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Magnetic Properties of Copper(II) Complexes of 6-Aminopurine and 6-Hydroxypurine

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The magnetic susceptibilities of bis(6-aminopurinato)copper(II) trihydrate, dichlorobis(6-aminopurine) copper(II) sesquihydrate, and dichlorobis(6-hydroxypurine)copper(II) monohydrate obey the Bleaney-Bowers equation for binuclear clusters in conformity with the results of X-ray crystal analysis. The exchange integrals within binuclear clusters were evaluated as $J/k=-156$ to -208°K. Superexchange interaction rather than the interaction of direct nature operates predominantly between copper atoms through the $p\pi$ orbitals of the heterocycles. The J/k values of the compounds are nearly equal to the value, -204°K, of copper(II) acetate monohydrate, although the Cu–Cu distance in the former is greater than that in the latter. The magnetic susceptibilities of dibromobis(6-aminopurine)copper(II) dihydrate, dibromobis(6-hydroxypurine)copper(II) dihydrate, dichloro(6-aminopurine)copper(II), dichloro(6-hydroxypurine)copper(II) monohydrate, and dibromo(6-hydroxypurine)copper(II) hemihydrate indicate the presence of paired copper atoms in the crystals.

Copper(II) acetate monohydrate presents a typical example of binuclear structure,[1] its magnetic susceptibility conforming to the simple triplet-singlet formula.[2,3] For the magnetic interaction within a binuclear cluster, two types of mechanism have been proposed, *i.e.*, direct exchange interaction through a δ-bond ($d_{x^2-y^2}-d_{x^2-y^2}$) and superexchange interaction through four Cu–O–C–O–Cu linkages.[3–6] Some experimental results suggest the predominance of the latter mechanism.[4–6] However, no conclusive evidence has been proposed as yet. A recent X-ray crystal analysis has shown that the crystals of bis(6-aminopurinato)copper(II) tetrahydrate, $Cu(ap)_2 \cdot 4H_2O$, contain binuclear clusters closely resembling those of copper(II) acetate monohydrate as shown in Fig. 1.[7] However, the detailed structure of the compounds reveals two significant differences that the Cu–Cu separation, 2.949 Å, in $Cu(ap)_2 \cdot 4H_2O$ is much greater than 2.64 Å in copper(II) acetate monohydrate and that 6-aminopurinato ligands involve a strong π-bond conjugation as compared with acetate groups. The crystals of dichlorobis(6-aminopurine)copper(II) trihydrate, $CuCl_2(apH)_2 \cdot 3H_2O$, and dichlorobis(6-hydroxypurine)copper(II) trihydrate, $CuCl_2(hpH)_2 \cdot 3H_2O$ also have binuclear clusters analogous to those of $Cu(ap)_2 \cdot 4H_2O$.[8,9] The neutral molecules of the heterocycles in the first two compounds have a stronger aromatic character than that of anionic heterocycles in the last compound. The present investigation has been undertaken in order to obtain some information about the mechanism of magnetic interaction between copper atoms in the binuclear clusters of the copper(II) complexes having the nitrogen heterocycles and of copper(II) acetate monohydrate. In addition, we have determined the susceptibilities of some $CuBr_2L_2$ and CuX_2L type complexes (X: halide ions, L: 6-aminopurine or 6-hydroxypurine) to discuss magnetic interaction in relation to crystal structure.

Preparation of Materials

Bis(6-aminopurinato)copper(II) tetrahydrate, $Cu(ap)_2 \cdot 4H_2O$, was prepared by a method described by Weiss and Venner[10] and recrystallized from a 10% ethanol-water mixture.[7] When the crystals were dried over phosphorus pentoxide or silica gel in a desiccator, $Cu(ap)_2 \cdot 3H_2O$ was obtained.[10] The results of chemical analysis are listed in Table 1. Dichlorobis(6-aminopurine)copper(II) sesquihydrate, $CuCl_2(apH)_2 \cdot 1.5H_2O$, dichlorobis(6-hydroxypurine)copper(II) monohydrate, $CuCl_2(hpH)_2 \cdot H_2O$, dichloro(6-aminopurine)copper(II), $CuCl_2(apH)$, and dichloro(6-hydroxypurine)copper(II) monohydrate, $CuCl_2(hpH) \cdot H_2O$, were prepared by methods reported in the literature.[10,11] X-ray crystal analysis has been

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Table 1. Analytical data for CuX$_2$(apH)$_m$·nH$_2$O and CuX$_2$(hpH)$_m$·nH$_2$O

Compound	Cu, %		C, %		H, %		N, %	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Cu(ap)$_2$·3H$_2$O	16.5	16.9	31.1	31.5	3.7	3.7	36.3	37.1
CuCl$_2$(apH)$_2$·1.5H$_2$O	14.7	14.7	27.8	28.5	3.0	2.9	32.5	32.3
CuCl$_2$(hpH)$_2$·H$_2$O	14.9	15.3	28.3	28.1	2.8	2.4	26.4	25.4
CuBr$_2$(apH)$_2$·2H$_2$O	11.9	12.2	22.7	22.9	2.7	2.6	26.4	25.9
CuBr$_2$(hpH)$_2$·2H$_2$O	11.9	12.5	22.6	22.8	2.7	2.2	21.1	21.2
CuCl$_2$(apH)	23.6	23.4	22.3	22.2	1.9	2.1	26.0	25.8
CuCl$_2$(hpH)·H$_2$O	22.1	21.8	20.8	21.0	2.4	2.1	19.4	19.4
CuBr$_2$(hpH)·0.5H$_2$O	17.2	17.1	16.3	16.4	1.6	1.6	15.2	15.3

apH: 6-aminopurine, hpH: 6-hydroxypurine.

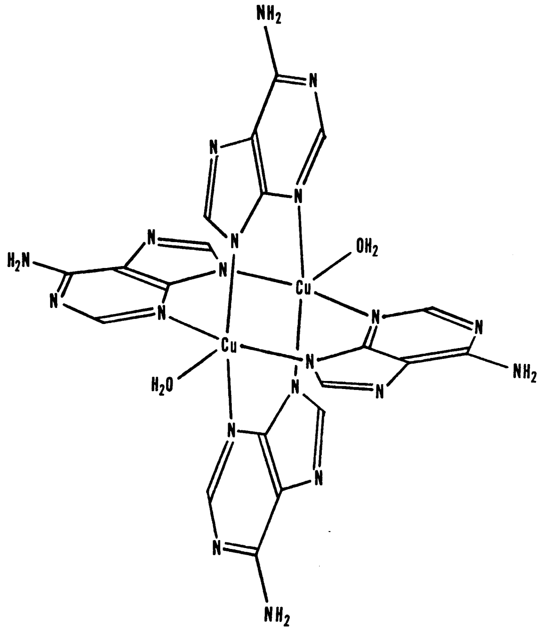

Fig. 1. Binuclear structure of bis(6-aminopurinato)copper(II) tetrahydrate.

carried out on Cu(ap)$_2$·4H$_2$O, CuCl$_2$(apH)$_2$·3H$_2$O, and CuCl$_2$(hpH)$_2$·3H$_2$O. However, the crystals of these complexes gradually lost water of crystallization in air. On standing over silica gel in a desiccator, the crystals yielded Cu(ap)$_2$·3H$_2$O, CuCl$_2$(apH)$_2$·1.5H$_2$O, and CuCl$_2$(hpH)$_2$·H$_2$O, which were no longer dehydrated in vacuum as well as in air. Therefore, these hydrates were used for magnetic measurements. Dibromobis(6-aminopurine)copper(II) dihydrate, CuBr$_2$(apH)$_2$·2H$_2$O, and dibromobis(6-hydroxypurine)copper(II) dihydrate, CuBr$_2$(apH)$_2$·2H$_2$O, and dibromobis(6-hydroxypurine)copper(II) dihydrate, CuBr$_2$(hpH)$_2$·2H$_2$O, were prepared by adding a dilute aqueous solution of copper(II) bromide (1 mol) to aqueous solutions of appropriate ligands (2 mol) acidified with a minimum quantity of hydrobromic acid. Dibromo(6-hydroxypurine)copper(II) hemihydrate, CuBr$_2$(hpH)·0.5 H$_2$O, was prepared in the same way as for CuCl$_2$(hpH)·H$_2$O using hydrobromic acid in place of hydrochloric acid. We tried to prepare CuBr$_2$(apH) by a method similar to that for CuBr$_2$(hpH)·0.5H$_2$O, but failed to obtain pure samples.

Magnetic Measurements and Results

Magnetic susceptibilities were determined using magnetic balances described in a previous paper.[12] The molar susceptibilities were corrected for diamagnetic contributions (in 10^{-6} emu/mole) from copper(II) ions (−11), chloride ions (−26), bromide ions (−36), water (−13), 6-aminopurine (−62), and 6-hydroxypurine (−59).[13,14] The last value is based

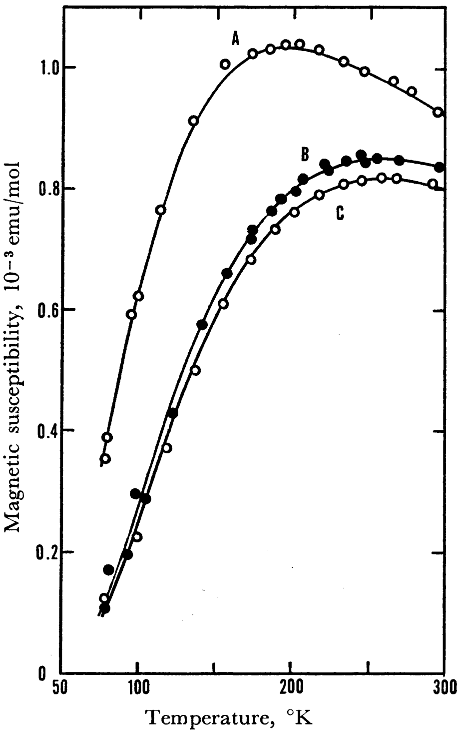

Fig. 2. Magnetic susceptibilities of bis(6-aminopurinato)copper(II) trihydrate (A), dichlorobis(6-aminopurine)copper(II) sesquihydrate (B), and dibromobis(6-aminopurine)copper(II) dihydrate (C). The solid curves show theoretical susceptibilities calculated by the triplet-singlet formula.

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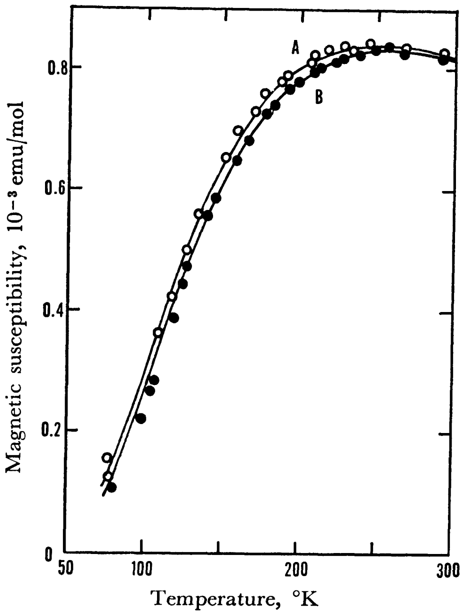

Fig. 3. Magnetic susceptibilities of dichlorobis(6-hydroxypurine)copper(II) monohydrate (A) and dibromobis(6-hydroxypurine)copper(II) dihydrate (B). The solid curves represent the triplet-singlet formula.

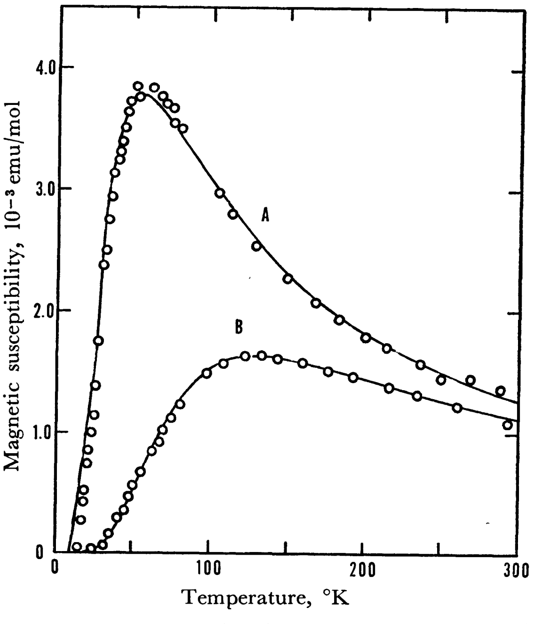

Fig. 4. Magnetic susceptibilities of dichloro(6-aminopurine)-copper(II) (A) and dichloro(6-hydroxypurine)copper(II) monohydrate (B). The solid curves represent the triplet-singlet formula.

on the observed values of 6-aminopurine (adenine) and 2-amino-6-hydroxypurine (guanine).[14] The temperature-independent paramagnetism was assumed to be equal to 60×10^{-6} emu/mol.[3] The corrected susceptibilities are plotted against the temperature in Figs. 2—5.

Discussion

The magnetic susceptibility of $Cu(ap)_2\cdot 3H_2O$ conforms to the theoretical susceptibility, χ, of binuclear clusters[2] (see Fig. 2).

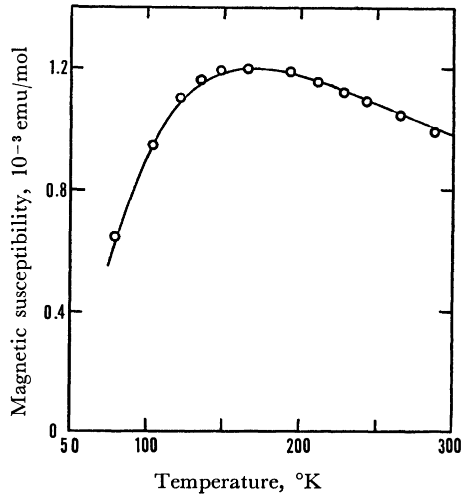

Fig. 5. Magnetic susceptibility of dibromo(6-aminopurine)-copper(II) hemihydrate. The solid curve represents the triplet-singlet formula.

$$\chi = \frac{Ng^2\beta^2}{3kT}\left[1+\frac{1}{3}\exp\left(-\frac{2J}{kT}\right)\right]^{-1} \qquad (1)$$

Here apart from obvious notations, J is the exchange integral between copper atoms within a cluster. The exchange integral and the g-value are evaluated as $J/k=-156$°K and $g=2.07$. The magnetic susceptibility of $Cu(ap)_2\cdot 4H_2O$, on which X-ray crystal analysis had been carried out, could not be determined in a reproducible manner because the crystals gradually lost water of crystallization even in air. By use of Eq. 1, the exchange integral, J/k, was roughly estimated to be about -170°K from the susceptibility *versus* temperature curve. Goodgame and Price[15] have measured the susceptibility of $Cu(ap)_2\cdot 4H_2O$ and evaluated the parameters as $J/k=-151$°K and $g=2.06$. The exchange integral and the g-value of $Cu(ap)_2\cdot 3H_2O$ are almost equal to those of $Cu(ap)_2\cdot 4H_2O$, indicating that the binuclear clusters are retained on dehydration without any significant change in bonding arrangement. The disagreement between the J/k values of $Cu(ap)_2\cdot 4H_2O$ is due probably to fluctuation in composition. In fact, the magnetic moment of $Cu(ap)_2\cdot 4H_2O$ gradually increased with time at room temperature. The J/k value of $Cu(ap)_2\cdot 3H_2O$ is more reliable than that of the tetrahydrate because the former crystals were no longer dehydrated in vacuum as well as in air. Therefore, the following discussion is based on the data of $Cu(ap)_2\cdot 3H_2O$ and an assumption that the crystals of the trihydrate contain binuclear clusters having the same bonding arrangement as in those of the tetrahydrate.

Dubicki and Martin[5] have pointed out that the δ-bond in the crystals of copper(II) acetate monohydrate is virtually nonbonding and that the configuration of the binuclear clusters is maintained by four bridging acetate groups. This has been supported by the following experimental results. The Cu–Cu

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[15] D. M. L. Goodgame and K. A. Price, *Nature*, **220**, 783 (1968).

bond length, 2.657 Å, in the crystals of copper(II) formate monourea is nearly equal to 2.64 Å in copper(II) acetate monohydrate,[6)] although the former compound shows a magnetic moment, 1.08 B.M. (17°C), much lower than that of the latter, 1.40 B.M. (21.2 °C).[16)] Because the Cu–Cu separation, 2.949 Å, in $Cu(ap)_2 \cdot 4H_2O$ is much greater than that in copper(II) acetate monohydrate, δ-bonds are presumed to be very weak in the former compound. Therefore, magnetic interaction is supposed to take place between copper atoms through Cu–ap–Cu linkages.

The crystals of $CuCl_2(apH)_2 \cdot 3H_2O$[8)] and $CuCl_2(hpH)_2 \cdot 3H_2O$[9)] have binuclear clusters bearing a striking resemblance to those of $Cu(ap)_2 \cdot 4H_2O$: neutral molecules of the heterocycles coordinate to two copper atoms in place of 6-aminopurinato groups and one of the two chloride ions in the chemical formula occupies the same position about a copper atom as does a water molecule coordinating weakly to a copper atom (see Fig. 6). $CuCl_2(apH)_2 \cdot 1.5H_2O$ and $CuCl_2(hpH)_2 \cdot H_2O$ show magnetic properties characteristic of binuclear clusters (see Fig. 3 and Table 2), indicating the retention of the binuclear structure on dehydration. The exchange integrals of $CuCl_2(apH)_2 \cdot 1.5H_2O$ and $CuCl_2(hpH)_2 \cdot H_2O$ are larger than that of $Cu(ap)_2 \cdot 3H_2O$ (see Table 2), although Cu–Cu distance, 3.066 and 3.024 Å, in the former are slightly greater than 2.949 Å in the latter. When paired copper atoms are separated from each other by three diamagnetic atoms (for example, Cu–N–C–N–Cu links), the π-path can give rise to a strong antiferromagnetic interaction between copper atoms,[17)] whereas if the contribution from the σ-path is predominant, unpaired electrons of copper atoms are coupled ferromagnetically.[17)] In the clusters of $CuCl_2(apH)_2 \cdot 1.5H_2O$ and $CuCl_2(hpH)_2 \cdot H_2O$, nitrogen atoms bonded to copper atoms have pπ orbitals, because neutral molecules of 6-aminopurine or 6-hydroxypurine coordinate to copper atoms as shown in Fig. 6. Hence, positive holes of copper atoms can migrate through the π-bond system of Cu–N–C–N–Cu links, giving rise to antiferromagnetic interaction in agreement with the sign of the exchange integrals. In the crystals of $Cu(ap)_2 \cdot 3H_2O$, 6-aminopurinato groups coordinate to copper atoms by nitrogen atoms having a negative formal charge (see Fig. 6). This hinders the migration of positive holes through the π-bond system and weakens antiferromagnetic interaction between copper atoms. Owing to this effect, the magnetic interaction is presumed to operate more strongly in $CuCl_2(apH)_2 \cdot 1.5H_2O$ and $CuCl_2(hpH)_2 \cdot H_2O$ than in $Cu(ap)_2 \cdot 3H_2O$ in accordance with the experimental results (see Table 2).

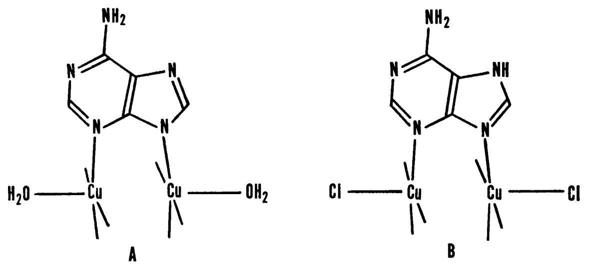

Fig. 6. Bonding arrangements in the binuclear clusters of bis(6-aminopurinato)copper(II) trihydrate (A) and dichlorobis(6-aminopurine)copper(II) sesquihydrate (B).

TABLE 2. EFFECTIVE MAGNETIC MOMENT μ_{eff} AT 17°C, EXCHANGE INTEGRAL J, AND g-VALUE g

Compound	μ_{eff}, B.M.	$-J/k$, °K	g
$Cu(ap)_2 \cdot 3H_2O$	1.46	156	2.07
$CuCl_2(apH)_2 \cdot 1.5H_2O$	1.39	206	2.15
$CuCl_2(hpH)_2 \cdot H_2O$	1.38	200	2.11
$CuBr_2(apH)_2 \cdot 2H_2O$	1.38	208	2.12
$CuBr_2(hpH)_2 \cdot 2H_2O$	1.38	206	2.13
$CuCl_2(apH)$	1.74	44	2.10
$CuCl_2(hpH) \cdot H_2O$	1.62	104	2.12
$CuBr_2(hpH) \cdot 0.5H_2O$	1.52	134	2.07
$Cu(CH_3COO)_2 \cdot H_2O$[a)]	1.40[b)]	204	2.13

a) Ref. 3, b) at 21.2°C.

The magnetic susceptibility *versus* temperature curves of $CuBr_2(apH)_2 \cdot 2H_2O$ and $CuBr_2(hpH)_2 \cdot H_2O$ conform to Eq. 1 (see Figs. 2 and 3), indicating the presence of binuclear clusters analogous to those in the crystals of the corresponding chlorides. The values of exchange integrals are almost equal to one another as listed in Table 2, indicating that the substitution of chlorine with bromine gives no appreciable effect on magnetic interaction.

The magnitude of superexchange interaction depends to a great extent on the electronic structure of bridging ligands. When superexchange interaction takes place through three diamagnetic atoms, a path through π-orbitals can give rise to a strong antiferromagnetic interaction.[17)] Therefore, one would suspect that magnetic interaction operates more strongly in the complexes of 6-aminopurine and 6-hydroxypurine than in copper(II) acetate monohydrate, because the heterocycles are expected to facilitate the migration of positive holes more strongly than do acetate groups. Contrary to this expectation, the exchange integral of copper(II) acetate monohydrate is almost equal to those of $CuX_2(apH)_2 \cdot nH_2O$ and $CuX_2(hpH)_2 \cdot nH_2O$ type complexes and is evidently larger than that of $Cu(ap)_2 \cdot 3H_2O$ (see Table 2). These facts suggest that the effect of direct exchange interaction is not entirely negligible in the binuclear clusters of copper(II) acetate monohydrate despite the predominance of superexchange interaction.

The susceptibilities of $CuCl_2(apH)$, $CuCl_2(hpH) \cdot H_2O$, and $CuBr_2(hpH) \cdot 0.5H_2O$ also can be fitted well to the curves of Eq. 1 (see Figs. 4 and 5). Presumably, paired copper atoms are bridged by the heterocycles in the crystals.

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16) M. Kishita, M. Inoue, and M. Kubo, *Inorg. Chem.*, **3**, 237 (1964).

17) M. Inoue and M. Kubo, *ibid.*, **9**, 2310 (1970).