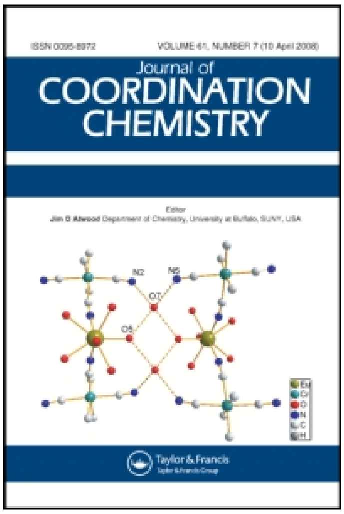

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THE MOLECULAR STRUCTURE OF THE ALKOXO-OXYGEN BRIDGED BINUCLEAR COPPER (II) COMPLEX, $[Cu_2\{(CH_3)_2N(CH_2)_3NH(CH_2)_2O\}_2(CH_3OH)_2](ClO_4)_2$

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The molecular structure of the title compound has been determined from single-crystal X-ray diffraction methods. The molecule consists of an alkoxo-oxygen bridged dimeric unit, $[Cu_2\{(CH_3)_2N(CH_2)_3NH(CH_2)_2O\}_2(CH_3OH)_2]^{2+}$, and two perchlorate anions as counter ions. The coordination geometry of each copper ion is a five coordinated tetragonal pyramid, of which the apical site is occupied by the oxygen atom of methanol. The magnetic moment of the compound is remarkably higher than that expected from Cu—O—Cu angle. This is explained in terms of the effect of axial coordination.

INTRODUCTION

Recently a number of oxygen-bridged copper(II) complexes have been prepared and their magnetic and spectral properties have been studied extensively.[1] Kida and his coworkers prepared numerous alkoxo-oxygen bridged copper(II) complexes with aminoalcohols, and studied their magnetic and spectral properties.[2-6] From these data, they proposed a classification scheme for those compounds based on their magnetic properties.[6] According to them, the compounds are classified into four groups, each of which have specific characteristics of magnetic and optical properties. Structural analyses of those compounds have been made to elucidate the characteristics of these groups in terms of their molecular structure.[7-15] In this paper we report the result of the single-crystal X-ray analysis of $Cu\{(CH_3)_2N(CH_2)_3NH(CH_2)_2O\}ClO_4\cdot CH_3OH$

EXPERIMENTAL

The complex was prepared according to ref. 4. Single-crystals for the X-ray work were obtained as deep-green rhombic prisms by slow evaporation of absolute methanol. Since the crystal readily effloresces in the atmosphere, it was enclosed in a glass capillary saturated with methanol vapor. The unit-cell parameters were determined from 15 reflections measured on a Syntex P$\bar{1}$ diffractometer. Crystal data: $CuClO_6N_2C_8H_{21}$, F.W. = 340.1, orthorhombic, space group Pbca, a = 14.760(5), b = 16.441(5), c = 11.911(4) Å, V = 2890.4 Å^3, Z = 8, D_m = 1.54, D_x = 1.56 g·cm^{-3}, μ(Mo Kα) = 16.8 cm^{-1}.

Intensity data were collected by the θ-2θ scan technique on a Syntex P$\bar{1}$ automated four-circle diffractometer, using Mo Kα radiation monochromated by graphite plate. Three reflections were monitored after every 47 reflections and the monitored data showed good stability. The intensities of 1332 independent reflections up to $2\theta = 42°$ were measured. 952 of them with $I > 2.33\sigma(I)$ were used for the determination of the crystal structure. The data were corrected for Lorentz and polarization effects.

Magnetic Measurement

Since crystals are so efflorescent, magnetic measurement over a temperature range could not be performed. Hence, the crystals were ground and packed in a Gouy cell in an atmosphere saturated with methanol vapor and the magnetic susceptibility was measured at room temperature by the Gouy method.

SOLUTION AND REFINEMENT OF THE STRUCTURE

The structure was solved from a Patterson function which was followed by successive fitting of a min-

TABLE I

Final atomic coordinates and thermal parameters with their standard deviations (x 10^4). The anisotropic thermal parameters are expressed in the form of $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$.

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	−124(0)	5499(0)	3939(1)	42(0)	33(0)	65(1)	0(1)	2(1)	6(1)
Cl	−1559(2)	3472(2)	1414(3)	64(1)	53(1)	124(3)	13(2)	−26(4)	−26(4)
O(1)	501(4)	4553(4)	4513(6)	58(4)	39(3)	63(6)	8(6)	12(8)	7(8)
O(2)	1158(5)	6336(5)	4107(8)	84(5)	56(4)	160(11)	−35(8)	−62(13)	46(12)
O(3)	−1751(10)	4164(7)	1864(22)	148(11)	84(7)	891(59)	33(15)	19(42)	−387(36)
O(4)	−2041(13)	2896(8)	1868(18)	304(21)	113(9)	503(39)	−176(24)	349(46)	112(30)
O(5)	−650(8)	3397(10)	1401(16)	86(7)	223(14)	387(27)	144(18)	−63(25)	−71(4)
O(6)	−1815(14)	3458(19)	381(14)	236(18)	535(36)	164(19)	−177(44)	−163(31)	187(46)
N(1)	203(6)	5033(5)	2433(7)	55(5)	48(4)	69(7)	19(8)	5(11)	8(10)
N(2)	−963(6)	6380(5)	3300(7)	56(5)	45(4)	70(8)	11(8)	0(11)	18(10)
C(1)	1011(8)	4512(7)	2624(10)	78(8)	61(6)	87(12)	70(13)	17(16)	35(17)
C(2)	798(8)	3988(7)	3670(9)	99(9)	56(6)	46(10)	63(13)	25(15)	4(13)
C(3)	370(8)	5598(7)	1467(10)	76(8)	70(7)	75(11)	35(11)	23(15)	42(16)
C(4)	−474(9)	6124(7)	1278(10)	94(9)	68(7)	71(12)	49(13)	0(17)	34(15)
C(5)	−674(9)	6738(7)	2173(10)	95(9)	51(6)	89(13)	10(12)	21(17)	46(14)
C(6)	−1890(7)	5977(7)	3174(11)	40(6)	65(7)	133(15)	−9(11)	−6(16)	44(17)
C(7)	−1066(9)	7099(6)	4045(12)	98(9)	34(5)	118(14)	22(12)	1(20)	−24(15)
C(8)	1808(10)	6174(10)	4966(13)	90(10)	99(10)	170(21)	−50(17)	−102(24)	33(24)

TABLE II

Bond lengths and angles with their standard deviations

(i) bond lengths (Å)

Cu–Cu*	3.034(2)	N(1)–C(3)	1.500(16)
Cu–O(1)	1.934(7)	C(3)–C(4)	1.533(19)
Cu–O(1)*	1.926(7)	C(4)–C(5)	1.502(19)
Cu–N(1)	2.010(9)	C(5)–N(2)	1.526(17)
Cu–N(2)	2.052(9)	N(2)–C(6)	1.529(17)
Cu–O(2)	2.348(10)	N(2)–C(7)	1.487(17)
O(2)–C(8)	1.429(20)	Cl–O(3)	1.294(27)
N(1)–C(1)	1.485(16)	Cl–O(4)	1.304(22)
C(1)–C(2)	1.547(18)	Cl–O(5)	1.348(20)
C(2)–O(1)	1.435(15)	Cl–O(6)	1.283(32)

(ii) bond angles (°)

Cu–O(1)–Cu*	103.6(3)	Cu–N(1)–C(3)	119.2(6)
O(1)–Cu–O(1)*	76.3(3)	C(1)–N(1)–C(3)	109.2(9)
O(1)–Cu–N(1)	83.8(3)	N(1)–C(3)–C(4)	109.0(10)
N(1)–Cu–N(2)	94.7(3)	C(3)–C(4)–C(5)	115.7(11)
N(2)–Cu–O(1)*	102.2(3)	C(4)–C(5)–N(2)	114.7(10)
O(2)–Cu–O(1)*	93.3(4)	C(5)–N(2)–Cu	115.5(6)
O(2)–Cu–N(1)	96.0(4)	C(5)–N(2)–C(6)	109.3(9)
O(2)–Cu–N(2)	95.9(4)	C(5)–N(2)–C(7)	104.2(9)
O(2)–Cu–O(1)*	100.2(4)	C(6)–N(2)–C(7)	108.1(9)
Cu–O(2)–C(8)	119.5(5)	O(3)–Cl–O(4)	110.0(15)
Cu–O(1)–C(2)	114.8(6)	O(3)–Cl–O(5)	107.7(14)
Cu*–O(1)–C(2)	136.8(5)	O(3)–Cl–O(6)	110.4(18)
O(1)–C(2)–C(1)	105.3(9)	O(4)–Cl–O(5)	118.9(13)
C(2)–C(1)–N(1)	106.3(9)	O(4)–Cl–O(6)	103.1(17)
Cu–N(1)–C(1)	105.9(6)	O(5)–Cl–O(6)	106.2(16)

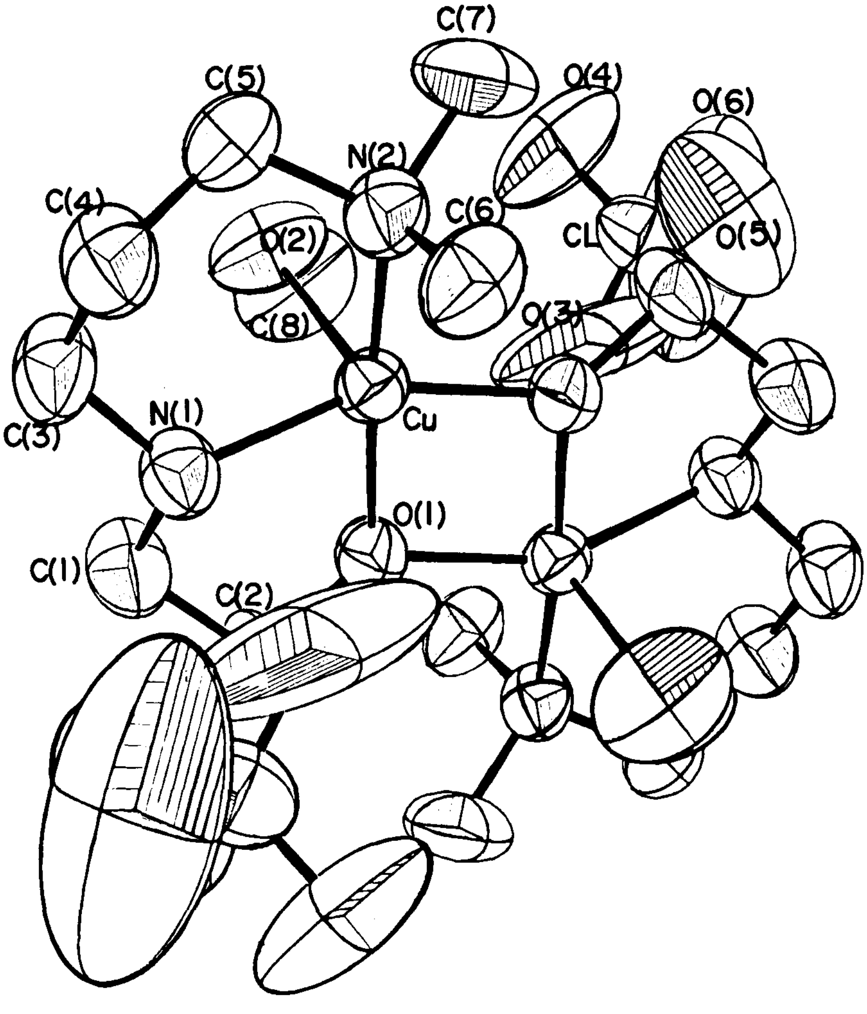

FIGURE 1 Perspective drawing of the molecule

imum function and by a Fourier synthesis. The structure was refined to R = 6.15% for 952 observed reflections by a block-diagonal least-squares method using anisotropic temperature factors for non-hydrogen atoms. The final atomic and thermal parameters, with their estimated standard deviations, are given in Table I. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[16] All the calculations were carried out on a FACOM 230-75 computer at the Computer Center of Kyushu University using the UNICS program system.[17]

DESCRIPTION OF THE STRUCTURE

The crystal consists of discrete binuclear units and perchlorate ions. Each of them contacts with van der Waals forces, the shortest intermolecular Cu··Cu distance being 8.1 Å.

A perspective drawing of the complex and the numbering system are illustrated in Figure 1. Bond distances and angles are listed in Table II. Some least-squares planes with the deviations of the atoms from the planes are given in Table III.

The molecule consists of the alkoxo-oxygen bridged dimeric unit, $[Cu_2\{(CH_3)_2N(CH_2)_3NH(CH_2)_2O\}_2(CH_3OH)_2]^{2+}$, and two perchlorate anions as counter ions. The coordination geometry of each copper ion is essentially five-coordinated tetragonal pyramidal, of which the apical site is occupied by the oxygen atom of methanol. The basal plane of the pyramidal unit, consisting of N(1), N(2), O(1) and O(1)*, is almost planar, the deviation of Cu being 0.22 Å toward the apical site.

TABLE III
Coefficients of Least-Squares Planens, $AX + BY + CZ = D$

Plane	Atoms	A	B	C	D	Distances from plane, Å
I	Cu, O(1), N(1)	0.8578	0.5173	0.0113	4.5408	C(1): 0.585, C(2): −0.112
II	N(1), N(2), C(3), C(5)	0.7847	0.4123	0.4628	5.0082	Cu: 0.747, C(4): −0.701, N(1): −0.020, N(2): 0.020, C(3): 0.023, C(5): −0.023
III	N(1), N(2), N(1)*, N(2)*	0.8062	0.5848	0.0893	5.3398	Cu: 0.219, O(1): 0.114
IV	Cu, Cu*, O(1), O(1)*	0.7757	0.5746	0.2607	6.2769	N(1): −0.533, N(2): −0.326
V	O(1), O(1)*, N(1), N(2)	0.7852	0.6095	0.1091	5.6553	Cu: 0.223, O(1): 0.074, O(1)*: −0.064, N(1): −0.060, N(2): 0.050
VI	Cu, Cu*, C(2)	0.8733	0.4565	0.1698	4.7643	O(1): 0.211

Interplanar Angle, Deg III–IV 10.0

The bridged-oxygen atom deviates from the plane defined by Cu, Cu* and C(2) by 0.21 Å. The five-membered chelate ring has an asymmetrical skew conformation, and C(1) and C(2) are deviated by 0.58 and −0.11 Å, respectively, from the plane through Cu,O(1) and N(1). The six-membered chelate ring has a chair conformation, and Cu and C(4) are located 0.74 and −0.70 Å, respectively, from the plane through N(1), N(2), C(3) and C(5).

DISCUSSION

Hatfield and his coworkers have investigated the structures and magnetic properties of numerous oxygen-bridged copper(II) complexes and pointed out that the Cu–O–Cu angle is the governing parameter for the antiferromagnetic interaction between copper(II) ions.[18,19] On the other hand, based on the spectral studies, as well as structural and magnetic measurements, Kida et al. claimed that the planarity of the bonds attached to the bridging oxygen atom is more fundamental in determining the nature of the antiferromagnetic interaction.[3] Structural data related to the discussion of some alkoxo-oxygen bridged complexes are listed in Table IV together with the effective magnetic moments at room temperature. The table shows that both criterions are consistent with the experimental data for (1) ~ (4). However, the magnetic moment of the present complex (5) is quite unusual on either of the criteria as is obviously seen in the Table IV.

It is not likely that there is any appreciable difference in the electron density at the bridging oxygen atom among the compounds listed in Table IV. Hence, the above magnetic anomaly should be accounted for in terms of the axial coordination effect. As already mentioned above, in the present compound (5), each copper ion is coordinated by methanol at the axial site with the Cu–O distance of 2.34 Å, whereas in compound (4) the copper ions of the binuclear unit are coordinated by H_2O and ClO_4^- with Cu–O distances of 2.52 and 2.62 Å, respectively. Thus, the effect of the axial coordination should be stronger in (5) resulting in a reduction of the antiferromagnetic interaction and producing a

TABLE IV
Structural and Magnetic Properties of Alkoxo-bridged Copper(II) Complexes

Complex		μ_{eff} (BM)	Cu–Cu (Å)	Cu–O–Cu (°)	ρ (°)	τ (°)	Cu-axial (Å)	ref.
(1)	Cu(pia)	0.41	3.026	106.4	360	0.5	–	15
(2)	$Cu(C_2H_5-2)Br$	0.50	3.033	105.0	360	8.3	–	13
(3)	$Cu(n-C_4H_9-2)Br$	0.60	3.019	104.2	360	0.3	–	7
(4)	$Cu(C_2H_5-2-3)H_2O\cdot ClO_4$	0.93	2.953	99.4	352.0	2.0	2.62, 2.52	9
(5)	$Cu(CH_3-3-2)CH_3OH\cdot ClO_4$	1.11	3.034	103.6	355.0	10.0	2.34	this work

(pia): $^-OC(CH_3)CHC(CH_3)N(CH_2)_3O^-$
(R–n): $R_2N(CH_2)_nO^-$
(R–n–m): $R_2N(CH_2)_nNH(CH_2)_mO^-$
ρ = sum of the angles, Cu–O(1)–Cu*, Cu–O(1)–C(2) and Cu*–O(1)–C(2)
τ is Sinn's parameter[21,22]

relatively larger magnetic moment (1.11 BM) compared to that for (4) (0.92 BM) which is contrary to the expectation deduced from comparison of the Cu–O–Cu angles and/or the ρ values in Table IV. Axial coordination should have the effect on the copper atom of reducing its electronegativity and of forcing the aminoalcohol ligand to lift from the basal plane. The latter effect may be the major factor of depressing the antiferromagnetic interaction.[20]

In the compound (3), there is no axial coordination, which may explain why the magnetic moment of (3) is remarkably lower than that of (5), in spite of the fact that the Cu–O–Cu angles of both compounds are nearly identical.

Sinn has pointed out that the intramolecular antiferromagnetic interaction between copper ions is closely related to tetrahedral distortion of the environment of copper ions, which was represented by a dihedral angle τ between the plane CuO(1)-Cu*O(1)* and that of the remaining coordinating atoms.[21,22] In Table IV, the angles τ are listed. However, it appears that there is no discrete relation between τ and magnetic moments for this series of compounds.

As a conclusion, this study shows that the fifth ligand plays an important role in depressing the antiferromagnetic interaction between copper(II) ions in these binuclear copper complexes.

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