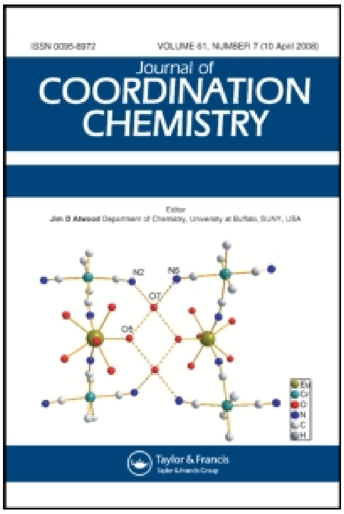

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# MAGNETIC PROPERTIES OF HEXAMMINECOBALT(III) TRIBROMODICHLOROCUPRATE(II)

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# MAGNETIC PROPERTIES OF HEXAMMINECOBALT(III) TRIBROMODICHLOROCUPRATE(II)

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The magnetic susceptibility of hexamminecobalt(III) tribromodichlorocuprate(II) has been measured in the temperature range 4.2–292° K. There is a distinct minimum in the $(\chi_m)^{-1}$ *versus* T plot near 6° K suggestive of an antiferromagnetic interaction. The data are interpreted in terms of a mechanism for the interaction involving inter-complex axial ligand contacts.

## INTRODUCTION

Since there are few known trigonal bipyramidal complexes of transition metal ions with inorganic ligands, there has been much interest in the pentahalocuprate(II) salts of hexamminecobalt(III) and hexamminechromium(III).[2–9] Detailed structural analyses by X-ray diffraction techniques have shown that the pentachlorocuprate(II) ions in both the hexamminechromium(III) salt[6] and the hexamminecobalt(III) salt,[7] have perfect trigonal bipyramidal structures with symmetry $D_{3h}$ although they sit on a site with 32 symmetry. While ligand–ligand repulsions in most trigonal bipyramidal complexes usually result in slightly longer metal-axial than metal-equatorial bond lengths, such is not the case for the $[CuCl_5]^{3-}$ ion. It has been suggested[6] that the shortening of the axial bond length is due to the electronic configuration of the metal ion. A recent report[8] of the preparation and structure of the novel mixed halocuprate, $[Cr(NH_3)_6][CuBr_3Cl_2]$, tends to support this suggestion although the halide ligands are randomly disordered among the five coordination positions. The magnetic properties of these metal complexes have attracted considerable attention following an initial report of a low magnetic moment for the $[CuCl_5]^{3-}$ ion in the compound $[Co(NH_3)_6][CuCl_5]$.[3] More extensive measurements,[9] in a higher temperature range, revealed that the low magnetic moment was a consequence of an antiferromagnetic interaction at about 8° K. It was postulated that the antiferromagnetic effect was probably transmitted through inter-complex axial chloride ligand contacts since from spectral studies[5, 10–13] it is apparent that the unpaired electron of each complex ion resides in the $d_z{}^2$ orbital. The magnetic properties of the mixed halide ion should provide additional insight into this cooperative magnetic behavior. For that reason we have prepared the analogous hexamminecobalt(III) salt, $[Co(NH_3)_6][CuBr_3Cl_2]$, and have measured the magnetic properties of the compound in the temperature range 4.2–292° K. The results of these studies are reported in this article.

## EXPERIMENTAL SECTION

### *Preparation of the Compound*

The new compound hexamminecobalt(III) tribromodichlorocuprate(II), $[Co(NH_3)_6][CuBr_3Cl_2]$, was prepared in a manner similar to that described by Raymond[8] for the chromium analogue. A solution of $[Co(NH_3)_6]Br_3$ in water was added to a fairly concentrated solution of $CuSO_4$ in aqueous HBr and HCl. The resulting solution was then evaporated slowly until most of the volume was gone. Upon cooling with ice very dark maroon colored crystals precipitated. These crystals were collected and air dried.

*Anal.* Calcd. for $[Co(NH_3)_6][CuBr_3Cl_2]$: Br, 44.80; Cl, 13.25; N, 15.69; H, 3.36. Found: Br, 45.02; Cl, 13.30; N, 15.58; H, 3.40.

Since the structure of the hexamminecobalt(III) salt has not been determined, it was taken to be isostructural with the chromium analogue based on a comparison of the intensities of the lines and the progression of the d-spacings of their respective powder patterns.

### *Magnetic Susceptibility Measurements*

The magnetic properties of a powdered sample of $[Co(NH_3)_6][CuBr_3Cl_2]$ were determined at 77°, 195°, and 292° K using a Faraday balance[14] calibrated with $Hg[Co(NCS)_4]$.[15] In the temperature range 4.2–48.7° K, measurements on a powdered sample contained in a plastic sample holder were made with a Foner-type vibrating sample magnetometer[16] built by Princeton Applied Research Corporation. The magnetometer was operated at a field strength of 10,000 G, and was also calibrated with $Hg[Co(NCS)_4]$. Temperature measurements were made with a calibrated germanium resistance thermometer and a high impedence AC resistance bridge. Appropriate diamagnetic corrections estimated from Pascal's constants[17] were applied. A correction for the temperature independent paramagnetism of the cobalt(III) ion[9] was also taken into account.

## RESULTS

In Figure 1 a plot of the inverse molar susceptibility *versus* temperature is shown. Except at very low temperatures, the data obey the Curie-Weiss law $X_m = C/(T+\theta)$ with $C = 0.513$ and $\theta = 55.8°$. From the relationship

$$\mu_{eff} = 2.828\, C^{1/2}$$

we calculate a magnetic moment of 2.03 B.M. As the plot of the data in Figure 1 shows, however, at very low temperatures the data deviate from this law, and a distinct minimum occurs near 6° K. It is probable that this low temperature behavior reflects an antiferromagnetic interaction.

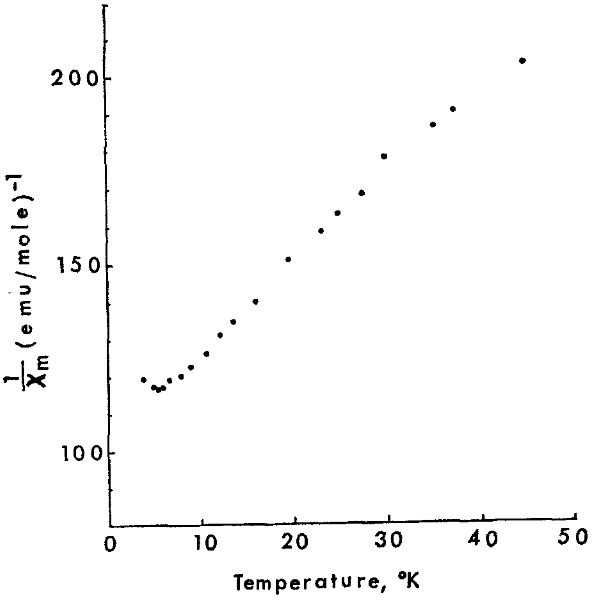

FIGURE 1 The temperature variation of the inverse molar susceptibility for $[Co(NH_3)_6][CuBr_3Cl_2]$ in the range 4.2 to 50° K.

## DISCUSSION

It is of considerable interest to compare the temperatures at which the minima in the $(X_m)^{-1}$ *versus* T plots occur for $[Co(NH_3)_6][CuCl_5]$ and $[Co(NH_3)_6][CuBr_3Cl_2]$, since these temperatures are probably a measure of the magnitude of the antiferromagnetic interaction in the two compounds. With this criterion it is apparent that the interaction is more pronounced in the $[CuCl_5]^{3-}$ salt since the temperature of maximum susceptibility for $[Co(NH_3)_6][CuCl_5]$ was observed near 8° K while that in the current system is about 6° K. Both structural and bonding factors would be expected to govern an antiferromagnetic interaction. The most important of these factors are inter-complex contact distances, intra-complex bond distances, and bond covalencies, the latter factor being a function of the identity of the halide ligand and the appropriate intra-complex bond length. This follows since the overlap of the wave functions must decrease with increasing internuclear separation.

The features of the chromium hexammine salts of the two anions (since the data for these are somewhat more complete) which are to be compared are the following:

| Space group | $[Cr(NH_3]_6][CuCl_5]$(6)<br>Fd3c | $[Cr(NH_3)_6][CuBr_3Cl_2]$(8)<br>Fd3c |
|---|---|---|
| a | 22.240 ± .007 Å | 22.644 ± .007 Å |
| $Cu\text{-}Cl_{ax}$ | 2.2964 ± .0012 | 2.375 ± .002 |
| $Cu\text{-}Cl_{eq}$ | 2.3912 ± .0013 | |

The somewhat larger unit cell for the mixed halide complex must reflect the additional volume of the bromide ligands, and may permit an increased inter-complex axial chloride contact distance.

We now consider the effect of the random disorder of chloride and bromide ligands among the five coordination positions. With such disorder the symmetry of the pentahalocuprate(II) ion is lowered, but the unpaired electron is still expected to be in the singly degenerate sigma anti-bonding orbital. This orbital will surely be mainly $d_z{}^2$

although, depending on the isomer under consideration, properties of the other *d*-orbitals may be mixed thereby complicating a mechanistic discussion. We proceed with the assumption that we can discuss the mechanism in terms of the $d_{z^2}$ orbital, only.

In the case of random disorder, it would be expected that 60% of the time a bromide ligand may occupy an axial site. Since the copper–bromine bond length is considerably longer than that for the copper–chlorine bond, there will be a diminished amplitude of the magnetic wave function on the ligand. A weaker antiferromagnetic interaction will naturally occur under those circumstances. One might argue, contrawise, that the copper-bromine bond should be more covalent since the electronegativity difference is not as pronounced, and that the interaction should be enhanced. This argument, however, neglects the increased bond length effect, and further, is not in agreement with the experimental facts.

It is not necessary to discuss the contribution of the equatorial inter-complex contacts between bromide ligands, since the considerations outlined above for the inter-complex axial contacts apply equally as well in this case.

Thus, we conclude by remarking that the magnetic data for the new and novel complex $[Co(NH_3)_6][CuBr_3Cl_2]$ tend to support a mechanism for the antiferromagnetic interaction involving axial inter-complex ligand-ligand contacts regardless of the degree of randomness among the ligands. It would be of great interest to further compare the magnetic properties of $[Co(NH_3)_6][CuCl_5]$ and $[Co(NH_3)_6][CuBr_3Cl_2]$ with those of a salt containing the $[CuBr_5]^{3-}$ ion. Unfortunately, we have not been able to prepare a compound containing the pentabromocuprate(II) ion with a diamagnetic cation. Efforts in this direction are continuing.

## ACKNOWLEDGEMENTS

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