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The Crystal Structure of the Trinuclear Complex, $[Cu_3\{(C_2H_5)_2N(CH_2)_2NH(CH_2)_3O\}_2(OH)_2](ClO_4)_2$

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The structure of the trinuclear complex, formed from *N*,*N*-diethyl-*N'*-(3-hydroxypropyl)ethylenediamine and copper(II) perchlorate, has been determined from three dimensional X-ray diffraction data. The crystals are monoclinic with the space group $P2_1/c$. The cell dimensions are $a=7.759(6)$, $b=13.21(1)$, $c=15.00(1)$ Å and $\beta=103.95(6)°$. The unit cell contains two molecules and the molecule has a centre of symmetry. The structure has been determined by the heavy atom method and refined by the block diagonal least squares method to give $R=6.83\%$ for 1368 observed reflections. Three copper atoms are arrayed on a straight line, the separations being 2.902 Å. The geometry around the two end copper atoms is best described as a slightly distorted tetragonal pyramid. The central copper atom has a square planar environment.

In the previous paper Nishida and Kida[1] reported the preparation of the binuclear (green) and the trinuclear (blue) copper(II) complexes from *N*,*N*-dialkyl-*N'*-(3-hydroxypropyl)ethylenediamine, $R_2N(CH_2)_2NH(CH_2)_3OH$ ($R=CH_3$, C_2H_5), copper(II) perchlorate and sodium hydroxide.

When the ligand, copper(II) perchlorate and sodium hydroxide were mixed with the mole ratio 1: 1.2: 1, green crystals were obtained. This complex was assumed to be binuclear on the bases of the elemental analysis and the magnetic susceptibility measurements over the temperature range 80—300 K. This was verified from the single crystal X-ray diffraction method by Villa *et al.*[2]

On the other hand, when the ligand, copper(II) perchlorate and sodium hydroxide were mixed with the mole ratio 1: 2: 1, blue crystals were obtained, which were assumed to be of a linear trinuclear structure on the bases of the elemental analysis and the magnetic susceptibility measurements (80—300 K). In the present work a single crystal X-ray diffraction study has been carried out for this compound in order to confirm the above assumption. The detailed structural data are desirable for the elucidation of magnetisms and electronic spectra of the alkoxo-bridged copper(II) complexes.

Experimental

The complex was prepared according to Ref. 1. Single crystals of the complex for the X-ray work were obtained as violet blue needles by slow evaporation of 99% methanol solution at room temperature. For cell parameter determination and intensity measurement an approximately cubic crystal of dimension 0.2 mm was prepared by cutting a larger specimen. The cell parameters were determined from fifteen reflections measured on Syntex $P\bar{1}$ diffractometer by the autoindexing and least squares programs.

The Crystal Data: $Cu_3Cl_2O_{12}N_4C_{18}H_{44}$, formula weight 770.1, monoclinic, space group $P2_1/c$, $a=7.759(6)$, $b=13.21(1)$, $c=15.00(1)$ Å, $\beta=103.95(6)°$, $V=1493.03$ Å^3, $Z=2$, $D_m=1.704$ g·cm^{-3} (by floatation), $D_x=1.712$ g·cm^{-3}, μ(Mo $K\alpha$)$=23.90$ cm^{-1}. Three dimensional intensity data were collected by the θ—2θ scan technique with a variable scan rate from 4.0 to 24.0°/min on a Syntex $P\bar{1}$ four-circle diffractometer using Mo$K\alpha$ radiation monochromated by a graphite plate. Three reflections were monitored after every measurement of 47 reflections, and the monitored data showed good stability. Of the 2650 reflections recorded, 1368 had intensities greater than 2.33 times their estimated standard deviations, and only these unique reflections were used for the structure determination. The data were corrected for Lorentz and polarization effects. Correction for absorption was not applied.

Determination and Refinement of Structure

In the space group $P2_1/c$, the general positions are fourfold. In this crystal, there are only two molecules in a unit cell and each molecule includes three copper atoms. Therefore, each molecule has a center of symmetry, which corresponds to the special position 0, 0, 0 or 0, 1/2, 1/2, and the central copper atom of each molecule is required to be in this special position.

TABLE 1. FRACTIONAL ATOMIC COORDINATES AND THEIR STANDARD DEVIATIONS IN PARENTHESES

	x	*y*	*z*
Cu(1)	0.0	1/2	1/2
Cu(2)	0.1320(1)	0.3363(0)	0.4056(0)
Cl	0.3066(4)	0.5661(2)	0.2998(2)
O(1)	0.1750(9)	0.3942(5)	0.5252(4)
O(2)	−0.0764(8)	0.4169(4)	0.3940(3)
N(1)	0.0580(10)	0.2770(6)	0.2813(4)
N(2)	0.3361(10)	0.2329(6)	0.4263(5)
C(1)	0.2173(14)	0.2360(8)	0.2603(6)
C(2)	0.3099(13)	0.1731(8)	0.3397(6)
C(3)	−0.0478(15)	0.3423(8)	0.2093(6)
C(4)	−0.2123(14)	0.3792(8)	0.2345(7)
C(5)	−0.1839(14)	0.4567(7)	0.3082(6)
C(6)	0.5088(14)	0.2923(8)	0.4433(7)
C(7)	0.6789(16)	0.2279(11)	0.4628(9)
C(8)	0.3386(14)	0.1654(8)	0.5072(6)
C(9)	0.1597(17)	0.1252(11)	0.5082(9)
O(3)$^{a)}$	0.3077(17)	0.4771(9)	0.3395(8)
O(4)$^{b)}$	0.1874(19)	0.6124(13)	0.3644(11)
O(5)	0.4547(11)	0.6289(7)	0.3222(6)
O(6)	0.1851(14)	0.5943(8)	0.2228(7)
O(7)$^{c)}$	0.3756(25)	0.4882(14)	0.2316(13)

a) Occupancy 0.82. b) Occupancy 0.65. c) Occupancy 0.53.

TABLE 2. FINAL ANISOTROPIC TEMPERATURE FACTORS ($\times 10^4$) AND THEIR STANDARD DEVIATIONS IN PARENTHESES
The temperature factor is of the form $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu(1)	137(3)	44(1)	28(0)	38(3)	18(2)	−21(1)
Cu(2)	131(2)	41(0)	25(0)	32(2)	17(1)	−11(1)
Cl	166(7)	71(2)	84(2)	−42(6)	−57(5)	61(3)
O(1)	216(18)	51(4)	29(3)	25(14)	42(12)	−28(6)
O(2)	173(16)	43(4)	29(3)	23(13)	11(10)	−16(5)
N(1)	166(20)	63(6)	20(3)	59(18)	−11(12)	−5(7)
N(2)	155(19)	39(5)	41(4)	35(16)	45(14)	−6(7)
C(1)	190(26)	64(7)	26(4)	106(23)	27(16)	−32(9)
C(2)	186(27)	56(7)	37(5)	68(23)	29(17)	−26(10)
C(3)	287(30)	50(7)	32(5)	−2(26)	17(19)	−16(10)
C(4)	146(26)	62(8)	54(6)	60(23)	−46(19)	−59(11)
C(5)	164(24)	48(6)	32(5)	73(21)	−45(16)	6(9)
C(6)	157(25)	52(7)	50(6)	5(22)	33(19)	1(10)
C(7)	159(29)	108(12)	79(8)	−15(31)	41(24)	30(17)
C(8)	225(27)	52(6)	34(4)	17(24)	9(17)	34(10)
C(9)	238(34)	110(12)	72(8)	−27(32)	87(27)	12(16)
O(3)	412(37)	95(10)	121(10)	−64(31)	−11(30)	168(16)
O(4)	264(39)	139(15)	120(15)	34(40)	185(36)	−10(22)
O(5)	218(21)	104(8)	86(6)	−91(20)	75(17)	−30(11)
O(6)	404(31)	121(9)	92(7)	40(29)	−40(23)	54(13)
O(7)	336(51)	91(15)	118(15)	−72(47)	−52(44)	−69(25)

TABLE 3. FRACTIONAL ATOMIC COORDINATES AND ISOTROPIC TEMPERATURE FACTORS OF HYDROGEN ATOMS
The average estimated standard deviations of the isotropic temperature factors is 2.0Å^2.

	x	y	z	B(Å^2)
H(1)	0.234(19)	0.382(11)	0.557(9)	8.0
H(2)	0.190(13)	0.204(7)	0.202(6)	2.5
H(3)	0.304(14)	0.294(8)	0.246(7)	4.3
H(4)	0.430(13)	0.131(7)	0.329(6)	3.1
H(5)	0.240(13)	0.110(8)	0.350(7)	3.2
H(6)	−0.079(17)	0.301(10)	0.150(8)	6.6
H(7)	0.022(17)	0.399(10)	0.197(8)	6.6
H(8)	−0.285(13)	0.318(7)	0.244(6)	2.8
H(9)	−0.297(13)	0.407(8)	0.177(6)	3.0
H(10)	−0.299(14)	0.495(9)	0.313(7)	4.2
H(11)	−0.122(14)	0.522(8)	0.288(7)	3.8
H(12)	0.515(13)	0.348(7)	0.495(6)	2.4
H(13)	0.496(14)	0.342(8)	0.389(7)	4.1
H(14)	0.383(16)	0.199(9)	0.564(7)	6.2
H(15)	0.421(15)	0.100(9)	0.508(8)	5.4
H(16)	−0.026(17)	0.218(9)	0.275(8)	6.1
H(17)	0.598(17)	0.179(10)	0.435(8)	6.4
H(18)	0.657(16)	0.197(9)	0.501(8)	5.8
H(19)	0.786(13)	0.275(8)	0.465(8)	3.5
H(20)	0.080(15)	0.198(8)	0.484(7)	4.9
H(21)	0.068(17)	0.094(10)	0.464(7)	6.3
H(22)	0.140(17)	0.357(10)	0.052(8)	6.7

The structure was solved by the heavy atom method. The coordinates of the copper atoms could be easily determined from the three-dimensional Patterson synthesis. The position of the chlorine atom was deduced 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 chlorine atoms. The resulting map showed the peaks corresponding to all the remaining non-hydrogen atoms except two oxygen atoms in perchlorate anion. The atomic positions and isotropic temperature factors were refined by the block diagonal least squares method. Further refinement was carried out, introducing anisotropic temperature factors, and the disagreement factor decreased to 11.67%. At this step a difference Fourier synthesis was calculated. The difference Fourier map showed three diffuse peaks, though only two peaks of the two oxygen atoms in perchlorate ion were expected. Accordingly, the occupancy factors of the oxygen atoms were assigned in proportion to the peak values, as shown in Table 1. Six cycles of the block diagonal least squares refinement were applied to the positional and anisotropic thermal parameters of all the non-hydrogen atoms. The disagreement factor was decreased from 8.96 to 7.69% for the observed 1368 reflections. At this stage a difference Fourier synthesis was calculated and the positions of about half of the hydrogen atoms could be determined. The positions of the remaining hydrogen atoms were assigned from the calculation. Introducing these hydrogen atoms, the final set of the least squares calculation was carried out.

The final disagreement factor was 6.83% for the observed 1368 reflections.** Maximum shifts of the positional and thermal parameters in the final cycle did not exceed half their standard deviations. In the least squares procedure, the quantity minimized was $\sum w(k|F_o|-|F_c|)^2$, where k is a scale factor and $w=1$ for $|F_o|\geqq 5.0$ and $w=0$ for $|F_o|<5.0$. The scattering factors for all the atoms were taken from the literature.[3] The final positional and thermal parameters are shown in Tables 1, 2 and 3.

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* The observed and calculated structure factors are available at the office of this Bulletin as Document No. 7604.

Description and Discussion of the Structure

A perspective drawing of the complex and the numbering system used in this text are illustrated in Fig. 1. The bond distances and the bond angles within a molecule are listed in Tables 4 and 5.

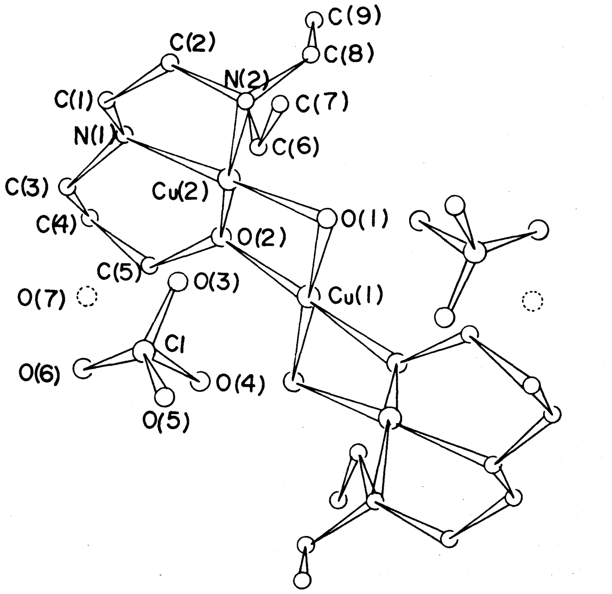

Fig. 1. A perspective drawing of the molecule.

Table 4. Interatomic distances

	Coordination sphere	
Cu(1)	Cu(2)	2.902(1)Å
Cu(1)	O(1)	1.922(7)
Cu(1)	O(2)	1.904(7)
Cu(1)	O(4)	3.13(1)
Cu(2)	O(1)	1.904(7)
Cu(2)	O(2)	1.910(7)
Cu(2)	N(1)	1.977(9)
Cu(2)	N(2)	2.059(9)
Cu(2)	O(3)	2.63(1)
	Six-membered ring	
N(1)	C(3)	1.46(1)Å
C(3)	C(4)	1.50(1)
C(4)	C(5)	1.48(1)
C(5)	O(2)	1.45(1)
	Five-membered ring	
N(1)	C(1)	1.45(1)Å
C(1)	C(2)	1.49(1)
C(2)	N(2)	1.49(1)
	Ethyl group	
N(2)	C(6)	1.52(1)Å
C(6)	C(7)	1.53(1)
N(2)	C(8)	1.50(1)
C(8)	C(9)	1.49(1)
	Perchlorate ion	
Cl	O(3)	1.31(1)Å
Cl	O(4)	1.62(1)
Cl	O(5)	1.39(1)
Cl	O(6)	1.35(1)
Cl	O(7)	1.62(2)

Table 5. Bond angles

	Coordination sphere		
Cu(1)	O(1)	Cu(2)	98.6(3)°
Cu(1)	O(2)	Cu(2)	99.1(3)
O(1)	Cu(1)	O(2)	79.0(3)
O(1)	Cu(2)	O(2)	79.3(3)
O(1)	Cu(2)	N(2)	99.8(3)
O(2)	Cu(2)	N(1)	95.0(3)
N(1)	Cu(2)	N(2)	85.2(3)
	Six-membered ring		
Cu(2)	N(1)	C(3)	116.4(6)°
N(1)	C(3)	C(4)	111.2(9)
C(3)	C(4)	C(5)	115.2(9)
C(4)	C(5)	O(2)	111.0(8)
C(5)	O(2)	Cu(2)	125.1(6)
	Five-membered ring		
Cu(2)	N(2)	C(2)	106.3(8)°
N(2)	C(2)	C(1)	109.8(8)
C(2)	C(1)	N(1)	107.6(8)
C(1)	N(1)	Cu(2)	106.4(6)
	Ethyl group		
Cu(2)	N(2)	C(6)	107.2(9)°
C(2)	N(2)	C(6)	110.4(8)
N(2)	C(6)	C(7)	114.9(9)
Cu(2)	N(2)	C(8)	112.0(9)
C(2)	N(2)	C(8)	111.2(8)
N(2)	C(8)	C(9)	112.7(9)
	Perchlorate ion		
O(5)	Cl	O(6)	113.9(6)°
O(5)	Cl	O(3)	120.6(7)
O(5)	Cl	O(7)	98.8(8)
O(5)	Cl	O(4)	100.6(7)
O(6)	Cl	O(3)	123.8(8)
O(6)	Cl	O(7)	84.4(9)
O(6)	Cl	O(4)	91.6(8)
O(3)	Cl	O(7)	75.6(9)
O(3)	Cl	O(4)	90.5(8)
O(7)	Cl	O(4)	160.0(9)

Three copper atoms are arrayed on a straight line, the separations being 2.902(1) Å. This arrangement has been expected from the magnetic susceptibility measurements over the temperature range 80—300 K.[1] The geometry around the two end copper atoms is best described as a slightly distorted tetragonal pyramid. One of the axial coordination site is occupied by an oxygen atom of perchlorate ion. The bond distance, Cu(2)–O(3), is 2.63(1) Å. The central copper atom has a square planar environment. The Cu–Cu distance (2.902(1) Å), the Cu–O distances (1.904(7)—1.922(7) Å) and the bridging Cu–O–Cu angles(98.6(3), 99.1(3)°) are very close to the corresponding values (2.953(3) Å, 1.915(6)—1.953(6) Å, 99.3(2)° and 99.5(2)°) in the green binuclear complex with the same ligand,[2] and are within the range of ones found in other di-μ-alkoxo copper(II) and di-μ-hydroxo copper(II) complexes.[4–9] The Cu(2)–N(2) distance(2.059(9) Å) is longer than the Cu(2)–N(1) distance(1.977(9) Å), such a tendency was also observed in the green binuclear complex.[2] The C–N, C–O and C–C bond distances of the chelate ring are also similar to those of the green binuclear

TABLE 6. BEST LEAST-SQUARE PLANES DEFINED BY ATOMIC POSITIONS

1) Plane defined by Cu(2), O(1), O(2), N(1), N(2)

$0.6176x+0.7193y-0.4572z=0.9609$

Distances of atoms from this plane (Å)

Cu(2)	0.08Å	N(1)	0.02Å
O(1)	0.02	N(2)	−0.06
O(2)	−0.06	O(3)	2.71

2) Plane defined by Cu(1), Cu(2), O(1), O(2)

$0.6453x+0.6563y-0.5373z=0.1818$

Distances of atoms from this plane (Å)

Cu(1)	0.12Å	O(1)	−0.12Å
Cu(2)	0.12	O(2)	−0.12

3) Plane defined by Cu(1), Cu(2), C(5)

$0.6989x+0.6419y-0.4744z=0.6817$

Distances of atoms from this plane (Å)

O(2)	−0.36Å

4) Plane defined by Cu(2), N(1), N(2)

$0.6686x+0.6645y-0.4849z=0.6868$

Distances of atoms from this plane (Å)

C(1)	0.61Å	C(2)	−0.02Å

5) Plane defined by N(1), O(2), C(3), C(9)

$0.7713x+0.6461y-0.1665z=2.017$

Distances of atoms from this plane (Å)

Cu(2)	0.58Å	C(4)	−0.68Å
N(1)	0.04	C(3)	0.05
O(1)	−0.04	C(5)	−0.05

x, y, and z denote atomic fractional coordinates.

complex.[2] The ethyl C(8)–C(9) bond length is a little shorter than the normal C–C bond length, and may be explained in terms of heavy thermal motion of C(9) atom. It is noteworthy that a second oxygen atom O(4) of perchlorate ion appears to be in proximity of the axial coordination site of the central copper atom, although the Cu(1)–O(4) separation of 3.13(1) Å is too large for any bonding to be assumed. The positions of oxygens of perchlorate ion were not determined unequivocally and the geometry of the perchlorate ion is different from that of tetrahedron. This may be due to the disorder and the hindered rotation. We attempted to interpret the disorder and the hindered rotation of the perchlorate ion, but no satisfactory interpretation was obtained.

Some least squares planes are given in Table 6, together with the distances of the individual atoms from these planes. The basal plane of pyramidal unit, consisting of Cu(1), O(1), O(2), N(1), N(2), is essentially planar, the deviation of Cu(2) being 0.08 Å in the direction of the axial site. The dihedral angle between the planes passing through Cu(1), O(1), O(2) and Cu(2), O(1), O(2) is 3.5°. The five membered chelate ring has an unsymmetrical skew conformation and C(1) and C(2) are at 0.61 Å and −0.02 Å respectively from the plane through Cu(2), N(1) and N(2). The six membered chelate ring has a chair conformation and Cu(2) and C(4) are at 0.58 Å and −0.68 Å respectively from the plane through N(1), O(2), C(3) and C(5).

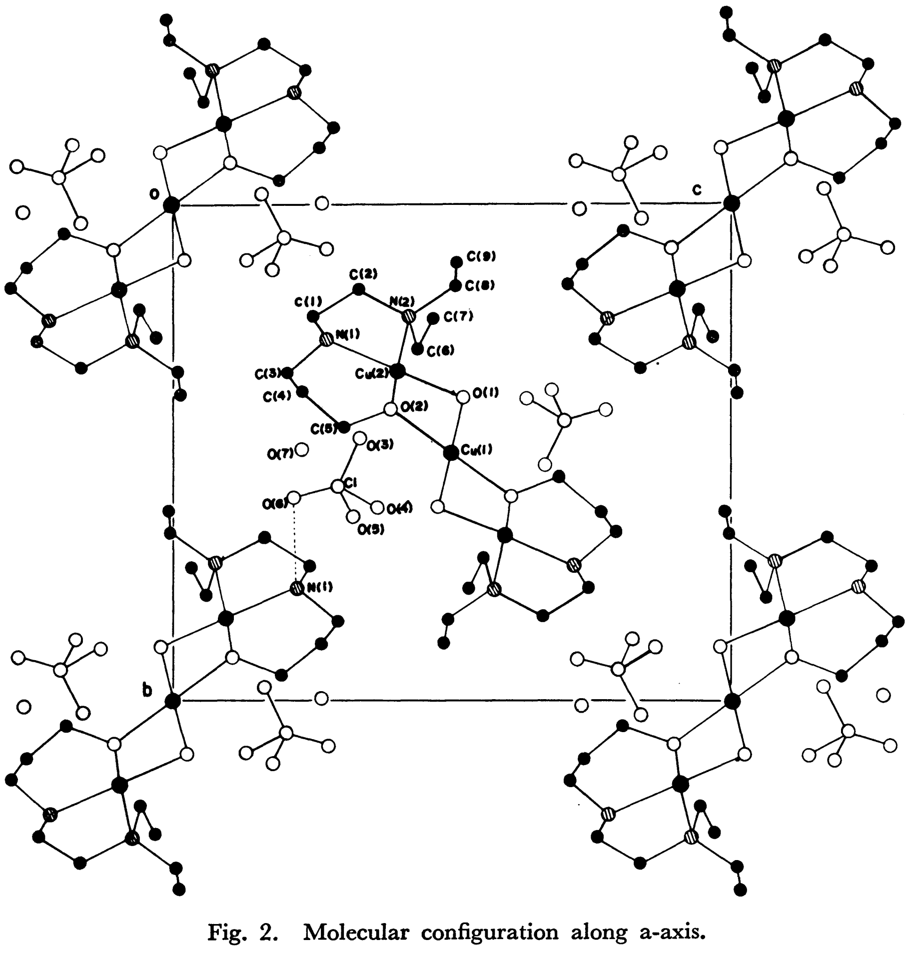

Fig. 2. Molecular configuration along a-axis.

Table 7. Intermolecular distances below 3.5Å

O(2)......C(1)	III	3.39Å
O(2)......C(2)	III	3.42
O(6)......N(1)	III	3.05
N(1)......O(4)	III	3.34
C(3)......N(1)	IV	3.32

Key to symmetry operations

I	x	y	z
II	$-x$	$-y$	$-z$
III	x	$1/2+y$	$1/2-z$
IV	x	$1/2-y$	$1/2+z$

The crystal structure projected along the a-axis is presented in Fig. 2. Intermolecular distances less than 3.5 Å are listed in Table 7. The molecules in the crystal are in contact at the normal van der Waals distances. There may be weak hydrogen bond between N(1) and O(6), whose distance is 3.05 Å.

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