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Contribution from the Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Fukuoka 812, Japan,
and Department of Applied Molecular Science, Institute for Molecular Science,
Okazaki National Research Institutes, Okazaki 444, Japan

# Temperature Dependence of Structure and Magnetic Interaction in a Dialkoxo-Bridged Binuclear Copper(II) Complex, Dichlorobis[$\mu$-2-[[2-(dipropylamino)ethyl]thio]ethanolato-*N*,*S*,$\mu$-*O*]dicopper(II)

MASAHIRO MIKURIYA,*[1] KOSHIRO TORIUMI,[2] TASUKU ITO,[2] and SIGEO KIDA[1]

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The crystal structure of dichlorobis[$\mu$-2-[[2-(dipropylamino)ethyl]thio]ethanolato-*N*,*S*,$\mu$-*O*]dicopper(II) was determined by the single-crystal X-ray diffraction method at 120 K. The structure was compared with that determined previously at 293 K in order to elucidate the temperature-dependent magnetic behavior, which can not be interpreted by the Van Vleck equation based on the Heisenberg model for a binuclear structure. The space group of the crystal does not change on cooling. Crystal data at 120 K: $[Cu(C_{10}H_{22}NOS)Cl]_2$, monoclinic, $P2_1/a$, $a = 17.647$ (3) Å, $b = 10.246$ (1) Å, $c = 7.636$ (1) Å, $\beta = 102.98$ (1)°, $Z = 2$. Although the overall structure was essentially the same as that at 293 K, a substantial change was observed in the deviation of the carbon atom linked to the bridging oxygen atom from the Cu–O–Cu plane. The increase of the deviation from the Cu–O–Cu plane is of a reasonable magnitude for the decrease of the $-2J$ value (340 → 230 cm$^{-1}$) on the basis of the comparison of the magnetic and structural data of many dialkoxo-bridged copper(II) complexes.

## Introduction

A great number of binuclear copper(II) complexes have been prepared and extensively studied for their magnetic properties. The temperature dependence of the magnetic susceptibility of many binuclear copper(II) complexes has been explained by Van Vleck's equation based on isotropic spin-exchange interaction (the Bleaney–Bowers equation):

$$\chi_A = \frac{Ng^2\beta^2}{3kT}\left[1 + \frac{1}{3}\exp(-2J/kT)\right]^{-1} + N\alpha$$

where $\chi_A$ and $-2J$ are susceptibility per copper atom and the energy separation of the ground singlet and the lowest triplet states, respectively, and other symbols have the usual meanings.[3] The parameter $J$ can be evaluated by the least-squares method or the best-fit method. Recently, we have found that binuclear copper(II) complexes, Cu(R-nso)X (where HR-nso = 2-[[2-(dialkylamino)ethyl]thio]ethanol, R = $CH_3$, $C_2H_5$, $n$-$C_3H_7$, $n$-$C_4H_9$, and X = Cl, Br), are classified into two groups on the basis of the temperature dependence of the magnetic susceptibilities: i.e., (i) complexes whose magnetic behavior can be interpreted in terms of the Bleaney–Bowers equation and (ii) complexes whose magnetic behavior cannot be interpreted by any conventional theoretical formulas based on the Heisenberg or Ising model.[4] Nevertheless, the X-ray structure analyses of a series of the Cu(R-nso)X complexes have revealed that complexes belonging to either group have a discrete dialkoxo-bridged binuclear structure.[5] We assumed that the magnetic behavior of the group ii complexes is attributable to the variation of the molecular structure with temperature. Comparing the structures of these complexes in detail, we have found that the five-membered chelate ring, $\overline{\mathrm{Cu{-}O{-}C{-}C{-}S}}$, takes a gauche conformation for the group i complexes, while the chelate ring has an envelope conformation[6] for the group ii complexes. On this basis, we have assumed that the envelope conformation changes into a more stable gauche conformation at lower temperature, making $J$ temperature dependent. On the other hand, Uryû et al. have proposed the introduction of anisotropy in the exchange interaction to account for this magnetic behavior.[7] However, in view of the structural data, the reason that anisotropy had to be invoked only in the case of the group ii complexes is not clear.

Table I. Crystal Data at 120 K and Collection Details

| | |
|---|---|
| formula | $C_{20}H_{44}Cl_2Cu_2N_2O_2S_2$ |
| fw | 606.70 |
| cryst syst | monoclinic |
| space group | $P2_1/a$ |
| $a$, Å | 17.647 (3) |
| $b$, Å | 10.246 (1) |
| $c$, Å | 7.636 (1) |
| $\beta$, deg | 102.98 (1) |
| $V$, Å$^3$ | 1345.3 (3) |
| $Z$ | 2 |
| $d_c$, g cm$^{-3}$ | 1.50 |
| $d_m$, g cm$^{-3}$ | 1.46 (at 293 K) |
| radiation | graphite-monochromated Mo K$\alpha$ ($\lambda$ = 0.710 73 Å) |
| scan type | $\theta$–$2\theta$ |
| scan speed, deg min$^{-1}$ | 3 |
| scan width, deg | 1.3 + 0.5 tan $\theta$ |
| reflcn forms recorded | $\pm h, +k, +l$ |
| $2\theta$ range, deg | 2–55 |
| total no. of obsd reflcns | 3356 |
| no. of unique reflcns with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$ | 2553 |
| final no. of variables | 225 |
| final residuals | |
| $R^a$ | 0.026 |
| $R_w{}^b$ | 0.044 |

[a] $R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$. [b] $R_w = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$.

In order to settle the controversy, in this study, the crystal structure of dichlorobis[$\mu$-2-[[2-(dipropylamino)ethyl]thio]ethanolato-*N*,*S*,$\mu$-*O*]dicopper(II), Cu($n$-$C_3H_7$-nso)Cl, which belongs to the group ii complexes, was determined at low temperature (120 K) by the single-crystal X-ray diffraction method.

## Experimental Section

Dark green crystals of Cu($n$-$C_3H_7$-nso)Cl were prepared by the method previously reported.[4] A crystal with dimensions 0.36 × 0.24 × 0.24 mm was used for crystal data and intensity data collections. A Rigaku AFC-5 automated four-circle diffractometer was used for all operations. The low-temperature measurement was carried out with an attached Rigaku variable-temperature apparatus based on the cold nitrogen stream method. The temperature was measured before and after the data collection with a thermocouple mounted at the same position of the crystal.[8] Lattice constants were determined by the least-squares refinement based

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**Table II.** Fractional Coordinates

| atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Cu | −0.01606 (1) | 0.14315 (3) | −0.03391 (3) |
| Cl | −0.02554 (3) | 0.27579 (6) | −0.27162 (7) |
| S | −0.09880 (3) | 0.26607 (6) | 0.10090 (8) |
| O | −0.0442 (1) | −0.0016 (2) | 0.1034 (2) |
| N | 0.0867 (1) | 0.2391 (2) | 0.1962 (3) |
| C(1) | −0.0616 (1) | 0.0261 (2) | 0.2702 (3) |
| C(2) | −0.1185 (1) | 0.1397 (2) | 0.2542 (3) |
| C(3) | −0.0273 (1) | 0.3713 (2) | 0.2423 (4) |
| C(4) | 0.0494 (1) | 0.3059 (2) | 0.3271 (3) |
| C(5) | 0.1263 (1) | 0.3367 (2) | 0.1040 (3) |
| C(6) | 0.1744 (1) | 0.2787 (2) | −0.0186 (3) |
| C(7) | 0.2006 (2) | 0.3848 (3) | −0.1315 (4) |
| C(8) | 0.1408 (1) | 0.1377 (2) | 0.2884 (3) |
| C(9) | 0.2083 (2) | 0.1873 (3) | 0.4369 (4) |
| C(10) | 0.2599 (2) | 0.0786 (3) | 0.5296 (4) |

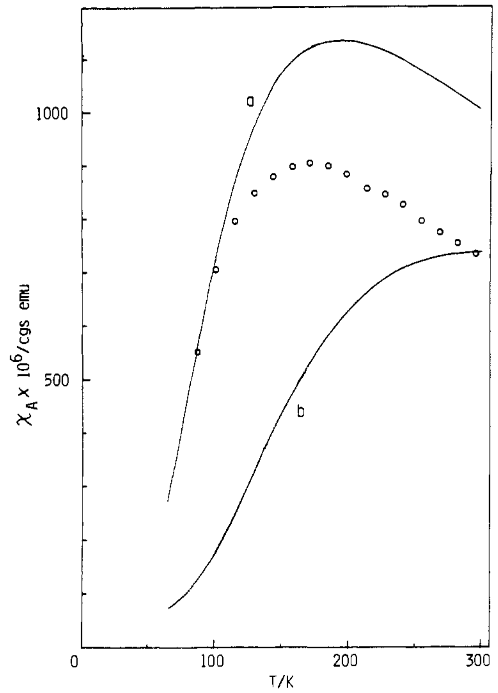

**Figure 1.** Temperature dependence of magnetic susceptibility of Cu($n$-$C_3H_7$-nso)Cl. The solid curves were calculated from the Bleaney–Bowers equation: (a) with $g = 2.10$ and $-2J = 215$ cm$^{-1}$; (b) with $g = 2.10$ and $-2J = 340$ cm$^{-1}$.

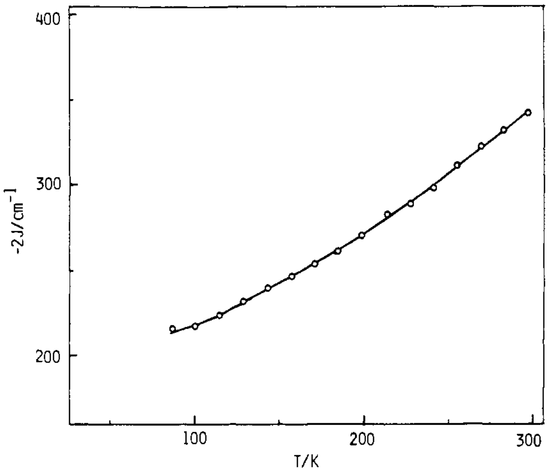

**Figure 2.** Temperature dependence of exchange integral $J$ calculated from the Bleaney–Bowers equation by use of the experimental $\chi_A$ values, with $g = 2.10$ and $N\alpha = 60 \times 10^{-6}$ cgs emu.

**Table III.** Selected Intramolecular Distances (Å) and Angles (deg) at 120[a] and 293 K[b]

| | 120 K[a] | 293 K[b] |
|---|---|---|
| (1) Copper Coordination Spheres[c] | | |
| Cu···Cu$^i$ | 3.010 (1) | 2.999 (1) |
| Cu–S | 2.335 (1) | 2.330 (2) |
| Cu–Cl | 2.244 (1) | 2.236 (2) |
| Cu–O | 1.943 (2) | 1.925 (4) |
| Cu–O$^i$ | 1.942 (2) | 1.945 (4) |
| Cu–N | 2.431 (2) | 2.468 (3) |
| Cu–O–Cu$^i$ | 101.6 (1) | 101.6 (2) |
| S–Cu–O | 85.0 (1) | 84.6 (1) |
| S–Cu–O$^i$ | 163.4 (1) | 163.0 (1) |
| S–Cu–Cl | 95.1 (1) | 94.8 (1) |
| S–Cu–N | 84.4 (1) | 83.9 (1) |
| O–Cu–O$^i$ | 78.4 (1) | 78.4 (2) |
| O–Cu–N | 99.1 (1) | 99.1 (1) |
| O–Cu–Cl | 156.5 (1) | 157.4 (1) |
| N–Cu–O$^i$ | 97.7 (1) | 99.3 (1) |
| N–Cu–Cl | 104.3 (1) | 103.3 (1) |
| Cl–Cu–O$^i$ | 100.2 (1) | 100.6 (1) |
| (2) $n$-$C_3H_7$-nso Moiety | | |
| O–C(1) | 1.404 (3) | 1.362 (8) |
| C(1)–C(2) | 1.524 (3) | 1.490 (8) |
| S–C(2) | 1.830 (3) | 1.814 (6) |
| S–C(3) | 1.818 (2) | 1.807 (5) |
| C(3)–C(4) | 1.520 (3) | 1.516 (7) |
| N–C(4) | 1.482 (3) | 1.476 (7) |
| Cu–O–C(1) | 118.0 (1) | 120.7 (3) |
| O–C(1)–C(2) | 110.8 (2) | 113.4 (5) |
| C(1)–C(2)–S | 112.0 (2) | 113.4 (5) |
| Cu–S–C(2) | 97.3 (1) | 97.1 (2) |
| Cu–S–C(3) | 99.4 (1) | 99.6 (2) |
| S–C(3)–C(4) | 115.1 (2) | 115.4 (4) |
| C(3)–C(4)–N | 113.8 (2) | 113.9 (4) |
| Cu–N–C(4) | 107.6 (1) | 106.6 (3) |

[a] This work. [b] Reference 5. [c] Superscript (i) refers to the equivalent position ($-x$, $-y$, $-z$).

on 40 reflections with $20° < 2\theta < 30°$. The intensity measurements were repeated until $\sigma_c(|F_o|)/|F_o|$ became less than 0.05, where $\sigma_c(|F_o|)$ denotes a standard deviation calculated from counting statistics. The maximum number of iterations was two. The intensities of three standard reflections were monitored at 50-reflection intervals. Fluctuations for the $|F_o|$ values were less than 2% during the data collection. The intensity data were corrected for Lorentz-polarization effects but not for absorption ($\mu$(Mo K$\alpha$) = 19.2 cm$^{-1}$). Details of the crystal data and data collection are listed in Table I.

The coordinates of non-hydrogen atoms determined at 293 K[5] were used as initial values in refinement by the block-diagonal least-squares method. The function minimized was $\sum w(|F_o| - k|F_c|)^2$, and the weighting scheme[9] was $w = (6.5 + |F_o| + 0.011|F_o|^2)^{-1}$. All the hydrogen atoms were located from the difference Fourier map and included in the final refinement with isotropic temperature factors. The final $R$ and $R_w$ values were 0.026 and 0.044, respectively. The final difference Fourier synthesis showed no peaks higher than 0.42 e/Å$^3$.

The atomic scattering factors and the anomalous dispersion corrections were taken from ref 10. All the calculations were carried out on the FACOM M-200 computer at the Computer Center of Kyushu University by the use of a local version of the UNICS-III[11] program and the ORTEP[12] program. Final values of the fractional coordinates are given in Table II.

## Results and Discussion

The temperature dependence of the magnetic susceptibility of Cu($n$-$C_3H_7$-nso)Cl is shown in Figure 1.[4] The $\chi_A$–$T$ curves calculated from the Bleaney–Bowers equation could not be fitted to the experimentally obtained one insofar as $J$ is assumed to be

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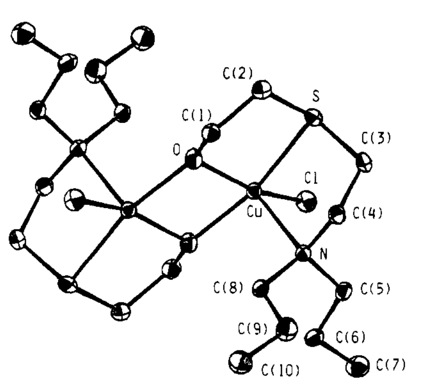

**Figure 3.** Molecular structure of Cu($n$-$C_3H_7$-nso)Cl at 120 K.

constant over the temperature range 80–300 K. Fixing $g$ and $N\alpha$ at 2.1 and $60 \times 10^{-6}$ cgs emu, respectively, we have calculated $J$ from the Bleaney–Bowers equation by use of experimental $\chi_A$ values. The result is shown in Figure 2. The $-2J$ value increases gradually as the temperature rises from 80 to 300 K.

The crystal and molecular structures of Cu($n$-$C_3H_7$-nso)Cl at 120 K are essentially the same as those found at 293 K.[5] The shortest separation of non-hydrogen atoms between binuclear units (Cl···C(4)) is 3.613 (3) Å at 120 K and 3.669 (6) Å at 293 K. Thus, the crystal consists of discrete binuclear units.

The molecular structure is shown in Figure 3. The coordination geometry of the copper atom is a distorted square pyramid with two alkoxo oxygen atoms, a thioether sulfur atom, and a chlorine atom in the basal plane and an amino nitrogen atom in the apical position. Contrary to our previous assumption, the five-membered chelate ring, $\overline{\text{Cu–O–C–C–S}}$, assumes the envelope conformation at low temperature as well. Bond lengths and angles in the equatorial plane showed no appreciable temperature variation. A slight contraction (2.468 (3) → 2.431 (2) Å) was observed in the axial Cu–N bond upon lowering the temperature. However, this does not seem to be the main factor for such a remarkable change in the $J$ value as observed in this complex, because the deviation of the copper atom from the basal plane (0.244 Å) was not altered on going from 293 to 120 K.

Since Hatfield and co-workers found a linear relation between $-2J$ and the bridging angle, Cu–O–Cu, for hydroxo-bridged binuclear copper(II) complexes, the Cu–O–Cu angle has been thought to be important in determining the nature of the magnetic spin-exchange interaction.[13] However, no such clear relation holds for dialkoxo-bridged binuclear copper(II) complexes.[5] This suggests that other structural factors are also important as well as the Cu–O–Cu angle. For the present complex, there was no change in the Cu–O–Cu angle at 293 and 120 K. Therefore, we must seek other structural parameters that can account for the temperature variation of the $J$ value. Kida et al. have claimed that the planarity of the bonds linked to the bridging oxygen atom is more fundamental in determining the magnitude of the antiferromagnetic interaction.[14] The planarity can be measured in terms of the deviation ($\delta$) of the carbon atom linked to the oxygen atom from the Cu–O–Cu plane.[15] In the case of the present complex, the $\delta$ value varies from 0.51 to 0.65 Å as the temperature decreases from 293 to 120 K. It is interesting to see if the magnitude of the variation in $\delta$ is large enough to cause the temperature variation of the $J$ value as observed here. Using available structural and magnetic data of dialkoxo-bridged copper(II) complexes, Nieminen plotted the $\delta$ values vs. $2J$ and obtained a fairly good linear relation as shown in Figure 4.[16] The $2J$ values at 293 and 120 K are calculated to be −340 and −230 $cm^{-1}$, respectively, from the Bleaney–Bowers equation by fixing $g$ and $N\alpha$ at 2.10 and $60 \times 10^{-6}$ cgs emu, respectively. When the above $\delta$ and $2J$ values are plotted in the Nieminen diagram, the data fall almost on the Nieminen least-squares line as indicated in Figure 4. This implies that the temperature variation of $\delta$ observed for the present complex is of a reasonable magnitude to cause the observed change in $J$. Hence, it is not necessary to invoke the anisotropy of spin-exchange interaction to account for the magnetic behavior of this complex.

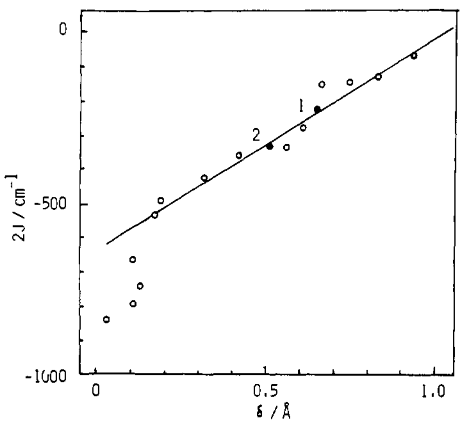

**Figure 4.** Plot of $2J$ vs. the deviation of the carbon atom from the Cu–O–Cu plane, $\delta$. The regression line was drawn through the data points with $2J \geq -600$ $cm^{-1}$: (1) Cu($n$-$C_3H_7$-nso)Cl at 120 K; (2) Cu($n$-$C_3H_7$-nso)Cl at 293 K;[5] other points quoted from ref 16.

The temperature dependence of magnetic susceptibility has been interpreted by the Bleaney–Bowers equation for most of the binuclear copper(II) complexes, assuming $J$ to be independent of temperature. However, there are some cases where this method does not work even though a discrete binuclear structure has been proved by X-ray analysis.[4,5,17] In such cases the origin of the phenomena has often been attributed to the temperature dependency of molecular structure. Nevertheless, no direct evidence by X-ray analysis has been reported yet. This is the first report of the direct evidence for the structural change with temperature to cause the abnormal magnetic behavior. As stated before, in the series of Cu(R-nso)X complexes the characteristic feature of the group ii complexes is the envelope conformation in the five-membered chelate ring, $\overline{\text{Cu–O–C–C–S}}$. This fact is understandable considering that the chelate conformation is deeply correlated to the $\delta$ value and an envelope conformation is more fluxional than a gauche conformation.

**Registry No.** Cu($n$-$C_3H_7$-nso)Cl, 74828-42-5.

**Supplementary Material Available:** Listings of anisotropic temperature factors for non-hydrogen atoms, isotropic temperature factors and atomic coordinates for hydrogen atoms, least-squares planes and atomic deviations therefrom, and observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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