2106 © *1993 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.,* ***66****, 2106—2108(1993)* [Vol. 66, No. 7

Phase-Change Behavior of a Dialkoxo-Bridged Dinuclear Copper(II) Complex: X-Ray Crystal Structure of {2-[2-(Dimethylamino)ethylthio]ethanolato}-isothiocyanatocopper(II) at 210 K

Masahiro MIKURIYA* and Koshiro TORIUMI†
Department of Chemistry, School of Science, Kwansei Gakuin University, Uegahara, Nishinomiya 662
†Department of Material Science, Faculty of Science, Himeji Institute of Technology, Kamigoricho, Ako-gun, Hyogo 678-12

(Received January 25, 1993)

Synopsis. The crystal structure of {2-[2-(dimethylamino)ethylthio]ethanolato}isothiocyanatocopper(II) at 210 K was determined by the single-crystal X-ray diffraction method. The unusual magnetic property was examined in terms of the temperature dependence of the magnetic susceptibility (85—290 K) and a differential scanning calorimetric analysis.

For many years, a great number of dinuclear copper(II) complexes have been prepared, and their structures and magnetic properties have been extensively studied. So far, most of their magnetic susceptibility data have been well explained by the Bleaney–Bowers equation[1)] based on the Heisenberg model. However, in very few cases, the Bleaney–Bowers formula is unable to explain the magnetic behavior of the dinuclear copper(II) system.[2—5)] One of the reasons for the unusual magnetic behavior is a phase transition. Although such a phase transition was already noticed by some authors,[6,7)] a dialkoxo-bridged dinuclear complex, {2-[2-(dimethylamino)ethylthio]ethanolato}isothiocyanatocopper(II) (**1**), may be a typical example of the phase change.[8)] In the course of studies on dinuclear copper(II) complexes with 2-[2-(dialkylamino)ethylthio]ethanol,[2—4)] we found that **1** exhibits a drastic change in the magnetic susceptibility in the temperature range 180—240 K, although the magnetic data can be fitted to the Bleaney–Bowers equation independently in the two temperature ranges ($-2J=595$ cm^{-1} for $90 \leq T < 170$ K; $-2J=535$ cm^{-1} for $240 < T < 300$ K). The X-ray crystal structure of **1** at 297 K excludes the possibility of an intermolecular interaction, and reveals that the complex comprises dialkoxo-bridged dinuclear units, in which the coordination geometry around each copper atom can be described as a distorted square pyramid with two bridging alkoxo-oxygen atoms, a thioether sulfur atom, and an isothiocyanate nitrogen atom in the basal plane, and an amino nitrogen atom in the apical position.[8)]

In the present study we tried to collect the X-ray diffraction data of **1** at low temperatures, especially at a temperature below 170 K, with a view to obtain more information concerning this unusual magnetic behavior (Table 1). However, upon cooling below 210 K, the crystals of **1** always became broken. We could barely obtain low-temperature X-ray data at 210 K without destroying the crystal. Judging from the magnetic data reported earlier,[8)] this temperature should correspond to the transition point. Thus, we expected a significant structural change in the crystal structure at 210 K, compared with the room-temperature structure. However, the crystal showed the same space group, and the crystal-packing feature is the same as that at 297 K. Figure 1 gives a view of **1** at 210 K. The dinuclear structure is essentially the same as that found at 297 K (Table 2), except that the low-temperature structure does not show any severe disorder, which is observed for the carbon atom of the chelate ring in the room-temperature structure, although the thermal parameters are still high. In order to check for the possibility of hysterisis, the magnetic susceptibility of **1** was measured between 290 and 85 K, by decreasing and increasing the temperature succesively (Fig. 2). Starting at 290 K, the temperature was gradually lowered to 85 K, as indicated by the downward-pointing arrow, and then increased up to 290 K, as indicated by the upward-pointing arrow. The χ_A vs. T curves show a hysterisis effect of ca. 20 K. Transitions were observed at around 208 and 230 K for decreasing and increasing temperatures, respectively. This hysterisis effect suggests a first-order nature of the phase transition. A differential scanning calorimetric analysis shows an endothermic peak

Table 1. Fractional Positional Parameters and Thermal Parameters of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

Atom	x	y	z	$B_{eq}/\text{Å}^2$ a)
Cu	0.1418(1)	0.0137(1)	−0.0248(1)	2.86(1)
S(1)	0.3676(1)	0.0063(1)	0.1961(2)	4.64(3)
S(2)	0.2113(2)	0.2022(1)	−0.4309(1)	5.17(4)
O	0.0656(3)	−0.0148(2)	0.1449(3)	3.79(8)
N(1)	0.2042(4)	−0.1290(2)	−0.0987(4)	3.58(9)
N(2)	0.1933(4)	0.0887(3)	−0.1813(5)	4.51(12)
C(1)	0.1484(5)	−0.0460(4)	0.3048(5)	4.44(13)
C(2)	0.2955(6)	−0.0031(4)	0.3609(6)	5.99(18)
C(3)	0.4080(7)	−0.1137(5)	0.1675(9)	7.81(23)
C(4)	0.3466(9)	−0.1503(6)	0.0180(11)	10.88(32)
C(5)	0.1001(8)	−0.1964(4)	−0.0875(10)	6.87(25)
C(6)	0.2080(9)	−0.1275(4)	−0.2658(8)	7.62(27)
C(7)	0.1994(4)	0.1354(3)	−0.2855(5)	3.25(10)

a) Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameters defined as $4/3[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

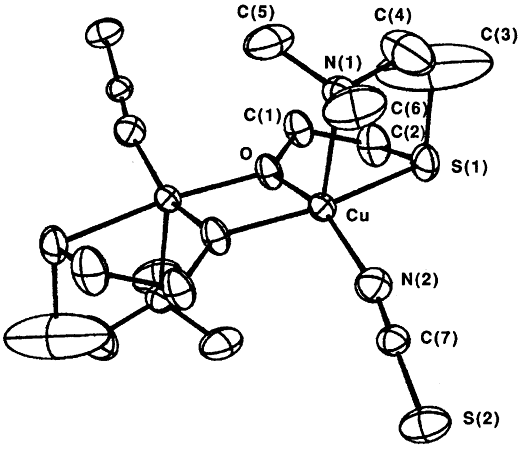

Fig. 1. Perspective view of **1** at 210 K.

Table 2. Selected Interatomic Distances (l/Å) and Bond Angles (ϕ/°) with Their Estimated Standard Deviations in Parentheses

	210 K[a)]	297 K[b)]
Cu···Cu^{i} [c)]	3.032(1)	3.009(2)
Cu–S(1)	2.367(1)	2.361(3)
Cu–O	1.918(3)	1.902(7)
Cu–O^{i}	1.949(3)	1.942(5)
Cu–N(1)	2.309(4)	2.296(7)
Cu–N(2)	1.936(5)	1.940(9)
Cu–O–Cu^{i}	103.3(1)	103.0(2)
S(1)–Cu–O	84.33(9)	84.1(2)
S(1)–Cu–O^{i}	160.9(1)	160.8(2)
S(1)–Cu–N(1)	84.74(8)	84.4(2)
S(1)–Cu–N(2)	99.8(1)	99.5(2)
O–Cu–N(1)	103.7(1)	102.3(3)
O–Cu–N(2)	157.9(2)	159.0(3)
O–Cu–O^{i}	76.7(1)	77.0(2)
N(1)–Cu–N(2)	98.3(2)	98.7(3)
N(1)–Cu–O^{i}	101.6(1)	102.5(2)
N(2)–Cu–O^{i}	97.1(1)	97.1(3)

a) This work. b) Ref. 8. c) Superscript (i) refers to the equivalent position ($-x$, $-y$, $-z$).

at around 230 K upon increasing the temperature. At present, although we cannot elucidate the origin of the unusual magnetic behavior, this type of phase change is the first example of a dinuclear copper(II) system.

Experimental

The synthesis of the complex has been described elsewhere.[8)] The magnetic susceptibilities were measured by the Faraday method over the 85—290 K temperature range. The apparatus was calibrated using [Ni($H_2NCH_2CH_2NH_2$)$_3$]S_2O_3.[9)] The susceptibilities were corrected for the diamagnetism of the constituent atoms by the use of Pascal's constants.[10)] A differential scanning calorimetric analysis was performed using a Du Pont 990 Thermal Analyzer.

Crystal Data: $C_{14}H_{28}Cu_2N_4O_2S_4$, F.W.=539.7, monoclinic, $P2_1/a$; $a=9.962(2)$, $b=14.456(3)$, $c=8.604(1)$ Å, $\beta=111.12(1)°$, $V=1155.8(4)$ Å^3, $D_m=1.52$, $D_c=1.55$ g cm^{-3}, $Z=2$, μ(Mo $K\alpha$)=21.7 cm^{-1}, $T=210$ K. The unit-cell parameters and intensities were measured on a Rigaku AFC-5 automated four-circle diffractometer attached to a variable-temperature apparatus based on a cold-nitrogen stream method. The intensity data were collected by the ω–2θ scan technique and corrected for Lorentz-polarization effects, but not for absorption. A total of 3055 reflections were measured in the $2<2\theta<60°$ range; 1793 with $|F_o|>3\sigma(|F_o|)$ were assumed as observed. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were inserted at their calculated positions. A weighting scheme $w=1/[5.7+|F_o|+0.0125|F_o|^2]$ was employed. The final discrepancy factors are $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|=0.038$ and $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}=0.057$.

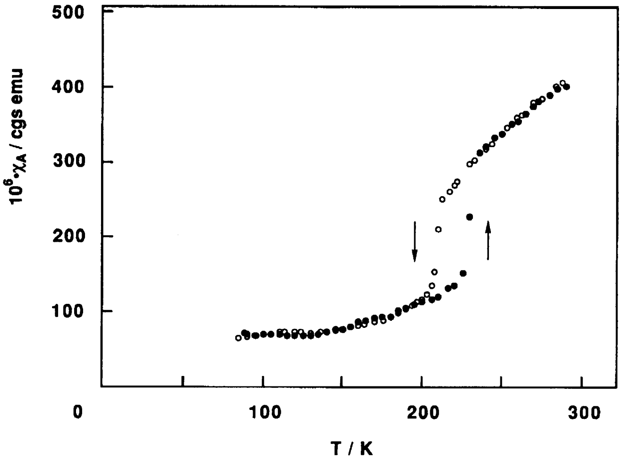

Fig. 2. Temperature dependence of the magnetic susceptibilities of **1**. The downward- and upward-pointing arrows indicate decreasing (○) and increasing (●) temperatures, respectively.

All of the calculations were carried out on the FACOM M-200 computer at the Computer Center of Kyushu University using the UNICS-III program.[11)] The atomic coordinates and thermal parameters of non-hydrogen atoms are listed in Table 1. The anisotropic thermal parameters of non-hydrogen atoms, and the F_o–F_c tables have been deposited as a Document No. 66022 at the Office of the Editor of Bull. Chem. Soc. Jpn.

References

1) B. Bleaney and K. D. Bowers, *Proc. R. Soc. London, Ser. A*, **214**, 451 (1952).

2) M. Mikuriya, H. Okawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **53**, 2871 (1980).

3) M. Mikuriya, H. Okawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **55**, 1086 (1982).

4) M. Mikuriya, K. Toriumi, T. Ito, and S. Kida, *Inorg. Chem.*, **24**, 629 (1985).

5) O. Kahn, I. M. -Badarau, J. P. Audiere, J. M. Lehn, and S. A. Sullivan, *J. Am. Chem. Soc.*, **102**, 5936 (1980).

6) H. Yokoi and M. Chikira, *J. Am. Chem. Soc.*, **97**, 3975 (1975).

7) A. -M. G. -Godquin, J. -M. Latour, and J. -C.

Marchon, *Inorg. Chem.*, **24**, 4452 (1985).

8) M. Mikuriya, H. Okawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **54**, 2979 (1981).

9) N. F. Curtis, *J. Chem. Soc.*, **1961**, 3147.

10) P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York (1965).

11) T. Sakurai and K. Kobayashi, *Rikagaku Kenkyusho Hokoku*, **55**, 69 (1979).