On Some Dark-colored Chlorocuprates(I, II) and Related Compounds. II. Magnetic Susceptibility and Color at Liquid Helium Temperatures

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A series of dark-colored chloroplumbates(II, IV) and chlorocuprates(I, II) of hexamminechromium(III) and hexamminecobalt(III) were reported in previous papers[1]. In the present paper a study on the magnetic susceptibility and the color of some of these compounds at liquid helium temperatures will be reported.

The samples studied in this research were "mixed valence compounds", $[Co(NH_3)_6]\cdot[PbCl_6]$ (I), $[Co(NH_3)_6][CuCl_5]_x[CuCl_4]_{1-x}$ ($x\sim0.75$) (II) and a single valence compound, $[Co(NH_3)_6][CuCl_5]$ (III). Measurements of magnetic susceptibility were carried out by the a. c. method[2] using a Hartshorn bridge in the temperature range, 1.3~4.2°K. The frequency used was 90 cycles/sec. The reciprocal values of the molar susceptibility (χ_M) of II and III obtained in this way are plotted against absolute temperature T in Fig. 1.

It is seen that the susceptibility obeys the Curie-Weiss law, $\chi_M=C/(T-\Theta)$, down to the temperature of about 2°K. The Weiss constant, ca. −2.3°K, for both II and III as seen from

1) M. Mori, This Bulletin, 24, 285 (1951); 33, 985 (1960).
2) C. J. Gorter, "Paramagnetic Relaxation", Elsevier, Amsterdam (1947).

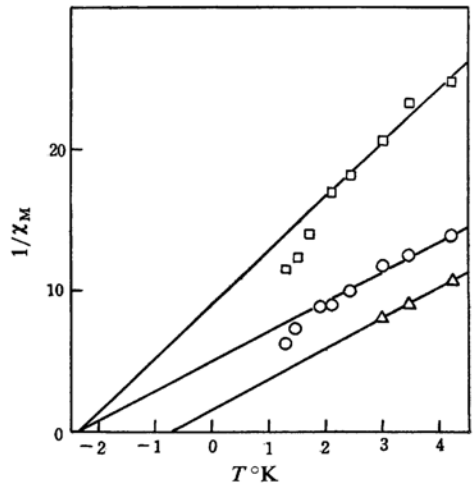

Fig. 1. Plots of $1/\chi_M$ vs. T°K.
—△— $CuSO_4 \cdot 5H_2O$
—○— $[Co(NH_3)_6][CuCl_5]_x[CuCl_4]_{1-x}$
—□— $[Co(NH_3)_6][CuCl_5]$

Fig. 1 is considerably different from that of $CuSO_4 \cdot 5H_2O$ (ca. −0.7°K). The magnetic moments per each bivalent copper atom calculated from the slopes are 1.57 B. M. for II and 1.47 B. M. for III*. These values are also abnormal as compared with the value of $CuSO_4 \cdot 5H_2O$, 1.92 B. M. These anomalies seem to be due to the trigonal-bipyramidal structure[3] of chlorocuprate ion, $[CuCl_5]^{3-}$, and not to the Cu^{I}–Cu^{II} interaction, since II and III exhibit similar magnetic behaviors.

No marked change of color was observed when II (brownish black) and III (yellowish orange) were dipped in liquid helium except that the color of III appeared a little lighter. On the other hand the color of I (brownish black) changed into brown in liquid air and brick red in liquid helium. The cause and reason of such different behaviors of chloroplumbate(II, IV) and chlorocuprate(I, II) are not yet clear.

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* In the calculation of this value the ratio of Cu^{II} content to the total copper was assumed to be $x=0.75$.

3) M. Mori, Y. Saito and T. Watanabe, This Bulletin, to be published.