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Crystal and Molecular Structure of μ-Imidazolato-bis{[tris(2-methylthioethyl)amine]copper(II)}perchlorate

Masatatsu SUZUKI,* Ikuhiko UEDA, Hajime KANATOMI, and Ichiro MURASE
Laboratory of Chemistry, College of General Education, Kyushu University,
Ropponmatsu, Chuo-ku, Fukuoka 810

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The structure of the title complex, $[Cu_2(NS_2\text{–}Me)_2im](ClO_4)_3$, has been determined by the single-crystal X-ray diffraction method, where NS_3–Me is tris(2-methylthioethyl)amine and im is imidazolate anion. The complex crystallizes in the monoclinic space group $P2_1/a$ with a unit cell with the dimensions of $a=13.114(3)$, $b=28.045(6)$, $c=10.481(2)$ Å, $\beta=98.70(2)°$, $V=3810.2(13)$ Å^3, and $Z=4$. The structure was solved by the heavy atom method. The residual R value was 0.0594 for 4431 independent reflections. The coordination geometries of the two copper atoms are different from each other; the Cu(1) is in a trigonal bipyramidal geometry with three sulfur atoms in the equatorial plane and two nitrogen atoms in the axial positions, while the coordination geometry of the Cu(2) can be best described as an intermediate between a trigonal bipyramid and a square pyramid. The intramolecular Cu(1)⋯Cu(2) distance is 5.930(2) Å. Temperature-dependent magnetic susceptibility data showed a strong antiferromagnetic exchange interaction with a coupling constant $-J=63\ \text{cm}^{-1}$. The Cu(1)-N(1)-C(1) and Cu(2)-N(2)-C(1) angles, which have been considered to be related to the magnitude of the antiferromagnetic exchange interaction, are 132.1(5) and 127.0(6)°, respectively. The magnetism of the complex is discussed in connection with the structural data.

Recently, a number of di- and tetra-nuclear copper (II) complexes bridged by various imidazolate groups have been reported as possible models for the active site of bovine erythrocyte superoxide dismutase.[1–8] Those studies have shown that antiferromagnetic exchange interactions operate between copper(II) ions and their magnitudes are highly dependent on the structure of the Cu–im–Cu moiety.

In the previous study,[9] we reported that the imidazolate-bridged dinuclear copper(II) complexes with tripod ligand (L) having NS_3 or N_2S_2 donor set, $[Cu_2(L)_2im](ClO_4)_3$, exhibited antiferromagnetic interactions with coupling constants ($-J$) of 58—66 cm^{-1}, where L is tris(2-alkylthioethyl)amine, 2-[bis(2-methylthioethyl)aminomethyl]pyridine, or *N,N*-bis-(2-methylthioethyl)ethylenediamine and im is imidazolate anion. The antiferromagnetic exchange interactions of those complexes are considerably strong compared with those of the other dinuclear complexes bridged by imidazolate itself.[2–8] Therefore, we are interested in the structure of the Cu–im–Cu moiety of the above complexes with tripod ligands containing sulfur atoms in connection with their magnetic properties.

In general, tripod ligands (L) such as tris(2-aminoethyl) amine (tren) tend to form trigonal bipyramidal copper(II) complexes, $[Cu(L)X]^{n+}$, with an additional unidentate ligand (X).[10–13] Previously, we demmonstrated that, in a series of $[Cu(NS_3\text{–}R)X]^{n+}$, the stereochemistry of the complexes depends on both alkyl substituent (R) and the unidentate ligand (X).[14] The electronic and esr spectra of the imidazole complex, $[Cu(NS_3\text{–}Me)Him]\ (ClO_4)_2$, suggested that the complex has a square pyramidal structure. Thus the stereochemistry of the dinuclear complex with tripod ligand, NS_3–Me, is also interesting. In this paper, we have undertaken a single-crystal X-ray analysis of $[Cu_2(NS_3\text{–}Me)_2im](ClO_4)_3$.

Mikuriya *et al.*[15,16] demonstrated that the replacement of nitrogen donor atom by sulfur donor atom causes an increase in antiferromagnetic exchange interaction; the alkoxo-bridged dinuclear copper(II) complexes with SNO and NSO donor sets exhibit a stronger antiferromagnetic exchange interaction than the complexes with NNO donor set. An influence of the sulfur donor atom on the antiferromagnetic exchange interaction is also described.

Experimental

The complex was prepared by the method previously reported.[9] Recrystallization from an aqueous solution at room temperature afforded dark green prisms.

The diffraction data were measured on a Rigaku AFC-5 automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The unit-cell parameters were determined by the least-squares refinement based on 20 reflections. A crystal with approximate dimensions of $0.3\times0.2\times0.2$ mm^3 was used for intensity measurement. Crystal data: $Cu_2Cl_3S_6O_{12}N_4C_{21}H_{45}$, F.W.$=971.4$, monoclinic, space group $P2_1/a$, $a=13.114(3)$, $b=28.045(6)$, $c=10.481(2)$ Å, $\beta=98.70(2)°$, $V=3810.2(13)$ Å^3, $D_m=1.68$, $D_x=1.69\ \text{g cm}^{-3}$, $Z=4$, and $\mu(\text{Mo}\ K\alpha)=17.4\ \text{cm}^{-1}$.

The intensity data were collected by θ-2θ scan technique with a scan rate of 8° min^{-1}. For weak reflections the peak scan was repeated up to three times depending on their intensities. Three standard reflections were monitored every 100 reflections and their intensities showed a good stability. A total of 7249 reflections with $2\theta<50°$ was collected and 4431 independent reflections with $|F_o|>3\sigma(|F_o|)$ were considered as "observed" and used for structure analysis. The intensity data were corrected for the Lorentz and polarization effects, but not for the absorption.

The structure was solved by the heavy-atom method. The positions of two copper atoms were obtained from the Patterson synthesis and those of the remaining 46 nonhydrogen atoms were obtained from successive Fourier syntheses. Refinement was carried out by the block-diagonal least-squares method. A difference Fourier synthesis gave several peaks around chlorine atoms of perchlorate ions, which were ascribed to the disordered oxygen atoms of perchlorate ions. The nonhydrogen atoms with occupancy factor larger than 0.5 were refined with anisotropic thermal parameters. Hydrogen atoms defined by the geometry of the complex were located at the calculated positions (C–H$=1.09$ Å)

TABLE 1. 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_{eq}/Å^3	b)	Atom	x	y	z	B_{eq}/Å^3	b)
Cu(1)	3615.6(8)	4374.6(3)	7311.4(9)	2.7		C(15)	3339(8)	6959(4)	7594(10)	5.1	
Cu(2)	1411.8(7)	6227.7(3)	6866.6(10)	2.8		C(16)	-194(8)	6955(4)	6240(11)	5.2	
S(1)	4950(2)	4529(1)	6069(2)	3.1		C(17)	445(9)	7131(4)	5258(9)	5.0	
S(2)	3790(2)	4605(1)	9561(2)	3.8		C(18)	2147(9)	6942(4)	4027(11)	5.7	
S(3)	2216(2)	3874(1)	6368(2)	4.0		C(19)	-299(8)	6473(4)	8174(11)	5.6	
S(4)	2690(2)	6531(1)	8468(2)	3.7		C(20)	-861(8)	6052(5)	7457(13)	6.4	
S(5)	1145(2)	6636(1)	4722(2)	3.9		C(21)	236(9)	5218(5)	7360(15)	7.8	
S(6)	-93(2)	5737(1)	6451(3)	4.7		Cl(1)	13371(2)	10675(1)	8823(3)	5.2	
N(1)	2911(5)	4965(2)	6661(6)	2.9		Cl(2)	11355(2)	8415(1)	6731(2)	4.3	
N(2)	2243(5)	5688(2)	6425(6)	2.9		Cl(3)	4189(2)	7687(1)	11197(2)	4.1	
N(3)	4408(6)	3760(2)	7931(6)	3.3		O(11)	12761(10)	10635(4)	9783(10)	11.5	
N(4)	414(5)	6726(3)	7405(7)	3.7		O(12)	13156(7)	10285(4)	7967(9)	8.2	
C(1)	2736(6)	5369(3)	7234(8)	3.0		O(13)	14422(8)	10671(5)	9316(12)	12.7	
C(2)	2119(6)	5476(3)	5242(7)	3.2		O(14)	13109(9)	11102(4)	8166(12)	10.8	
C(3)	2526(7)	5029(3)	5368(8)	3.4		O(21)	12083(6)	8119(3)	6232(9)	7.3	
C(4)	5532(7)	3798(4)	7760(9)	4.2		O(22)	11470(7)	8892(3)	6398(11)	8.9	
C(5)	5661(7)	3990(3)	6454(9)	4.0		O(23)	10382(6)	8248(4)	6122(10)	8.9	
C(6)	5677(7)	4957(4)	7106(9)	4.2		O(24)	11157(15)	8299(7)	8009(16)	7.6	0.50
C(7)	4370(8)	3674(4)	9333(9)	4.3		O(25)	11714(15)	8408(7)	8026(14)	8.0	0.50
C(8)	4623(8)	4120(4)	10127(8)	4.6		O(31)	3482(7)	8011(3)	10517(8)	8.0	
C(9)	2609(8)	4429(4)	10158(10)	7.1		O(32)	4430(9)	7344(4)	10368(9)	9.0	0.90
C(10)	3927(8)	3348(3)	7152(10)	4.2		O(33)	3655(15)	7384(7)	12002(21)	10.7	0.55
C(11)	2768(8)	3322(3)	7069(10)	4.4		O(34)	5177(12)	7901(7)	11464(17)	9.4	0.55
C(12)	1122(8)	3968(4)	7238(11)	5.1		O(35)	3954(16)	7559(8)	12406(20)	8.2	0.45
C(13)	975(8)	7113(4)	8202(11)	5.2		O(36)	4452(28)	7801(13)	12452(35)	10.0	0.30
C(14)	1834(8)	6914(4)	9214(9)	4.3		O(37)	4887(29)	7977(14)	11906(36)	8.0	0.25

b) Occupancy factors.

In the final cycles of the refinement, hydrogen atoms were included with isotropic thermal parameters (4.0 Å^2). The final value of R was 0.0594.

The difference Fourier map showed a peak (1.4 eÅ^3) near the S(6) atom which was probably due to the fact that the absorption correction had not been applied.

The atomic scattering factors and the anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$, for Cu, Cl, S, O, N, and C, were taken from the international tables for X-ray Crystallography.[17] For the hydrogen atoms, the scattering factors were adopted from the tables of Stewart *et al.*[18] All the calculations were carried out on the FACOM M-200 computor at the Computor Center of Kyushu University by the use of a local version of the UNICS III[19,20] and the ORTEP[21] programs. The final positional parameters with their standard deviations are given in Table 1. Observed and calculated structure factors, anisotropic thermal parameters of the nonhydrogen atoms, and hydrogen atom coordinates have been deposited as a Document NO. 8351 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

A perspective drawing of the complex cation and the numbering system are illustrated in Fig. 1. Bond distances and angles are listed in Table 2.

The crystal structure consists of a discrete imidazolate bridged dinuclear cation, $[Cu_2(NS_3\text{-}Me)_2im]^{3+}$, and perchlorate anions. The intramolecular Cu(1)···Cu(2) distance is 5.930(2) Å. Each copper atom is five-coordinate. The coordination geometries of the Cu(1) and Cu(2) atoms are different from each other. The Cu(1) atom is in a trigonal bipyramidal coordination geometry, while the Cu(2) is in an intermediate between a trigonal bipyramid and a square pyramid (Fig. 2). In the former, the equatorial positions are occupied by three sulfur atoms and the axial positions

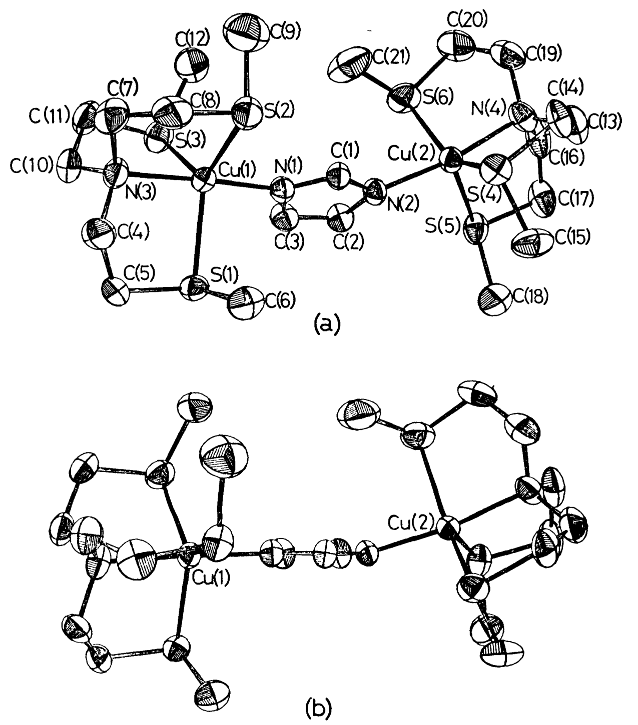

Fig. 1. Two views (a) and (b) of the complex cation, $[Cu_2(NS_3\text{-}Me)_2im]^{3+}$, showing the atomic numbering. The thermal ellipsoid was drawn at the 50% probability level.

by two nitrogen atoms. The three trigonal angles formed by S–Cu–S are close to 120°, *i.e.*, 121.11(9), 117.47(9), and 120.71(10)°, and the trigonal axis (N(1)–Cu(1)–N(3)) is nearly linear (177.1(3)°). The three equatorial Cu–S distances are 2.374(2), 2.423(3), and 2.402(3) Å, which are in agreement with those in trigonal bipyramidal complexes with tripod ligand containing sulfur atoms, $[Cu(NS_3\text{–}Me)Br]ClO_4$ [22] and $[Cu(pam)SO_4]$[23] (pam=2-[bis(2-ethylthioethyl)-aminomethyl]pyridine). The Cu(1)–N(3) distance is comparable to Cu–N distances of the above complexes.

The Cu(1) atom does not exactly fit in the trigonal plane through S(1), S(2), and S(3), and is displaced 0.12 Å toward the direction of the bridging imidazolate. This type of displacement of the Cu atom is quite commom in the trigonal bipyramidal complexes with tripod ligands.[10–13]

The coordination geometry around the Cu(2) atom is an intermediate between a trigonal bipyramid and a square pyramid. The distorted nature from a trigonal bipyramid becomes evident from an examination of the S–Cu–S bond angles, 95.77(9), 117.71(9), and 145.10(10)°. Viewing the structure as a square pyramid, N(2), N(4), S(4), and S(6) atoms form a basal plane, and the S(5) atom occupies the axial position. In a regular square pyramid, The S(4)–Cu(2)–S(6) and the N(2)–Cu(2)–N(4) angles should be 180°. In the typical square pyramidal complex, $K[Cu(NH_3)_5](PF_6)_3$[24], however, the corresponding angles are 164 and 167°, where the decrease

Table 2. Interatomic distances and angles with estimated standard deviations in parentheses

Bond distance	l/Å	Bond distance	l/Å
Cu(1)···Cu(2)	5.930(2)	N(3)-C(7)	1.498(11)
Cu(1)-S(1)	2.374(3)	N(3)-C(10)	1.498(11)
Cu(1)-S(2)	2.423(3)	N(4)-C(13)	1.492(13)
Cu(1)-S(3)	2.402(3)	N(4)-C(16)	1.498(13)
Cu(1)-N(1)	1.968(7)	N(4)-C(19)	1.502(14)
Cu(1)-N(3)	2.065(7)	C(2)-C(3)	1.362(12)
Cu(2)-S(4)	2.345(2)	C(4)-C(5)	1.504(14)
Cu(2)-S(5)	2.500(3)	C(7)-C(8)	1.512(14)
Cu(2)-S(6)	2.392(3)	C(10)-C(11)	1.511(14)
Cu(2)-N(2)	1.961(7)	C(13)-C(14)	1.531(14)
Cu(2)-N(4)	2.051(8)	C(16)-C(17)	1.505(16)
S(1)-C(5)	1.790(9)	C(19)-C(20)	1.528(17)
S(1)-C(6)	1.795(10)	Cl(1)-O(11)	1.381(13)
S(2)-C(8)	1.789(11)	Cl(1)-O(12)	1.416(10)
S(2)-C(9)	1.825(12)	Cl(1)-O(13)	1.398(11)
S(3)-C(11)	1.817(10)	Cl(1)-O(14)	1.395(12)
S(3)-C(12)	1.832(12)	Cl(2)-O(21)	1.424(9)
S(4)-C(14)	1.813(11)	Cl(2)-O(22)	1.396(9)
S(4)-C(15)	1.799(12)	Cl(2)-O(23)	1.417(9)
S(5)-C(17)	1.800(11)	Cl(2)-O(24)	1.440(18)
S(5)-C(18)	1.812(13)	Cl(2)-O(25)	1.368(15)
S(6)-C(20)	1.797(13)	Cl(3)-O(31)	1.411(10)
S(6)-C(21)	1.757(14)	Cl(3)-O(32)	1.364(11)
N(1)-C(1)	1.319(11)	Cl(3)-O(33)	1.452(21)
N(1)-C(3)	1.385(10)	Cl(3)-O(34)	1.417(17)
N(2)-C(1)	1.331(10)	Cl(3)-O(35)	1.395(22)
N(2)-C(2)	1.363(10)	Cl(3)-O(36)	1.347(36)
N(3)-C(4)	1.515(12)	Cl(3)-O(37)	1.359(36)

Bond angle	ϕ/°	Bond angle	ϕ/°	Bond angle	ϕ/°
S(1)-Cu(1)-S(2)	121.11(9)	Cu(2)-S(4)-C(14)	95.8(3)	N(1)-C(3)-C(2)	107.0(7)
S(1)-Cu(1)-S(3)	117.47(9)	Cu(2)-S(4)-C(15)	102.7(3)	N(3)-C(4)-C(5)	112.2(7)
S(2)-Cu(1)-S(3)	120.71(10)	C(14)-S(4)-C(15)	101.3(5)	S(1)-C(5)-C(4)	112.4(7)
S(1)-Cu(1)-N(1)	90.2(2)	Cu(2)-S(5)-C(17)	94.7(3)	N(3)-C(7)-C(8)	111.7(8)
S(1)-Cu(1)-N(3)	87.0(2)	Cu(2)-S(5)-C(18)	124.5(4)	S(2)-C(8)-C(7)	112.1(6)
S(2)-Cu(1)-N(1)	94.7(2)	C(17)-S(5)-C(18)	101.3(5)	N(3)-C(10)-C(11)	114.0(8)
S(2)-Cu(1)-N(3)	87.0(2)	Cu(2)-S(6)-C(20)	97.5(4)	S(3)-C(11)-C(10)	108.5(7)
S(3)-Cu(1)-N(1)	93.4(2)	Cu(2)-S(6)-C(21)	104.5(4)	N(4)-C(13)-C(14)	111.8(8)
S(3)-Cu(1)-N(3)	87.6(2)	C(20)-S(6)-C(21)	101.7(7)	S(4)-C(14)-C(13)	110.9(7)
N(1)-Cu(1)-N(3)	177.1(3)	Cu(1)-N(1)-C(1)	132.1(5)	N(4)-C(16)-C(17)	114.6(8)
S(4)-Cu(2)-S(5)	117.71(9)	Cu(1)-N(1)-C(3)	122.0(6)	S(5)-C(17)-C(16)	108.9(7)
S(4)-Cu(2)-S(6)	145.10(10)	C(1)-N(1)-C(3)	105.8(7)	N(4)-C(19)-C(20)	113.2(10)
S(5)-Cu(2)-S(6)	95.77(9)	Cu(2)-N(2)-C(1)	127.0(6)	S(6)-C(20)-C(19)	113.4(8)
S(4)-Cu(2)-N(2)	94.9(2)	Cu(2)-N(2)-C(2)	123.9(5)	O(11)-Cl(1)-O(12)	108.5(6)
S(4)-Cu(2)-N(4)	88.4(2)	C(1)-N(2)-C(2)	105.5(7)	O(11)-Cl(1)-O(13)	112.2(7)
S(5)-Cu(2)-N(2)	98.6(2)	Cu(1)-N(3)-C(4)	110.9(5)	O(11)-Cl(1)-O(14)	107.6(7)
S(5)-Cu(2)-N(4)	85.8(2)	Cu(1)-N(3)-C(7)	110.7(6)	O(12)-Cl(1)-O(13)	108.5(7)
S(6)-Cu(2)-N(2)	89.2(2)	Cu(1)-N(3)-C(10)	108.8(5)	O(12)-Cl(1)-O(14)	109.8(6)
S(6)-Cu(2)-N(4)	84.2(2)	C(4)-N(3)-C(7)	107.7(7)	O(13)-Cl(1)-O(14)	110.2(8)
N(2)-Cu(2)-N(4)	172.5(3)	C(4)-N(3)-C(10)	109.1(7)	O(21)-Cl(2)-O(22)	111.4(6)
Cu(1)-S(1)-C(5)	97.1(3)	C(7)-N(3)-C(10)	109.7(7)	O(21)-Cl(2)-O(23)	104.4(6)
Cu(1)-S(1)-C(6)	99.1(3)	Cu(2)-N(4)-C(13)	111.6(6)	O(21)-Cl(2)-O(24)	115.7(8)
C(5)-S(1)-C(6)	102.6(4)	Cu(2)-N(4)-C(16)	110.5(6)	O(21)-Cl(2)-O(25)	101.9(9)
Cu(1)-S(2)-C(8)	94.7(3)	Cu(2)-N(4)-C(19)	107.5(6)	O(22)-Cl(2)-O(23)	109.2(6)
Cu(1)-S(2)-C(9)	107.5(3)	C(13)-N(4)-C(16)	107.6(7)	O(22)-Cl(2)-O(24)	119.4(9)
C(8)-S(2)-C(9)	100.8(5)	C(13)-N(4)-C(19)	109.7(8)	O(22)-Cl(2)-O(25)	103.2(10)
Cu(1)-S(3)-C(11)	95.7(3)	C(16)-N(4)-C(19)	110.0(7)	O(23)-Cl(2)-O(24)	93.9(9)
Cu(1)-S(3)-C(12)	108.5(4)	N(1)-C(1)-N(2)	112.8(7)	O(23)-Cl(2)-O(25)	126.4(10)
C(11)-S(3)-C(12)	102.5(5)	N(2)-C(2)-N(3)	108.8(7)	O(24)-Cl(2)-O(25)	32.5(11)

a) The angles around Cl(3) are omitted because of serious disorder.

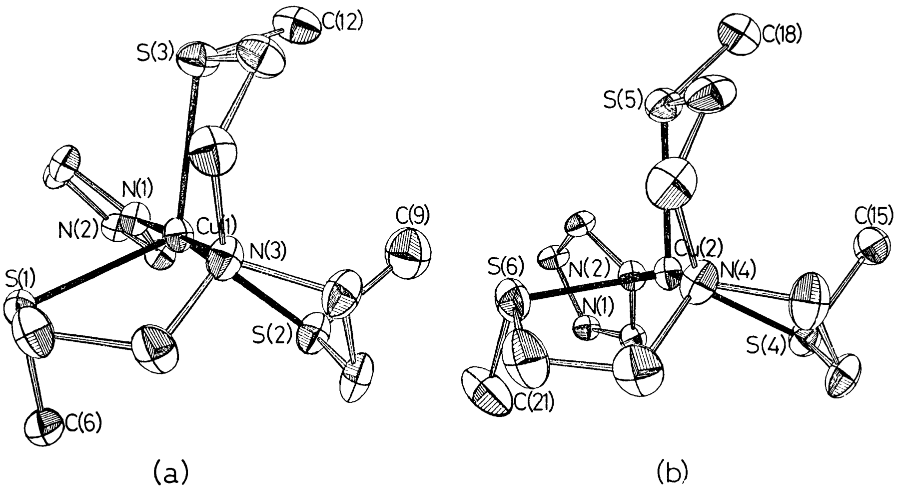

Fig. 2. Coordination geometries around the Cu(1) (a) and the Cu(2) (b) of $(Cu_2(NS_3\text{-}Me)_2im]^{3+}$.

in those angles from 180° is due to the displacement of the Cu atom from the basal plane toward the fifth ligand. In the present complex, the S(4)–Cu(2)–S(6) and the N(2)–Cu(2)–N(4) angles are 145.10(10) and 172.5(3)°, respectively. In general, the apical bonds are longer than the basal ones in square pyramidal complexes.[25] The S(5)–Cu(2) bond distance (2.500 (3) Å) is apparently longer than the S(4)–Cu(2) (2.345 (3) Å) and the S(6)–Cu(2) (2.392(3) Å). Thus the coordination geometry around the Cu(2) atom can be best described as an intermediate between a trigonal bipyramid and a square pyramid.

In general, tripod ligands tend to enforce a trigonal bipyramidal structure, *i.e.*, in the tren complexes, the range of the trigonal angles are from 105 to 140°.[10–13] The larger variation in the trigonal angles of the present complex may be due to the packing effects.

All of the bond distances and angles of the NS_3–Me ligands are within the range observed for $[Cu(NS_3\text{-}Me)Br]ClO_4$,[22] and $[Co(NS_3\text{-}Bu)Br]PF_6$.[26] All the five-membered chelate rings adopt gauche conformation with the exception of the $\overline{Cu(2)\text{-}N(3)\text{-}C(19)\text{-}S(6)}$ chelate ring which assumes envelop conformation. The torsion angles about C–C bonds of the chelate rings in the gauche conformation are in the range of 50.8—58.9°, while that in the envelop conformation is 35.2°.

The bond distances and angles of the imidazolate ring are in agreement with those previously reported.[3,4,6] The five atoms constituting the imidazolate ring lie within 0.009 Å of the best plane through them. The Cu(1) atom is 0.039 Å out of this plane and the Cu(2) atom deviates 0.603 Å from the plane on the opposite side, which is considerably larger than those previously reported.[3,4,27] Thus the Cu(2)–N(2) bond is bent out of the imidazolate plane (Fig. 1b). The angle of this bending is *ca.* 17°.

The Cu–N(imidazolate) bond distances are 1.968 (7) and 1.961(7) Å, which are quite normal.

Magnetism. Di- and tetra-nuclear copper(II) complexes bridged by various imidazolate groups show antiferromagnetic exchange interactions with coupling constants ($-J$) ranging from *ca.* 0—90 cm^{-1}.[1,2,8] The magnitude of antiferromagnetic exchange interaction is a reflection of the interaction of the orbitals of the bridging ligand with copper orbitals in which the unpaired electrons reside; the extent of the overlap between the copper d orbitals and the appropriate orbitals of the bridging ligand, and the energy difference between those orbitals are two important factors which determine the J value.[2,8,28]

It has been suggested that a π-exchange mechanism is not important in the imidazolate-bridged copper(II) complexes.[2,4,8] Haddad and Hendrickson[2] demonstrated that, in a series of $[Cu_2(tren)_2Y]^{3+}$, (Y=benzimidazolate, imidazolate, or 2-methylimidazolate), the difference in antiferromagnetic exchange interactions mediated by a variety of the bridging imidazolates are related to the angle α (in the present complex, α is defined by the Cu(1)–N(1)–C(1) and Cu(2)–N(2)–C(1) angles). Increasing the angles α improves the overlap between the metal d orbitals and the σ orbitals of the bridging imidazolate, leading to an increase in $|J|$.

In addition, Dewan and Lippard[27] suggested that the angle θ between two Cu–N(imidazolate) vectors is also important in determining $|J|$. This angle can be also considered to be a measure of the extent of the overlap between the d orbitals and the σ molecular orbitals of the bridging imidazolate.

In the present complex, the values of α are 127.0(6) and 132.1(5)°, and that of θ is 145°. These values suggest that an overlap between the d orbitals and the σ molecular orbitals of the bridging imidazolate is not larger than those in $[Cu_2(tmdt)_2im(ClO_4)_2]ClO_4$[3] ($\alpha$=129°, θ=143°, $-J$=25.8 cm^{-1}) (Table 3). Furthermore, the Cu(2)–N(2) bond significantly bends out of the imidazolate plane (*ca.* 17°). Thus, the effect of the overlap of the Cu–N bonds in a geometrical sense could not explain such a large $|J|$ value (63 cm^{-1}) of the present complex.

Kolks *et al.*[8] pointed out that the magnitude of the coupling constant is also proportional to the pK_a of imidazolium group. This was interpreted in terms of the energy change of the σ molecular orbitals of the bridging imidazolate groups. The higher the pK_a of the imidazolium is, the higher the energies of the σ

TABLE 3. COMPARISON OF THE COPPER-IMIDAZOLATE GEOMETRY AND COUPLING CONSTANT

Complex[a)]	α/°	θ/°	$-J$/cm^{-1}	Reference
$[Cu_2(bpim)(NO_3)_2(ClO_4)(OH_2)]\cdot H_2O$	143, 142	170	81.3	27
$[Cu_2(NS_3\text{-}Me)_2im](ClO_4)_3$	127, 132	145	63	This work
$[Cu_2(pmdt)_2(2\text{-}Meim)]ClO_4)_3$	121, 121		38	8
$[Cu_2(tmdt)_2im(ClO_4)_2]ClO_4$	129, 129	143	25.8	3
$[Cu_2(L)im](ClO_4)_3$	129, 134	146[b)]	21.0	5
$Na[Cu_2(gly\text{-}glyO)_2im]\cdot 6H_2O$	124, 125	135	19	4
$[Cu_2(pmdt)_2(Bzim)](ClO_4)_3\cdot H_2O$	123, 128		17	8

a) Abbreviations for the ligands are bpim=4,5-bis[2-(2-pyridyl)ethyliminomethyl]imidazolate; pmdt=*N,N,N′,N″,*-*N″*-tetramethyldiethylenetriamine; tmdt=*N,N,N′,N′*-tetramethyldiethylenetriamine; L=30-membered macrocyclic Schiff base in Ref. 5,6; gly-glyO=glycylglycinate. b) The value given in Table 2 in Ref. 5 is 163°, which is incorrect.

molecular orbitals of the imidazolate become. This results in a decrease in energy separation between the d orbitals and the σ molecular orbitals, and an increase in $|J|$. One of the other possibilities of the large $|J|$ value of the present complex is the lowering of the d orbital energies compared with those of $[Cu_2(tmdt)_2im(ClO_4)_2]$ ClO_4.[3)] Mikuriya *et al.*[15,16)] demonstrated that, in a series of the alkoxo-bridged dinuclear copper (II) complexes, the replacement of the nitrogen donor atom by the sulfur donor atom causes an increase of $|J|$. Although direct evidence is lacking, it seems that the sulfur donor atom has a larger effect which lowers the d orbital energy than the nitrogen donor atom.

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