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The Crystal Structure and Magnetic Property of the Alkoxo-Oxygen Bridged Tetranuclear Copper(II) Complex, $Cu_4\{(n\text{-}C_3H_7)_2N(CH_2)_2O\}_4Cl_4$

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The crystal structure of the alkoxo-oxygen bridged tetranuclear copper(II) complex, $Cu_4\{(n\text{-}C_3H_7)_2N(CH_2)_2O\}_4Cl_4$, has been determined from the three-dimensional X-ray diffraction method. The crystals are orthorhombic with the space group Pbcn. The cell dimensions are $a=15.965$ (4), $b=14.941$ (1), $c=19.305$ (2) Å. The structure has been determined from the heavy atom method and refined by the block-diagonal least-squares method to give $R=7.52\%$. The complex is of a cubane type structure formed by four copper and four alkoxide oxygen atoms. Each copper atom has a distorted square pyramidal environment. The correlation between the magnetic property and the structure was discussed on some homologous compounds of cubane structure.

Hein and his coworkers[1)] prepared a series of copper(II) complexes of *N,N*-dialkylaminoethanol with the general formula $Cu(R_2NCH_2CH_2O)X$ ($R=CH_3$, C_2H_5, $n\text{-}C_4H_9$ *etc.* and $X=Cl$, Br) whose basic structure was assumed to be a binuclear unit as shown in Fig. 1.

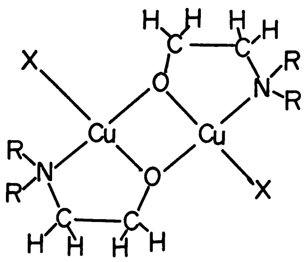

Fig. 1. An assumed basic structure of $[Cu(R_2(CH_2)_2O)X]$, where R = alkyl group and X = Cl, Br, NCS.

Uhlig and Staiger[2)] measured magnetic moments and optical spectra, and found that their magnetic moments at room temperature distribute in a wide range (from 1.9 BM to practically zero). Recently Kida and his coworkers[3—5)] prepared a number of copper(II) complexes of various aminoalcohols with the general formulas $[Cu(R_2N(CH_2)_nO)X]$ (hereafter abbreviated as Cu(R-*n*)X, where $R=CH_3$, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$ and X = Cl, Br, NCS) and $[Cu(R_2N(CH_2)_nNH(CH_2)_mO)]Y$ (hereafter abbreviated as [Cu(R-*n*-*m*)]Y, where *n* and $m=2$ or 3, and Y denotes a mono-negative ion), and proposed a new criterion for the classification of the extended series of alkoxo-bridged copper(II) complexes on the basis of temperature dependence of the magnetic susceptibilities,[5)] *i.e.*, (A) those whose χ_A-T curves can be fitted by the Bleaney-Bowers equation[6)], (B) those whose χ_A-T curves obey the Curie-Weiss law with positive Weiss constant, (C-1) those whose χ_A-T curves obey Curie-Weiss law with negative Weiss constant, and (C-2) whose χ_A-T curves can not be fitted by the Bleaney-Bowers equation, though showing subnormal magnetic moments at room temperature. They also showed that there is a close relationship between the presence of the near-ultraviolet absorption band and the intramolecular spin-exchange interaction.

In order to elucidate the above properties on the molecular structural basis, single-crystal X-ray analyses are desirable for a series of key compounds. The structures of some alkoxo-bridged copper(II) complexes were already determined.[7—12)] In this study, crystal structure of chloro *N,N*-dipropyl-2-aminoethanolato copper(II), Cu(pr-2)Cl, which belongs to the above-mentioned C-1 group, was determined by the three-dimensional X-ray diffraction techniques. It was found that the compound is of a cubane type structure formed by four copper and four alkoxide oxygen atoms. This result and the already reported data of the three related compounds[7—9,12)] make a series of cubane structures with stepwise differing magnetic properties. Thus, the present result has made it possible to discuss the correlation between magnetic property and molecular structure.

Experimental

The complex was prepared according to Hein.[1)] Single-crystals were obtained by slow evaporation of absolute ethanol solution at room temperature. They are green rhombic prisms elonagated along the c-axis. Unit cell dimensions were determined by the least-squares method from fifteen reflections measured on a Syntex P$\bar{1}$ diffractometer. The crystal data are listed in Table 1. A suitable crystal for the intensity measurement was ground to a sphere of radius $r=0.151$ mm. Since the crystal is liable to decompose in the air, it was coated with clear varnish. Three-dimensional intensity data were collected by the 2θ-θ scan technique on a Syntex P$\bar{1}$ four-circle diffractometer using Mo*Kα* radiation monochromated by a graphite plate. Three reflections were monitored after every measurement of 47 reflections, and the monitored data showed a satisfactory stability. Of 3929

TABLE 1. CRYSTAL DATA OF Cu(pr-2)Cl

$Cu_2Cl_2O_2N_2C_{16}H_{36}$ F.W. = 486.4
Orthorhombic
$a=15.965$ (4) Å
$b=14.941$ (1)
$c=19.305$ (2)
$V=4596.8$ Å^3
$D_m=1.399$ g·cm^{-3} (by floatation)
$D_x=1.405$ g·cm^{-3} (for $Z=8$)
μ(Mo*Kα*, $\lambda=0.71069$Å) = 21.24 cm^{-1}
Space group = Pbcn
systematic absences;
$h\ k\ 0$ for $h+k=$ odd
$h\ 0\ l$ for $l=$ odd
$0\ k\ l$ for $k=$ odd

TABLE 2. FRACTIONAL ATOMIC COORDINATES AND FINAL ANISOTROPIC TEMPERATURE FACTORS ($\times 10^4$) WITH THEIR STANDARD DEVIATIONS IN PARENTHESES

The temperature factor is of the form; $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
CuOA	4496 (2)	6792 (1)	3227 (1)	72 (1)	56 (1)	21 (0)	40 (2)	−6 (2)	−12 (1)
CuOB	4118 (2)	5276 (1)	2108 (1)	54 (1)	62 (1)	31 (0)	−26 (2)	13 (2)	−31 (2)
CLOA	4929 (5)	6942 (4)	4313 (2)	105 (5)	86 (4)	22 (1)	40 (8)	−9 (5)	−20 (4)
CLOB	2828 (4)	5070 (4)	2531 (3)	59 (3)	80 (4)	51 (2)	−47 (6)	21 (5)	−33 (6)
OXBA	4209 (9)	6695 (8)	2241 (6)	52 (7)	47 (7)	24 (4)	10 (12)	3 (9)	−10 (9)
OXBB	5296 (8)	5357 (8)	1854 (6)	52 (7)	41 (6)	24 (4)	3 (11)	6 (9)	−22 (9)
NITA	3553 (13)	7693 (14)	3305 (10)	65 (12)	86 (14)	43 (7)	42 (22)	−10 (16)	−34 (18)
NITB	4043 (13)	4380 (12)	1318 (8)	72 (12)	62 (10)	26 (5)	−6 (19)	25 (14)	−29 (13)
CAR1	3556 (15)	7274 (15)	2040 (12)	56 (13)	55 (12)	40 (8)	35 (21)	−22 (18)	0 (18)
CAR2	3050 (17)	7499 (15)	2700 (13)	93 (18)	86 (18)	43 (10)	−50 (25)	63 (22)	−72 (23)
CAA1	3724 (18)	8533 (16)	3697 (16)	75 (17)	52 (13)	78 (14)	26 (26)	36 (26)	−48 (24)
CAA2	4555 (26)	9017 (23)	3491 (19)	148 (31)	96 (23)	76 (16)	−64 (45)	70 (38)	−8 (32)
CAA3	4954 (31)	9519 (22)	4222 (22)	186 (36)	90 (21)	107 (21)	−35 (50)	70 (48)	−69 (37)
CAB1	2845 (19)	7263 (27)	3745 (29)	47 (16)	156 (33)	214 (38)	−66 (39)	63 (43)	−254 (62)
CAB2	2072 (29)	7470 (44)	3729 (26)	127 (34)	322 (69)	111 (24)	−159 (84)	−32 (38)	−29 (71)
CAB3	1595 (26)	6916 (32)	4314 (31)	86 (25)	163 (38)	184 (37)	−66 (53)	56 (53)	−18 (65)
CBR1	4782 (18)	4555 (18)	880 (13)	91 (19)	96 (18)	42 (9)	−88 (30)	81 (22)	−96 (22)
CBR2	5570 (17)	4763 (15)	1317 (12)	82 (16)	58 (13)	37 (8)	37 (25)	15 (20)	−46 (18)
CBA1	4060 (20)	3471 (14)	1659 (13)	116 (21)	38 (11)	46 (9)	13 (26)	24 (25)	−34 (17)
CBA2	3968 (27)	2634 (20)	1155 (20)	161 (33)	61 (17)	91 (19)	30 (40)	20 (42)	−34 (31)
CBA3	4130 (22)	1803 (19)	1654 (22)	99 (22)	63 (16)	117 (22)	−8 (33)	35 (39)	40 (33)
CBB1	3232 (21)	4470 (23)	894 (17)	89 (20)	124 (25)	60 (13)	−67 (38)	−63 (28)	10 (30)
CBB2	3029 (21)	5392 (22)	663 (16)	95 (21)	117 (24)	52 (12)	14 (38)	−37 (27)	−5 (29)
CBB3	2296 (28)	5495 (34)	192 (21)	132 (33)	223 (47)	81 (18)	−19 (64)	−132 (42)	54 (50)

independent reflections collected in $2\theta \leqq 48°$, 1557 ones greater than 2.33σ (F) were used in the analysis. They were corrected for Lorentz and polarization effects, but corrections for absorption were not applied ($\mu r=0.32$).

Solution and Refinement

There are eight formula units (a formula unit= $Cu_2Cl_2O_2N_2C_{16}H_{36}$) in a unit cell. The structure has been determined by the heavy atom method. The positions of copper atoms were obtained from the three-dimensional Patterson syntheses. Those of chlorine atoms were obtained from the minimum function based on the copper atoms. A three-dimensional electron-density map was then calculated with all observed reflections phased by the copper and chloride atoms, thus obtaining the positions of oxygen and nitrogen atoms. By successive Fourier syntheses and the block-diagonal least-squares method the positions of all the nonhydrogen atoms were determined except some carbon atoms of the propyl group, whose most probable positions were determined by the D-Fourier syntheses. Six-cycles of the block-diagonal least-squares refinement was applied to the positional and isotropic thermal parameters of the non-hydrogen atoms. Further five-cycles refinement was carried out, introducing anisotropic temperature factors, and R decreased to 7.52%. Maximum shifts of the positional and thermal parameters in the final cycle did not exceed half of their standard deviations. The scattering factors for all the atoms were taken from the International Tables for X-ray Crystallography.[13] In the least-squares procedures, weight w was taken equal to one for $|F_o| \geqq 5.0$ and zero for $|F_o| < 5.0$. The F_o–F_c table is kept at the office of this Bulletin, as Document No. 7617. The final positional and thermal parameters with the standard deviations are shown in Table 2.

Description of the Structure

The projection along the b-axis and the numbering system are shown in Fig. 2. The unit cell contains four molecules, each of which has a so-called "cubane" structure formed by four copper and four alkoxide

TABLE 3. INTERATOMIC DISTANCES WITH THEIR STANDARD DEVIATIONS

Coordination sphere			Chelate ring (B)		
CuOA	CuOA′	3.237 (5)	OXBB	CBR2	1.43 (2)
CuOB	CuOB′	3.219 (5)	CBR2	CBR1	1.54 (3)
CuOA	CuOB	3.190 (5)	NITB	CBR1	1.47 (3)
CuOA	CuOB′	3.238 (5)			
CuOA	OXBA	1.963 (11)	Propyl group (A)		
CuOA	OXBA′	2.260 (14)	NITA	CAA1	1.49 (3)
CuOB	OXBB	1.947 (13)	CAA1	CAA2	1.56 (4)
CuOB	OXBB′	2.212 (12)	CAA2	CAA3	1.71 (6)
CuOA	OXBB′	2.175 (12)	NITA	CAB1	1.55 (4)
CuOB	OXBA	2.140 (12)	CAB1	CAB2	1.27 (8)
CuOA	NITA	2.025 (20)	CAB2	CAB3	1.60 (9)
CuOB	NITB	2.032 (16)			
CuOA	CLOA	2.220 (4)	Propyl group (B)		
CuOB	CLOB	2.236 (6)	NITB	CBA1	1.50 (2)
			CBA1	CBA2	1.59 (6)
Chelate ring (A)			CBA2	CBA3	1.59 (6)
OXBA	CAR1	1.40 (2)	NITB	CBB1	1.53 (3)
CAR1	CAR2	1.54 (3)	CBB1	CBB2	1.48 (4)
NITA	CAR2	1.45 (3)	CBB2	CBB3	1.49 (6)

oxygen atoms. Each molecule contacts with Van der Waals forces, the shortest intermolecular Cu–Cu distance being 8.12 Å. The molecule has a twofold axis which passes through the center of the top and the bottom faces of the cubane structure. The symmetry group of the molecule may be approximated by S_4 point group. Each copper atom of the molecule has a distorted tetragonal pyramidal environment. The bond lengths and angles with their standard deviations are given in Tables 3 and 4.

Some least-squares planes are given in Table 5 together with the distances of the individual atoms from

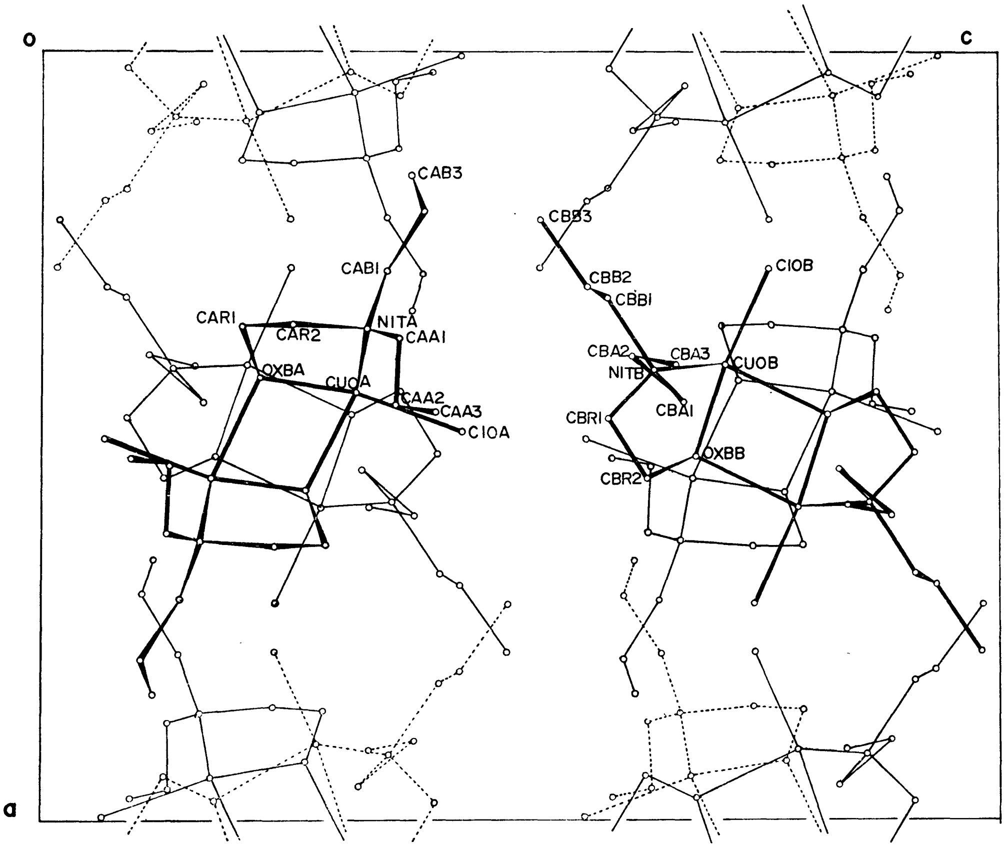

Fig. 2. Projection of the crystal structure along the b-axis

Table 4. Bond angles and estimated standard deviations

CuOA	OXBA	CuOA′	99.8 (5)	CuOA′	OXBB	CBR2	120 (1)
CuOB	OXBB	CuOB′	100.1 (5)				
CuOA	OXBA	CuOB	101.8 (5)	CuOA	NITA	CAT2	103 (1)
CuOA	OXBB′	CuOB	93.1 (4)	NITA	CAR2	CAR1	114 (1)
CuOA	OXBA′	CuOB′	94.4 (5)	CAR2	CAR1	OXBA	107 (1)
CuOA	OXBB′	CuOB′	103.0 (5)				
OXBA	CuOA	OXBA′	79.6 (5)	CuOB	NITB	CBR1	105 (1)
OXBA	CuOA	NITA	87.0 (6)	NITB	CBR1	CBR2	111 (1)
NITA	CuOA	CLOA	95.3 (5)	CBR1	CBR2	OXBB	105 (1)
CLOA	CuOA	OXBA′	95.7 (3)				
OXBA	CuOA	OXBB′	83.8 (4)	CuOA	NITA	CAA1	117 (1)
OXBA′	CuOA	OXBB′	76.6 (4)	NITA	CAA1	CAA2	114 (2)
OXBB	CuOB	OXBB′	79.4 (4)	CAA1	CAA2	CAA3	108 (3)
OXBB	CuOB	NITB	84.8 (6)	CuOA	NITA	CAB1	107 (1)
NITB	CuOB	CLOB	97.3 (6)	NITA	CAB1	CAB2	126 (5)
CLOB	CuOB	OXBB′	93.7 (3)	CAB1	CAB2	CAB3	108 (5)
OXBB	CuOB	OXBA	84.4 (5)				
OXBB′	CuOB	OXBA	78.9 (4)	CuOB	NITB	CBA1	105 (1)
CuOA	OXBA	CAR1	113 (1)	NITB	CBA1	CBA2	115 (2)
CuOA′	OXBA	CAR1	121 (1)	CBA1	CBA2	CBA3	103 (3)
CuOB	OXBA	CAR1	121 (1)	CuOB	NITB	CBB1	113 (1)
CuOB	OXBB	*CBR2*	*116 (1)*	*NITB*	*CBB1*	*CBB2*	*115 (2)*
CuOB′	OXBB	CBR2	119 (1)	CBB1	CBB2	CBB3	116 (3)

TABLE 5. BEST LEAST-SQUARES PLANES DEFINED BY ATOMIC POSITIONS

1) Plane defined by CuOA, CuOA′, OXBA, OXBA′			
Distances of atoms from this plane (Å)			
CuOA	0.07	ClOA	0.29
CuOA′	0.07	NITA	1.41
OXBA	−0.07	CAR1	0.79
OXBA′	−0.07	CAR2	1.12
2) Plane defined by CuOB, CuOB′, OXBB, OXBB′			
Distances of atoms from this plane (Å)			
CuOB	−0.06	ClOB	−0.36
CuOB′	−0.06	NITB	−1.39
OXBB	0.06	CBR2	−0.81
OXBB′	0.06	CBR1	−1.13

these planes. The carbon atoms of the chelate ring, and nitrogen and chlorine atoms are situated far from the plane, probably due to a steric repulsion.

Discussion

The cubane type structure similar to the present complex has been known in the related complexes, Cu(et-2)Cl[7,8] and Cu(bu-2)Cl.[9] The copper complex with a tridentate ligand, Cu(eia), where eia is a Schiff base formed by the condensation of aminoethanol and acetylacetone has also been known to be of a cubane structure.[12] A remarkable trend is found in those compounds that in-plane Cu–O bonds involving chelate ring are of normal Cu–O bond lengths, while the other in-plane Cu–O bonds (labeled with (d) in Fig. 3) are considerably elongated.[7–9,12] It is also to be noted that in all the above complexes the bridging alkoxide group is involved in a five-membered chelate ring. No cubane type tetranuclear complex, which has a six-membered chelate ring involving bridging alkoxide, has yet been known.

TABLE 6. BOND LENGTHS AND ANGLES OF CUBANE STRUCTURE

	Cu(et-2)Cl[7,8]	Cu-(eia)[12]	Cu(pr-2)Cl	Cu(bu-2)Cl[9]
μ_{eff} (BM) (k)	1.66	1.83	1.85	1.95
	−102	+10	−27	+32
group	C-1	B	C-1	B
Cu–Cu (a)	2.935	3.006	3.228	3.383
(b)	3.435	3.259	3.214	3.169
Cu–O (c)	1.945	1.98	1.955	1.942
(d)	1.986	2.00	2.236	2.410
(e)	2.471	2.32	2.157	2.069
Cu–O–Cu (α)	96.6	97.8	100.4	101.3
(β)	102.1	98.2	102.4	105.7
(γ)	99.5	97.6	93.8	90.5

The notations of bonds are defined in Fig. 3.

Some bond distances and angles of the series of cubane type structure are listed in Table 6 in the order of increasing μ_{eff} values. As seen in Table 6, bond distances and angles are closely related to magnetic moments for the three homologous compounds.* In this series, Cu(et-2)Cl and Cu(bu-2)Cl take both extreme values in either structural and magnetic data. In the former, the in-plane Cu–O (d and c) bonds are much stronger than the out-of-plane Cu–O (e) bonds and the molecule may be regarded to be formed from two basic binuclear units of Fig. 1. On the other hand, in the latter the out-of-plane Cu–O (e) bonds are much shortened and Cu–O (d) bonds are elongated. Thus the axis of the squar pyramid of copper ion is changed from the Cu–O (e) (in the case of Cu(et-2)Cl) to the Cu–O (d) (in the case of Cu(bu-2)Cl) axis. The presently analysed complex, Cu(pr-2)Cl, lies between the both extremes in either structural and magnetic values. However, it should be remarked that the structural trend of Cu(pr-2)Cl is definitely similar to that of Cu(bu-2)Cl rather than that of Cu(et-2)Cl, *i.e.*, in Cu(pr-2)Cl and Cu(bu-2)Cl Cu–Cu (a)>(b) and Cu–O (d)>(e)>(c), though magnetically Cu(pr-2)Cl belongs to the same group C-1[5] as Cu(et-2)Cl, since they both give negative Weiss constant, while Cu(bu-2)-Cl gives positive Weiss constant as shown in Table 6. This implies that in this series of compounds the change of sign in Weiss constant accompanies no discontinueous change of structure.

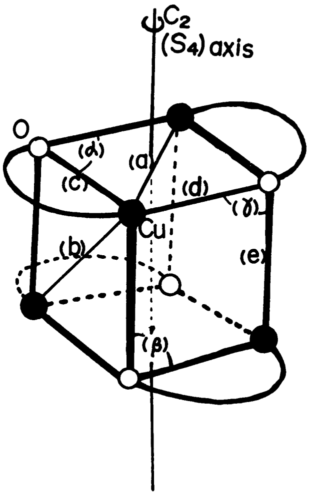

Fig. 3. The cubane type structure formed by the copper and oxygen atoms.
The bond distances and angles, which may be closely related to the magnetic property, are defined in the figure.

The calculations were performed on the FACOM 230-75 computer of the Computer Center of Kyushu University, using the UNICS program system.[14]

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* For Cu(eia) the μ_{eff} value slightly deviates from the value expected from the interpolation of the data of the three homologous compounds, probably due to the change of the chemical environment of copper atom.

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