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Magnetic Study of α- and β-Diamminecopper(II) Chlorides and Bromides

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The magnetic susceptibilities, χ, of α- and β-$Cu(NH_3)_2X_2$($X=Cl$, Br) were measured from 4.2 to 360 K. Those of β-$Cu(NH_3)_2X_2$ obeyed the Curie-Weiss law above 50 K. The Weiss constants and effective Bohr magneton numbers are $-3.5(\pm1)$ K and $1.75(\pm0.01)$ for X=Cl, and -9.7 K and 1.82 for X=Br. α-$Cu(NH_3)_2Cl_2$ showed a rounded maximum for χ at 30 K. A linear Heisenberg model with the parameters, $J=-23.5(\pm1)$ K and $g=2.03(\pm0.03)$, gave good agreement with observations. α-$Cu(NH_3)_2Br_2$ had a peak for χ at $47(\pm2)$ K. This temperature is probably a Neèl temperature. The strong magnetic interaction of the α-form compounds is related to the compressed coordination octahedron of $[Cu(NH_3)_2X_4]^{2-}$. All samples used were solid solutions of $Cu(NH_3)_2X_2$ and NH_4X. An analysis of χ suggests that the Cu^{2+} cations in α-$Cu(NH_3)_2Cl_2$ are distributed inhomogeneously over a short range. A similar inhomogeneity was also found for the β-$Cu(NH_3)_2X_2$ samples. In this sense, the β-form may be better described as a solid solution of α-$Cu(NH_3)_2X_2$ and NH_4X rather than as a dimorph.

Diamminecopper(II) chloride and bromide have interesting stereochemical features. The copper(II) cation of these halides is situated at the center of a compressed $[Cu(NH_3)_2X_4]^{2-}$ (X=Cl, Br) octahedron, whereas in many copper(II) compounds the copper(II) cation is in an elongated octahedral environment. Studies have been made on the crystal structures of these compounds,[1-3] and their IR and optical absorption,[4] and ESR spectra.[4] Similarly, these compounds diluted with NH_4X[5] and ammonium halides doped with copper(II) ions[6-10] have also been studied. In the present study, the magnetic susceptibilities of α- and β-$Cu(NH_3)_2X_2$ were measured in order to learn the effect of a particular coordination on a magnetic property.

However, these halides are dimorphous. One of them has a chain structure of the coordination octahedra, $[Cu(NH_3)_2X_4]^{2-}$, while the other consists of isolated octahedra. Since both dimorphs exist at room temperature, it is questionable whether they are a thermodynamically-stable phase. In analyzing the magnetic susceptibility of α-$Cu(NH_3)_2Cl_2$, information on the distribution of copper(II) cations was obtained. From this information the phase relationship will be discussed.

Experimental

Preparation. Preparation of α- and β-$Cu(NH_3)_2X_2$ (X=Cl, Br) samples followed a known method.[1] The process always resulted in precipitates containing NH_4X. Moreover, the precipitates of the α-form partially transformed into the β-form during washing with an NH_4X aqueous solution. This partial transformation was prevented by washing the precipitate with acetone immediately after the parent solution had been filtered off. Ammonium halides contaminating precipitates were separated by decantation from acetone. This separation was repeated until the X-ray diffraction powder pattern of the sample indicated the disappearance of diffraction lines from NH_4X or indicated that the intensity ratio of several strong lines no longer varied.

Magnetic Measurements. The magnetic susceptibilities were measured from 4.2 to 360 K on a Faraday balance. The apparatus was calibrated for $CoHg(SCN)_4$.[11] Corrections were made for diamagnetism (-1.21 and -1.46 mm^3 mol^{-1} for the chlorides and bromides, respectively)[12] and for Van Vleck paramagnetism (0.75 mm^3 mol^{-1}).[13]

Results

The results of chemical analysis of the samples are given in Table 1. All samples obtained in this study contain more N and X than their stoichiometric composition of $Cu(NH_3)_2X_2$ (X=Cl, Br). Considering the caution exercised in their preparation, these samples are not a mixture of $Cu(NH_3)_2X_2$ and NH_4X, but are a solid solution of these two compounds. These preparations always gave solid solutions with no pure $Cu(NH_3)_2X_2$.

TABLE 1. RESULTS OF CHEMICAL ANALYSIS AND THE MOLAR FRACTIONS OF $Cu(NH_3)_2X_2$ DEDUCED THEREFROM

Compound	Mass fraction[a]				Molar fraction of $Cu(NH_3)_2X_2$
	Cu	N	H	X	
α-$Cu(NH_3)_2Cl_2$	0.3520	0.174	0.041	0.4334	0.814
β-$Cu(NH_3)_2Cl_2$	0.2392	0.206	0.052	0.5069	0.353
α-$Cu(NH_3)_2Br_2$	0.2243	0.112	0.026	0.6375	0.792
β-$Cu(NH_3)_2Br_2$	0.1836	0.119	0.031	0.6662	0.525

a) Calcd for $Cu(NH_3)_2Cl_2$: Cu 0.3771, N 0.1663, H 0.0359, Cl 0.4208; for $Cu(NH_3)_2Br_2$: Cu 0.2469, N 0.1088, H 0.0235, Br 0.6208.

The magnetic susceptibilities are shown in Figs. 1—4. Throughout this paper, values of the magnetic susceptibility, χV_m, are given for one mole of copper(II) cations.

For both compounds having β-form, the magnetic susceptibility decreased monotonically with increasing temperature and obeyed the Curie-Weiss law above 50 K. The Weiss constants, θ, and effective Bohr magneton numbers, n_μ, deduced therefrom are given in Table 2.

In contrast to the features of the β-form compounds, the magnetic susceptibilities of the α-form compounds

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Table 2. Weiss constants θ and effective Bohr magneton numbers n_μ obtained by application of the Curie-Weiss law

Compound	θ/K[a)]	n_μ[b)]
α-$Cu(NH_3)_2Cl_2$	−36	1.85
α-$Cu(NH_3)_2Br_2$	−70	1.95
β-$Cu(NH_3)_2Cl_2$	−3.5	1.75
β-$Cu(NH_3)_2Br_2$	−9.7	1.82

a) Maximum e.s.d. is ±2 K. b) Maximum e.s.d. is ±0.02.

clearly indicate that strong magnetic interaction occurs among copper(II) cations. The magnetic susceptibility of the α-form chloride compound exhibits a round maximum at 30 K. Combined with the crystal structure (Fig. 5), this suggests the magnetic interaction to be of a one-dimensional character. The temperature dependence agreed well with that of the linear Heisenberg spin system[14)] having the parameters, $J=-23.5(\pm1)$ K and $g=2.03(\pm0.03)$. Fitting to the equation for a linear Ising spin system was unsuccessful.

Since the above-mentioned analysis neglected the fact that the sample was a solid solution, the following model was checked by taking the $Cu(NH_3)_2Cl_2$ molar fraction into account. If the cations are distributed randomly, a linear chain of $[Cu(NH_3)_2Cl_4]^{2-}$ octahedra is cut into smaller chains and the proportion of each smaller chain is determined by the $Cu(NH_3)_2Cl_2$ molar fraction. Assuming that the Heisenberg-type interaction operates only between the nearest neighbor cations in a chain and that the values of parameters J and g are the same for all types of chains, the magnetic susceptibility of the system was calculated as the statistical sum of that of each component. It indicated, however, no maximum, in contrast with the data. Therefore, this model is not applicable to the present case.

The magnetic susceptibility of α-$Cu(NH_3)_2Br_2$ showed a peak at 47(±2) K, and not a round maximum. This suggests that 47 K is a Neèl temperature and that below this temperature copper(II) spins are ordered antiferromagnetically. In support of this, the reduced magnetic

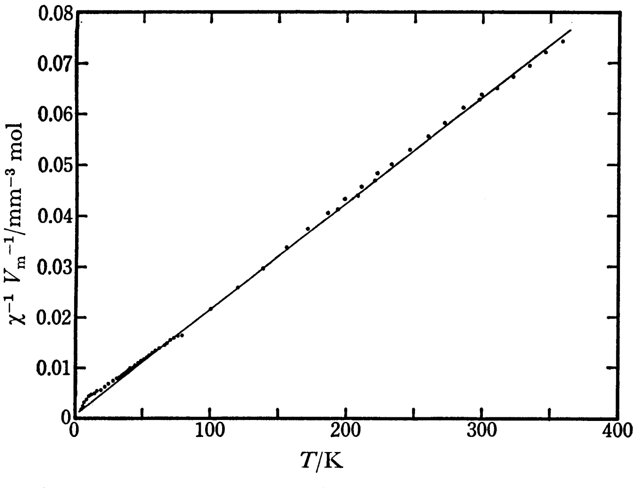


Fig. 1. Temperature dependence of the reciprocal susceptibility of β-$Cu(NH_3)_2Cl_2$. The solid line shows a Curie-Weiss relation.

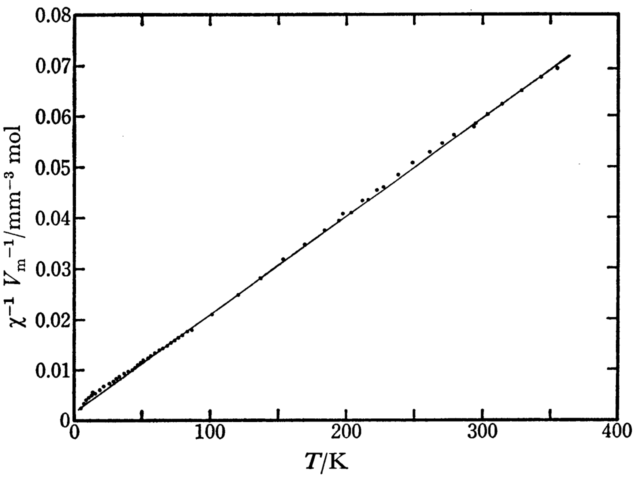


Fig. 2. Temperature dependence of the reciprocal susceptibility of β-$Cu(NH_3)_2Br_2$. The solid line shows a Curie-Weiss relation.

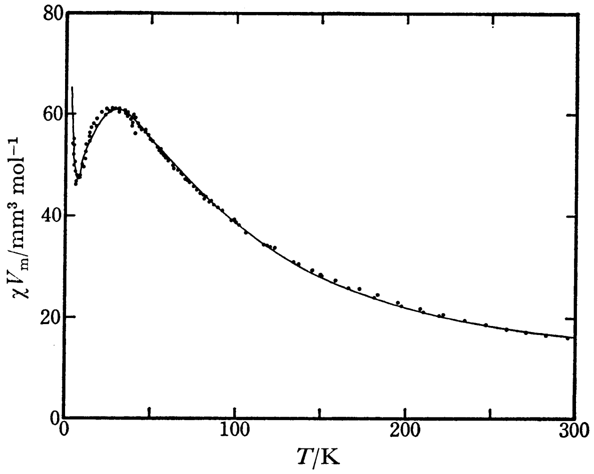


Fig. 3. Temperature dependence of the susceptibility of α-$Cu(NH_3)_2Cl_2$. The solid line shows a calculated one with contributions from a linear Heisenberg model ($J=-23.5$ K, $g=2.03$) and another paramagnetic term. The latter was included to explain the dependence below 10 K and was calculated by the relation of $\chi_p V_m$/mm^3 mol$^{-1}=16.7/(T/\text{K}-3.3)$.

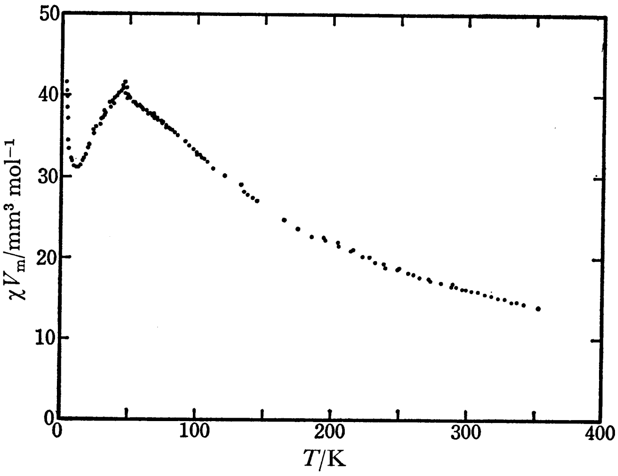


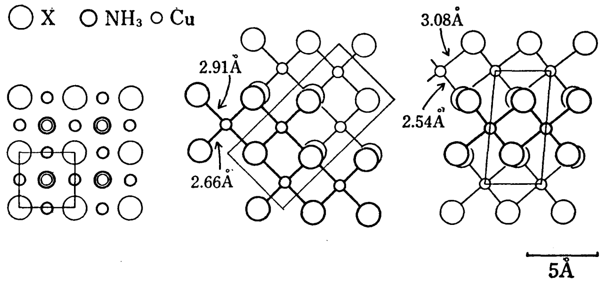
Fig. 4. Temperature dependence of the susceptibility of α-$Cu(NH_3)_2Br_2$.

susceptibility $\chi(T)/\chi(T_N)$ below T_N agreed well with that predicted by simple molecular field theory,[18] although the theory was not applicable to the data over the entire temperature range measured.

For both α-form compounds, the values of parameters θ and n_μ were deduced from data above 110 K for the chloride and above 190 K for the bromide. They are given in Table 2.

Discussion

Crystal Structure. Diamminecopper(II) chloride and bromide are dimorphous.[1] The crystal structures of β-$Cu(NH_3)_2Br_2$[1] and β-$Cu(NH_3)_2Cl_2$ are isomorphous and belong to the cubic system (Fig. 5). The arrangement of the NH_3 molecules and halogen anions is of the CsCl type. The copper(II) cations are situated at the face-centered sites of the anion lattice, forming a $[Cu(NH_3)_2X_4]^{2-}$ compressed octahedron. These copper sites are occupied only with a small probability of 1/6 and the orientation of the octahedron is random along the three crystallographic axes.



(a) β-$Cu(NH_3)_2X_2$ (b) α-$Cu(NH_3)_2Cl_2$ (c) α-$Cu(NH_3)_2Br_2$

Fig. 5. Projection of crystal structure. Atoms at $z'=0$ is shown by a thin line and those at $z'=1/2$ by a thick one, where z' is a positional parameter along the axis perpendicular to the sheet of the paper. A nitrogen atom in α-forms is situated above and below a Cu atom and omitted for simplicity. Chlorine atoms overlapping each other in the α-chloride are shifted for easy view.

The crystal structures of the α-form result from ordering of the octahedron found in the structure of the β-form. This ordering brings about deformation of the lattice and the coordination octahedron itself. The deformation of the octahedron is such that short and long Cu–X distances are distinguished as is often seen in many halo-copper(II) complexes, $CuX_2 \cdot 2L$ (L= H_2O or organic molecules containing an N atom).[15] In α-$Cu(NH_3)_2Br_2$,[2] the coordination octahedron shares two opposite Cl–Cl edges to form an infinite linear chain like that in $CuCl_2 \cdot 2H_2O$ whereas, in α-$Cu(NH_3)_2Cl_2$,[3] zigzag chains result from the sharing of two adjacent Cl–Cl edges of the octahedron.

Magnetic Properties. For the β-forms, the observed magnetic susceptibilities show mainly the behavior expected for an isolated copper(II) ion (Figs. 1 and 2). This observation is compatible with the crystal structure together with a large dilution of NH_4X molecules (Table 1). However, deviation from the Curie-Weiss law was observed below 50 K and the Weiss constants have a non-zero value. This means that the copper(II) ions in these compounds are not fully isolated. This is discussed further below.

The magnetic susceptibility of α-$Cu(NH_3)_2Cl_2$ agrees well with a one-dimensional Heisenberg spin system having a J value of −23.5 K. Thus, an antiferromagnetic interaction must occur along the zigzag chain. Since the separation between copper(II) ions exceeds 3.9 Å, the direct interaction of copper(II) spins should be negligible. A copper(II) cation has four Cu^{2+} neighbors in a chain and two types of paths along which the superexchange interaction are possible. One of the paths passes the short (2.61 Å) and long (2.91 Å) Cu–Cl bonds between two nearest neighbor cations, whereas the other passes the two long Cu–Cl bonds between two alternate neighboring cations. Since the latter includes only long Cu–Cl bonds, only the former should be effective in this compound. This view is consistent with the result obtained from the ESR study of a doped copper ion in NH_4Cl at 4.2 K[8,10] for which a superhyperfine interaction was detected only between a copper spin and two nearest Cl nuclei in the center of the $[Cu(H_2O)_2Cl_4]^{2-}$ with orthorhombic symmetry. The value of J obtained is about twice that of a typical one-dimensional chloro-complex of $CuCl_2 \cdot 2C_5H_5N$ ($J=-13.6$ K).[16] The accuracy in the structural analysis of α-$Cu(NH_3)_2Cl_2$, however, is not enough to permit a discussion of the difference in the J values.

The magnetic susceptibility of α-$Cu(NH_3)_2Br_2$ indicates a three-dimensional ordering of copper(II) spins below 47 K. Therefore, a magnetic interaction must occur between linear chains, as well as within a chain. On inspection of the crystal structure, it appears that $NH_3 \cdots Br$ hydrogen bonds probably play the principal role in the interchain interaction. There are four such paths with an N···Br distance of 3.51 Å. Boettcher and Spaeth have shown that in the paramagnetic center of $[Cu(NH_3)_2Cl_4]^{2-}$ in NH_4Cl, an ammonia molecule reorients about the Cu–N bonding axis at 4.2 K.[10] The situation is probably the same in α-$Cu(NH_3)_2Br_2$ and hence the hydrogen bonding is weak. In $K_2CuCl_4 \cdot 2H_2O$, copper(II) cations interact through $H_2O \cdots Cl$ hydrogen bonding the magnitude of the interaction being of the order of 0.1 K.[17] On the other hand, Cu–Br chemical bonding plays a role in the intrachain interaction. Therefore, in α-$Cu(NH_3)_2Br_2$, the intrachain interaction should be stronger than the interchain interaction. The ratio of their magnitudes was estimated to be 1×10^{-1} from T_N and θ by application of molecular field theory.[18] This value is very large compared with the usual values of the order of 10^{-3} or less.[19] Furthermore, the value of the ratio T_N/θ, which is 0.67 for α-$Cu(NH_3)_2Br_2$, is much greater than the corresponding values, which are less than 0.2, for typical antiferromagnetic Heisenberg chains, and is close to values of 0.7—0.8 for three-dimensional Heisenberg magnets.[19] These facts indicate that the interchain interaction is very strong in α-$Cu(NH_3)_2Br_2$.

Strong magnetic interaction was observed in the α-form compounds. This is the result of the particular coordination of the copper(II) cation. As the coordination octahedron $[Cu(NH_3)_2X_4]^{2-}$ is compressed along the Cu–N bonding axis,[1] the unpaired electron of the copper(II) cation occupies the $3d_{x^2-y^2}$ orbital.[4–10] Because the lobes of this orbital point to four chlorine neighbors, stronger magnetic interaction is expected in this case than in the case in which the unpaired electron occupies the $3d_{z^2}$ orbital in the elongated octahedral coordination.

Phase Relationship. The samples in this study were all solid solutions. However, the magnetic susceptibility of the α-$Cu(NH_3)_2Cl_2$ sample cannot be explained on the assumption that the copper(II) cations are distributed randomly and that the magnetic interaction between them is isotropic. A calculation based on this assumption showed that the maximum magnetic susceptibility χ_{max} is much larger for small chains than for an infinite chain; *e.g.* the χ_{max} of a tetramer, which is the most predominant species in the case of random distribution, is greater by 26.5% than that of the infinite chain. Therefore, the fact that the observed magnetic susceptibility agree well with an infinite linear Heisenberg model strongly suggests that the sample is not homogeneous over a short range. The copper(II) cations group together and form a chain long enough to exhibit the magnetic feature of an infinite chain.

In this connection, Tomlinson and Hathaway[4] have published an interesting observation for β-$Cu(NH_3)_2X_2$. They observed an isotropic ESR spectrum for the chloride and no signal for the bromide. They explained this by the effect of exchange coupling between the copper(II) cations. Because the occupancy factor of the copper site is only 1/6, their ESR results indicate that their samples of the β-form are inhomogeneous over a short range like the present sample of α-$Cu(NH_3)_2Cl_2$. On the contrary, the magnetic susceptibility of the β-form in the present study has primarily the character of that of an isolated copper(II) ion. The difference may be due to a greater local inhomogeneity in their samples than in the present ones. Local inhomogeneity is suggested also for the present samples due to small Weiss constants and deviation from the Curie-Weiss law below 50 K.

The preparation data[1] support this view. When a concentrated NH_4X solution was used as a solvent, the precipitate was of the β-form and remained stable. When a dilute NH_4X solution was used, the first precipitate was also of the β-form, which then transformed into the α-form. This means that, for a high concentration of copper, the system is more stabilized by clustering than by random distribution of the cations. The latter situation is probably stable only at very low copper concentrations. Thus, the local inhomogeneity needs to be taken into consideration for certain physical measurements on samples of the β-form, although a statistical distribution of copper(II) ions has been derived from X-ray analysis.[20] Together with the similarity between the crystal structures of β-$Cu(NH_3)_2X_2$ and NH_4X, the β-form may be better described as a solid solution of α-$Cu(NH_3)_2X_2$ and NH_4X rather than as one of dimorphs.

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20) The idea of local inhomogeneities is not contrary to the result of X-ray analysis. Ususal X-ray analysis gives information on the average structure. Local inhomogeneities, if present, yield a large temperature factor. Hanic and Cakajdova give a large value for the temperature factor (Ref. 1). The inhomogeneities discussed here may contribute to this in some degree.