On Some Dark-colored Chlorocuprates(I, II) and Related Compounds. I. The Method of Preparation and Some Properties*

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A considerable amount of data has now been accumulated concerning the characteristic properties of "mixed valence" compounds, i. e. compounds containing atoms of the same element in different valence states. Mixed valence compounds having a comparatively covalent character have been fairly well studied and are now utilized in the field of semiconductors. One of the most characteristic features of such mixed valence semiconductors is that the ratio of atoms in two valence states can often be changed arbitrarily, thus resulting in a change in the properties of the substance, as if the valence of the metal could take a continuous non-integral number. Such a technique of preparing semiconductors, termed *valence control*, is often useful for giving desired electrical properties to these substances1). On the other hand the properties of the mixed valence compounds of ionic character containing halometallate ions have scarcely ever been elucidated. Most of of these mixed valence halometallates show an "interaction color" due to an abnormal light absorption2).

The interaction color of copper(I) and copper(II) chlorides in hydrochloric acid solution has been known from an early date. Doehlemann and Fromherz measured the absorption spectrum of this system and found a broad interaction absorption in the visible region3). However, the present-day knowledge of the structure of chlorocuprate ions is very meager, and it is not known what kinds of chlorocuprate ion are responsible for the interaction color. This is mainly due to the fact that the phenomenon has hitherto been observed only in aqueous solution. It occurred, therefore, to the present author that an investigation on crystalline compounds showing an interaction color of copper(I) and copper(II) might be helpful in throwing light on the nature of this problem and he succeeded in obtaining dark brown chlorocuprates(I, II) of hexamminechromium(III) and hexamminecobalt(III) cations. For comparison the chlorocuprates(I) and chlorocuprates(II) of these

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1) E. J. W. Verwey, *Philips Research Repts.*, 5, 173 (1950).

* A part of this study was presented at the Symposium on Coordination Chemistry, Tokyo, November, 1958.

2) The paper of J. E. Whitney and N. Davidson [*J. Am. Chem. Soc.*, 71, 3809 (1949)] contains a survey of the literature up to that time.

3) E. Doehlemann and H. Fromherz, *Z. physik. Chem.*, 171A, 353 (1934).

complex cations were also prepared and they were found to form yellow or orange crystals. In the following paragraphs the methods of preparation and some properties of these compounds will be described.

Experimental

Methods of Preparation.—*Hexamminechromium(III) Chlorocuprate(I, II) and Hexamminecobalt(III) Chlorocuprate(I, II).*—Five tenths grams of copper(I) chloride was dissolved in 100 ml. of hot water containing 15 g. of ammonium chloride and 40 ml. of concentrated hydrochloric acid. When the color of the solution was found to be greenish yellow, a dilute solution of titanium(III) chloride was added dropwise, until the very moment when the yellow color disappeared. The solution was quickly filtered and the filtrate was poured into a solution of 2.7g. of hexamminechromium(III) chloride mono-hydrate and 3 g. of copper(II) chloride di-hydrate in 100 ml. of water. The same amount of hexamminecobalt(III) chloride was used in preparing the corresponding cobalt compound. It seemed preferable to heat both solutions to about 60°C before mixing, for the precipitate formed in the cold solution was very fine and liable to decomposition. The mixture was cooled in a cold water bath for 30 min. with occasional stirring. The dark brown or almost black crystalline precipitate thus formed was filtered off, washed with 2 N hydrochloric acid and then with ethanol, and dried in air. (Samples No. 3 and 8 in Table I.)

Found for the chromium compound: Cr, 14.2, 13.8, 13.6; N, 21.5, 21.7, 21.8; total Cu, 16.8, 15.7; Cl, 42.3; loss in wt. at 110°C, 1.05, 1.23. Calcd. for $[Cr(NH_3)_6]_2Cu_2Cl_9(H_2O)_{1/2}$: Cr, 13.6; N, 22.0; Cu, 16.6; Cl, 41.8; H_2O, 1.14%.

Found for the cobalt compound: Cu, 15.2; N, 21.3; total Cu, 16.5, 16.9; Cl, 41.1; loss in wt. at 110°C, 1.15. Calcd. for $[Co(NH_3)_6]_2Cu_2Cl_9(H_2O)_{1/2}$: Co, 15.2; N, 21.6; Cu, 16.4; Cl, 41.1; H_2O, 1.13%.

The total copper content in the above analytical data was determined gravimetrically. The content of bivalent copper was determined iodometrically in 3 N acetic acid using finely powdered sample. The chromium compound gave a fairly sharp end point of titration and it was found to contain about a half of the total copper in the bivalent state (Found, 8.4; calcd., 8.3). In the cobalt compound the end point of the iodometric titration was very obscure, and the results were less reproducible (Found, 8.7, 9.0, 9.1, 9.3. Calcd., 8.2). It was found, however, that the composition of the chlorocuprate(I, II) depends on the quantity of copper(I) and copper(II) chlorides and used in the preparation. An outline of this relationship is given in Table I. Samples Nos. 1—6 are chromium compounds and Nos. 7—11 cobalt compounds. The procedure adopted in preparing these samples was the same as that given above except the difference in the quantities of the copper chlorides used.

Hexamminechromium(III) Chlorocuprate(I) and Hexamminecobalt(III)Chlorocuprate(I).—One gram of copper(I) chloride and 15 g. of ammonium chloride were dissolved in a mixture of 100 ml. of hot water, 20 ml. of 15% titanium(III) chloride solution in hydrochloric acid and 40 ml. of concentrated hydrochloric acid. The solution was quickly filtered and the filtrate was poured into a solution at 60°C of 2.7 g. of hexamminechromium(III) chloride mono-hydrate in 100 ml. of water. The same amount of hexamminecobalt(III) chloride was used in preparing the corresponding cobalt compound. The mixture was cooled in a cold water bath for 30 min. with occasional stirring. The yellow or orange precipitate was filtered off and washed with 2 N hydrochloric acid and ethanol, and then it was

TABLE I. THE RELATIONSHIP BETWEEN THE QUANTITIES OF THE STARTING MATERIALS AND THE CHEMICAL COMPOSITION OF THE CHLOROCUPRATE

Sample No.	Starting Material[a]		Product		
	CuCl (in g.)	$CuCl_2 \cdot 2H_2O$ (in g.)	Total Cu (in %)	Bivalent Cu (in %)	Color
1	0	3	16.1	16.1	yellow
2	0.2	3	17.0	12.7	brownish black
3	0.5	3	16.8	8.4	black
4	1	3	19.5	2.0	grayish brown
5	1	1	20.0	1.0	brown
6	1	0	20.4	0	yellow
7	0	3	15.8	16.8[b]	orange
8	0.5	3	16.4	9.2[b]	black
9	1	3	19.0	2.3[b]	dark brown
10	1	1	19.8	1.6[b]	brown
11	1	0	19.8	0	orange

a) For samples Nos. 1—6 the complex cation used was hexamminechromium(III) ion and for samples Nos. 7—11 hexamminecobalt(III) ion.

b) The end point of the iodometry of the cobalt compound is very obscure.

dried in vacuo over potassium hydroxide. (Samples No. 6 and No. 11 in Table I.)

Found for the chromium compound: Cr, 13.6; N, 21.7; Cu, 20.4; Cl, 39.2. Calcd. for $[Cr(NH_3)_6]_4 \cdot Cu_5Cl_{17}$: Cr, 13.5; N, 21.9; Cu, 20.7; Cl, 39.2%.

Found for the cobalt compound: Co, 15.4; N, 20.8; Cu, 19.8; Cl, 38.5. Calcd. for $[Co(NH_3)_6]_4 \cdot Cu_5Cl_{17}$: Co, 15.1; N, 21.5; Cu, 20.3; Cl, 38.5%.

Hexamminechromium(III) Chlorocuprate(II).—Two grams of hexamminechromium(III) chloride monohydrate and 2 g. of copper(II) chloride di-hydrate were dissolved in 60 ml. of water. The solution was filtered and the filtrate was heated to 60°C and mixed with 20 ml. of concentrated hydrochloric acid. The mixture was cooled in a cold water bath for 30 min. with occasional stirring and the precipitated complex was filtered and washed with ethanol. (Sample No. 1, Table I.)

Found: Cr, 13.8; N, 21.5; Cu, 16.1; Cl, 44.9. Calcd. for $[Cr(NH_3)_6]CuCl_5$: Cr, 13.2; N, 21.3; Cu, 16.1; Cl, 44.5%.

The corresponding cobalt compound had already been prepared by Levi[4]. (Sample No. 7, Table I).

Hexamminechromium(III) Bromocuprate(II).—Two grams of hexamminechromium(III) bromide, 2.4 g. of copper(II) sulfate penta-hydrate, 10 g. of sodium bromide, 20 ml. of water and 20 ml. of 48% hydrobromic acid were mixed and the mixture was occasionally stirred. After 1 hour the resulting black crystals were filtered off through a glass filter under strong suction, washed quickly with fuming hydrobromic acid (ca. 66%) and dried in vacuo over sulfuric acid.

Found: Cr, 9.0; N, 13.9; Cu, 9.6; Br, 65.1. Cacld. for $[Cr(NH_3)_6]CuBr_5$; Cr, 8.4; N, 13.6; Cu, 10.3; Br, 64.7%.

An attempt to prepare the corresponding cobalt compound was unsuccessful.

Absorption Spectrum Measurement.—The absorption spectrum of copper sulfate dissolved in 48% hydrobromic acid was measured with a Beckman spectrophotometer, model DU. The result is given in Fig. 1. The concentration of copper sulfate was 0.0000870 M and the extinction coefficient is expressed on the basis of g. ion of copper.

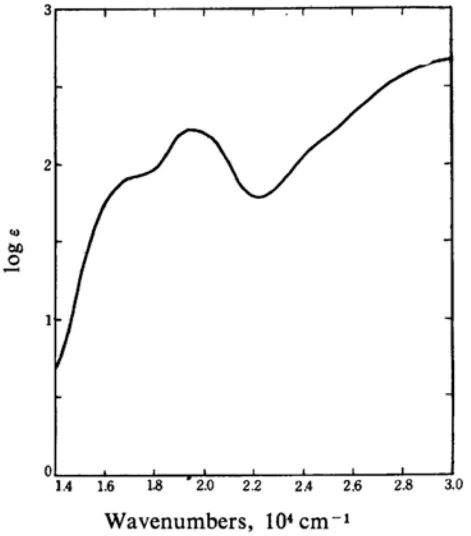

Fig. 1. Absorption spectrum of copper(II) sulfate in 48% hydrobromic acid.

Measurement of Magnetic Susceptibility.—Dr. Saburo Fujii* of the Tokyo Institute of Technology kindly measured the magnetic susceptibility of hexamminecobalt(III) chlorocuprate(I, II) by Weiss-Foex's zero point compensation method.

Results and Discussion

All the foregoing chlorocuprates crystallize in regular octahedra. As has been pointed out in the preceding section, the composition of the chlorocuprate(I, II) depends on the quantities of copper(I) and copper(II) chlorides used in the preparation (Table I). Observation under a microscope as well as with the naked eye shows that the color changes from sample to sample as the chemical composition changes, although it is uniform in a given sample. This fact indicates that the product is not a mixture of two chemical species, but a nearly uniform chemical compound whose composition can change continuously. As far as is known to the present author, this series of chlorocuprates form the only known typical ionic crystals consisting of well-defined cations and anions in which the valence control is possible.

From the total copper content given in Table I it will be seen that the atomic ratio of chromium to copper is 1:1 when more than a half of the total copper is bivalent, and that this ratio gradually decreases to the limiting value of 4:5 when the bivalent copper is less than a half. In this extreme case the product is a pure chlorocuprate(I) (samples No. 6 and No. 11 in Table 1). The reason why compounds having such different chemical formulae belong to one series of compounds would be made clear only by a crystallographic investigation with X-rays. A research along this line is now in progress and the results will be published shortly.

An interesting phenomenon is observed when crystals of hexamminecobalt(III) chlorocuprate-(I, II) are digested in the mother liquor at 30~40°C for many hours. The crystals reach 0.1 ~1 mm. in size and often present a tortoise-shell appearance. The black or dark brown crystals are spotted with yellow transparent portions although the crystals as a whole are well developed octahedra. This may be explained as follows. By the oxidation of the mother liquor in the air the quantity of univalent copper therein is gradually decreased. The portions of the crystals that grow at later stages, therefore, have a poorer content of

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[4] G. R. Levi, *Atti Accad. Lincei*, (5) 32 I, 633 (1923).

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univalent copper and consequently the interaction color is feeble in these portions.

Hexamminechromium(III) bromocuprate(II) is black in contrast to yellow chlorocuprate(II). This difference of color is probably due to the strong absorption band of bromocuprate(II) ion with a peak at 1.95×10^4 cm^{-1} as is observed in the spectrum of copper(II) sulfate in hydrobromic acid in Fig. 1. An investigation of hexamminechromium(III) bromocuprate(II) may give some information about the ionic species to which this absorption band belongs.

Magnetic study on $[Co(NH_3)_6]_2Cu_2Cl_9(H_2O)_{1/2}$ showed, after a correction being made for the presence of diamagnetic groups, a magnetic moment of 1.9 Bohr magnetons per each formula unit. This value may be considered quite reasonable as the magnetic moment ascribed to the bivalent copper atom present in the crystals. The magnetic moment of the bivalent copper atom, therefore, seems to be little affected even when an interaction color is observed.

Summary

A series of dark-colored chlorocuprates(I, II) of hexamminechromium(III) and hexamminecobalt(III) have been prepared. The chemical composition and the color of these compounds have been found to change continuously with the composition of the mother liquor in which they were crystallized.

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