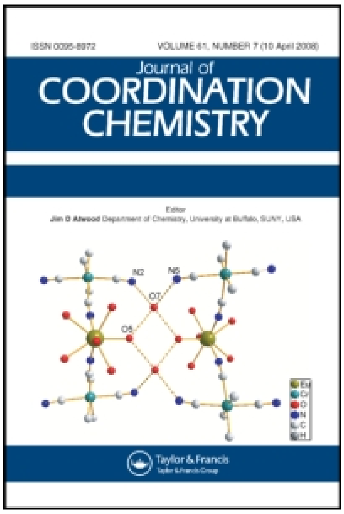

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MAGNETIC SUSCEPTIBILITIES AND POLYMERIC STRUCTURES OF COPPER(II) COMPLEXES WITH PYRAZOLE, IMIDAZOLE, AND TRIAZOLE

Motomichi Inoue[a]; Masaji Kubo[a]
[a] Department of Chemistry, Nagoya University, Nagoya, Japan

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MAGNETIC SUSCEPTIBILITIES AND POLYMERIC STRUCTURES OF COPPER(II) COMPLEXES WITH PYRAZOLE, IMIDAZOLE, AND TRIAZOLE

MOTOMICHI INOUE and MASAJI KUBO

Department of Chemistry, Nagoya University, Chikusa, Nagoya 464, Japan

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The magnetic susceptibilities of some copper(II) complexes with pyrazole (pyH), imidazole (imH), and 1,2,4-triazole (trH) were determined at temperatures between 78 and 300 K. On the basis of the observed susceptibilities, the crystal structures of the complexes were proposed in relation to the type of spin aggregation: linear chains consisting of –Cu–N–N–Cu– links are formed in $Cu(py)_2 \cdot \frac{1}{2}H_2O \cdot \frac{1}{2}NH_3$ and $CuSO_4(trH)_2 \cdot 3H_2O$, whereas –Cu–N–C–N–Cu– links construct network structures in $Cu(tr)_2$ and $Cu(im)_2$. The exchange integral and the Weiss constant depend to a great extent on the kind of bridging ligands and the type of spin aggregation.

INTRODUCTION

In the crystals of copper(II) complexes with pyrazole (pyH), imidazole (imH), and 1,2,4-triazole (trH), –Cu–L–Cu– links are expected to be formed for steric reasons inherent in nitrogen heterocycles. In fact, X-ray crystal analysis[1] carried out on $CuCl_2(trH)$ has shown that the neighboring nitrogen atoms of a triazole molecule coordinate to two copper atoms as shown in Fig. 1A and that the resulting infinite linear chain is the structural unit. The formation of –M–(trH)–M– links has been reported for $Ni(NO_3)_2(trH)_2 \cdot \frac{8}{3}H_2O$ also,[2] in which a trinuclear cluster, $[\{(H_2O)_3(trH)_3Ni\}_2Ni]^{6+}$, is the structural unit. The magnetic susceptibility and broad-line PMR of the complex have indicated the presence of superexchange interaction through the bridging nitrogen-heterocyclic ligand.[3,4] For the same steric requirement, the neighboring nitrogen atoms of a pyrazolate ion can coordinate to two copper atoms, constituting the same type of –Cu–N–N–Cu– links as shown in Fig. 1A. Jarvis and Wells[5,6] have carried out X-ray crystal analysis on $Cu(im)_2$, and reported the formation of –Cu–N–C–N–Cu– links in the crystal. 1,2,4-Triazole also possibly forms –Cu–N–C–N–Cu– links as shown in Fig. 1B. It is expected that 1,2,4-triazole acting as a uninegative bidentate ligand forms –Cu–(tr)–Cu– links closely resembling those in $Cu(im)_2$ (see Fig. 1C). For these reasons, the five-membered nitrogen heterocycles are expected to form copper(II) complexes of magnetic interest. In fact, a variety of copper(II) complexes with these ligands have been prepared, and low magnetic moments have been observed for the majority of the complexes at room temperature.[7] Bis(imidazolato)copper(II), $Cu(im)_2$, has been reported to form three modifications differing in the effective magnetic moment: a blue modification (μ_{eff} = 1.57 B.M.), a green modification (1.62 B.M.), and a brown modification (1.46 B.M.).[7,8] For these reasons, the structures of the complexes attract attention from the viewpoint of magnetic interaction. Unfortunately, it is difficult to get single crystals available for X-ray crystal analysis. The temperature dependence of magnetic susceptibility often gives a valuable information about the type of spin aggregation closely related to crystal structure, because rigorous formulas for susceptibility have been derived theoretically for various types of isolated clusters and linear chains.[9–12] In the present investigation, the magnetic susceptibilities of the complexes have been determined as functions of temperature to obtain informations about magnetic interaction and the type of spin lattices in the crystals of the complexes.

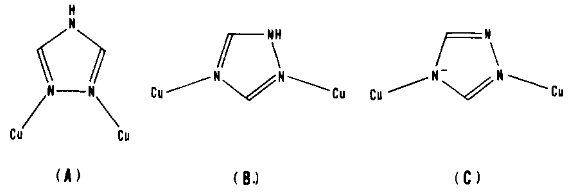

FIGURE 1 Types of Cu–(trH)–Cu and Cu–(tr)–Cu links.

EXPERIMENTAL

The compounds were prepared by methods described in a previous report.[7] The magnetic susceptibility was determined by the Gouy method with a field strength of 5000 Oe in a temperature range of 78–300 K. It was corrected for diamagnetic contributions (10^{-6} emu mol^{-1}) from copper ions (-11), chloride ions (-26), sulfate ions (-40), water (-13), ammonia (-18), pyrazole (-33), imidazole (-33), and 1,2,4-triazole (-38).[7,13,14] The temperature-independent paramagnetic susceptibility, $N\alpha$, was assumed to be equal to 60×10^{-6} emu mol^{-1}.

RESULTS AND DISCUSSION

Figures 2–4 show the observed magnetic susceptibilities. The magnetic susceptibility of $Cu(tr)_2$ and the blue modification of $Cu(im)_2$ obey the Curie–Weiss law, $\chi = C/(T - \theta) + N\alpha$, over the temperature range investigated. The Curie constant C and the Weiss constant θ were determined as $C = 0.428$ emu K mol^{-1} and $\theta = -87$ K for $Cu(tr)_2$, and $C = 0.449$ emu K mol^{-1} and $\theta = -156$ K for the blue modification of $Cu(im)_2$. The susceptibility of the green modification of $Cu(im)_2$ obeys the Curie–Weiss law above about 170 K: $C = 0.417$ emu K mol^{-1} and $\theta = -101$ K.[15]

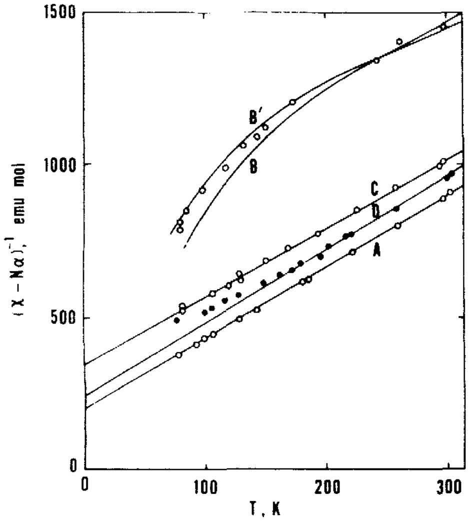

FIGURE 2 Reciprocal susceptibilities of $Cu(tr)_2$ (A), $CuCl(tr)\cdot 2H_2O$ (B), blue $Cu(im)_2$ modification (C), and green $Cu(im)_2$ modification (D). Curves B and B' show the theoretical reciprocal susceptibilities of isolated trinuclear clusters and coupled trinuclear clusters, respectively.

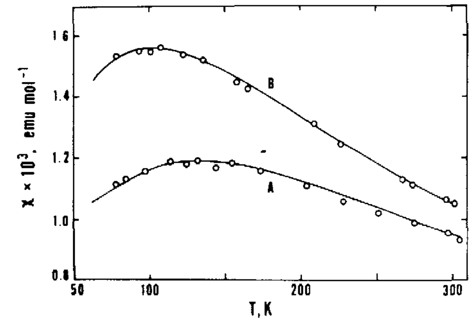

FIGURE 3 Magnetic susceptibilities of $Cu(py)_2\cdot\frac{1}{2}H_2O\cdot\frac{1}{2}NH_3$ (A) and $CuSO_4(trH)_2\cdot 3H_2O$ (B). The solid curves represent the theoretical curves of linear Heisenberg chains.

Complex with Pyrazole

The susceptibility of $Cu(py)_2\cdot\frac{1}{2}H_2O\cdot\frac{1}{2}NH_3$ exhibits a broad maximum attributable to a short-range magnetic interaction. Linear chains and isolated clusters are typical spin systems showing a short-range interaction. For polymeric rings involving magnetic interaction of the Heisenberg type, the spin Hamiltonian is given by

$$\mathcal{H} = -2J \sum_{i=1}^{n} (\mathbf{S}_i\cdot\mathbf{S}_{i+1} + g\mu_B\mathbf{S}_i\cdot\mathbf{H}) \tag{1}$$

where a periodic boundary condition, $\mathbf{S}_{n+1} = \mathbf{S}_1$, holds. Bonner and Fisher[10] have calculated the susceptibility for $S = 1/2$ and $n = 3$–11, and have estimated the susceptibility of an infinite linear

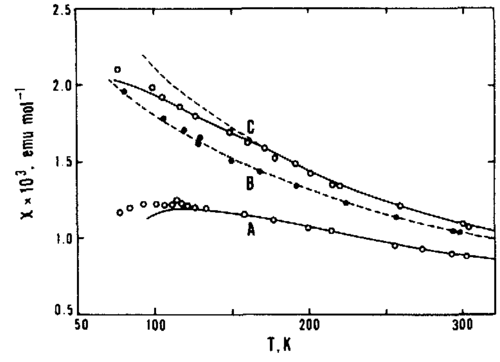

FIGURE 4 Magnetic susceptibilities of $Cu(im)_2$. A: Brown modification. B: Blue modification. C: Green modification. The solid curves were calculated theoretically on the basis of the high-temperature expansion method (A: $g = 2.00$, $J/k = -62$ K; C: $g = 2.10$, $J/k = -40$ K). The broken curves were calculated on the basis of the Curie–Weiss law (B: $g = 2.19$, $\theta = -156$ K; C: $g = 2.11$, $\theta = -101$ K).

chain by an extrapolation method. In Fig. 3, curve A shows the theoretical curve of a linear chain with $J/k = -105$ K and $g = 2.08$, which well reproduces the observed susceptibility of $Cu(py)_2 \cdot \frac{1}{2}H_2O \cdot \frac{1}{2}NH_3$. The observed curve is difficult to explain theoretically by any formula already proposed for clusters. These suggest that the complex contains one-dimensional spin lattices each consisting of –Cu–N–N–Cu– links in crystals. On the basis of the Ising model, rigorous formulas have been derived for the susceptibility of linear chains.[12] However, in conformity with the fact that the Heisenberg model rather than the Ising model is applicable adequately to most of copper(II) complexes,[4,16] it is difficult to reproduce the observed curve by the formulas.

Complexes with 1,2,4-Triazole

Alternatives are conceivable for a 1,2,4-triazole molecule to coordinate to two copper atoms as shown in Fig. 1. Broad-line PMR spectra have been recorded by use of the crystal powders of $CuCl_2(trH)$ and $Cu(tr)_2$.[17] The spectrum of $CuCl_2(trH)$ shows two absorptions of intensity ratio equal to 2:1 indicating the presence of two kinds of nonequivalent hydrogen atoms in crystals in agreement with the result of X-ray crystal analysis. The PMR spectrum of $Cu(tr)_2$ comprises two absorptions of equal intensity. On the basis of this result, two possible structures have been suggested for the complex:[17] a network structure consisting of –Cu–N–C–N–Cu– links and an alternating linear-chain structure involving –Cu–N–N–Cu– links. Either of the proposed structures can explain the presence of antiferromagnetic interaction yielding the large Weiss constant. The relation between the Weiss constant and the temperature of the maximum susceptibility has been derived as $|\theta|/T_{max} = 0.40–0.78$ for alternating linear chains.[11] The relation indicates that an alternating linear chain having the Weiss constant of –87 K might exhibit the maximum susceptibility in a temperature range of 112–218 K. Contrary to the expectation, no maximum was observed in the temperature range investigated. For two- and three-dimensional spin lattices, no rigorous formulas have been derived for susceptibility as yet. The high-temperature expansion method[18] has given a relation, $\theta = zJ/2k$, where z denotes the number of the nearest neighbors: for a fixed value of J, the Weiss constants of two- and three-dimensional spin lattices ($z \geqslant 3$) are larger than that of a one-dimensional lattice ($z = 2$). Hence, the network structure already proposed does not conflict with the observed magnetic susceptibility. X-ray crystal analysis[5,6] on $Cu(im)_2$ has provided an example of a three-dimensional network of copper atoms linked by imidazolato groups, which are isoelectronic with 1,2,4-triazolato groups. These support the network structure proposed for $Cu(tr)_2$.

The susceptibility versus temperature curve of $CuSO_4(trH)_2 \cdot 3H_2O$ can be reproduced by Bonner–Fisher's curve with $J/k = -80$ K and $g = 2.09$ (see curve B in Fig. 3). In addition, the value of $\chi_{max}kT_{max}/Ng^2\mu_B^2$ approximately equal to 0.09 agrees with the theoretical value of 0.0943 for regular chains.[11] These suggest that a one-dimensional lattice is the structural unit. Two types of –Cu–(trH)–Cu– links constructing one-dimensional lattices are conceivable: –Cu–N–N–Cu– and –Cu–N–C–N–Cu– links. So far as two equivalent trH molecules in the chemical formula are assumed to be coordinated to two copper atoms, steric consideration requires that the former links are formed in one-dimensional lattices. An example of one-dimensional –Cu–N–C–N–Cu– links has been presented by X-ray analysis[19] carried out on $Cu(im)(imH)_2Cl$: an imidazolate ion is coordinated to two copper atoms whereas imidazole molecules act as unidentate ligands. Therefore, the formation of infinite –Cu–N–C–N–Cu– chains is conceivable in the crystals of the triazole complex also, provided that one trH molecule in the chemical formula functions as a unidentate ligand.

The crystalline powders of $CuCl(tr) \cdot 2H_2O$ show a low effective magnetic moment of 1.32 B.M. at room temperature,[7] and the susceptibility increases with decreasing temperature without obeying the Curie–Weiss law as shown in Fig. 2, in which the reciprocal susceptibility is plotted against the temperature. The magnetic behavior is characteristic of magnetic clusters consisting of an odd number of copper atoms. For instance, the susceptibility of a trimeric aggregate of equivalent spins ($S = 1/2$ and $n = 3$ in Eq. 1) is given given by[9]

$$\chi = \frac{Ng^2\mu_B^2}{12kT}\left[\frac{1 + 5\exp(-3J/kT)}{1 + \exp(-3J/kT)}\right] + N\alpha \qquad (2)$$

In Fig. 2, curve B shows the reciprocal susceptibility calculated by Eq. 2 with $J/k = -155$ K and $g = 2.00$. Although it reproduces the observed curve fairly well, the g value is much smaller than the value, 2.1–2.2, normally observed for copper(II) complexes. The small g value can be explained by assuming that an additional magnetic interaction operates between trinuclear clusters. For coupled trinuclear clusters, the susceptibility is approximated by[20]

$$\chi = \frac{Ng^2\mu_B{}^2}{12k(T-\Delta)}\left[\frac{1+5\exp(-3J/kT)}{1+\exp(-3J/kT)}\right] + N\alpha \quad (3)$$

where Δ denotes the Weiss constant that takes into account interaction between clusters. Assuming $g = 2.10$ and $J/k = -155$ K, one can well reproduce the observed curve with $\Delta = -25$ K (see curve B' in Fig. 2). Although the analysis is tentative, we can conclude that the structural unit is a cluster containing an odd number of copper atoms, and that a trinuclear cluster is highly probable as the structural unit because the molecular model of a trimer is easily constructed by –Cu–N–N–Cu– links.

Complexes with Imidazole

Three magnetically different crystal modifications have been found for $Cu(im)_2$.[7,8] Jarvis and Wells[5,6] have carried out an X-ray crystal analysis on $Cu(im)_2$, although they failed to describe the method of preparation of their sample. The X-ray powder patterns of the blue modification agree with Jarvis–Wells' data in regard to major peaks. In the crystals, imidazolato groups construct –Cu(1)–L–Cu(2)–L–Cu(1)– chains, in which the coordination is square planar around Cu(1) atoms, whereas Cu(2) atoms take a flattened tetrahedral coordination. The chains are kinked at Cu(2) atoms so that the whole assembly forms a three-dimensional network. The large Weiss constant of the blue modification indicates that a strong antiferromagnetic interaction takes place through imidazolato groups. The susceptibility *versus* temperature curve of the brown modification exhibits a broad maximum at about 100 K, but it is difficult to explain the behavior by any model of isolated clusters or linear chains. In the crystals of $Cu(im)_2$, the square coordination of copper cannot be completed unless –Cu–L–Cu– links are formed. Therefore, a network structure with –Cu–N–C–N–Cu– links are contained in the crystals of the brown and green modifications as well. A preliminary X-ray analysis[6] carried out on $Zn(im)_2$ has presented another example of a three-dimensional network: each zinc atom has a tetrahedral coordination of nitrogen atoms from four different imidazolato groups, each of which forms a –Zn–L–Zn– link. One of the modifications of $Cu(im)_2$ may contain a similar type of network in crystals. For two- or three-dimensional lattices, susceptibility has not been calculated rigorously. The high-temperature expansion method[18] gives a good approximation in a temperature range of $kT \gg |J|$. In any network structure discussed above, each copper atom has four nearest neighboring copper atoms, because it is coordinated by four imidazolate ions each bonded to two metal ions. Therefore, we have tentatively analyzed the susceptibility of $Cu(im)_2$ using a formula for square lattices ($z = 4$) on the basis of the high-temperature expansion method.[21] Solid curves in Figure 4 were calculated by the formula normalized in such a way that it agrees with the Curie–Weiss law in the high-temperature limit. In a high-temperature range, the theoretical curves reproduce fairly well the susceptibilities of the green and brown modifications, which deviate from the Curie–Weiss law. The difference in the type of network between the modifications leads to a difference in their magnetic properties.

Superexchange Interaction

In the crystals of $CuCl_2(trH)$, neighboring copper atoms are 3.40_5 Å distant from each other and are bridged by two chlorine atoms and one –Cu–N–N–Cu– link.[1] The Cu–Cu distance is too long to form metal–metal bonding. Fermi contact shift evaluated from the broad-line PMR spectrum has indicated that a positive hole diffuses from a copper atom to the molecules of the heterocycle and hence that superexchange interaction is operative through 1,2,4-triazole molecules.[4,17] Because –Cu–L–Cu– links are the only exchange pathway conceivable in $Cu(im)_2$ and $Cu(tr)_2$, the strong antiferromagnetic interaction is caused by spin delocalization through the π-electron clouds of the heterocyclic ligands. A PMR study on anhydrous copper(II) formate[22] has shown that strong antiferromagnetic interaction is induced by the migration of a positive hole through the π-electron clouds of formate groups forming a network structure of –Cu–O–C–O–Cu– links. The same mechanism is presumed to be operative in the –Cu–N–C–N–Cu– bonding systems of $Cu(im)_2$ and $Cu(tr)_2$. The present investigation along with previous reports[4,23,24] has provided a convincing example in support of a conclusion that the magnitude of exchange interaction depends to a great extent on the kind of bridging ligands. Undoubtedly this effect is due to the difference in the aromatic character of the ligands as well as in the nature of metal–ligand bonding.

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