

## Binuclear Metal Complexes.

## XLVIII [1]. Crystal and Molecular Structure of Binuclear Copper(II) Complex with 2-[2-(2-Pyridyl)ethylthio] ethanol

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The crystal structure of the binuclear copper(II) complex with 2-[2-(2-pyridyl)ethylthio] ethanol,  $\text{Cu}(\text{py-3}\cdot\text{2-nso})\text{NO}_3\cdot\frac{1}{2}\text{H}_2\text{O}$  (where  $\text{Hpy-3}\cdot\text{2-nso}$  denotes 2-[2-(2-pyridyl)ethylthio] ethanol) was determined by the single-crystal X-ray diffraction method. The crystals are triclinic, space group  $\text{P}\bar{1}$ ,  $a = 11.234(2)$ ,  $b = 15.605(2)$ ,  $c = 8.535(2)$  Å;  $\alpha = 95.13(2)$ ,  $\beta = 121.74(1)$ ,  $\gamma = 72.90(1)^\circ$ . The structure was solved by the heavy atom method and refined by the block-diagonal least-squares method to an R factor of 0.043. The crystal consists of two crystallographically independent binuclear units. In both units, the coordination around the copper atom is a distorted square pyramid with two alkoxo oxygen, thioether sulfur and pyridine nitrogen atoms in the basal plane and an oxygen atom of nitrate ion or water molecule in the apical position. The magnetic property was discussed in terms of the structure, especially the conformation of the chelate ring.

## Introduction

Recently, we have found that binuclear copper(II) complexes with 2-[2-(dialkylamino)ethylthio] ethanol,  $\text{Cu}(\text{R-2}\cdot\text{2-nso})\text{X}$  (where  $\text{HR-2}\cdot\text{2-nso} = 2\text{-[2-(dialkylamino)ethylthio] ethanol}$ ,  $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{n-C}_3\text{H}_7, \text{n-C}_4\text{H}_9$ , and  $\text{X} = \text{Cl}, \text{Br}$ ), are classified into two groups on the basis of the temperature dependence of the magnetic susceptibilities [2]: *i.e.*, (i) complexes whose magnetic behavior can be interpreted in terms of the Bleaney-Bowers equation [3] and (ii) complexes which do not obey the equation. The X-ray structure analyses of a series of  $\text{Cu}(\text{R-2}\cdot\text{2-nso})\text{X}$  complexes revealed that the five-membered chelate ring,  $\text{Cu-O-C-C-S}$ , has a gauche conformation for the group (i) complexes,  $\text{Cu}(\text{C}_2\text{H}_5\cdot\text{2}\cdot\text{2-nso})\text{Cl}$  and  $\text{Cu}(\text{n-C}_4\text{H}_9\cdot\text{2}\cdot\text{2-nso})\text{Cl}$ ; while the chelate ring has an envelope conformation for the group (ii) complexes,  $\text{Cu}(\text{CH}_3\cdot\text{2}\cdot\text{2-nso})\text{Cl}$ ,  $\text{Cu}(\text{CH}_3\cdot\text{2}\cdot\text{2-nso})\text{Br}$ ,  $\text{Cu}$

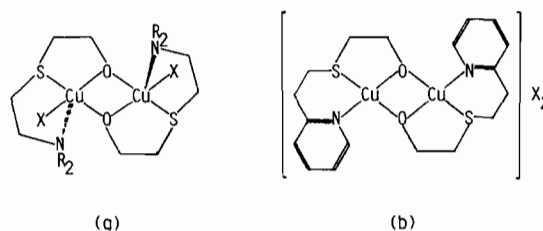


Fig. 1. Basic structures of the complexes. (a)  $\text{Cu}(\text{R-2}\cdot\text{2-nso})\text{X}$  and (b)  $\text{Cu}(\text{py-3}\cdot\text{2-nso})\text{X}$ .

( $\text{n-C}_3\text{H}_7\cdot\text{2}\cdot\text{2-nso}$ )Cl,  $\text{Cu}(\text{n-C}_3\text{H}_7\cdot\text{2}\cdot\text{2-nso})\text{Br}$  and  $\text{Cu}(\text{n-C}_4\text{H}_9\cdot\text{2}\cdot\text{2-nso})\text{Br}$  [4].

In the previous paper of this series [5], we reported synthesis and spectral, magnetic, and electrochemical properties of binuclear copper(II) complexes,  $\text{Cu}(\text{py-3}\cdot\text{2-nso})\text{X}$  and  $\text{Cu}(\text{py-3}\cdot\text{3-nso})\text{X}$  (where  $\text{Hpy-3}\cdot\text{2-nso}$  and  $\text{Hpy-3}\cdot\text{3-nso}$  represent 2-[2-(2-pyridyl)ethylthio] ethanol and 3-[2-(2-pyridyl)ethylthio]-1-propanol, respectively, and  $\text{X}$  denotes Cl, Br,  $\text{ClO}_4$ ,  $\text{NO}_3$ ,  $\text{BF}_4$ , and  $\text{PF}_6$ ). In most of them, the temperature dependence of the magnetic susceptibilities (80–300 K) can be interpreted in terms of the Bleaney-Bowers equation, showing that an antiferromagnetic spin-exchange interaction is operating between the copper(II) ions. However, in the case of  $\text{Cu}(\text{py-3}\cdot\text{2-nso})\text{NO}_3$ ,  $\text{Cu}(\text{py-3}\cdot\text{2-nso})\text{-ClO}_4$ , and  $\text{Cu}(\text{py-3}\cdot\text{2-nso})\text{BF}_4$ , the  $\chi_A$ -T curves deviate from the binuclear model. (In the previous paper, the  $2J$  values of these complexes were evaluated as a rough estimate.) The general trend of these curves resembles those of the group (ii) complexes. This prompted us to determine the crystal structure of  $\text{Cu}(\text{py-3}\cdot\text{2-nso})\text{NO}_3$  by the X-ray diffraction technique in order to examine the validity of the assumption proposed in the preceding paper, *i.e.*, binuclear complexes with envelope conformation do not obey the Bleaney-Bowers equation.

## Experimental

Dark green crystals of  $\text{Cu}(\text{py}\cdot 3\cdot 2\text{-nso})\text{NO}_3\cdot \frac{1}{2}\text{H}_2\text{O}$  were prepared by the method previously reported [5]. A crystal with dimensions of  $0.25 \times 0.25 \times 0.13$  mm was used for the X-ray analysis. The unit-cell parameters and intensities were measured on a Rigaku AFC-5 automated diffractometer with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71069$  Å) at  $24 \pm 1$  °C. The unit-cell parameters were determined by the least-squares refinement based on the 20 reflections in the range of  $20 < 2\theta < 32$ °.

### Crystal Data

$\text{C}_{18}\text{H}_{26}\text{Cu}_2\text{N}_4\text{O}_9\text{S}_2$ , F.W. = 633.64; triclinic;  $P\bar{1}$ ;  $a = 11.234(2)$ ,  $b = 15.605(2)$ ,  $c = 8.535(2)$  Å;  $\alpha = 95.13(2)$ ,  $\beta = 121.74(1)$ ,  $\gamma = 72.90(1)$ °;  $D_m = 1.72$  (by flotation in  $\text{CCl}_4\text{-BrCH}_2\text{CH}_2\text{Br}$ );  $D_c = 1.74$  g  $\text{cm}^{-3}$ ;  $Z = 2$ ;  $\mu(\text{Mo } K\alpha) = 19.8$   $\text{cm}^{-1}$ .

The intensity data were collected by the  $2\theta$ - $\omega$  scan technique with a scan rate of  $8$ °  $\text{min}^{-1}$ . For weak reflections the peak scan was repeated up to four times depending on the intensities. Three standard reflections were monitored every 100 reflections, and their intensities showed a good stability. A total of 3604 reflections with  $2\theta \leq 49$ ° were collected. The intensity data were corrected for the Lorentz and the polarization effects, but not for absorption. Independent 3082 reflections with  $|F_o| > 3\sigma(|F_o|)$  were considered as 'observed' and were used for the structure analysis.

The structure was solved by the heavy atom method and refined by the block-diagonal least-squares method. The weighting scheme [6],  $w = (8.0 + |F_o| + 0.01|F_o|^2)^{-1}$ , was employed. All hydrogen atoms were located from the difference Fourier map and included in the final refinement with the isotropic temperature factors. The final  $R$  values were  $R = 0.043$  and  $R_w = 0.063$ . The final difference Fourier synthesis showed no peaks higher than  $0.73$  e/Å<sup>3</sup>.

The atomic scattering factors for Cu, S, O, N and  $C_{\text{val}}$  and the anomalous dispersion corrections,  $\Delta f'$  and  $\Delta f''$  for Cu and S, were taken from the International Tables for X-Ray Crystallography [7]. For the hydrogen atom, the scattering factors were adopted from the tables of Stewart *et al.* [8]. 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 [9] of the UNICS-II [10] and the ORTEP [11] programs.

Lists of structure factors and anisotropic thermal parameters are available from the Editor. The final positional and thermal parameters with

TABLE I. Fractional Positional Parameters ( $\times 10^4$ ) and Thermal Parameters of Non-hydrogen Atoms with their Estimated Standard Deviations in Parentheses.

Atom	x	y	z	$B_{\text{eq}}/\text{Å}^2$
Cu(A)	530(1)	769.8(4)	1001(1)	2.2
Cu(B)	3857(1)	4751.7(4)	5125(1)	2.5
S(A)	-526(1)	1710(1)	2504(2)	3.0
S(B)	3003(2)	5441(1)	7051(2)	3.4
O(1A)	-1220(4)	403(2)	-241(5)	2.8
O(2A)	3(5)	1521(4)	-1529(7)	5.1
O(3A)	-1888(6)	1852(5)	-4225(6)	6.5
O(4A)	-1962(5)	2437(3)	-1918(7)	5.0
O(1B)	5410(4)	5306(3)	6504(5)	3.3
O(2B)	2744(10)	3188(6)	-2936(13)	9.9
O(3B)	2708(8)	2490(7)	-1078(11)	10.7
O(4B)	4689(7)	2374(7)	-919(11)	11.7
OW	5003(5)	3380(3)	6461(8)	5.0
N(1A)	2441(5)	985(3)	2633(7)	2.8
N(2A)	-1292(5)	1925(3)	-2586(6)	3.2
N(1B)	1974(5)	4502(3)	3334(6)	2.5
N(2B)	3404(7)	2647(5)	-1610(9)	5.5
C(1A)	-2245(7)	725(5)	254(10)	4.6
C(2A)	-1590(8)	954(6)	2196(10)	4.9
C(3A)	924(7)	1417(5)	4917(9)	4.2
C(4A)	2230(7)	644(5)	5192(8)	3.9
C(5A)	3059(6)	899(4)	4484(8)	3.1
C(6A)	4382(6)	1076(4)	5650(9)	4.3
C(7A)	5088(6)	1320(4)	4953(10)	4.5
C(8A)	4458(7)	1413(4)	3073(11)	4.5
C(9A)	3114(6)	1249(4)	1930(9)	3.4
C(1B)	5384(9)	5880(6)	7829(12)	5.9
C(2B)	4027(9)	6251(6)	7669(13)	6.7
C(3B)	1181(7)	6119(4)	5363(9)	4.0
C(4B)	814(6)	6078(4)	3408(8)	3.1
C(5B)	716(6)	5164(4)	2710(7)	2.5
C(6B)	-618(6)	5007(4)	1516(7)	3.1
C(7B)	-672(6)	4170(5)	910(8)	3.6
C(8B)	611(7)	3495(4)	1525(8)	3.4
C(9B)	1926(6)	3674(4)	2758(8)	3.4

their estimated standard deviations are given in Tables I and II.

## Description of the Structure and Discussion

The crystal contains two crystallographically independent binuclear units; they are abbreviated as A and B. Figures 2 and 3 show their molecular structures. Both comprise an alkoxo-bridged  $\text{Cu}_2(\text{py}\cdot 3\cdot 2\text{-nso})_2$  unit which has a center of symmetry. In each unit, the coordination about the copper atom may be regarded as distorted square pyramid. The two alkoxo oxygen, thioether sulfur, and pyridine nitrogen atoms of the ligands occupy the equatorial positions of the square pyramid. The most obvious difference between A and B is in the

TABLE II. Fractional Positional Parameters ( $\times 10^3$ ) and Isotropic Temperature Factors of Hydrogen Atoms with their Estimated Standard Deviations in Parentheses.

Atom	x	y	z	B/ $\text{\AA}^2$
H1(OW)	604(8)	308(5)	709(10)	6(2)
H2(OW)	516(8)	370(5)	756(10)	5(2)
H1(C(1A))	-278(9)	21(5)	7(11)	7(2)
H2(C(1A))	-304(8)	134(5)	-62(10)	5(2)
H1(C(2A))	-89(7)	33(5)	311(10)	5(2)
H2(C(2A))	-243(7)	127(5)	250(9)	5(2)
H1(C(3A))	50(7)	124(4)	568(8)	4(1)
H2(C(3A))	130(8)	199(5)	548(10)	6(2)
H1(C(4A))	185(7)	8(4)	447(9)	5(2)
H2(C(4A))	295(8)	44(5)	663(10)	5(2)
H(C(6A))	483(8)	103(5)	713(10)	6(2)
H(C(7A))	612(8)	143(5)	585(10)	6(2)
H(C(8A))	500(8)	160(5)	249(11)	7(2)
H(C(9A))	260(7)	134(4)	45(8)	4(1)
H1(C(1B))	576(8)	644(5)	778(10)	5(2)
H2(C(1B))	608(12)	552(8)	919(15)	12(3)
H1(C(2B))	340(11)	680(7)	659(15)	12(3)
H2(C(2B))	413(9)	652(6)	888(11)	7(2)
H1(C(3B))	104(8)	682(5)	567(10)	6(2)
H2(C(3B))	38(7)	591(4)	545(9)	4(1)
H1(C(4B))	167(6)	623(4)	334(8)	3(1)
H2(C(4B))	-21(6)	656(4)	254(8)	3(1)
H(C(6B))	-161(7)	555(4)	105(9)	5(2)
H(C(7B))	-172(7)	405(4)	-4(8)	4(1)
H(C(8B))	60(7)	283(5)	104(9)	5(2)
H(C(9B))	295(8)	314(5)	329(10)	6(2)

apical ligation; the fifth coordination site in A is occupied by the oxygen atom of the nitrate ion, while in B it is occupied by a water oxygen atom. The equatorial Cu–O distances are 1.918(4) and 1.963(4) Å in A and 1.931(5) and 1.939(6) Å in B. These values fall in the range observed for other alkoxy-bridged binuclear copper(II) complexes [2, 4, 12]. The Cu–S distances (2.335(2) Å for A and 2.348(2) Å for B) are comparable to the values found in the Cu(R-2·2-nso)Cl complexes [4]. The Cu–N distances (1.964(5) Å for A and 1.985(4) Å for B) are near the lower limits of the values (1.980–2.161 Å) reported for other copper(II) complexes of pyridine [13] and substituted pyridines [14–23]. The fifth coordinating atoms, O(2A) and OW, lie at the apex of the square pyramid with Cu–O distances of 2.255(6) and 2.193(5) Å, respectively. The deviations of the basal atoms from the mean planes are –0.141–0.136 Å for A and –0.057–0.059 Å for B (Table IV). The tetrahedral distortion in A is larger than that in B. The copper atoms in A and B are shifted from the basal planes toward the apical oxygen atom by 0.299 and 0.313 Å, respectively.

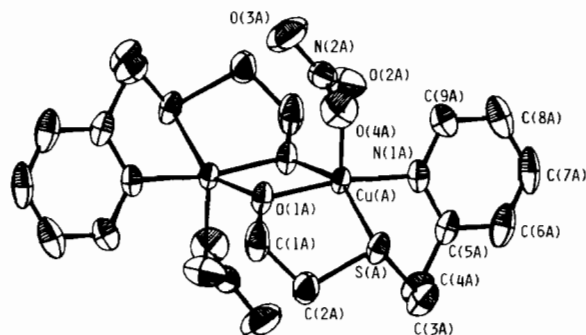


Fig. 2. Molecular structure of A with thermal ellipsoids (50% probability level).

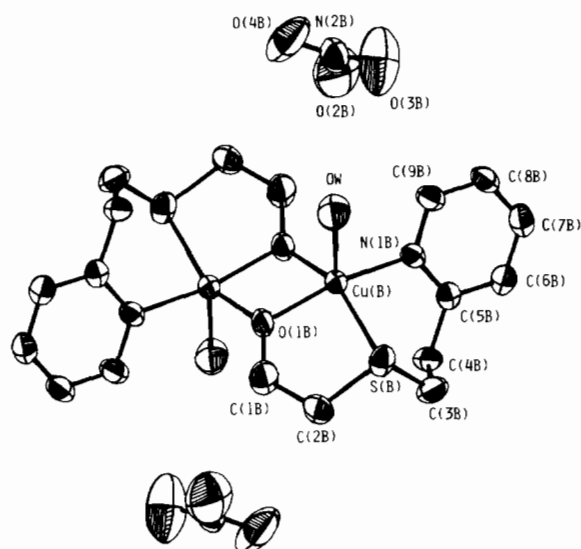


Fig. 3. Molecular structure of B with thermal ellipsoids (50% probability level).

No significant difference in the geometries of the py-3·2nso ligands can be recognized between A and B. The five-membered chelate ring formed by Cu, O(1), C(1), C(2) and S assumes the envelope conformation, *i.e.*, both carbon atoms, C(1) and C(2), are placed in the same side of the Cu–S–O(1) plane (Table IV). The chelating angles O(1)–Cu–S subtended at copper by the five-membered rings are 85.5(1)° for A and 85.6(2)° for B, respectively; these angles are slightly larger than the values in the Cu(R-2·2-nso)X complexes, which range from 84.6 to 85.0° [2, 4]. The six-membered chelate ring formed by Cu, S, C(3), C(4), C(5) and N(1) adopts the boat conformation. The base portion of the boat formed by S, C(3), C(5) and N(1) is nearly planar, while Cu and C(4) are located above this plane by 0.993 (in A) and 1.033 Å (in B) and 0.730 (in A) and 0.712

TABLE III. Interatomic Distances (1/Å) and Bond Angles ( $\phi^\circ$ ) with their Estimated Standard Deviations in Parentheses.<sup>a</sup>

## (I) Binuclear molecule A

## (a) Copper coordination spheres

Cu(A)···Cu(A) <sup>i</sup>	2.986(1)	Cu(A)–S(A)	2.335(2)
Cu(A)–O(1A)	1.918(4)	Cu(A)–N(1A)	1.964(5)
Cu(A)–O(1A) <sup>i</sup>	1.963(4)	Cu(A)–O(2A)	2.255(6)
Cu(A)–O(1A)–Cu(A) <sup>i</sup>	100.6(2)	S(A)–Cu(A)–N(1A)	93.2(2)
O(1A)–Cu(A)–O(1A) <sup>i</sup>	79.4(2)	O(2A)–Cu(A)–O(1A)	94.8(2)
O(1A)–Cu(A)–S(A)	85.5(1)	O(2A)–Cu(A)–O(1A) <sup>i</sup>	92.9(2)
O(1A)–Cu(A)–N(1A)	169.6(2)	O(2A)–Cu(A)–S(A)	110.1(1)
O(1A) <sup>i</sup> –Cu(A)–S(A)	153.4(2)	O(2A)–Cu(A)–N(1A)	95.3(2)
O(1A) <sup>i</sup> –Cu(A)–N(1A)	97.8(2)		

## (b) py-3·2-nso moiety

O(1A)–C(1A)	1.375(11)	C(5A)–C(6A)	1.382(8)
C(1A)–C(2A)	1.478(11)	C(6A)–C(7A)	1.357(14)
C(2A)–S(A)	1.825(10)	C(7A)–C(8A)	1.372(12)
S(A)–C(3A)	1.818(6)	C(8A)–C(9A)	1.389(9)
C(3A)–C(4A)	1.519(9)	C(9A)–N(1A)	1.344(11)
C(4A)–C(5A)	1.499(12)	N(1A)–C(5A)	1.351(8)
Cu(A)–O(1A)–C(1A)	119.5(4)	C(4A)–C(5A)–C(6A)	122.3(6)
Cu(A) <sup>i</sup> –O(1A)–C(1A)	132.4(5)	C(5A)–C(6A)–C(7A)	120.5(7)
O(1A)–C(1A)–C(2A)	112.4(6)	C(6A)–C(7A)–C(8A)	119.4(6)
C(1A)–C(2A)–S(A)	107.1(7)	C(7A)–C(8A)–C(9A)	119.0(9)
Cu(A)–S(A)–C(2A)	90.8(3)	C(8A)–C(9A)–N(1A)	121.2(7)
Cu(A)–S(A)–C(3A)	101.8(3)	C(9A)–N(1A)–C(5A)	119.7(5)
C(2A)–S(A)–C(3A)	100.9(4)	Cu(A)–N(1A)–C(5A)	119.5(5)
S(A)–C(3A)–C(4A)	113.3(5)	Cu(A)–N(1A)–C(9A)	120.8(4)
C(3A)–C(4A)–C(5A)	112.3(6)	N(1A)–C(5A)–C(6A)	120.2(7)
		C(4A)–C(5A)–N(1A)	117.5(5)

## (c) Nitrate ion

N(2A)–O(2A)	1.299(5)	N(2A)–O(4A)	1.243(9)
N(2A)–O(3A)	1.203(7)		
Cu(A)–O(2A)–N(2A)	116.2(5)	O(3A)–N(2A)–O(4A)	120.7(5)
O(2A)–N(2A)–O(3A)	121.4(6)	O(4A)–N(2A)–O(2A)	117.9(5)

## (II) Binuclear molecule B

## (a) Copper coordination spheres

Cu(B)···Cu(B) <sup>ii</sup>	3.004(1)	Cu(B)–S(B)	2.348(2)
Cu(B)–O(1B)	1.931(5)	Cu(B)–N(1B)	1.985(4)
Cu(B)–O(1B) <sup>ii</sup>	1.939(6)	Cu(B)–OW	2.193(5)
Cu(B)–O(1B)–Cu(B) <sup>ii</sup>	101.9(2)	S(B)–Cu(B)–N(1B)	92.5(2)
O(1B)–Cu(B)–O(1B) <sup>ii</sup>	78.1(2)	OW–Cu(B)–O(1B)	100.1(2)
O(1B)–Cu(B)–S(B)	85.6(2)	OW–Cu(B)–O(1B) <sup>ii</sup>	99.4(2)
O(1B)–Cu(B)–N(1B)	164.6(2)	OW–Cu(B)–S(B)	101.0(2)
O(1B) <sup>ii</sup> –Cu(B)–S(B)	155.8(1)	OW–Cu(B)–N(1B)	95.2(2)
O(1B) <sup>ii</sup> –Cu(B)–N(1B)	98.4(2)		

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TABLE III. (continued)

## (b) py-3·2-nso moiety

O(1B)–C(1B)	1.386(11)	C(5B)–C(6B)	1.381(8)
C(1B)–C(2B)	1.398(15)	C(6B)–C(7B)	1.368(9)
C(2B)–S(B)	1.815(11)	C(7B)–C(8B)	1.369(8)
S(B)–C(3B)	1.812(5)	C(8B)–C(9B)	1.387(9)
C(3B)–C(4B)	1.493(10)	C(9B)–N(1B)	1.347(7)
C(4B)–C(5B)	1.507(8)	N(1B)–C(5B)	1.340(6)
Cu(B)–O(1B)–C(1B)	119.2(6)	C(5B)–C(6B)–C(7B)	120.1(5)
Cu(B) <sup>ii</sup> –O(1B)–C(1B)	133.6(6)	C(6B)–C(7B)–C(8B)	118.8(6)
O(1B)–C(1B)–C(2B)	116.4(7)	C(7B)–C(8B)–C(9B)	119.3(6)
C(1B)–C(2B)–S(B)	112.5(7)	C(8B)–C(9B)–N(1B)	121.5(5)
Cu(B)–S(B)–C(2B)	92.2(4)	C(9B)–N(1B)–C(5B)	119.0(5)
Cu(B)–S(B)–C(3B)	101.0(3)	Cu(B)–N(1B)–C(5B)	119.6(4)
C(2B)–S(B)–C(3B)	101.0(3)	Cu(B)–N(1B)–C(9B)	121.4(3)
S(B)–C(3B)–C(4B)	114.7(5)	N(1B)–C(5B)–C(6B)	121.2(5)
C(3B)–C(4B)–C(5B)	112.6(6)	C(4B)–C(5B)–N(1B)	117.4(5)
C(4B)–C(5B)–C(6B)	121.4(5)		

## (c) Nitrate ion

N(2B)–O(2B)	1.210(12)	N(2B)–O(4B)	1.183(9)
N(2B)–O(3B)	1.176(16)		
O(2B)–N(2B)–O(3B)	116.2(8)	O(3B)–N(2B)–O(4B)	126.8(9)
O(2B)–N(2B)–O(4B)	116.8(11)		

<sup>a</sup>Superscripts (i) and (ii) refer to the equivalent positions (–x, –y, –z) and (1 – x, 1 – y, 1 – z), respectively.

TABLE IV. Deviations of the Atoms from Least-Squares Planes (1/Å).

(I)	Plane through O(1A), O(1A) <sup>i</sup> , N(1A), S(A) –0.3071X – 0.6390Y + 0.7658Z = 0.0024 <sup>a</sup> [O(1A) –0.141, O(1A) <sup>i</sup> 0.136, N(1A) –0.106, S(A) 0.111, Cu(A) –0.299, O(2A) –2.519] <sup>b</sup>
(II)	Plane through Cu(A), S(A), O(1A) –0.1489X – 0.6865Y + 0.6470Z = –0.3607 [Cu(A) 0.000, S(A) 0.000, O(1A) 0.000, C(1A) 0.100, C(2A) 0.817]
(iii)	Plane through S(A), C(3A), C(5A) N(1A) 0.3353X + 0.9964Y – 0.0507Z = 2.3459 [S(A) 0.006, C(3A) –0.008, C(5A) 0.010, N(1A) –0.009, Cu(A) –0.993, C(4A) –0.730]
(IV)	Plane through N(1A), C(5A), C(6A), C(7A), C(8A), C(9A) –0.2771X + 0.8367Y + 0.1955Z = 0.9726 [N(1A) –0.007, C(5A) –0.003, C(6A) 0.010, C(7A) –0.007, C(8A) –0.003, C(9A) 0.010]
(V)	Plane through O(2A), O(3A), O(4A), N(2A) 0.6482X + 0.9088Y – 0.3942Z = 2.6696 [O(2A) 0.003, O(3A) 0.003, O(4A) 0.003, N(2A) –0.010]
(VI)	Plane through O(1B), O(1B) <sup>ii</sup> , N(1B), S(B) 0.0334X – 0.8222Y + 0.3393Z = –4.7806 [O(1B) 0.059, O(1B) <sup>ii</sup> –0.057, N(1B) 0.044, S(B) –0.046, Cu(B) 0.313, OW 2.502]

(continued overleaf)

TABLE IV. (continued)

(VII) Plane through Cu(B), S(B), O(1B)
$0.0283X - 0.7166Y + 0.4852Z = -3.0687$
[Cu(B) 0.000, S(B) 0.000, O(1B) 0.000, C(1B) -0.094, C(2B) -0.618]
(VIII) Plane through S(B), C(3B), C(5B), N(1B)
$-0.8076X - 0.7247Y + 0.6415Z = -5.0334$
[S(B) 0.017, C(3B) -0.022, C(5B) 0.028, N(1B) -0.023, Cu(B) -1.033, C(4B) -0.712]
(IX) Plane through N(1B), C(5B), C(6B), C(7B), C(8B), C(9B)
$-0.6102X - 0.3469Y + 0.9640Z = -1.0479$
[N(1B) 0.001, C(5B) -0.009, C(6B) 0.008, C(7B) 0.000, C(8B) -0.008, C(9B) 0.008]
(X) Plane through O(2B), O(3B), O(4B), N(2B)
$0.0309X + 0.7813Y + 0.5378Z = 2.6275$
[O(2B) 0.007, O(3B) 0.008, O(4B) 0.007, N(2B) -0.021]

<sup>a</sup>The equation of the plane is expressed as  $LX + MY + NZ = D$ , where X, Y and Z are in Å units referred to the crystallographic axes. <sup>b</sup>Deviations (1/Å) of atoms from the planes are listed in square brackets. Superscript (i) and (ii) refer to the equivalent positions (-x, -y, -z) and (1 - x, 1 - y, 1 - z), respectively.

Å (in B), respectively (Table IV). The boat conformation has been observed in copper(II) complexes of 2-(2-aminoethyl)pyridine [16], 2-(2-methylaminoethyl)pyridine [17] and 2-(2-dimethylaminoethyl)pyridine [19]. In these complexes, it has been noted that when the chelating angle, N-Cu-N, (corresponding to S-Cu-N(1) angle in the present complex), is acute, the copper atom is farther from the basal plane, and when this angle is obtuse, the carbon atom (corresponding to C(4) in the present complex) is farther from the plane. This correlation does not hold for the present complex whose chelating angles, S-Cu-N(1), are 93.2(2) and 92.5(2)°, although the copper atoms are farther from the planes. The obtuse chelating angles may be ascribed to the large radius of the sulfur atom.

The pyridine rings are planar and the bond distances and angles in the pyridine rings are in the normal ranges [13-23].

The nitrate ions are approximately planar with no deviations from the least-squares planes greater than 0.03 Å. There were no definite differences in the coordinated and uncoordinated nitrate ions [24]. The nitrate oxygen atoms participate in hydrogen bonding with the coordinated water molecule (O(4A)···OW(x - 1, y, z - 1) 2.856(7), O(2B)···OW(x, y, z - 1) 2.94(2), O(4B)···OW(x, y, z - 1) 3.06(1) Å).

The temperature dependence of magnetic susceptibilities for the present complex is shown in Fig. 4. The susceptibility data could not be fitted by the Bleaney-Bowers equation. The closest interdimer contact is the hydrogen bond, O(4A)···OW(x - 1, y, z - 1) 2.856(7) Å. Therefore, interdimer magnetic interaction may be negligibly small: hence it seems

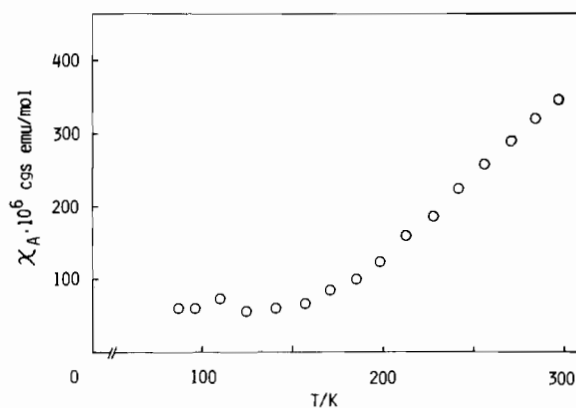


Fig. 4. Temperature dependence of magnetic susceptibilities of  $\text{Cu}(\text{py-3}\cdot\text{2-nso})\text{NO}_3\cdot\frac{1}{2}\text{H}_2\text{O}$ .

to be difficult to explain the magnetic behavior in terms of the interdimer interaction [12]. Since there are two independent binuclear units in the unit cell, use of the different  $-2J$  values for both dimers is required. However, the experimental data could not be interpreted by any theoretical formulas based on the two independent dimers. For a reasonable explanation, some change of the crystal structure may take place with lowering of temperature, and this may cause the deviation of the  $\chi_A$ -T curve from the theoretical one. In the  $\text{Cu}(\text{R-2}\cdot\text{2-nso})\text{X}$  complexes, a similar magnetic behavior was observed for the complexes whose chelate ring,  $\text{Cu-O(1)-C(1)-C(2)-S}$ , assumes an envelope conformation [2, 4]. We supposed that this conformation may be responsible for a structural change with tempera-

ture and hence for the temperature dependence of the J value [4]. The chelate ring,  $\text{Cu}-\text{O}(1)-\text{C}(1)-\text{C}(2)-\text{S}$ , of the present complex also adopts the envelope conformation. This result again fits in our assumptions.

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