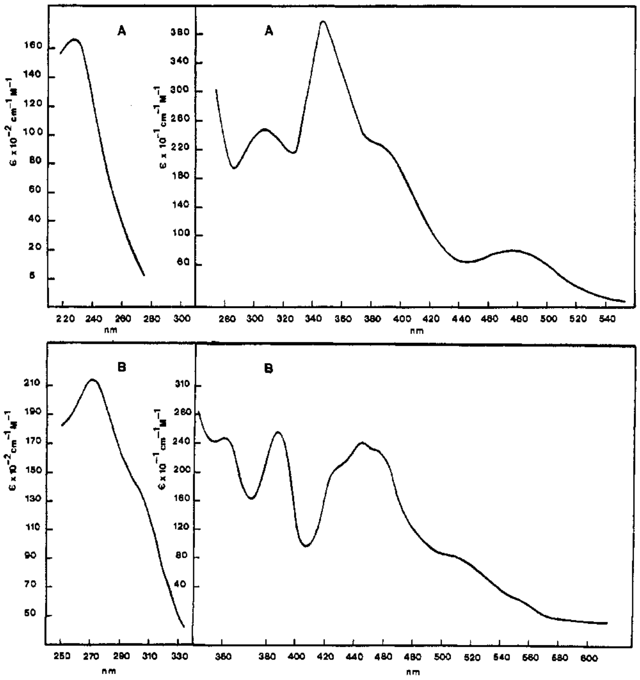

Figure 1.—A, electronic spectrum of $[RuCl_6]^{3-}$ in 12 *M* HCl; B, electronic spectrum of $[RuBr_6]^{3-}$ in 9 *M* HBr.

situ[11,12] and by Hartmann and Buschbeck[13] for K_3RuCl_6. No attempt was made in this study to assign the observed absorption bands since detailed assignments have been given considerable attention by Jorgensen.[11,12]

There is no supporting evidence for the presence of $H_5O_2^+$ in **1** although Gillard and Wilkinson[14] have reported that this ion is present in a number of rhodium(III) complexes. It may then be concluded that $[RuCl_6]^{3-}$ and $[RuBr_6]^{3-}$ are stabilized by $N(CH_2CH_2NH_3)_3{}^{3+}$ and that crystal packing considerations probably require one molecule of HX to be present in the solid. This situation would be similar to that observed for the anilinium salts, $(C_6H_8N)_6RuX_9$.[4] Attempts to stabilize $[RuF_6]^{3-}$ and $[RuI_6]^{3-}$ by $N(CH_2CH_2NH_3)_3{}^{3+}$ by the general method presented herein were unsuccessful.

Experimental Section

Infrared spectra were recorded on a Beckman IR-12 spectrophotometer as Nujol mulls between CsI plates. Electronic spectra were obtained with a Cary-14 spectrophotometer. Beer's law was obeyed over the concentration range $\sim 1 \times 10^{-5}$–1×10^{-4} *M*. A Radiometer pH meter model 28 was used to measure the pH of aqueous solutions. Microanalyses were performed by A. B. Gygli, Toronto or by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Ruthenium was determined by reduction to the metal in an atmosphere of hydrogen at 700°. Halogen analyses were determined by potentiometric titration with silver nitrate solution. Magnetic susceptibility measurements were carried out using a Gouy balance at room temperature.

Materials.—Ruthenium trichloride was purchased from Engelhard Industries, N. J. Potassium tris(oxalato)ruthenate(III) tetrahydrate was prepared according to the method of Witschy and Beattie.[15] Other chemicals used were reagent grade. The ligand, $[N(CH_2CH_2NH_3)_3]Cl_3$, was purchased from Strem Chemicals, Inc., Danvers, Mass.

$[N(CH_2CH_2NH_3)_3][RuCl_6]\cdot HCl\cdot 2H_2O$.—To an acidic solution (pH <3) made from 5.0 ml of concentrated HCl and 5 ml of water was added $K_3[Ru(ox)_3]\cdot 4H_2O$ (0.5 g) and $[N(CH_2CH_2NH_3)_3]Cl_3$ (0.5 g). The resulting mixture was heated on a steam bath for 15–20 min during which time the solution changed from dark green to red-brown in color. After cooling the solution the product was filtered and washed successively with cold water, methanol, and ether. The crude product was recrystallized by dissolving it in the minimum volume of hot water followed by filtration of the hot solution into an equal volume of concentrated HCl. The reddish brown powder was washed as before and dried *in vacuo* over boiling H_2O. *Anal.* Calcd for $C_6H_{26}Cl_7N_4O_2$: C, 13.46; H, 4.86; N, 10.47; Cl, 46.36; Ru, 18.88. Found: C, 13.41; H, 4.40; N, 10.60; Cl, 46.64; Ru, 19.51.

$[N(CH_2CH_2NH_3)_3][RuBr_6]\cdot HBr$.—This dark brown complex salt was prepared in a manner similar to that used for the $[RuCl_6]^{3-}$ salt except that HBr (9 *M*) was used instead of HCl. *Anal.* Calcd for $C_6H_{22}Br_7N_4Ru$: C, 8.89; H, 2.71; N, 6.91; Br, 69.01; Ru, 12.47. Found: C, 8.80; H, 2.90; N, 6.89; Br, 68.11; Ru, 13.81.

Acknowledgment.—The authors thank the National Research Council of Canada for financial support in the form of an operating grant to C. V. S.

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The Identity of So-Called "Cupric Iodate Monohydrate" and Bellingerite, $3Cu(IO_3)_2\cdot 2H_2O$

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Received February 2, 1972

Despite some early confusion,[1] the product of the metathetic reaction between copper salts and iodic acid or alkali iodates has long been considered to be the cupric iodate hydrate $Cu(IO_3)_2\cdot H_2O$.[1-5] At the same time the mineral bellingerite, found in Chuquicamata, Chile, was reported by Berman and Wolfe[6] to have the formula $3Cu(IO_3)\cdot 2H_2O$, *i.e.*, only two-thirds of the water content of the synthetic product; they also found this formula to apply to one of the previously reported products (that of Granger and de Schulten[4,5]).

A variety of physical data, including thermodynamic,[7-9] infrared,[10] and magnetic[11] properties, have nevertheless been reported under the designation $Cu(IO_3)_2\cdot H_2O$. The differences in analysis expected from these two formulations are quite small (the water has frequently been determined by difference, and direct water determinations are easily vitiated by in-

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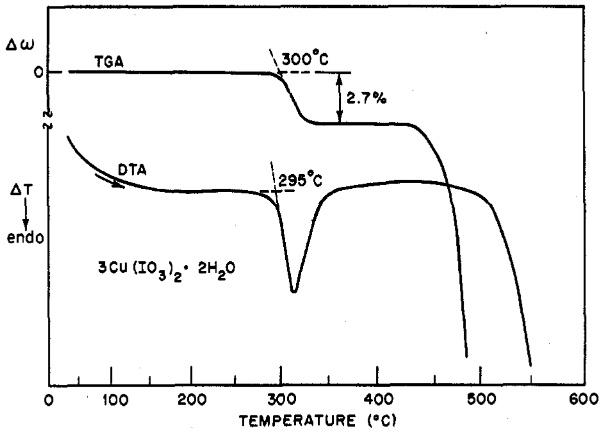

Figure 1.—Differential thermal analysis and thermogravimetric analysis of $3Cu(IO_3)_2 \cdot 2H_2O$, sample a; testing rate 5°/minute.

sufficient drying) and the relationship between these two materials seemed worthy of reexamination. The material usually designated $Cu(IO_3)_2 \cdot H_2O$ was indeed found to be identical with bellingerite, $3Cu(IO_3)_2 \cdot 2H_2O$, the structure of which has symmetry $P\bar{1}$ (triclinic) with unit cell $a = 7.228$ Å, $b = 7.829$ Å, $c = 7.940$ Å, $\alpha = 105.039°$, $\beta = 96.985°$, and $\gamma = 92.942°$.[12,13]

Experimental Section

Precipitations were carried out by mixing 0.1 mol of $CuSO_4$ in 100 ml of H_2O with 0.2 mol of HIO_3 or KIO_3 in 100 ml of H_2O with continuous agitation at 3°, at room temperature, or at the boiling point. After 0.5 hr the product was filtered, washed with water at the same temperature, and air-dried. Some preparations were also dried at 110°.

Crystal growth was carried out by the use of the HIO_3-boiling-point-precipitated compounds. Saturated solutions (~2 l.) were prepared in water at 47° and at the boiling point and in concentrated nitric acid at its boiling point (about 120°) and permitted to evaporate slowly over a 2-week period. In the case of the boiling mixtures evaporation was permitted under reflux conditions at a controlled[14] rate of about 100 ml/day until about 200 ml remained and several grams of ~1-mm crystals was harvested. These crystals were used as seeds in repeat runs and crystals up to 10 mm resulted. A very fine crystalline powder was obtained from water at 47°.

A Du Pont 900 differential thermal analyzer (dta) and the thermogravimetric analyzer (tga) attachment were used with flowing nitrogen or air atmospheres (no differences) and a heating rate of 20°/min or 5°/min (no significant difference). X-Ray powder diffraction patterns were taken with vanadium-filtered Cr Kα radiation in a 114.6-mm diameter Straumanis-type Norelco camera. Copper analyses were performed by dissolving the samples in HCl and using atomic absorption spectrometry determinations with reference standards.

Results and Discussion

All samples made, which cover essentially all of the preparative techniques used previously, gave powder X-ray diffraction patterns identical with that of each other and with that of the mineral bellingerite, $3Cu(IO_3)_2 \cdot 2H_2O$.[12]

The dta and tga results shown in Figure 1 were typical of the high-temperature crystal growth for which the water loss occurred at 290–300° and the weight loss at that temperature corresponded to 2.7–2.9 wt % H_2O, *i.e.*, to 1.92–2.06 H_2O on the bellingerite formulation. Decomposition of the iodate began at about 450°.

TABLE I

	% Cu[a]	% H_2O[b]
Precipitate using HIO_3 and boiling H_2O	15.45	2.9
Crystals grown from boiling H_2O	15.10	2.7
Crystals grown from boiling HNO_3	14.97	2.85
Calculated for $3Cu(IO_3)_2 \cdot 2H_2O$	14.94	2.82

[a] Estimated accuracy ±0.10. [b] Estimated accuracy ±0.1.

A sample of natural bellingerite from the type locality Chuquicamata, Chile, from the Harvard University collection gave a dta pattern essentially identical with that of Figure 1. Another sample from the same location from the Smithsonian Institution showed an additional endotherm at about 380°; the presence of an extra phase in the Smithsonian specimen has been previously noted by Kaplan.[13] There was an insufficient amount of this material for further investigation.

Precipitations ranged in water content from 2.9 to 3.6% and main water loss temperature from 135 to 295°; some water was, however, lost below 100° in these specimens. It was found that incomplete washing, and in particular the presence of free iodic acid, had the effect of lowering the main water evolution temperature. The addition of 5% HIO_3 lowered the water evolution temperature from 295 to 230°.

Analytical results on three high-temperature preparations are given in Table I. These are considered by us to be the best conditions for the preparation of $3Cu(IO_3)_2 \cdot 2H_2O$.

In view of the identity of the X-ray powder diffraction patterns and the excellent analysis results on the slowly grown crystals, the identity of "$Cu(IO_3)_2 \cdot H_2O$" with bellingerite, $3Cu(IO_3)_2 \cdot 2H_2O$, can be considered to be established.

Acknowledgments.—We wish to thank Mrs. A. C. Cooper for the X-ray powder diffraction patterns and C. Frondel of Harvard University and J. S. White, Jr., of the Smithsonian Institution, for the gift of the natural bellingerite specimens.

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Synthesis of Tautomeric Schiff Base Complexes and Ketimine → Aldimine Conversion Rates of Copper(II) Complexes

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Received February 14, 1972

Transamination is one of the key reactions catalyzed by pyridoxal-dependent enzymes.[2,3] It and other nonoxidative transformations of amino acids effected

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