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Preparation and Crystal Structures of Binuclear Copper(II) Complexes of *N,N′,N″,N‴*-Tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane Containing Azide, Cyanate, or Thiocyanate Ion

Masahiro MIKURIYA,* Sigeo KIDA,*,† and Ichiro MURASE††
Coordination Chemistry Laboratories, Institute for Molecular Science, Myodaiji, Okazaki 444
†Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka 812
††Laboratory of Chemistry, College of General Education, Kyushu University 01, Ropponmatsu, Chuo-ku, Fukuoka 810
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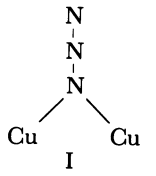
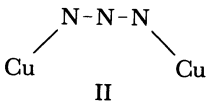
Three binuclear copper(II) complexes of *N,N′,N″,N‴*-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (taec), $[Cu_2(taec)N_3](ClO_4)_3$ (**1**), $[Cu_2(taec)(NCO)](ClO_4)_3$ (**2**), and $[Cu_2(taec)(NCS)_2](ClO_4)_2 \cdot H_2O$ (**3**), were prepared and characterized. The crystal structures of these complexes were determined by single-crystal X-ray analysis. In all the complexes taec coordinates to each copper through two ring- and two pendant-nitrogen atoms. Complexes **1** and **2** adopt similar structures, where N_3^- and NCO^- are incorporated into the cavity of taec as a bridging group (end-on fashion). The structure of **3** is substantially different from those of **1** and **2** in that each copper is independently coordinated by NCS^--nitrogen. The spectral and magnetic properties were discussed in relation to the molecular structures.

μ-Azidodicopper(II) complexes have been extensively studied in the last half decade, because of the interest in the fields of molecular magnetism and bioinorganic chemistry.[1-4] It is well-known that azide ion can bridge two copper(II) ions either in end-on fashion I or in end-to-end fashion II.[1] It has been established



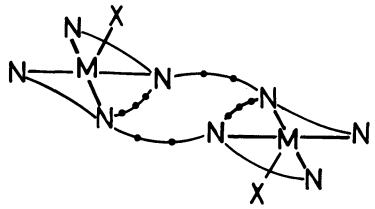
I



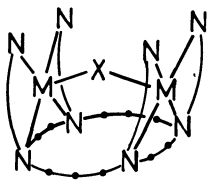
II

that the end-on bridge of azide ion favors the triplet ground state whereas the end-to-end bridge brings about a strong antiferromagnetic interaction.[2] The latter type of μ-azido complexes is of interest as models for azide derivatives of the active site of methemocyanine and met-tyrosinase in which a pair of copper(II) ions are strongly coupled antiferromagnetically.[3]

Recently we have prepared a new octadentate ligand, *N,N′,N″,N‴*-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (abbreviated as taec) and its metal complexes.[5-7] Interestingly, all the complexes obtained are 2 : 1 (metal : taec) binuclear complexes. So far, two types of coordination modes are known for the taec ligand: one is the trans III form[8] concerning the cyclam ring (chair form, Fig. 1 (A)) as found for $[Cu_2(taec)](ClO_4)_4$[5] and the other is the trans I form[8] (boat form, Fig. 1 (B)) as found for $[Cu_2(taec)Br](ClO_4)_3$.[6] In the latter case, single bromide ion is incorporated into the cavity of the ligand and coordinated to both copper ions. Using this unique property, we have prepared μ-azidocopper(II) complex of taec, $[Cu_2(taec)N_3](ClO_4)_3$, and determined the X-ray crystal structure in order to examine the bridging mode of the azide ion in the cavity of taec. We have also prepared copper(II) complexes with the isoelectronic cyanate and thiocyanate ions, $[Cu_2(taec)(NCO)](ClO_4)_3$ and $[Cu_2(taec)(NCS)_2](ClO_4)_2 \cdot H_2O$. Here, we report the preparation, the crystal structures, and the magnetic and spectral properties of these binuclear copper(II) complexes.



(A)



(B)

Fig. 1. Coordination mode of taec.

Experimental

Preparation. The preparative method for taec was already reported in the preceding papers.[5,6]

$[Cu_2(taec)N_3](ClO_4)_3$: To an aqueous solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (185 mg) and taec (93 mg) was added NaN_3 (16 mg), and the mixture was heated at 80 °C for 20 min. The resulting blue solution was filtered. When the filtrate was allowed to stand overnight, blue needles were separated. The crystals were collected and desiccated over P_2O_5. Found: C, 25.64; H, 5.31; N, 18.19%. Calcd for $C_{18}H_{44}Cl_3Cu_2N_{11}O_{12}$: C, 25.74; H, 5.28; N, 18.34%.

$[Cu_2(taec)(NCO)](ClO_4)_3$: The complex was obtained as blue needles in the same way as that of $[Cu_2(taec)N_3](ClO_4)_3$

Table 1. Crystal Data and Data Collection Details[a)]

Complex	$[Cu_2(taec)N_3](ClO_4)_3$	$[Cu_2(taec)(NCO)](ClO_4)_3$	$[Cu_2(taec)(NCS)_2](ClO_4)_2\cdot H_2O$
Formula	$C_{18}H_{44}Cl_3Cu_2N_{11}O_{12}$	$C_{19}H_{44}Cl_3Cu_2N_9O_{13}$	$C_{20}H_{46}Cl_2Cu_2N_{10}O_9S_2$
F. W.	840.06	840.06	832.76
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$Pmn2_1$	$Pmn2_1$	$Pnnm$
a/Å	8.875(4)	8.885(2)	10.926(3)
b/Å	8.076(1)	8.047(1)	16.005(3)
c/Å	21.756(9)	21.847(4)	9.923(2)
V/Å^3	1559.3(9)	1562.0(5)	1735.2(7)
Z	2	2	2
D_c/g cm^{-3}	1.79	1.79	1.56
D_m/g cm^{-3}	1.79	1.78	1.60
$F(000)$	868	868	864
μ(Mo $K\alpha$)/cm^{-1}	17.0	17.0	15.5
Crystal dimensions (mm)	0.35×0.35×0.35	0.20×0.30×0.41	0.28×0.28×0.32
2θ range (°)	1.5—68.0	1.5—68.0	2.0—66.0
Total no. of observed reflections	3613	3622	3696
No. of unique reflections with $\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)$	2785	2438	2000
Final no. of variables	361	361	203
Final residual R	0.054	0.062	0.066
Final residual R'	0.082	0.089	0.096
Goodness of fit[b)]	0.31	0.34	0.36
Largest peak in final diff Fourier (e/Å^3)	1.07	1.19	1.39

a) Common data: graphite-monochromated Mo $K\alpha$ radiation (λ=0.71073 Å), scan type θ—2θ, scan speed 3 °min^{-1}, scan width $(1.4+0.5\tan\theta)$°. b) GOF=$[\sum w(\lvert F_o\rvert-\lvert F_c\rvert)^2/(N_{observns}-N_{params})]^{1/2}$.

except for using potassium cyanate instead of sodium azide. Found: C, 26.72; H, 5.32; N, 14.83%. Calcd for $C_{19}H_{44}Cl_3Cu_2N_9O_{13}$: C, 27.17; H, 5.28; N, 15.01%.

$[Cu_2(taec)(NCS)_2](ClO_4)_2\cdot H_2O$: The complex was obtained as blue needles in the same way as that of $[Cu_2(taec)N_3](ClO_4)_3$ except for using potassium thiocyanate instead of sodium azide. Found:, C, 29.43; H, 5.75; N, 17.37%. Calcd for $C_{20}H_{46}Cl_2Cu_2N_{10}O_9S_2$: C, 28.85; H, 5.57; N, 16.82%.

Measurements. Carbon, hydrogen, and nitrogen analyses were carried out at the Service Center of Elemental Analysis, Kyushu University. Electronic spectra were measured with a Shimadzu Multipurpose Spectrophotometer Model MSP-5000 at room temperature. Magnetic susceptibility was measured by the Faraday method over the temperature range 80—300 K. The apparatus was calibrated by the use of $[Ni(H_2NCH_2CH_2NH_2)_3]S_2O_3$. The susceptibilities were corrected for the diamagnetism of the constituent atoms by the use of Pascal's constants.[9)] Effective magnetic moments were calculated from the equation, $\mu_{eff}=2.828\sqrt{(\chi_A-N\alpha)T}$, where χ_A is the atomic magnetic susceptibility and Nα is the temperature-independent paramagnetism.

X-Ray Crystal Structure Analysis. A Rigaku AFC-5 automated four-circle diffractometer was used for all measurements at 18 °C. Crystal data and details of the data collection are given in Table 1. Lattice constants were determined by least-squares refinement based on 40 reflections with $20<2\theta<30°$. The intensity data were corrected for Lorentz-polarization effects, but not for absorption. The structures were solved by the direct methods. Refinements were carried out by the block-diagonal least-squares methods. In the course of refinement it became apparent that the carbon atom, C(3), is subjected to disorder in $[Cu_2(taec)X](ClO_4)_3$ (X=N_3 and NCO). The carbon atom was divided into 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. The final discrepancy factors were $R=\sum||F_o|-|F_c||/\sum|F_o|=0.054$, $R'=[\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}=0.082$ for $[Cu_2(taec)N_3](ClO_4)_3$, $R=0.062$, $R'=0.089$ for $[Cu_2(taec)(NCO)](ClO_4)_3$, and $R=0.066$, $R'=0.096$ for $[Cu_2(taec)(NCS)_2](ClO_4)_2\cdot H_2O$. The weighting schemes were $w=(6.1+|F_o|+0.010|F_o|^2)^{-1}$ for $[Cu_2(taec)N_3](ClO_4)_3$, $(7.6+|F_o|+0.010|F_o|^2)^{-1}$ for $[Cu_2(taec)(NCO)](ClO_4)_3$, and $(8.0+|F_o|+0.008|F_o|^2)^{-1}$ for $[Cu_2(taec)(NCS)_2](ClO_4)_2\cdot H_2O$.

The atomic scattering factors for Cu, Cl, S, O, N, C, and H and the anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$, for Cu, Cl, S, O, N, and C were taken from Ref. 10. All the calculations were carried out on the FACOM M-200 computer at the Computer Center of Kyushu University using a local version of the MULTAN 78,[11)] UNICS-III,[12)] and ORTEP[13)] programs. The final positional and thermal parameters with their estimated standard deviations are given in Table 2. The coordinates and isotropic temperature factors of hydrogen atoms, the anisotropic thermal parameters of the non-hydrogen atoms, the remaining bond distances and angles, and the F_o—F_c tables have been deposited as a Document No. 8731 at the Office of the Editor.

Results and Discussion

Crystal Structures. $[Cu_2(taec)N_3](ClO_4)_3$: A perspective drawing of the complex cation of $[Cu_2(taec)N_3](ClO_4)_3$ and the numbering system are illustrated in Fig. 2. The complex cation has a mirror plane containing Cu(1), Cu(2), N(5), N(6), and N(7). The cyclam ring assumes the trans I form[8)] and the coordination mode of taec is similar to that of $[Cu_2(taec)Br](ClO_4)_3$.[6)] The taec ligand forms two 5-5-5 fused che-

Table 2. 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$^{2a)}$
(1) $[Cu_2(taec)N_3](ClO_4)_3$				
Cu(1)	0	6434(1)	3330(1)	1.7
Cu(2)	0	6417(1)	5312(1)	1.5
Cl(1)	0	8901(2)	7171(1)	2.4
Cl(2)	0	8929(3)	1494(1)	2.5
Cl(3)	0	10752(2)	−673(2)	2.8
O(1)	0	10079(9)	6646(4)	3.9
O(2)	0	7295(12)	6901(5)	6.7
O(3)	1301(9)	9159(11)	7552(4)	5.8
O(4)	0	10040(15)	1949(6)	6.4
O(5)	0	7217(10)	1722(4)	5.7
O(6)	−1321(8)	9137(11)	1161(5)	6.2
O(7)	0	9058(16)	−638(14)	11.2
O(8)	0	11438(24)	−117(6)	15.9
O(9)	−1214(24)	11244(25)	−893(13)	29.5
N(1)	1614(5)	4539(5)	3234(2)	1.9
N(2)	1574(5)	4598(6)	5442(2)	2.2
N(3)	1680(7)	7990(6)	3029(3)	2.7
N(4)	1684(5)	7948(6)	5579(2)	2.2
N(5)	0	7229(6)	4316(5)	2.1
N(6)	0	8708(7)	4344(6)	2.5
N(7)	0	10133(10)	4413(6)	4.8
C(1)	790(8)	3495(9)	2798(4)	3.7
C(2)	2544(8)	4200(9)	3759(3)	3.0
C(3)	1681(12)	3742(12)	4278(8)	1.9
C(3)′	2639(10)	4386(12)	4313(9)	2.1
C(4)	2151(7)	3452(7)	4907(3)	2.4
C(5)	767(9)	3073(9)	5662(5)	4.1
C(6)	2418(7)	5274(9)	2689(3)	2.7
C(7)	2777(8)	6999(9)	2708(5)	4.6
C(8)	3035(7)	5344(9)	5680(3)	2.9
C(9)	2835(11)	6922(13)	5923(5)	5.2
(2) $[Cu_2(taec)(NCO)](ClO_4)_3$				
Cu(1)	0	6463(1)	3327(1)	1.8
Cu(2)	0	6433(1)	5314(1)	1.6
Cl(1)	0	8886(3)	7172(1)	2.3
Cl(2)	0	8934(3)	1485(1)	2.6
Cl(3)	0	10734(3)	−664(3)	2.8
O(1)	0	10078(13)	6679(4)	4.3
O(2)	0	7281(14)	6881(6)	6.9
O(3)	1256(12)	9167(13)	7560(5)	6.4
O(4)	0	10082(16)	1978(9)	6.9
O(5)	0	7233(14)	1706(5)	6.5
O(6)	−1335(10)	9073(13)	1156(6)	6.4
O(7)	0	9055(20)	−597(18)	13.8
O(8)	0	11454(31)	−102(8)	15.1
O(9)	−1107(27)	11183(34)	−934(15)	28.9
O(10)	0	10208(11)	4429(9)	5.8
N(1)	1589(6)	4579(7)	3216(3)	1.7
N(2)	1607(8)	4579(8)	5421(3)	2.5
N(3)	1648(7)	8026(9)	3034(3)	2.6
N(4)	1728(7)	7950(8)	5612(4)	2.7
N(5)	0	7290(10)	4329(8)	2.6
C(1)	836(10)	3521(11)	2780(4)	3.1
C(2)	2538(9)	4229(11)	3761(4)	2.7
C(3)	1670(16)	3751(15)	4276(10)	1.8
C(3)′	2623(14)	4418(16)	4387(8)	1.9
C(4)	2139(9)	3480(9)	4909(4)	2.4
C(5)	714(10)	3079(10)	5655(5)	3.0
C(6)	2393(10)	5246(11)	2687(4)	3.0
C(7)	2834(11)	6968(13)	2762(6)	4.5
C(8)	3020(9)	5356(11)	5697(5)	3.3
C(9)	2796(15)	6932(15)	5989(7)	5.1
C(10)	0	8748(12)	4357(12)	2.8
(3) $[Cu_2(taec)(NCS)_2](ClO_4)_2 \cdot H_2O$				
Cu	2190(1)	5887(1)	0	2.3
Cl	2693(4)	8757(2)	0	7.5
S	3914(2)	3012(1)	0	4.4
O(1)	3296(12)	8122(8)	0	12.0
O(2)	3485(19)	9420(9)	0	14.9
O(3)	1324(28)	9023(19)	0	11.8
O(3)′	2267(24)	8719(14)	−1289(21)	16.4
OW	0	0	2025(11)	8.1
N(1)	892(3)	6031(2)	1541(4)	2.4
N(2)	3412(4)	6201(3)	1462(5)	3.9
N(3)	2803(6)	4584(4)	0	4.1
C(1)	−180(4)	5461(3)	1735(5)	2.8
C(2)	411(5)	6899(3)	1303(6)	3.1
C(3)	−291(7)	7021(4)	0	3.2
C(4)	1621(5)	6021(3)	2819(5)	3.1
C(5)	2790(5)	6497(4)	2678(6)	3.7
C(6)	3302(7)	3933(4)	0	3.1

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

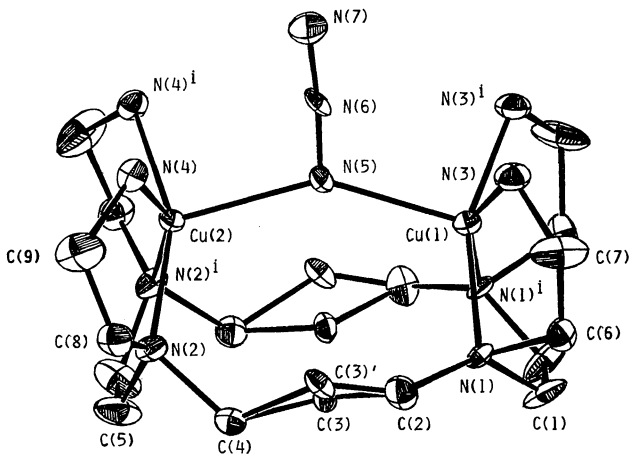


Fig. 2. ORTEP diagram of $[Cu_2(taec)N_3]^{3+}$. Superscript i refers to the equivalent position $(-x, y, z)$.

late rings with two copper ions. The coordination geometry of each copper ion is an elongated square pyramid. The basal plane is formed by two nitrogens of the cyclam ring and two nitrogens of the pendant amino groups. The basal plane is perfectly planar as required from the symmetry (the mirror plane) of the molecule and the copper ion is displaced by 0.45 Å from the plane toward the azide ion. The azide ion lies on the mirror plane and bridges the two copper ions at the apical positions with Cu-N distances of 2.240(12) and 2.263(12) Å. This is the first example of an end-on bridging of azide ion at axial sites of copper(II) ions. The Cu(1)-Cu(2) distance and Cu(1)-N(5)-Cu(2) angle are 4.312(1) Å and 146.5(3)°, respectively.

Of the three perchlorate ions, two are hydrogen bonded to the pendant amino groups (O(1)⋯N(4) 3.253(9), O(2)⋯N(4) 3.283(11), O(4)⋯N(3) 3.238(13),

Table 3. Selected Interatomic Distances (l/Å) and Angles (ϕ/°) with Their Estimated Standard Deviations in Parentheses

(1) $[Cu_2(taec)N_3](ClO_4)_3$[a]			
Cu(1)-N(1)	2.107(5)	Cu(2)-N(2)	2.047(5)
Cu(1)-N(3)	2.057(6)	Cu(2)-N(4)	2.025(5)
Cu(1)-N(5)	2.240(12)	Cu(2)-N(5)	2.263(12)
Cu(1)····Cu(2)	4.312(1)		
N(5)-N(6)	1.196(8)	N(6)-N(7)	1.160(10)
N(1)-Cu(1)-N(1)^i	85.7(2)	N(2)-Cu(2)-N(2)^i	86.0(2)
N(1)-Cu(1)-N(3)	85.4(2)	N(2)-Cu(2)-N(4)	84.0(2)
N(3)-Cu(1)-N(3)^i	92.9(2)	N(4)-Cu(2)-N(4)^i	95.1(2)
N(1)-Cu(1)-N(5)	107.6(2)	N(2)-Cu(2)-N(5)	109.9(2)
N(3)-Cu(1)-N(5)	97.5(2)	N(4)-Cu(2)-N(5)	95.6(2)
Cu(1)-N(5)-Cu(2)	146.5(3)	Cu(2)-N(5)-N(6)	104.0(9)
Cu(1)-N(5)-N(6)	109.5(9)	N(5)-N(6)-N(7)	175.4(15)
(2) $[Cu_2(taec)(NCO)](ClO_4)_3$[b]			
Cu(1)-N(1)	2.085(5)	Cu(2)-N(2)	2.078(7)
Cu(1)-N(3)	2.034(7)	Cu(2)-N(4)	2.066(7)
Cu(1)-N(5)	2.287(17)	Cu(2)-N(5)	2.260(16)
Cu(1)····Cu(2)	4.340(2)		
N(5)-C(10)	1.175(12)	C(10)-O(10)	1.186(14)
N(1)-Cu(1)-N(1)^i	85.2(2)	N(2)-Cu(2)-N(2)^i	86.8(3)
N(1)-Cu(1)-N(3)	85.7(2)	N(2)-Cu(2)-N(4)	83.0(3)
N(3)-Cu(1)-N(3)^i	92.1(3)	N(4)-Cu(2)-N(4)^i	96.0(3)
N(1)-Cu(1)-N(5)	108.8(2)	N(2)-Cu(2)-N(5)	109.0(2)
N(3)-Cu(1)-N(5)	97.0(3)	N(4)-Cu(2)-N(5)	96.9(3)
Cu(1)-N(5)-Cu(2)	145.3(4)	Cu(2)-N(5)-C(10)	104.7(16)
Cu(1)-N(5)-C(10)	109.9(2)	N(5)-C(10)-O(10)	175.4(27)
(3) $[Cu_2(taec)(NCS)_2](ClO_4)_2\cdot H_2O$[c]			
Cu-N(1)	2.098(4)	Cu-N(3)	2.191(7)
Cu-N(2)	2.034(5)	Cu····Cu^{ii}	5.565(1)
N(3)-C(6)	1.176(10)	S-C(6)	1.618(7)
N(1)-Cu-N(2)	84.1(2)	N(2)-Cu-N(3)	92.0(2)
N(1)-Cu-N(1)^i	93.6(2)	Cu-N(3)-C(6)	170.1(6)
N(2)-Cu-N(2)^i	91.0(2)	N(3)-C(6)-S	176.7(7)
N(1)-Cu-N(3)	108.1(2)		

a) Superscript i refers to the equivalent position ($-x$, y, z). b) Superscript i refers to the equivalent position ($-x$, y, z). c) Superscript i and ii refer to the equivalent positions (x, y, $-z$) and ($-x$, $1-y$, z), respectively.

O(5)··· N(3) 3.271(11) Å), and one (designated as Cl(3), O(7), O(8), O(9), and O(9)($-x$, y, z)) is not bound to any special atoms.

$[Cu_2(taec)(NCO)](ClO_4)_3$: The crystal of $[Cu_2(taec)(NCO)](ClO_4)_3$ is isomorphous to that of $[Cu_2(taec)N_3](ClO_4)_3$. The complex cation, $[Cu_2(taec)(NCO)]^{3+}$, has a mirror plane containing Cu(1), Cu(2), N(5), C(10), and O(10) (Fig. 3). The nitrogen atom of NCO^- bridges the two copper ions. The Cu(1)-Cu(2) distance and Cu(1)-N(5)-Cu(2) angle are 4.340(2) Å and 145.3(4)°, respectively. This bridging mode of NCO^- was found in $[Cu_2(C_{17}H_{27}N_4O)(CH_3COO)(NCO)][PF_6]$ recently.[4]

$[Cu_2(taec)(NCS)_2](ClO_4)_2\cdot H_2O$: A perspective drawing of the complex cation, $[Cu_2(taec)(NCS)_2]^{2+}$, is shown in Fig. 4. The cation has the center of symmetry and a mirror plane formed by C(3), Cu, N(3), C(6), S, C(3)^{ii}, Cu^{ii}, N(3)^{ii}, C(6)^{ii}, and S^{ii}. Contrary to $[Cu_2(taec)X](ClO_4)_3$ (X=N_3 and NCO), the cyclam ring assumes the trans III form and the coordination mode of taec is the same as that of $[Cu_2(taec)](ClO_4)_4$[5] in which axial coordination sites do not face to each other but face rather opposite directions and are independently coordinated with NCS^-. The coordination geometry of each copper is a square pyramid with a thiocyanate nitrogen at the top (Cu-N(3) 2.191(7) Å).

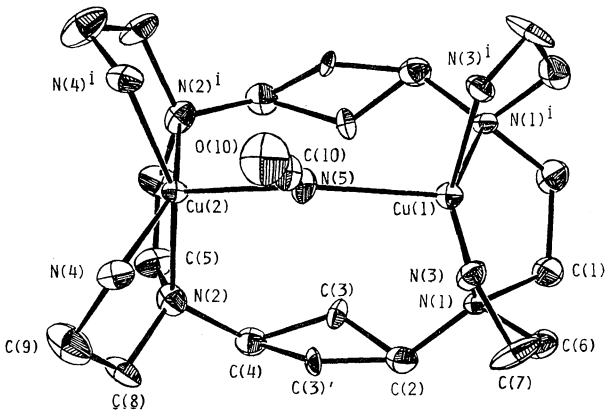


Fig. 3. ORTEP diagram of $[Cu_2(taec)(NCO)]^{3+}$. Superscript i refers to the equivalent position ($-x$, y, z).

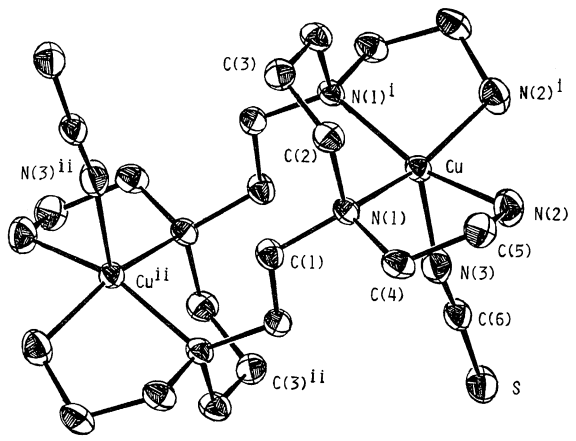


Fig. 4. ORTEP diagram of $[Cu_2(taec)(NCS)_2]^{2+}$. Superscripts i and ii refer to the equivalent positions (x, y, $-z$) and ($-x$, $1-y$, z), respectively.

The basal plane formed by two nitrogens of the cyclam ring and two terminal nitrogens is perfectly planar as required from the symmetry (C_{2h}) of the molecule, and the copper atom deviates by 0.37 Å from the basal plane toward thiocyanate ion.

Each water molecule is located in a vicinity of the pendant amino group of taec forming hydrogen bonds with the amino nitrogen and a perchlorate ion (N(2)$\cdots$OW($1/2+x$, $1/2-y$, $1/2-z$) 2.993(7) Å, O(3)$\cdots$OW(x, $1+y$, z) 2.929(23) Å).

Spectral and Magnetic Properties and Crystal Structures. Nujol mull spectra of $[Cu_2(taec)N_3](ClO_4)_3$, $[Cu_2(taec)(NCO)](ClO_4)_3$, and $[Cu_2(taec)(NCS)_2](ClO_4)_2\cdot H_2O$ each show a d-d band at 15.7, 15.6, and 17.1×10^3 cm^{-1}, respectively. The difference of the wavenumber in these complexes must be mainly due to the degree of the deviation of copper ion from the basal plane, i.e., 0.45, 0.46, and 0.37 Å, respectively. The bands of the azido and cyanato complexes are blue-shifted in aqueous solution relative to those in nujol mull, i.e., 15.7→16.1 (ε=217) and 15.6→15.8×10^3 cm^{-1} (ε=203), indicating the hydrolysis of coordinated anions in aqueous solution in more or less degree (the thiocyanato complex is sparingly soluble in water).[14]

The magnetic moments per copper ion of $[Cu_2(taec)N_3](ClO_4)_3$, $[Cu_2(taec)(NCO)](ClO_4)_3$, and $[Cu_2(taec)(NCS)_2](ClO_4)_2\cdot H_2O$ are 1.82, 1.77, and 1.75 B.M., respectively, at room temperature. All the complexes obey the Curie-Weiss law in the temperature range 80—300 K with the Weiss constants, −1, 0, and −5 K for the azido, cyanato, and thiocyanato complexes, respectively. The very small values indicate that there is no significant magnetic interaction between the copper ions. The result is quite understandable in view of that in these complexes an unpaired electron of a copper(II) ion is localized in the $d_{x^2-y^2}$ orbital of the basal plane of the CuN_5 square-based pyramid so that no overlapping of the magnetic orbitals is feasible.

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14) $[Cu_2(taec)](ClO_4)_4$ shows a d-d band at $17.7\times10^3 cm^{-1}$ in aqueous solution.