $HCb_3(SO_4)_6 \cdot xH_2O$ was assigned which contained two trivalent columbium atoms and one pentavalent atom. The washing with concentrated sulfuric acid prevented the amount of water associated with the compound from being obtained.

Salts of the alkali metals and ammonium were much more stable than the free acid. They were prepared by mixing sulfuric acid solutions of the reduced columbium with sulfuric acid solutions of the alkali sulfates. About 50 g. of the electrolytic reaction mixture was dissolved in

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(1) Ott, *Z. Elektrochem.*, **18**, 349 (1912).

(2) Kiehl and Hart, THIS JOURNAL, **50**, 2337 (1928).

(3) Kiehl, Fox and Hardt, *ibid.*, **59**, 2395 (1937).

(4) Kiehl and Hart, *ibid.*, **50**, 1608 (1928).

TABLE I

ANALYSIS OF COMPOUNDS CONTAINING TRI- AND PENTAVALENT COLUMBIUM

	Monovalent ion	Columbium, %	Sulfate, %	Average oxidation number	M^{+1}:Cb:SO_4	Radius of monovalent ions, Å.
Acid salt empirical formula,		24.76	51.10	3.69	1.00:2.00	
$HCb_3(SO_4)\cdot xH_2O$		23.15	47.41	3.65	1.00:1.99	
Sodium salt						
Prep. no. 1	8.25%	23.11	47.67	3.68	1.44:1.00:2.00	0.95
Check analysis	8.24	23.17				
Prep. no. 2	8.74	23.66	48.57		1.49:1.00:1.99	
Potassium salt						
Prep. no. 1	12.64	22.66	46.64	3.69	1.33:1.00:1.99	1.33
Prep. no. 2	12.92	22.72	46.79	3.67	1.33:1.00:2.00	
Theory $(K_8Cb_6(OH)_6(SO_4)_{12}\cdot 18H_2O$	12.77	22.76	47.07	3.67	1.33:1.00:2.00	
Ammonium salt						
Prep. no. 1	5.10	24.55	50.70	3.66	1.07:1.00:2.00	1.48
Prep. no. 2	4.97	24.43	50.51	3.66	1.05:1.00:2.00	

150 g. of 28% sulfuric acid. The columbium content was approximately 0.015 mole. The alkali sulfate, 0.07 mole, was dissolved in 200 g. of 40% sulfuric acid. The two solutions were added simultaneously to a flask provided with stirrer, and after a thorough mixing the solution was allowed to stand. All operations were carried out in a carbon dioxide atmosphere. In about an hour the precipitated crystals were collected on a sintered glass filter, washed with 40% sulfuric acid, alcohol and ether and dried in a stream of carbon dioxide. All were red-brown in color and in the dry state sufficiently stable to be exposed to atmospheric oxygen for short periods without noticeable oxidation. Analyses are given in Table I. In all cases the ratio SO_4:Cb was found to be 2.00 ± 0.01, and the average oxidation number of the columbium 3.68 ± 0.02. The atomic ratio, however, of the alkali metal to columbium varied with the different alkalies and decreased with increase in the ionic size of the ion.

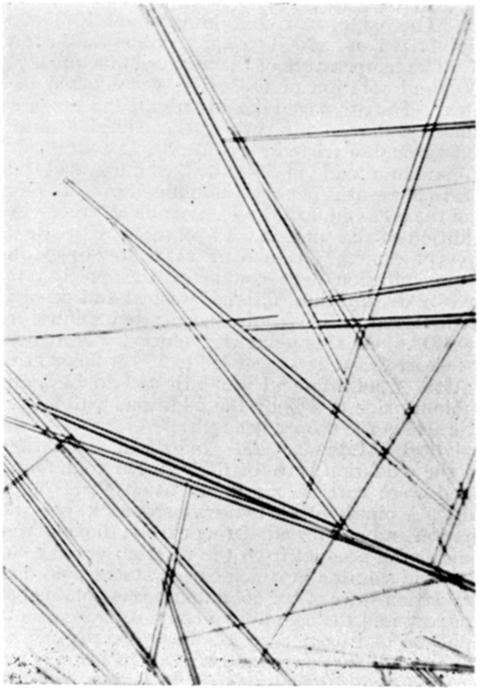

Fig. 2.—Complex columbium sulfate: magnified 12.5 times; proposed formula $HCb_3(SO_4)_6\cdot xH_2O$.

Well defined crystals were obtained by adjusting concentrations to cause slow precipitation. For example, when 0.04 mole of potassium sulfate was used in the previously described procedure hexagonal crystals were obtained as shown in Fig. 3. The picture was taken with polarized light to indicate twinning. Under similar conditions of

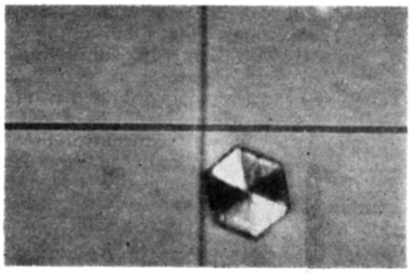

Fig. 3.—Potassium salt of complex columbium sulfate: magnified 550 times; proposed formula $K_8Cb_6(OH)_6(SO_4)_{12}\cdot 18H_2O$.

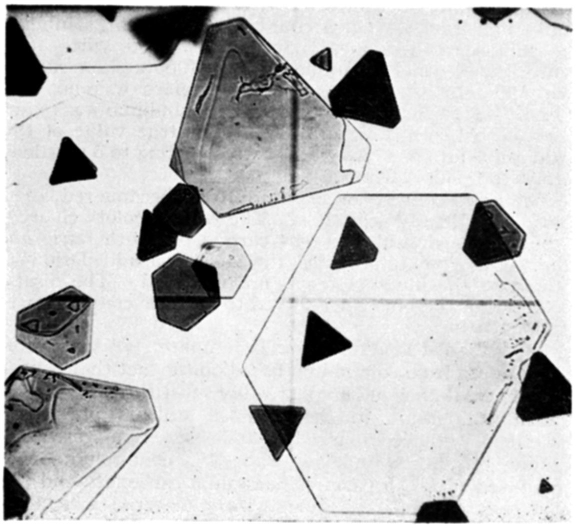

Fig. 4.—Ammonium salt of complex columbium sulfate: magnified 107 times.

concentration the ammonium salt was precipitated as needle-shaped crystals identical in appearance to those shown in Fig. 2. In the presence of a high concentration of ammonium sulfate large thin hexagonal plates, shown in Fig. 4, were formed which changed to the needle-like variety upon removal of the excess ammonium sulfate. The thallous ion also formed two varieties of crystals but cesium only the needle-like type. Six preparations of the potassium salt were made in which the concentration of sulfuric acid was varied from 3.7 to 9 molar and the concentration of potassium sulfate from 0.08 to 0.23 molar but the analyses of the product did not vary from those given for the potassium salt in Table I. Single crystals, large enough for obtaining X-ray diffraction patterns, were prepared. Two 200-g. quantities of a 40% solution of sulfuric acid, one containing 2.5% potassium sulfate and the other 0.7% columbium of average valence 3.67 were mixed. After being warmed to 50° the mixture was filtered, the filtrate being collected in a large Dewar flask and allowed to cool slowly to room temperature over a period of days. The crystals obtained were well formed, about 1 mm. on edge and could be exposed to air for some time without noticeable oxidation. The analyses are given in Table I. The crystallographic data were obtained by Dr. Howard T. Evans of this Institute, using a Buerger precession camera. Crystal type, monoclinic; space group P2, Pm or Pm/2; a_0 = 10.16 Å.; b_0 = 17.61 Å.; c_0 = 10.03 Å.; $a:b:c$ = 0.5776:1.000:0.5707; β = 58° 55′; density, calcd. for $K_8Cb_6(OH)_6(SO_4)_{12}\cdot 18H_2O$ per unit cell: 2.62 g./cc. Found: 2.55 g./cc.

Preparation of a Complex Sulfate Containing Columbium in an Average Oxidation State of 3.33.—Because of the insolubility of the complex sulfate containing columbium in an oxidation state of 3.67 in 75% sulfuric acid, further reduction required that a more dilute solution be employed. The red-brown crystals obtained from reduction of 100 g. of the 75% sulfuric acid solution were filtered and pressed to remove the relatively concentrated acid and redissolved in 41% acid. The reduction was carried out at a current density of 0.025 amp. per sq. cm. at 20° for one-half hour and then at 5° for an additional three hours. The solution assumed a deep green color; and after it had been warmed to 20°, 25 g. of 40% sulfuric acid containing 1 g. of potassium sulfate was added. The solution was cooled to 5°: air was of course excluded in all operations. Bright green hexagonal crystals precipitated which were found to be dichroic, green light being transmitted through the large hexagonal faces and red light through the 6 narrow sides. Oxidation or incomplete reduction cause the appearance of red crystals or crystals with green nuclei and red surfaces. On account of their great solubility in sulfuric acid alone, they were washed with 40% sulfuric acid which contained 1.5 g. of potassium sulfate per 100 ml. Complete analysis therefore was not obtained, but the oxidation state of the columbium was found to vary between 3.37 and 3.39. The true value of the oxidation state was likely 3.33 corresponding to 5 trivalent atoms to 1 pentavalent.

The green solution on exposure to air became red, then blue and finally colorless. The same color changes occurred when oxidation was carried out with ferric ion and permanganate provided the latter was added slowly, otherwise the blue color was not observed. The disappearance of the blue color served to indicate complete oxidation.

Separation of Tantalum from Columbium.—A separation of tantalum from columbium based on the fact that pentavalent tantalum could not be readily substituted for pentavalent columbium in the complex sulfates previously described was accomplished as follows. A mixture containing 6% tantalum oxide and 94% columbium oxide was fused with 2.5 parts of potassium carbonate and the melt was dissolved in water. Any material which remained insoluble was retreated in order to obtain complete solution. The solution of potassium tantalate and columbate was then treated as described later to make a solution containing 4% of the mixed oxides and 75% sulfuric acid, and the columbium contained therein was reduced to an average oxidation state of approximately 3.67.

One hundred grams of the solution and suspended crystals was diluted with 300 g. of 28% sulfuric acid and added at 20° to a solution of 30 g. of ammonium sulfate in 400 g. of 40% sulfuric acid. After standing an hour at 0° the thin hexagonal and triangular crystals which formed were filtered on a sintered glass filter, washed with 75 cc. of 40% sulfuric acid containing 3.75% ammonium sulfate and decomposed by heating to yield about 3.5 g. of oxide.

Dr. J. Rand McNally, of the Spectroscopy Laboratory at Massachusetts Institute of Technology, compared the purity of the above sample with that of a sample of columbium oxide containing according to the manufacturers not more than 0.2% tantalum oxide by spectrographic analysis as follows. The samples were mixed 1:1 with pure graphite powder to permit better excitation and 25-milligram samples were burned to completion (with a burning time of approximately five minutes). A high dispersion grating spectrograph (35-foot Paschen mounting giving about 0.76 Å. per millimeter dispersion) was used to separate the tantalum line from those of the considerably more intense columbium lines.

Inspection of six tantalum lines (λ = 2603.82, 2653.28, 2656.6, 2661.3, 2694.8, 2714.68 Å.) indicated that the tantalum concentration of the columbium oxide obtained from the ammonium salt was less than that of the reference sample. Although the absolute purity of the columbium oxide was not determined, it was evident that a high degree of purification had been obtained.

Solution of Columbium Oxide in Sulfuric Acid.—A solution containing 4% columbium oxide was used for previously described electrolytic reductions. The hydrous columbium oxide employed was prepared from a pure grade of columbium oxide. Twenty-five grams of this oxide was fused with 62.5 g. of potassium carbonate in a platinum crucible. The cooled melt was dissolved in 300 ml. of water, diluted to 1 liter, filtered if necessary, and finally diluted to 3.5 liters. The hydrous oxide was precipitated by acidifying the hot solution with sulfuric acid. After filtration and washing, the oxide was dried at 80° for twelve hours. The oxide, now containing about 10% of water, was pulverized and added to 300 g. of 95% sulfuric acid at 140°. The temperature of the mixture was quickly raised to 190° and solution of the oxide was effected in a few minutes. Too prolonged heating resulted in the precipitation of oxysulfates. If turbid, the cooled solution was filtered through a fritted glass filter. It contained about 6% columbium oxide in 85 to 90% sulfuric acid, but also retained a few tenths per cent. of potassium. To eliminate most of the potassium the hydrous oxide was reprecipitated by addition of the sulfuric acid solution, with stirring, to 3.5 liters of water. The mixture was heated to near boiling until precipitation was complete, the precipitate was washed by decantation, filtered, washed and dried at 80° and redissolved in 300 g. of concentrated sulfuric acid at about 240°.[5] At this point the solution was made ready for the electrolysis: it was cooled to 10° or below, the concentration of sulfuric acid was adjusted to 75% and the columbium oxide to 4% by the addition, with stirring, of sulfuric acid of the proper strength.

Analytical Methods.—All analytical operations in which the oxidation state of the reduced columbium was obtained were carried out in an atmosphere of carbon dioxide. A pipet with a two-way stopcock, one way for evacuation and one for admitting carbon dioxide was used to transfer the product from the reaction vessel to a 30% sulfuric acid solution in which the crystals would dissolve. The oxidation state of the columbium was obtained on one aliquot part and the columbium content on a second part. Bromine or hydrogen peroxide was used to oxidize the columbium to the pentavalent state. The columbium was precipitated and finally weighed as Cb_2O_5.

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(5) The operation was repeated if necessary until the potassium content was reduced to a negligible amount.

Discussion

The information available at present would not permit one to distinguish between formulas such as $HCb_3(SO_4)_6 \cdot xH_2O$ and $H_8Cb_6O_3(SO_4)_{12} \cdot xH_2O$ or between $K_4Cb_3(OH)_3(SO_4)_6 \cdot 9H_2O$ and $K_8Cb_6O_3(SO_4)_{12} \cdot 21H_2O$. The latter compound is undoubtedly the same as that previously represented as $4K_2O \cdot Cb_2O_5 \cdot 2Cb_2O_3 \cdot 12H_2SO_4 \cdot 12H_2O$,[3] but no evidence has been found from this work to indicate a variation in composition as previously reported.

The numerous compounds of molybdenum, vanadium, columbium and tantalum which can be represented as containing six metal atoms[6] would lead one to favor a similar structure for the complex sulfates. The latter also bear an interesting resemblance to a complex chloride prepared by dry methods[7] which contained columbium in a lower oxidation state. This compound and its solutions were deep green in color and were reported to be remarkably stable with respect to oxidation, but could be oxidized and decolorized by strong oxidizing agents. Lack of accurate data on the oxidation number of the columbium has caused it to be variously represented as $Cb_6Cl_{14} \cdot 7H_2O$ (oxidation number 2.33) and $Cb_3OCl_7 \cdot 3H_2O$ (oxidation number 3) but the possibility of the columbium having an oxidation number of 3.333 or 3.67 should not be overlooked. In solution, only two of the fourteen chlorides are precipitated by silver nitrate, the other twelve apparently existing in a complex which may resemble that of the complex sulfate.

The various intense colors exhibited by solutions of columbium in lower oxidation states have been the cause of much speculation and have often been attributed to the formation of different complexes in different concentrations of sulfuric acid and to different hydrates of trivalent columbium.

While the acid concentration was found to affect these colors it should be noted that all three colors mentioned previously could be produced in approximately 45% acid by varying the average oxidation number of the columbium only. It is of further interest that a red compound containing columbium with an average oxidation number of 3.67 was isolated from the red solutions and a green substance (actually dichroic) containing columbium with an average oxidation number approximating 3.33 was obtained from the green solutions. Both these oxidation numbers are represented by simple ratios of tri- and pentavalent columbium.

Summary

A complex columbium sulfate having a ratio of two trivalent columbium atoms to one pentavalent atom and a SO_4:Cb ratio of 2.00 precipitated from 75% sulfuric acid during electrolytic reduction of pentavalent columbium.

Sodium, potassium and ammonium salts were prepared all containing columbium with an average oxidation number of 3.67 and having an SO_4:Cb ratio of 2.00. The monovalent ion content varied for different ions.

The crystal type of the potassium salt was found to be monoclinic and density measurements indicated $K_8Cb_6(OH)_6(SO_4)_{12} \cdot 18H_2O$ per unit cell.

A green (actually dichroic) complex sulfate containing columbium with an average oxidation number approximating 3.33 was prepared.

The complex sulfates described offer a possible means of separating tantalum from columbium.

CAMBRIDGE, MASS. RECEIVED JULY 10, 1948

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[6] Pauling, *Chem. Eng. News*, **25**, 2970 (1947).

[7] Harned, THIS JOURNAL, **35**, 1078 (1913).

[CONTRIBUTION FROM METCALF RESEARCH LABORATORY, BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XL. Conductance of Aluminum Bromide in Several Solvents and of Methylaluminum Bromides in Methyl Bromide[1]

BY WILLIAM J. JACOBER[2] AND CHARLES A. KRAUS

I. Introduction

The properties and, particularly, the conductance of uni-univalent salts in a number of non-aqueous solvents, as well as in water, have been measured with a reasonable degree of precision. Higher types of salts, however, have received but little attention and, except for aqueous solutions, little is known concerning their properties. In general, the salts of multivalent ions of the more electropositive elements are difficultly soluble in non-aqueous solvents. Salts of multiply charged ions of less electropositive elements are often soluble in non-aqueous solvents but they are ordinarily weak electrolytes. The properties of solutions of such salts are often greatly influenced by interaction with solvent molecules or with impurities that may be present.

It seemed worth while to study the conductance of aluminum bromide in nitrobenzene, pyridine and methyl bromide; the dielectric constants of these solvents are, nitrobenzene, 34.5 and pyridine 12.3 (at 25°) and methyl bromide 10.6 (at 0°) and 15.7 (at −78°). The dielectric

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[1] This paper is based on a portion of a thesis presented by William J. Jacober in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in the Graduate School of Brown University, October, 1942.

[2] University Fellow, Brown University, 1940–1941; Ethyl Corporation Fellow, 1941–1942.