Binuclear Metal Complexes. XLI.[1] Crystal Structure and Unusual Magnetic Property of Isothiocyanato{2-[2-(dimethylamino)-ethylthio]ethanolato}copper(II)

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A binuclear copper(II) complex, isothiocyanato{2-[2-(dimethylamino)ethylthio]ethanolato}copper(II), (Cu(CH_3-nso)NCS), was prepared and characterized by elemental analysis, infrared and electronic spectra, magnetic susceptibility (90—300 K), and single-crystal X-ray diffraction. The complex exhibits a band at 25×10^3 cm^{-1} characteristic of alkoxo-bridged structure. The temperature dependence of the magnetic susceptibility is unusual and shows a dramatic change in the temperature range 240—180 K. The magnetic data were fitted to the Bleaney-Browers equation separately in the two temperature ranges ($-2J=535$ cm^{-1} for $300\geq T\geq240$ K; $-2J=595$ cm^{-1} for $170\geq T\geq90$ K).

In the previous paper[2] of this series, we reported the synthesis, structure, spectra, and magnetic properties of binuclear copper(II) complexes with 2-[2-(dialkylamino)ethylthio]ethanols, Cu{$R_2N(CH_2)_2S(CH_2)_2O$}X (abbreviated as Cu(R-nso)X, where R=CH_3, C_2H_5, n-C_3H_7, n-C_4H_9; X=Br, Cl, NO_3). With Cu(CH_3-nso)Br we found that its crystal consists of discrete binuclear units but that its magnetic susceptibility exhibits a temperature dependence which does not obey the Bleaney-Bowers equation[3] based on a binuclear structure; similar temperature dependence applies also to all the other Cu(R-nso)X but Cu(n-C_4H_9-nso)Cl. In order to elucidate this unusual magnetic behavior, we have continued collecting information on magnetic properties of similar complexes. In the course of this activity, we found that isothiocyanato{2-[2-(dimethylamino)ethylthio]ethanolato}copper(II), Cu(CH_3-nso)NCS, exhibits a magnetic behavior suggestive of a phase transition between two binuclear structures at 240—180 K. The present investigation was undertaken to characterize Cu(CH_3-nso)NCS by means of elemental analysis, infrared and electronic spectra, magnetic susceptibility, and single-crystal X-ray diffraction, for the purpose of elucidating the unusual magnetic behavior.

Experimental

Preparation of the Complex. 2-[2-(Dimethylamino)ethylthio]ethanol was prepared by the method previously described.[2] To an ethanol solution (50 ml) of 2-[2-(dimethylamino)ethylthio]ethanol (298 mg) and copper(II) acetate monohydrate (200 mg) was added an ethanol solution (10 ml) of potassium thiocyanate (97 mg). On standing overnight, dark green crystals were formed, which were separated by filtration, washed with ethanol and dried *in vacuo* over P_2O_5.

Found: C, 31.16; H, 5.24; N, 10.33%. Calcd for $C_7H_{14}CuN_2OS_2$: C, 31.16; H, 5.23; N, 10.38%.

Measurements. Infrared spectra were measured with a Hitachi Grating Infrared Spectrophotometer Model 215 in the region 4000—650 cm^{-1} on a KBr disk. Electronic spectra were measured with a Shimadzu Multipurpose Spectrophotometer Model MSP-5000 at room temperature. Magnetic susceptibility was measured by the Faraday method in the temperature range from liquid nitrogen temperature to room temperature. The apparatus was calibrated by the use of $[Ni(en)_3]S_2O_3$.[4] The susceptibility was corrected for the diamagnetism of the constituent atoms by the use of Pascal's constants.[5] Effective magnetic moment was calculated from the equation, $\mu_{\text{eff}}=2.828\sqrt{(\chi_A-N\alpha)T}$, where χ_A is the atomic magnetic susceptibility and $N\alpha$ is the temperature-independent paramagnetism. For the present complex, $N\alpha$ is assumed to be 60×10^{-6} cgs emu.[6]

X-Ray Crystal Structure Analysis. A crystal with dimensions of 0.19 mm × 0.25 mm × 0.31 mm was used for the X-ray analysis. The unit-cell parameters and intensities were measured on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.71069$ Å) at 24 ± 1 °C. The unit-cell parameters were determined by the least-squares refinement based on the 15 reflections in the range of $23<2\theta<33°$.

Crystal Data: $C_{14}H_{28}N_4O_2S_4Cu_2$, F.W.=539.73; monoclinic; $P2_1/a$; $a=10.025(3)$, $b=14.421$ (3), and $c=8.595$ (2) Å; $\beta=110.49$ (2)°; $D_m=1.52$ (by floatation in n-C_6H_{14}-CCl_4); $D_c=1.54$ g cm^{-3}; $Z=2$; μ(Mo $K\alpha$)=21.7 cm^{-1}.

The intensity data were collected by the 2θ-ω scan technique with a scan rate of 8° min^{-1}. For weak reflections the peak scan was repeated up to four times depending on thier intensities. Three standard reflections were monitored every 100 reflections, and their intensities showed a good stability. A total of 2282 reflections with $2\theta<50°$ were collected. The intensity data were corrected for the Lorentz and the polarization effects, but not for absorption. Independent 1605 reflections with $|F_o|>3\sigma(|F_o|)$ were considered as "observed" and were used for the structure analysis.

The systematic absences observed, h odd for $h0l$ and k odd for $0k0$, uniquely define the space group as $P2_1/a$. The structure was solved by the heavy atom method. The position of the copper atom was obtained from a three-dimensional Patterson synthesis. Successive Fourier Synthesis revealed all the nonhydrogen atoms. Refinement was carried out by the block-diagonal least-squares method. Anisotropic thermal parameters being introduced, the block-diagonal least-squares refinement yielded discrepancy factors $R_1=\sum||F_o|-|F_c||/\sum|F_o|=0.068$ and $R_2=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}=0.103$. In the course of refinement, it became apparent that the carbon atom of the chelate ring, C(4), is subjected to disorder. The carbon atom was divided between two positions with an occupancy factor 0.5 on the basis of a difference Fourier map. Hydrogen atoms were inserted in their calculated positions and included in the refinement. Further refinement with anisotropic thermal parameters for nonhydrogen atoms and isotropic temperature factors for hydrogen atoms gave final values of 0.062 and 0.093 for R_1 and R_2, respectively. In the least-squares refinement the function minimized was $\sum w(|F_o|-k|F_c|)^2$, and the weighting scheme was $w=(6.0+|F_o|+0.012|F_o|^2)^{-1}$.[7] The final difference Fourier synthesis showed no peaks higher than 0.65 e/Å^3.

The atomic scattering factors for Cu, S, O, N, and C_{val} and the anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$ for Cu and S, were taken from the International Tables for X-Ray Crystallography.[8] For the hydrogen atom, the scattering factors were adopted from the tables of Stewart et al.[9] All the calculations were carried out on the FACOM M-200 computer in the Computer Center of Kyushu University by the use of a local version[10] of the UNICS-II[11] and the ORTEP[12] programs.

Lists of structure factors and anisotropic thermal parameters have been deposited at the Chemical Society of Japan as Document No. 8142. The final positional and thermal parameters with their estimated standard deviations are given in Table 1.

TABLE 1. FRACTIONAL POSITIONAL PARAMETERS (×10^4) AND THERMAL PARAMETERS OF NON-HYDROGEN ATOMS WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	B_{eq}/Å^2
Cu	1386(1)	120(1)	−290(1)	4.7
S(1)	3628(3)	24(2)	1860(4)	7.4
S(2)	2254(3)	1977(2)	−4259(3)	7.8
O	663(6)	−171(4)	1424(7)	6.2
N(1)	1953(7)	−1317(4)	−1029(8)	5.4
N(2)	1906(8)	862(5)	−1872(9)	6.7
C(1)	1492(10)	−477(8)	2993(10)	7.1
C(2)	2961(13)	−130(9)	3519(13)	8.9
C(3)	4026(12)	−1154(10)	1397(17)	11.3
C(4A)	2829(26)	−1784(15)	494(28)	8.6
C(4B)	3402(21)	−1586(16)	−180(28)	8.6
C(5)	823(14)	−1964(7)	−1121(18)	9.7
C(6)	2158(18)	−1296(9)	−2612(16)	11.4
C(7)	2024(8)	1326(5)	−2860(9)	5.1

Results and Discussion

The molecular packing in the unit cell is shown in Fig. 1. As is evident from the packing diagram and the closest interdimer contact (C(4A)–C(7) 3.37(2)Å), the crystal consists of discrete binuclear units.

As shown in Fig. 2, the complex consists essentially of alkoxo-bridged centrosymmetric binuclear units. The coordination geometry around each copper atom is best described as a distorted square pyramid with two 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. The copper atom deviates from the basal plane toward the apical N(1) atom by 0.233Å (Table 3). There is a tetrahedral distortion in the basal plane, because the deviations of the basal atoms from the least-squares plane are 0.088—0.129Å and the dihedral angle between the planes

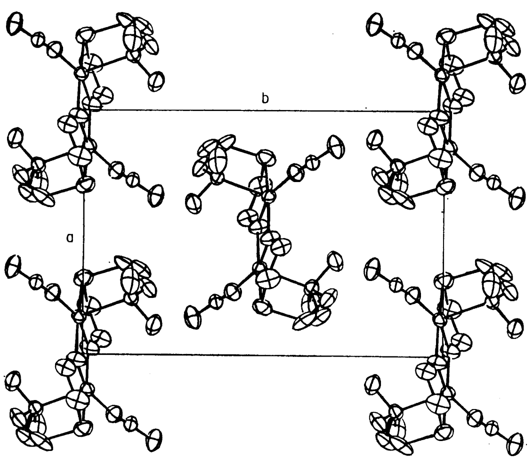

Fig. 1. Projection of the unit cell on the ab plane.

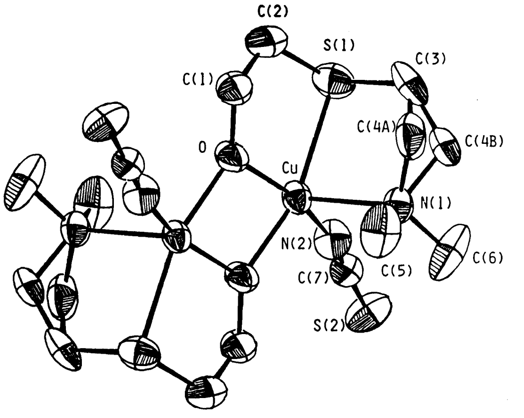

Fig. 2. Molecular structure of Cu(CH$_3$-nso)NCS. Thermal ellipsoids are drawn at 30% probability level.

TABLE 2. INTERATOMIC DISTANCES (l/Å) AND BOND ANGLES (ϕ/°) WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(a) Copper coordination spheres			
Cu–Cu^i	3.009(2)	Cu–O^i	1.942(5)
Cu–S(1)	2.361(3)	Cu–N(1)	2.296(7)
Cu–O	1.902(7)	Cu–N(2)	1.940(9)
Cu–O–Cu^i	103.0(2)	O–Cu–N(2)	159.0(3)
S(1)–Cu–O	84.1(2)	O–Cu–O^i	77.0(2)
S(1)–Cu–O^i	160.8(2)	N(1)–Cu–N(2)	98.7(3)
S(1)–Cu–N(1)	84.4(2)	N(1)–Cu–O^i	102 5(2)
S(1)–Cu–N(2)	99.5(2)	N(2)–Cu–O^i	97.1(3)
O–Cu–N(1)	102.3(3)		
(b) CH$_3$ -nso moiety			
O–C(1)	1.386(9)	C(3)–C(4B)	1.422(26)
C(1)–C(2)	1.469(16)	N(1)–C(4A)	1.460(21)
S(1)–C(2)	1.788(14)	N(1)–C(4B)	1.432(20)
S(1)–C(3)	1.820(15)	N(1)–C(5)	1.448(15)
C(3)–C(4A)	1.489(25)	N(1)–C(6)	1.446(18)
Cu–O–C(1)	124.2(6)	C(3)–C(4B)–N(1)	113.4(18)
Cu^i–O–C(1)	132.0(6)	Cu–N(1)–C(4A)	107.3(10)
O–C(1)–C(2)	112.7(9)	Cu–N(1)–C(4B)	114.1(10)
C(1)–C(2)–S(1)	114.3(7)	Cu–N(1)–C(5)	109.4(7)
C(2)–S(1)–Cu	96.4(4)	Cu–N(1)–C(6)	111.9(6)
Cu–S(1)–C(3)	96.1(3)	C(4A)–N(1)–C(5)	88.0(11)
C(2)–S(1)–C(3)	103.4(7)	C(4B)–N(1)–C(5)	119.2(11)
S(1)–C(3)–C(4A)	119.0(12)	C(4A)–N(1)–C(6)	127.9(14)
S(1)–C(3)–C(4B)	124.0(12)	C(4B)–N(1)–C(6)	91.8(13)
C(3)–C(4A)–N(1)	107.9(15)	C(5)–N(1)–C(6)	109.1(9)
(c) Isothiocyanato group			
N(2)–C(7)	1.119(12)	C(7)–S(2)	1.605(9)
Cu–N(2)–C(7)	170.9(7)	N(2)–C(7)–S(2)	177.8(8)

i) $-x$, $-y$, $-z$.

TABLE 3. DEVIATION OF THE ATOMS FROM LEAST-SQUARES PLANES (l/Å) AND DIHEDRAL ANGLES BETWEEN THE PLANES (ϕ/°)

(I) Plane through Cu, O, Cu$^{\rm i}$, O$^{\rm i}$
$-0.0782X+0.9713Y+0.2380Z=0$[a]
[Cu 0.000, O 0.000, Cu$^{\rm i}$ 0.000, O$^{\rm i}$ 0.000, S(1) 0.129, S(2) 1.721, N(1) −2.208, N(2) 0.675, C(1) −0.173, C(2) 0.306, C(3) −1.646, C(4A) −2.619, C(4B) −2.525, C(5) −3.045, C(6) −2.519, C(7) 1.113][b]

(II) Plane through Cu, S(1), O
$-0.1195X+0.9747Y+0.2187Z=-0.0519$
[Cu 0.000, S(1) 0.000, O 0.000, N(1) −2.226, N(2) 0.683, C(1) −0.235, C(2) 0.176, C(3) −1.790, C(4A) −2.701, C(4B) −2.618, C(5) −3.018, C(6) −2.520]

(III) Plane through Cu, S(1), N(1)
$-0.6796X-0.4300Y+0.7946Z=-1.2163$
[Cu 0.000, S(1) 0.000, N(1) 0.000, O 1.843, N(2) −1.895, C(1) 2.540, C(2) 1.682, C(3) 0.142, C(4A) 0.732, C(4B) −0.241, C(5) 1.108, C(6) −1.234]

(IV) Plane through O, N(1), N(2)
$0.7333X+0.0973Y+0.3736Z=0.9207$
[O 0.000, N(1) 0.000, N(2) 0.000, Cu 0.022, S(1) 2.347, S(2) −0.354, O$^{\rm i}$ −1.841, C(1) 1.071, C(2) 2.368, C(3) 2.326 C(4A) 1.067, C(4B) 1.300, C(5) −0.951, C(6) −0.355, C(7) −0.165]

(V) Plane through O, O$^{\rm i}$, N(2), S(1)
$-0.2113X+0.9128Y+0.4013Z=-0.0027$
[O 0.129, O$^{\rm i}$ −0.123, N(2) 0.088, S(1) −0.093, Cu −0.233, S(2) 0.659, N(1) −2.499,C(1) 0.091, C(2) 0.419, C(3) −1.887, C(4A) −2.774, C(4B) −2.867, C(5) −3.114, C(6) −3.062, C(7) 0.333]

(VI) Plane through Cu, S(1), N(2)
$-0.3706X+0.8335Y+0.5136Z=-0.4986$
[Cu 0.000, S(1) 0.000, N(2) 0.000, S(2) 0.157, O 0.675, O$^{\rm i}$ 0.322, N(1) −2.264, C(1) 0.692, C(2) 0.796, C(3) −1.768, C(4A) −2.478, C(4B) −2.751, C(5) −2.663, C(6) −3.014, C(7) 0.078]

Dihedral angles between the planes (ϕ/°)

(I) and (II)	3.1	(II) and (VI)	20.9
(I) and (III)	103.4	(III) and (IV)	98.1
(I) and (IV)	79.1	(III) and (V)	92.4
(I) and (V)	11.0	(III) and (VI)	82.1
(I) and (VI)	21.5	(IV) and (V)	80.3
(II) and (III)	103.0	(IV) and (VI)	85.1
(II) and (IV)	82.3	(V) and (VI)	10.8
(II) and (V)	11.2		

a) The equation of the plane is expressed as $LX+MY+NZ=D$, where X, Y, and Z are in Å units refered to the crystallographic axes. b) Deviations (l/Å) of atoms from the planes are listed in square brackets. Superscript (i) refers to the equivalent position ($-x$, $-y$, $-z$).

Cu-O-O$^{\rm i}$ and Cu-S(1)-N(2) is 21.5°. This distortion is smaller than that in Cu(CH$_3$-nso)Br.[2] The bond distances and angles with their estimated standard deviations are listed in Table 2. The Cu-Cu$^{\rm i}$ distance (3.009(2)Å) agrees well with the value found for Cu(CH$_3$-nso)Br (3.004(2) Å), while the Cu-O-Cu$^{\rm i}$ angle (103.0(2)°) is larger than that found for Cu(CH$_3$-nso)Br (102.2(2)°).[2]

The Cu-O and Cu-N(1) distances of Cu(CH$_3$-nso)-NCS are 1.902(7) and 2.296(7)Å, respectively, which are slightly shorter than those of Cu(CH$_3$-nso)Br (Cu-O 1.930(5), Cu-N 2.334(6)Å). On the other hand, the Cu-S(1) bond length (2.361(3)Å) is longer than that (2.316(2)Å) of Cu(CH$_3$-nso)Br. The shortening of the Cu-O and Cu-N bonds should bring about a considerable strain in the fused chelate ring, although the elongated Cu-S bond may contribute to the releasing of the strain. In fact, the carbon atom of the chelate ring, C(4), is disordered. This is probably due to the strain of two adjacent five-membered chelate rings.[2] It is noteworthy that all the atoms of the complex have considerably large temperature factors. This fact suggests that the conformation of the complex easily fluctuates.

The isothiocyanate group coordinates to the copper atom with the nitrogen atom. The infrared spectrum ($\nu_{\rm CN}=2075$ cm^{-1}; $\nu_{\rm CS}=760$ cm^{-1}) is consistent with this coordination mode.[13] The Cu-N(2) distance (1.940(9) Å) is in the range of the normal in-plane coordination. The NCS group is nearly linear (the N(2)-C(7)-S(2) angle 177.8(8)°) and of nearly the same structure as found for other alkoxo-bridged copper(II) complexes containing an NCS group.[14–17]

The electronic absorption spectrum in 1,2-dichloroethane solution resembles the diffuse reflectance spectrum, indicating that the molecular structure is essentially the same in the solution as in the solid state. The absorption spectrum shows a band centered at 13.9×10^3 cm^{-1} ($\varepsilon=130$) with a shoulder at *ca.* 11.1×10^3 cm^{-1}. These bands can be assigned to the d-d transitions of a five-coordinate copper(II) complex.[18] A more intence band ($\varepsilon=2350$) occurs at 24.9×10^3 cm^{-1}. This is the band characteristic of alkoxo-bridged structure assigned to a charge transfer from a p$_\pi$ orbital of the bridging oxygen atom to the unfilled d orbital of the copper ion.[2]

The magnetic susceptibility was measured over the temperature range 90—300 K. The magnetic moment per copper atom is 0.90 BM at 299 K. The temperature dependence of the magnetic susceptibility is shown in Fig. 3. The susceptibility decreases gradually with lowering temperature from 300 to 240 K and then

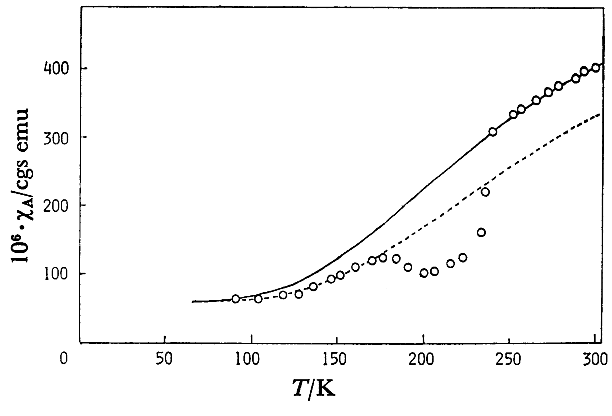

Fig. 3. Temperature dependence of magnetic susceptibility of Cu(CH$_3$-nso)NCS. The solid curve was calculated from Eq. 1 with $g=2.10$ and $-2J=535$ cm^{-1}; the bloken curve, from Eq. 1, using $g=2.10$ and $-2J=595$ cm^{-1}.

suddenly decreases in the range 240—230 K, reaching a minimum at 200 K. Below 200 K, the susceptibility increases to a maximum at about 180 K and finally decreases again. This fact suggests that a phase transition occurs in the temperature range 240—180 K. The susceptibility data were fitted to Eq. 1 (the Bleaney-Bowers equation[3]) separately in the two temperature ranges:

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

where $-2J$ is equal to the energy separation between the spin-singlet ground state and the lowest spin-triplet state and the other symbols have their usual meanings. Between 300 and 240 K, the experimental data fit Eq. 1 with $-2J=535\ \mathrm{cm}^{-1}$ and $g=2.10$. Below 170 K, the susceptibility follows Eq. 1 with $-2J=595\ \mathrm{cm}^{-1}$ and $g=2.10$. Although temperature dependence of J value was already noticed in some binuclear copper(II) complexes,[19—21] the present complex provides the most remarkable instance. Such a magnetic behavior may be attributed to the fact that the conformation of the chelate ring readily fluctuates with temperature variation. It is known that J values of binuclear copper(II) complexes depend sensitively on the Cu–O–Cu angle[22] or the tetrahedral distortion about the copper coordination.[23] Therefore, a slight variation in the conformation of the complex may lead to a marked change in the J value.

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