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X-Ray Structure and Magnetism of μ-Bromo-μ-pyrazolatobis(diethylenetriaminecopper(II)) Perchlorate Monohydrate

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Synopsis. The structure of the title compound has been determined by an X-ray method. The dinuclear complex is composed of two Cu(dien) units which are bridged by pyrazolate and Br$^-$ anions. The geometry around each copper(II) may be described as a square pyramid. The antiferromagnetic interaction within the dinuclear complex has been observed ($J=-14\,\mathrm{cm}^{-1}$, $H=-2JS_1\cdot S_2$).

A number of studies have been conducted on magneto-structural correlation of dinuclear copper(II) complexes bridged by imidazolate anion (im), in view of their importance as structural models for the active site of bovine erythrocyte superoxide dismutase.[1] On the other hand, there has been continuing interest in the magnetic properties of dinuclear copper(II) complexes bridged by pyrazolate anion (pz) which is similar to im.[2–4] Few such studies, however, have been appeared. We report here on the structure and magnetism of $[\mathrm{Cu_2(dien)_2(pz)(Br)}](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$ (**1**) (dien=diethylenetriamine).

Experimental

Preparation of $[\mathrm{Cu_2(dien)_2(pz)(Br)}](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$ (1). An aqueous solution of $\mathrm{AgClO_4}$ (0.38 g, 1.8 mmol) was added to an aqueous solution of $[\mathrm{Cu_2(dien)_2(pz)}]\mathrm{Br_3}\cdot\mathrm{H_2O}$[4] (0.60 g, 0.92 mmol), and the mixture was stirred for 15 min. After removing precipitated AgBr, the filtrate was evaporated to dryness. The violet-blue solids obtained were recrystallized from ethanol containing a small quantity of water. Found: C, 18.86; H, 4.38; N, 16.03%. Calcd for $\mathrm{C_{11}H_{29}O_8N_8Cl_2Cu_2Br}\cdot\mathrm{H_2O}$: C, 18.94; H, 4.49; N, 16.07%.

Crystal Data. $\mathrm{C_{11}H_{31}O_9N_8Cl_2Cu_2Br}$, $F.W.=697.4$, triclinic, space group $P\bar{1}$, $a=23.294(10)$ Å, $b=14.084(5)$ Å, $c=7.750(2)$ Å, $\alpha=92.50(2)°$, $\beta=92.07(2)°$, $\gamma=90.98(2)°$, $Z=4$, $D_m=1.80\ \mathrm{g\,cm^{-3}}$, $D_c=1.82$, $\mu(\mathrm{Mo}\,K\alpha)=36.8\ \mathrm{cm^{-1}}$, $\lambda(\mathrm{Mo}\,K\alpha)=0.71069$ Å, $U=2538.1(15)$ Å^3.

X-Ray Data Collection. The crystal chosen for data collection and lattice constants determination had dimensions of $0.12\times0.30\times0.38\ \mathrm{mm}^3$. It was mounted in an arbitrary orientation on a Philips PW1100 automated diffractometer. The PW1100 program obtained 23 centered reflections and an orientation matrix, and then identified the triclinic cell. The space group $P\bar{1}$ was assumed throughout the structure analysis and confirmed by the successful refinement of the structure. The unit cell dimensions with standard deviations were derived from a least-squares fit from the angular positions of 25 centered reflections. The intensity data ($4°\leqq2\theta\leqq50°$) were collected at room temperature by the use of graphite monochromated Mo $K\alpha$ radiation. The ω-scan method was employed. The scan range was $(1.0+0.3\tan\theta)°$ and the scan speed $0.05°\ \mathrm{s}^{-1}$; the background was counted for 10 s at each side of the scan range. During the data collection, intensities of 3 standard reflections were monitored every 4 h in order to check the orientation and stability of the crystal. The compound remained quite stable. A total of 3635 reflections $[F_o^2\geqq3\sigma(F_o^2)]$ were considered as observed. The intensities were corrected for Lorenz-polarization effects,[5] but not for absorption.

Structure Solution and Refinement. MULTAN 78[6] provided the positions of the copper and bromine atoms. Subsequent least-squares refinement followed by difference Fourier syntheses revealed the positions of all non-hydrogen atoms. The least-squares refinement with anisotropic temperature factors for the non-hydrogen atoms gave $R=0.068$ and $R'=(\sum w\Delta F^2/\sum wF_o^2)^{1/2}=0.092$. The hydrogen atoms were located on calculated positions (N–H, C–H=1.0 Å). In the final cycles of refinement, the hydrogen atoms, except for the water hydrogen atoms, were included with a common isotropic temperature factor $B=5.0$ Å^2, but their parameters were not refined. The function minimized was $\sum w(F_o-|F_c|)^2$, where $w=1/(\sigma^2(F_o)+0.005\,F_o^2)$ was used. All the parameter shifts were less than 0.5σ. The atomic scattering factors for Cu, Br, O, N, C, and H atoms were taken from Ref. 7, with corrections for anomalous scattering for the Cu and Br atoms. The final difference Fourier map was featureless and showed no peaks greater than 0.8 e Å^{-3}. Observed and calculated structure factors, thermal parameters, and hydrogen atom coordinates are preserved by the Chemical Society of Japan (Document No. 8763). Final atomic coordinates for non-hydrogen atoms are given in Table 1. The computer programs used in the calculations were a local version of the UNICS.[8] Figure 1 was drawn by the use of ORTEP.[9] Calculations were performed on a FACOM M 180II AD computer at Osaka City University.

Measurement. The Faraday method was applied for the measurement of magnetic susceptibility over the range from liquid helium temperature to room temperature.

Results and Discussion

Figure 1 gives a perspective view of the complex cation of **1**. There are two crystallographically independent complexes in a cell and their structures are similar to each other. Each complex is composed of two Cu(dien) units which are bridged by pyrazolate and bromine anions, forming a dimeric $[\mathrm{Cu_2(dien)_2(pz)(Br)}]^{2-}$. The complexes are described as an intermediate between a trigonal bipyramid and a square pyramid. From the trigonal bipyramidal view point, N(1)[N(9)], N(3)[N(11)], and Br(1)[Br(2)] atoms, and N(4)[N(12)], N(6)[N(14)], and Br(1)[Br(2)] atoms form the equitorial planes and, N(2)[N(10)] and N(7)[N(15)], and N(5)[N(13)] and N(8)[N(16)] atoms occupy the apical positions. In the square pyramidal approximation, Br(1) and Br(2) occupy the apical positions. N(1)[N(9)], N(2)[N(10)], N(3)[N(11)], and N(7)[N(15)] atoms, and N(4)[N(12)], N(5)[N(13)], N(6)[N(14)] and N(8)[N(16)] atoms form the basal planes. The intermediate coordination geometry has been characterized by the structural index parameter $\tau=(\beta-\alpha)/60$,[10] where α and β are the two largest metal ligand bond angles in the complex. Application of the formula to the present complex gives the τ values of 0.33, 0.31, 0.29, and 0.35, indicating that the complex lies closer

Table 1. Fractional Coordinates and Temperature Factors for **1**

Atom	x	y	z	U_{eq}[a)]	Atom	x	y	z	U_{eq}[a)]
Cu(1)	0.3342(1)	0.2690(1)	0.4010(2)	0.0345(6)	C(12)	−0.0057(8)	0.910(1)	0.297(3)	0.11(1)
Cu(2)	0.4922(1)	0.2293(1)	0.4651(2)	0.0333(6)	C(13)	−0.0608(7)	0.872(1)	0.194(3)	0.11(1)
Br(1)	0.4272(1)	0.3421(1)	0.2553(2)	0.0528(6)	C(14)	−0.0959(7)	0.775(1)	−0.049(3)	0.079(8)
N(1)	0.3213(5)	0.3642(9)	0.602(1)	0.049(5)	C(15)	−0.0696(8)	0.717(2)	−0.189(3)	0.093(9)
N(2)	0.2843(4)	0.3576(8)	0.264(1)	0.036(4)	C(16)	0.191(1)	0.707(1)	−0.495(3)	0.10(1)
N(3)	0.3065(5)	0.1690(9)	0.219(2)	0.059(5)	C(17)	0.2362(7)	0.774(1)	−0.440(2)	0.072(7)
N(4)	0.4951(4)	0.1137(8)	0.302(2)	0.045(4)	C(18)	0.2592(7)	0.889(1)	−0.212(2)	0.069(7)
N(5)	0.5618(4)	0.2727(7)	0.338(1)	0.037(4)	C(19)	0.2368(8)	0.921(1)	−0.041(3)	0.090(9)
N(6)	0.5225(4)	0.3254(9)	0.648(1)	0.044(4)	C(20)	0.0832(6)	0.594(1)	0.202(2)	0.056(6)
N(7)	0.3731(4)	0.1793(7)	0.551(1)	0.034(4)	C(21)	0.1292(7)	0.538(1)	0.182(2)	0.061(7)
N(8)	0.4299(4)	0.1788(7)	0.598(1)	0.035(4)	C(22)	0.1631(6)	0.584(1)	0.065(2)	0.062(7)
C(1)	0.2979(7)	0.452(1)	0.525(2)	0.060(6)	Cl(1)	0.3811(2)	0.9174(3)	0.2736(5)	0.045(1)
C(2)	0.2548(6)	0.423(1)	0.382(2)	0.054(6)	O(11)	0.3314(5)	0.918(1)	0.358(2)	0.126(8)
C(3)	0.2452(7)	0.299(1)	0.146(2)	0.058(6)	O(12)	0.3866(5)	0.9959(8)	0.165(1)	0.068(5)
C(4)	0.2780(7)	0.218(1)	0.072(2)	0.064(7)	O(13)	0.4286(6)	0.920(1)	0.388(2)	0.119(7)
C(5)	0.5329(7)	0.135(1)	0.157(2)	0.051(6)	O(14)	0.386(1)	0.834(1)	0.178(2)	0.19(1)
C(6)	0.5846(6)	0.192(1)	0.237(2)	0.043(5)	Cl(2)	0.3242(2)	0.5972(3)	0.0062(5)	0.051(1)
C(7)	0.6016(5)	0.324(1)	0.460(2)	0.041(5)	O(21)	0.2943(5)	0.653(1)	−0.113(2)	0.093(6)
C(8)	0.5649(6)	0.385(1)	0.575(2)	0.052(6)	O(22)	0.3113(6)	0.627(1)	0.177(2)	0.108(7)
C(9)	0.3429(6)	0.123(1)	0.663(2)	0.049(6)	O(23)	0.3846(4)	0.6087(8)	−0.018(2)	0.067(5)
C(10)	0.3827(6)	0.087(1)	0.780(2)	0.053(6)	O(24)	0.3068(6)	0.4996(8)	−0.019(2)	0.087(6)
C(11)	0.4352(6)	0.123(1)	0.733(2)	0.039(5)	Cl(3)	0.1592(2)	0.0331(3)	0.3887(6)	0.068(2)
Cu(3)	0.0231(1)	0.7552(1)	0.0512(3)	0.0534(7)	O(31)	0.1036(6)	0.069(1)	0.377(2)	0.117(7)
Cu(4)	0.1694(1)	0.7535(1)	−0.1413(2)	0.0425(6)	O(32)	0.1939(6)	0.069(1)	0.269(2)	0.125(8)
Br(2)	0.0751(1)	0.8562(2)	−0.1891(3)	0.095(1)	O(33)	0.1859(8)	0.051(1)	0.556(2)	0.143(9)
N(9)	0.0341(6)	0.832(1)	0.280(2)	0.080(6)	O(34)	0.1548(6)	−0.0691(9)	0.364(2)	0.095(6)
N(10)	−0.0488(5)	0.8318(9)	0.030(2)	0.068(6)	Cl(4)	0.0827(2)	0.4253(3)	0.6615(6)	0.074(2)
N(11)	−0.0192(6)	0.665(1)	−0.119(2)	0.069(6)	O(41)	0.0494(9)	0.350(1)	0.630(4)	0.23(2)
N(12)	0.1688(7)	0.655(1)	−0.347(2)	0.081(7)	O(42)	0.1392(7)	0.418(1)	0.659(4)	0.23(2)
N(13)	0.2126(5)	0.8353(8)	−0.305(2)	0.049(5)	O(43)	0.070(1)	0.498(2)	0.583(4)	0.34(2)
N(14)	0.2125(5)	0.836(1)	0.044(2)	0.057(5)	O(44)	0.065(1)	0.451(3)	0.803(3)	0.33(3)
N(15)	0.0870(5)	0.6708(8)	0.097(2)	0.052(5)	O(1)	0.2105(5)	0.253(1)	0.669(2)	0.106(7)
N(16)	0.1369(5)	0.6630(8)	0.015(2)	0.049(5)	O(2)	0.4271(6)	0.418(1)	0.845(1)	0.092(6)

Standard deviations of the least significant figures are given in parentheses.
a) $U_{eq}=1/3(U_{11}+U_{22}+U_{33}+2U_{12}\cos\gamma+2U_{13}\cos\beta+2U_{23}\cos\alpha)$.

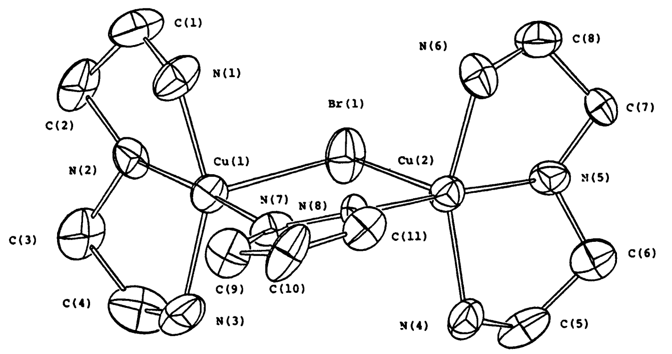

Fig. 1. A perspective view of one of the two crystallographically independent complex cations. Similar numbering scheme is used in the other complex.

to the idealized square pyramidal limit (τ=0) than the trigonal bipyramidal limit (τ=1.0). Selected bond lengths and angles are given in Tables 2 and 3. The five-membered rings in the bridges are nearly planar; deviations of the atoms from the respective best planes are: 0.029(4) [0.020(4)], −0.055(4) [0.067(4)], 0.012(3)-[−0.039(3)], −0.11(1)[0.04(1)], and 0.12(1)[−0.09(1)]Å for Cu(1)[Cu(3)], Cu(2)[Cu(4)], Br(1)[Br(2)], N(7)[N(15)], and N(8)[N(16)].

Table 2. Bond Distances (l/Å) of **1**

Cu(1)-Br(1)	2.690(2) Å	Cu(3)-Br(2)	2.702(3) Å
Cu(2)-Br(1)	2.756(2)	Cu(4)-Br(2)	2.673(3)
Cu(1)-N(1)	2.042(12)	Cu(3)-N(9)	2.044(16)
Cu(1)-N(2)	2.028(11)	Cu(3)-N(10)	2.014(12)
Cu(1)-N(3)	2.031(13)	Cu(3)-N(11)	2.010(14)
Cu(1)-N(7)	1.966(10)	Cu(3)-N(15)	1.953(12)
Cu(2)-N(4)	2.021(11)	Cu(4)-N(12)	2.064(14)
Cu(2)-N(5)	2.027(11)	Cu(4)-N(13)	2.032(12)
Cu(2)-N(6)	2.018(11)	Cu(4)-N(14)	2.034(12)
Cu(2)-N(8)	1.954(10)	Cu(4)-N(16)	1.959(12)

Cu···Cu distance (l/Å) for **1**

Cu(1)···Cu(2)	3.752(2) Å
Cu(3)···Cu(4)	3.769(3)

Short contact (l/Å) less than 3.10 Å

Cu(2)···O(13)(1−x, 1−y, 1−z)	3.05(2) Å
N(1)···O(1)(x, y, z)	3.07(2)
N(2)···O(24)(x, y, z)	3.09(2)
N(3)···O(32)(x, y, z)	3.00(2)
N(4)···O(13)(1−x, 1−y, 1−z)	3.00(2)
N(6)···O(2)(x, y, z)	3.02(2)
O(1)···O(33)(x, y, z)	2.97(2)
O(1)···O(42)(x, y, z)	2.89(2)
O(2)···O(23)(x, y, 1+z)	3.04(2)

The standard deviation of the least significant figure of each distance is given in parenthesis.

Table 3. Bond Angles ($\phi/^\circ$) of **1**

Br(1)-Cu(1)-N(1)	102.7(3)°
Br(1)-Cu(1)-N(2)	89.1(3)
Br(1)-Cu(1)-N(3)	101.7(4)
Br(1)-Cu(1)-N(7)	98.6(3)
N(1)-Cu(1)-N(2)	84.1(5)
N(1)-Cu(1)-N(3)	152.7(5)
N(1)-Cu(1)-N(7)	92.9(5)
N(2)-Cu(1)-N(3)	84.3(5)
N(2)-Cu(1)-N(7)	172.2(4)
N(3)-Cu(1)-N(7)	95.3(5)
Br(1)-Cu(2)-N(4)	97.9(3)
Br(1)-Cu(2)-N(5)	87.5(3)
Br(1)-Cu(2)-N(6)	101.3(3)
Br(1)-Cu(2)-N(8)	97.9(3)
N(4)-Cu(2)-N(5)	83.7(4)
N(4)-Cu(2)-N(6)	156.1(4)
N(4)-Cu(2)-N(8)	94.7(4)
N(5)-Cu(2)-N(6)	83.2(4)
N(5)-Cu(2)-N(8)	174.5(4)
N(6)-Cu(2)-N(8)	96.5(4)
Cu(1)-Br(1)-Cu(2)	87.1(1)
Br(2)-Cu(3)-N(9)	106.6(4)
Br(2)-Cu(3)-N(10)	91.8(4)
Br(2)-Cu(3)-N(11)	95.6(4)
Br(2)-Cu(3)-N(15)	96.4(4)
N(9)-Cu(3)-N(10)	83.1(6)
N(9)-Cu(3)-N(11)	154.5(6)
N(9)-Cu(3)-N(15)	94.5(5)
N(10)-Cu(3)-N(11)	83.7(6)
N(10)-Cu(3)-N(15)	171.7(6)
N(11)-Cu(3)-N(15)	95.5(5)
Br(2)-Cu(4)-N(12)	105.5(5)
Br(2)-Cu(4)-N(13)	90.5(3)
Br(2)-Cu(4)-N(14)	100.3(4)
Br(2)-Cu(4)-N(16)	97.4(3)
N(12)-Cu(4)-N(13)	83.1(5)
N(12)-Cu(4)-N(14)	150.8(6)
N(12)-Cu(4)-N(16)	93.4(5)
N(13)-Cu(4)-N(14)	83.3(5)
N(13)-Cu(4)-N(16)	172.0(5)
N(14)-Cu(4)-N(16)	96.6(5)
Cu(3)-Br(2)-Cu(4)	89.0(1)

The standard deviation of the least significant figure of each angle is given in parenthesis.

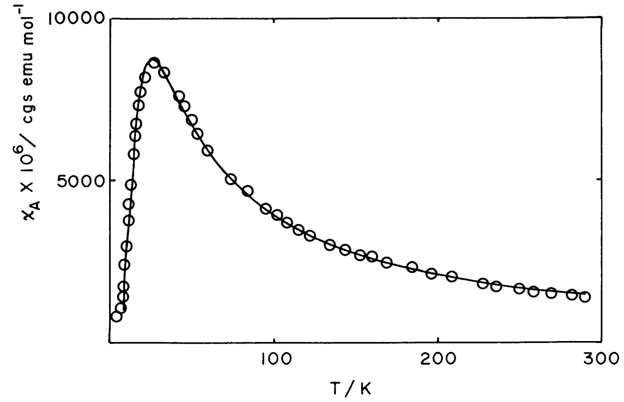

Fig. 2. Temperature dependence of the magnetic susceptibility of **1**. The open circles indicate observed susceptibility. The solid line shows the theoretical susceptibility calculated by the Bleaney-Bowers equation.

The magnetic moment(μ_{eff} value) for **1** was found to be 1.83 B.M. at 291.5 K using a Gouy magnetic apparatus. Figure 2 gives the temperature-dependence of the magnetic susceptibility for **1**. The magnetic data show a peak near 25 K and a rapid decrease to zero at lower temperatures, indicating an antiferromagnetic interaction within the dinuclear complex. The magnetic parameters are estimated as g=2.15, $N\alpha$=60×10^{-6} cgs emu mol^{-1}, and J=−14 cm^{-1} from the best fit of the χ_a values to the Bleaney-Bowers equation.[11] In 1, the pyrazolate anion bridges two basal planes of the two square pyramids, while the bridging Br atom shares the common apical position of the two square pyramids. It appears that the present complex has the $d_{x^2-y^2}$ ground state. The coordination geometries around the two copper(II) ions in **1** are unfavorable for exchanging two unpaired electrons through the bridging Br$^-$ ion. Accordingly, the antiferromagnetic exchange interaction of the two magnetic orbitals through pz seems to be more important than that through Br atom. The antiferromagnetic interaction is also observed in some complexes which are bridged by pz and J values range from −35.0 to −12.3 cm^{-1}.[2,4,12,13] Since no detailed stereochemistry around copper(II) in other pz-bridged copper(II) complexes[2,4,12,13] except **1** is available, a discussion concerning the relationship between the structure and the magnetism in these compounds is difficult at present. The exchange interaction in pz-bridged complexes, however, seems to be weaker than those in the dinuclear copper(II) complexes connected by imidazolate anion.[1]

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