

# Appendix 4

# Synthesis and Crystal Structure and Properties of a Novel Macrocyclic Copper Complex Bridged with $\mu$ -Oxalate

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## ABSTRACT

A novel binuclear copper complex,  $[(CuL)_2(ox) \cdot H_2O \cdot C_2H_5OH]$  (L=1, 15-diaza-3,4:9,10-dibenzo-5,8,-trioxacyclo-pentadecane-N-acetate) bridged  $\mu$ -oxalate, is synthesized and characterized by single crystal x-ray analysis, EPR spectra and thermal analysis. The crystal is monoclinic space group  $P2(1)/n$ , with  $a=12.493(1)$  Å,  $b=8.632(1)$  Å,  $c=22.709(2)$  Å,  $\beta=103.75(1)^\circ$ ,  $V=2378.7(4)$  Å<sup>3</sup>, and  $Z = 2$ ,  $R_1=0.0606$  for 1822 observed reflection [ $I > 2\sigma(I)$ ]. The determination of magnetic susceptibility in the temperature of 300—4.2K indicates that the copper sites are in the state of antiferromagnetically couple ( $J=145.3$  cm<sup>-1</sup>).

Keywords: Crystal Structure, Macrocyclic Complex, Copper, Magnetic Susceptibility

## INTRODUCTION

In last decade, a great deal interests have been devoted to the development of rational synthetic routes to novel one- to three dimensional, polymeric coordination compounds which have been applied as molecular-based magnetic material<sup>(1)</sup>. Many of recent reports have focused on the synthesis, structure and magnetic interaction of binuclear or polynuclear transition metal compounds bridged with oxalate<sup>(2)</sup>, azide<sup>(3)</sup>, cyanate<sup>(4)</sup>, bipyrimidine<sup>(5)</sup> and TCNQ<sup>(6)</sup>. The magnetic interaction of binuclear oxalate bridged complex has been thoroughly discussed by Hoffmann<sup>(7)</sup> on the basis of molecular orbital theory. Kahn and his co-workers<sup>(8,9)</sup> have described a theory to predict the magnetic interaction and further demonstrated that five-coordinate  $\mu$ -oxalatodicopper(II) complexes can be designed with  $J$ -value from approximately zero to approximately 400  $\text{cm}^{-1}$  by modifying the ligands. Up to now, many complexes have been designed such as copper binuclear complexes of amine derivative<sup>(8,9,10)</sup>, mepirizole<sup>(11)</sup> and phenanthroline<sup>(12)</sup>, but the copper binuclear complex of functional macrocycle abridged with oxalate has not reported. In this paper, we reported the synthesis, structure and properties of a novel binuclear complex bridged with  $\mu$ -oxalate, and thermal analysis EPR and magnetic property of the complex corresponding to its crystal structure are discussed. The measurement of the magnetic property in the range of 4.2-300 K shows the antiferromagnetic interaction of the binuclear complex of macrocycle is stronger than that of amine, mepirizole, and phenanthroline binuclear ones bridged with oxalate.

## EXPERIMENT

All chemical reagents used were of analytical grade. The solvents were purified by conventional method. The ligand (HL), 1,5-diaza-3,4;9,10-dibenzo-5,8-dioxyacyclopentadecane-N- acetate acid, was reported in our previous paper<sup>(13)</sup>.

Elemental analysis was carried out on a Perkin-Elmer 240 analytical instrument. IR Spectra were recorded as KBr pellet on a Fourier Transfer Infrared Spectrometer(U.S.A). Electronic spectra in DMF solutions were performed on a Shimaduz UV-240 spectrometer (Japan). Variable-temperature magnetic susceptibility measurement was carried out in the range of 4.2K-300K with a SQUID apparatus. The EPR spectra were recorded on a Bruker 200D spectrometer.

#### *Synthesis of Microcrystalline $\text{CuL}(\text{ox}) \cdot \text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH}$*

A solution containing stoichiometric amounts of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.01mol) and HL (0.010mol) in ethanol 60 mL was mixed with a stoichiometric ethanol solution of oxalate of ammonia. Instantaneously, green microcrystalline precipitate started to appear, it was filtered off, washed with ethanol and dried in air. The yield of the reaction is 92%. The results of IR and elemental analysis showed that the product  $(\text{CuL}(\text{ox}) \cdot \text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH})$  was structurally isomorphous to the single crystals mentioned below.

#### *Growth of Single Crystals of $\text{CuL}(\text{ox}) \cdot \text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH}$*

In the process of diffusion of oxalate of ammonia(1.0 mmol) in methanol 40 mL into the mixed solution containing 0.001 mol/L  $\text{CuCl}_2$  and 0.001 mol/L HL, the single crystal of green color complex grew slowly. Anal. Calcd. for  $\text{C}_{46}\text{H}_{56}\text{N}_4\text{O}_{14}\text{Cu}_2$  (M=1016.03): C 53.38; H 5.61; N 5.41. Found: C 53.15; H 5.67; N 5.50.

#### *Crystal Structure Determination*

A crystal selected with dimensions 0.4 $\times$ 0.3 $\times$ 0.3 mm was mounted on a glass fiber and scanned on a Siemens SMART-CCD area-detecting diffractometer with graphite - monochromatic  $\text{MoK}\alpha$  ( $\lambda=0.71073$ ) radiation. Intensity data were obtained by using an

$\omega$  scan mode with a scan speed of 10s/frame and 0.3 °/frame in the range of  $2.02^\circ < \theta < 27.5^\circ$ . Data reductions and cell refinements were performed with SMART<sup>(14)</sup> and SAINT<sup>(15)</sup> softwares.

A total of 5417 unique reflections were collected and 1822 observed reflections with  $I > 2\sigma(I)$  were used in structure determination. All calculations were performed on a workstation of Silicon Graphics with SHELXTL program<sup>(16)</sup>. The structure was solved by direct method. All non-hydrogen atoms were located on the E-map or successive difference fourier syntheses. Non-hydrogen atom scattering factors were taken from Cromer and Waber<sup>(17)</sup>. The structure was refined by full-matrix least-squares techniques on  $F^2$ . Hydrogen atoms were located theoretically and not refined. The final cycle of full-matrix least-squares refinement converged with  $R = \Sigma(|F_0| - |F_c|) / \Sigma|F_0| = 0.0294$  and  $wR = [\Sigma [w(F_0^2 - F_c^2)^2] / \Sigma[w(F_0^2)^2]] = 0.0757$ ,  $w = 1 / [\sigma^2(F_0^2) + (0.0453P)^2 + 1.1783P]$ , where  $P = (F_0^2 + 2 F_c^2) / 3$ . The largest and smallest peak in the final difference Fourier map had a height of 1.088 and -0.457 e/Å<sup>3</sup>, respectively. The crystal data together with some experimental details were listed in Table 1.

## RESULTS AND DISCUSSION

### *Synthesis of the complex*

The reaction of coordination is easier at room temperature owing to the stability of the complex, but the solubility of this complex is very low in many solvents such as dimethyl formamide (DMF) or dimethyl sulphoxide(DMSO), thus the single crystals have to be grown by using diffusion method.

### *ESR Spectra*

The EPR spectra of the complex in a solid state are shown in Figure 1. The spectrum of the complex at room temperature [Fig. 1(a)] exhibits a shoulder peak with  $g = 2.1569$  in low field, but the information on the electronic ground state can not be analyzed. At 110K, the spectrum of the complex [Fig. 2(b)] appears four-line hyperfine splitting of copper with an average hyperfine spacing  $A=82$  G,  $g_{\perp} = 2.011$ , which is in agreement with the presence of exchange couple of copper(II) ion<sup>(18)</sup>, and an intense spectrum with  $g_{\parallel} = 2.263$ . The fact  $g_{\parallel} > g_{\perp}$  agrees with the square pyramidal structure with a  $d_{x^2-y^2}$  ground state for copper(II) complex system<sup>(19)</sup>.

### *Thermal analysis*

Thermal stability was studied in air. Figure 2 is the TG and DTA curves of  $\text{Cu}_2\text{L}_2(\text{OX}) \cdot \text{H}_2\text{O} \cdot \text{C}_2\text{H}_5\text{OH}$ . The former curve shows that the complex loses weight 6.5% (calc. value: 6.3 %) assigned to loss of a molecule of ethanol and a molecule of water of crystallization in the range of 68-108.5°C. There are an endothermic peak at 75°C in the DTA curve corresponding to TG curve. TG curve shows the complex lose 18.0% weight rate in the range of 196.5-215°C assigned as decomposition of four carbonyls including oxalate and pendant acetate (calc. 17.3%). After this complex was heated for 30 minutes at 210°C, the residue has no absorptive peak in the region of 1750-1600  $\text{cm}^{-1}$  analyzed by IR. The result shows that there is no carbonyl group in the residue. The result of elemental analysis also demonstrated the above-mentioned conclusion. There are two neighbor exothermic peaks at 203°C and 241°C in DTA curve of the complex corresponding to the TG curve. The complex absorbs heat in the process of melting (m.p. 240.5°C), the exothermic curve is divided into two neighbor peaks by this endothermic process. The break-up of the macrocycle occurs at 246°C and completely decomposition

at 547;æ based on TG curve. The results of Thermal analysis exhibit the complex is not stable over 200;æ

### *Crystal Structure of Complex*

Green single crystals of  $(\text{CuL})_2(\text{OX}) \cdot \text{H}_2\text{O} \cdot \text{C}_2\text{H}_6\text{OH}$  are obtained from ethanol at room temperature. They crystalline in the monoclinic system, space group  $P2(1)/n$ , with  $a=12.493(1)\text{\AA}$ ,  $b=8.632(1)\text{\AA}$ ,  $c=22.709(2)\text{\AA}$ ,  $\beta=103.75(1)^\circ$ . The binuclear neutral entities are centrosymmetrical(Figure 3). The two (L)Cu moieties are bridged by an oxalato group. The coordinated number is five for each Cu(II) ion with a slightly distorted square pyramid(SP) geometry [ $\tau= 0.14$  based on a formula  $(\theta - \phi)/60^{(18)}$ ]. An oxygen atom of oxalate, O(6), takes a axial sites. The equatorial plane sites are occupied by an oxygen atom O(5) from oxalate, two nitrogen atoms N(1), N(2) and a oxygen atom O(3) from carboxyl group of macrocyclic ligand. The displacement of Cu(II) ion above the equatorial plane toward the axial site O(6) is 0.1041 Å with mean deviations less than 0.0002 Å from the basal plane. The intramolecular Cu(1)...Cu(1A) distance is 5.490(1) Å. The approximate square axis of each Cu(II) ion is slightly bent with an angle of O(5)-Cu(1)-O(6)=78.86(9) $^\circ$ . The bond angles in the equatorial plane deviate appreciably from 90 $^\circ$  expected for SP geometry. The four oxygen atoms in the deprotonated oxalate are in a plane. The dihedral angle between the equatorial plane and the oxygen atom plane of oxalate is 58.74 $^\circ$ .

The two equivalence Cu-N whose bond lengths 2.032(3)Å are slightly longer than that reported values of a similar CuL<sup>(13)</sup>, are in the normal range for Cu-amine distance (1.957-2.08Å)<sup>(19-21)</sup>. Cu-O(3) length, 1.968(3), falls within the range of values(1.88-2.24)

reported for five-coordinate copper(II) complexes which have carboxyl group(-COO<sup>-</sup>) oxygen, donor sets<sup>(13,21)</sup>. Cu-O(6) bond length[2.253(2)Å] is in range of 2.23-2.48Å, but Cu-O(5) one(1.987Å) is only slightly longer than that of a chelating, nonbridging Cu-oxalate complex(1.935(6)Å)<sup>(22)</sup>, but shorter than that in [Cu(bpym)(ox)Cl<sub>2</sub>]<sub>n</sub><sup>[5g]</sup>, which is a three-dimensional net-framed structure. The packing pattern is illustrated in Fig. 4. No intramolecular hydrogen bond is observed but there are two intermolecular H-bonds: one is that O(3) atom of the acetate group forms with hydrogen of the crystalline water[O(1w)-H...O(3), 2.892(1) Å]; the other is O(4) atom of the acetate group forms with hydrogen atom of the hydroxyl group of ethanol[O(7)-H...O(4), 2.559(1) Å].

The ether oxygen atoms of parent macrocycle don't coordinate to copper ion in this complex, which agree with previous reports<sup>(13,23)</sup>.

### *Magnetic Properties*

The data of magnetic susceptibility of copper atom in a powder sample of Cu<sub>2</sub>L<sub>2</sub>(ox) is collected in the temperature range of 4.2-300K. A steep increase of the magnetic susceptibility from about 25K with decreasing T indicates the antiferromagnetic interaction between two copper (II) centers. In high temperature there is no magnetic exchange coupling between these two copper(II), since the fitted value of 2.45 μB based on the data is close to the theoretical effective magnetic moment 2.78 μB for two uncoupled d<sup>9</sup>copper ions at 298K.

For a binuclear metal complex, exchange coupling may be described by the Hamiltonian,  $H = -2J S_1 \cdot S_2$ , where J is the bilinear exchange coupling constant.



The susceptibility data for this compound were least-squares fitted to the Bleaney-Bowers equation for isotropic exchange in a dimer Cu(II).

$$\chi_m = \frac{2Ng^2\beta^2}{kT} [3 + \exp(-2J/kT)]^{-1} + N\alpha$$

where  $J$  is singlet-triplet gap in the binuclear complex. The other symbols in this equation stand for their usual meanings. When  $g$  and  $N\alpha$  are fixed, there is only one fitting parameter, the exchange parameter  $J$ . The  $g$  value has to be adjusted to 2.18 to fit the data in order to obtain a satisfactory fit to the magnetic data. If  $g$  value is fixed at 2.18, least-squares fitting of the data give a  $J$  value of  $-154.3 \text{ cm}^{-1}$ . The result shows the antiferromagnetic interaction of the complex is stronger than that of amine derivatives<sup>(8,9,10)</sup>, mepirizole<sup>(11)</sup>, phenanthroline<sup>(12)</sup> binuclear ones bridged with oxalate, but weaker than that of pyridine binuclear one that is a square pyramid structure because of a large conjugate system for Cu(II). Kahn and co-workers have demonstrated that the magnetic exchange pathway is dominated by the interaction between  $d_{x^2-y^2}$  orbitals of copper(II) and  $\sigma$  orbitals of oxalate for copper(II) complexes and that five-coordinate  $\mu$ -oxalatodicopper(II) complex can be designed with  $J$  value from approximately zero to approximately  $400 \text{ cm}^{-1}$  by modifying the ligand. In a Cu(II) dimer, each Cu(II) ion has one unpaired electron in an essential d-type orbital, the antiferromagnetic interaction reflects the level of interaction of the two unpaired-electron orbitals for each Cu(II) ion. The interaction between the two Cu(II) d orbitals is effected by an interaction of copper d orbitals with molecular orbitals of the bridging group. The structure of the complex is square pyramid with  $d_{x^2-y^2}$  for Cu(II) ion in the dimer. There are two square planar Cu(II) centers in the complex, leading to an entirely planar [LCu(OX)CuL] array, thus the magnetic orbital  $d_{x^2-y^2}$  for Cu(II) will be ideally directed toward  $\sigma$  orbital of the oxalate. This is the reason that the  $J$  value in the complex is large.

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Empirical formula	$C_{46}O_{56}Cu_2N_4O_{14}$
Formula weight	1016.03
Temperature	293(2) K
Wavelength	0.71073
Crystal system	monoclinic
Space group	P2(1)/n
Unit cell dimensions	
	$a = 12.493(1)\text{\AA} \quad \alpha = 90^\circ$
	$b = 8.632(1)\text{\AA} \quad \beta = 103.750(10)^\circ$
	$c = 22.709(2)\text{\AA} \quad \gamma = 90^\circ$
Volume, Z	$2378.7(4)\text{\AA}^3, 2$
Density (calculated)	$1.419\text{ Mg/m}^3$
Absorption coefficient	$0.963\text{ mm}^{-1}$
F(000)	1060
Crystal size	$0.40 \times 0.30 \times 0.30\text{ mm}^3$
$\theta$ range for data collection	$1.85$ to $27.5^\circ$
Limiting indices	$-1 \leq h \leq 16, -1 \leq k \leq 11, -29 \leq l \leq 29$
Reflections collected	6939
Independent reflections	5417 [R(int) = 0.0490]
Refinement method	Full-matrix least-squares on $F^2$
Data / restraints / parameters	5417 / 2 / 297
Goodness-of-fit on $F^2$	1.032
Final R indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0606, wR2 = 0.1586$
R indices (all data)	$R1 = 0.1111, wR2 = 0.1743$
Largest diff. peak and hole	$1.088$ and $-0.457\text{ e\AA}^{-3}$

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Table 2. Bond lengths [Å] and angles [°] for the complex

Cu(1)-O(3)	1.970(4)	C(1)-C(6)	1.408(7)
Cu(1)-O(5)	1.981(3)	C(1)-C(19)	1.504(6)
Cu(1)-N(2)	2.028(4)	C(2)-C(3)	1.417(8)
Cu(1)-N(1)	2.053(4)	C(3)-C(4)	1.373(8)
Cu(1)-O(6)#1	2.250(3)	C(4)-C(5)	1.394(8)
O(1)-C(6)	1.367(6)	C(5)-C(6)	1.369(7)
O(1)-C(7)	1.426(6)	C(7)-C(8)	1.499(7)
O(2)-C(9)	1.359(6)	C(9)-C(14)	1.400(7)
O(2)-C(8)	1.457(6)	C(9)-C(10)	1.409(6)
O(3)-C(21)	1.274(7)	C(10)-C(11)	1.370(7)
O(4)-C(21)	1.253(7)	C(11)-C(12)	1.417(8)
O(5)-C(22)	1.273(5)	C(12)-C(13)	1.386(8)
O(6)-C(22)	1.236(5)	C(13)-C(14)	1.395(7)
O(6)-Cu(1)#1	2.250(3)	C(14)-C(15)	1.498(6)
N(1)-C(20)	1.483(6)	C(16)-C(17)	1.522(7)
N(1)-C(16)	1.484(6)	C(17)-C(18)	1.510(7)
N(1)-C(15)	1.504(5)	C(20)-C(21)	1.517(8)
N(2)-C(18)	1.489(6)	C(22)-C(22)#1	1.545(8)
N(2)-C(19)	1.500(6)	C(23)-O(7)	1.34(2)
C(1)-C(2)	1.392(7)	C(23)-C(24)	1.58(2)
O(3)-Cu(1)-O(5)	89.3(2)	C(3)-C(4)-C(5)	120.1(5)
O(3)-Cu(1)-N(2)	162.53(14)	C(6)-C(5)-C(4)	119.4(5)
O(5)-Cu(1)-N(2)	94.64(14)	O(1)-C(6)-C(5)	124.4(5)
O(3)-Cu(1)-N(1)	84.4(2)	O(1)-C(6)-C(1)	113.6(4)
O(5)-Cu(1)-N(1)	170.95(14)	C(5)-C(6)-C(1)	122.1(5)
N(2)-Cu(1)-N(1)	93.3(2)	O(1)-C(7)-C(8)	106.4(4)
O(3)-Cu(1)-O(6)#1	98.34(13)	O(2)-C(8)-C(7)	106.9(4)
O(5)-Cu(1)-O(6)#1	78.90(11)	O(2)-C(9)-C(14)	116.3(4)
N(2)-Cu(1)-O(6)#1	99.12(13)	O(2)-C(9)-C(10)	123.1(4)
N(1)-Cu(1)-O(6)#1	95.48(12)	C(14)-C(9)-C(10)	120.5(5)
C(6)-O(1)-C(7)	118.1(4)	C(11)-C(10)-C(9)	119.4(5)
C(9)-O(2)-C(8)	118.2(4)	C(10)-C(11)-C(12)	121.3(5)
C(21)-O(3)-Cu(1)	112.7(4)	C(13)-C(12)-C(11)	118.4(5)
C(22)-O(5)-Cu(1)	117.6(3)	C(12)-C(13)-C(14)	121.6(5)
C(22)-O(6)-Cu(1)#1	108.8(3)	C(13)-C(14)-C(9)	118.9(4)
C(20)-N(1)-C(16)	108.9(4)	C(13)-C(14)-C(15)	119.9(5)
C(20)-N(1)-C(15)	109.7(4)	C(9)-C(14)-C(15)	120.8(4)
C(16)-N(1)-C(15)	108.0(4)	C(14)-C(15)-N(1)	118.0(4)
C(20)-N(1)-Cu(1)	100.8(3)	N(1)-C(16)-C(17)	115.0(4)
C(16)-N(1)-Cu(1)	108.9(3)	C(18)-C(17)-C(16)	114.9(4)
C(15)-N(1)-Cu(1)	120.0(3)	N(2)-C(18)-C(17)	113.4(4)
C(18)-N(2)-C(19)	110.4(3)	N(2)-C(19)-C(1)	112.5(4)
C(18)-N(2)-Cu(1)	112.7(3)	N(1)-C(20)-C(21)	111.5(4)
C(19)-N(2)-Cu(1)	115.5(3)	O(4)-C(21)-O(3)	123.9(6)
C(2)-C(1)-C(6)	118.4(5)	O(4)-C(21)-C(20)	119.6(6)
C(2)-C(1)-C(19)	121.9(4)	O(3)-C(21)-C(20)	116.5(5)
C(6)-C(1)-C(19)	119.7(4)	O(6)-C(22)-O(5)	125.4(4)
C(1)-C(2)-C(3)	119.2(5)	O(6)-C(22)-C(22)#1	118.5(4)
C(4)-C(3)-C(2)	120.8(5)	O(5)-C(22)-C(22)#1	116.1(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+2,-z+1

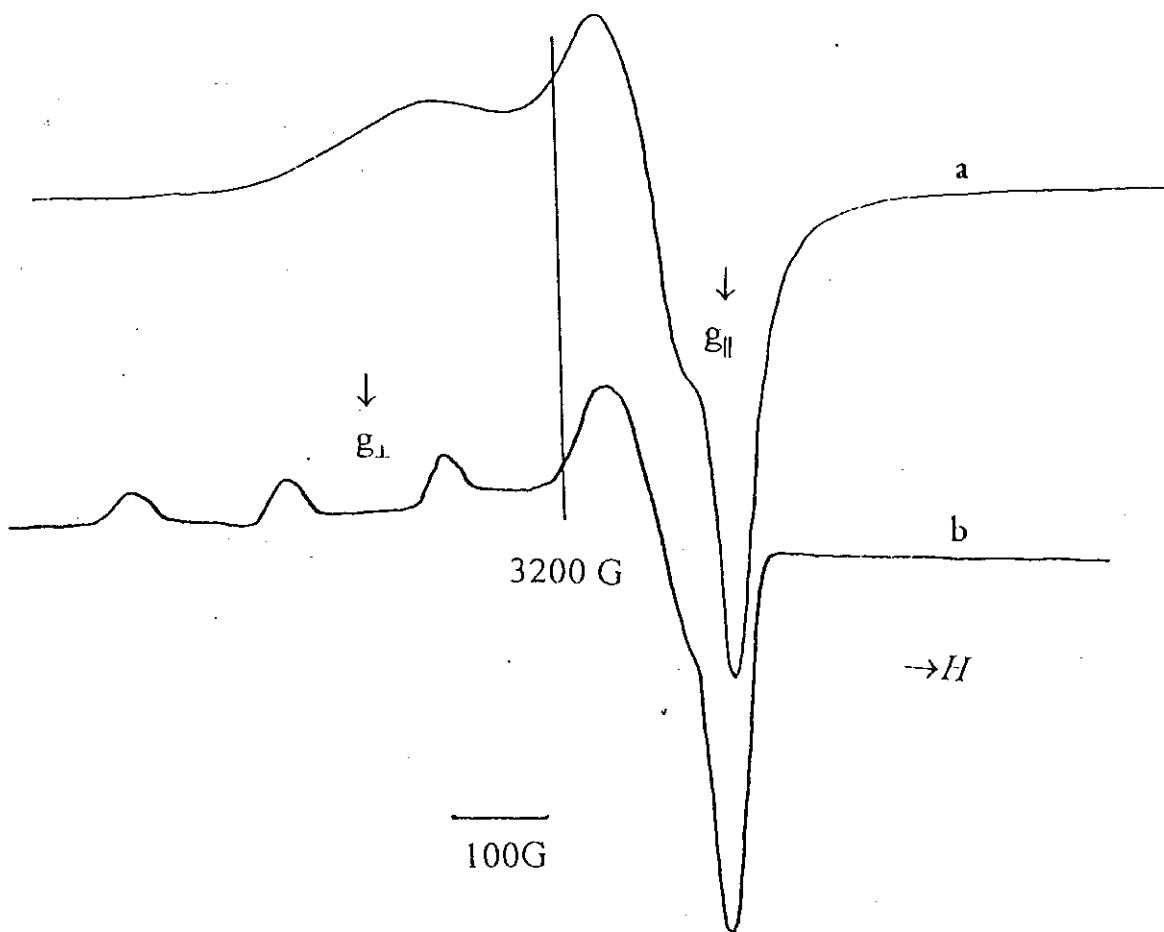


Fig. 1 EPR spectra of the complex at room temperature (a) and at 110 K (b)

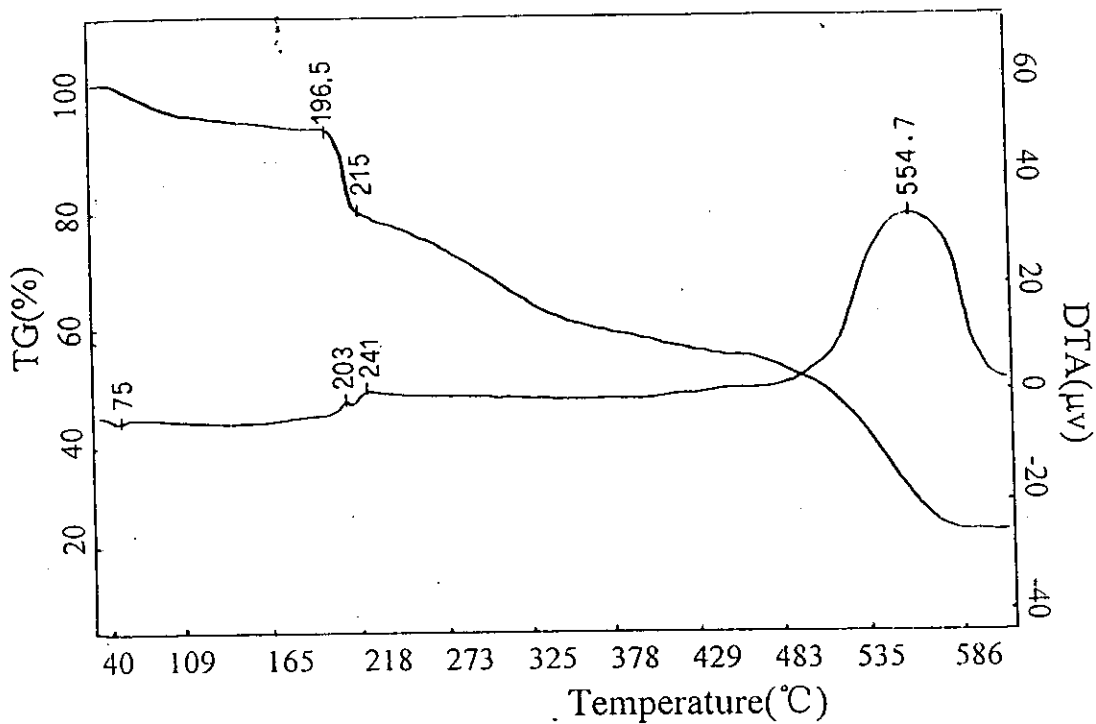


Fig. 2 TG- DTA curve of the copper complex



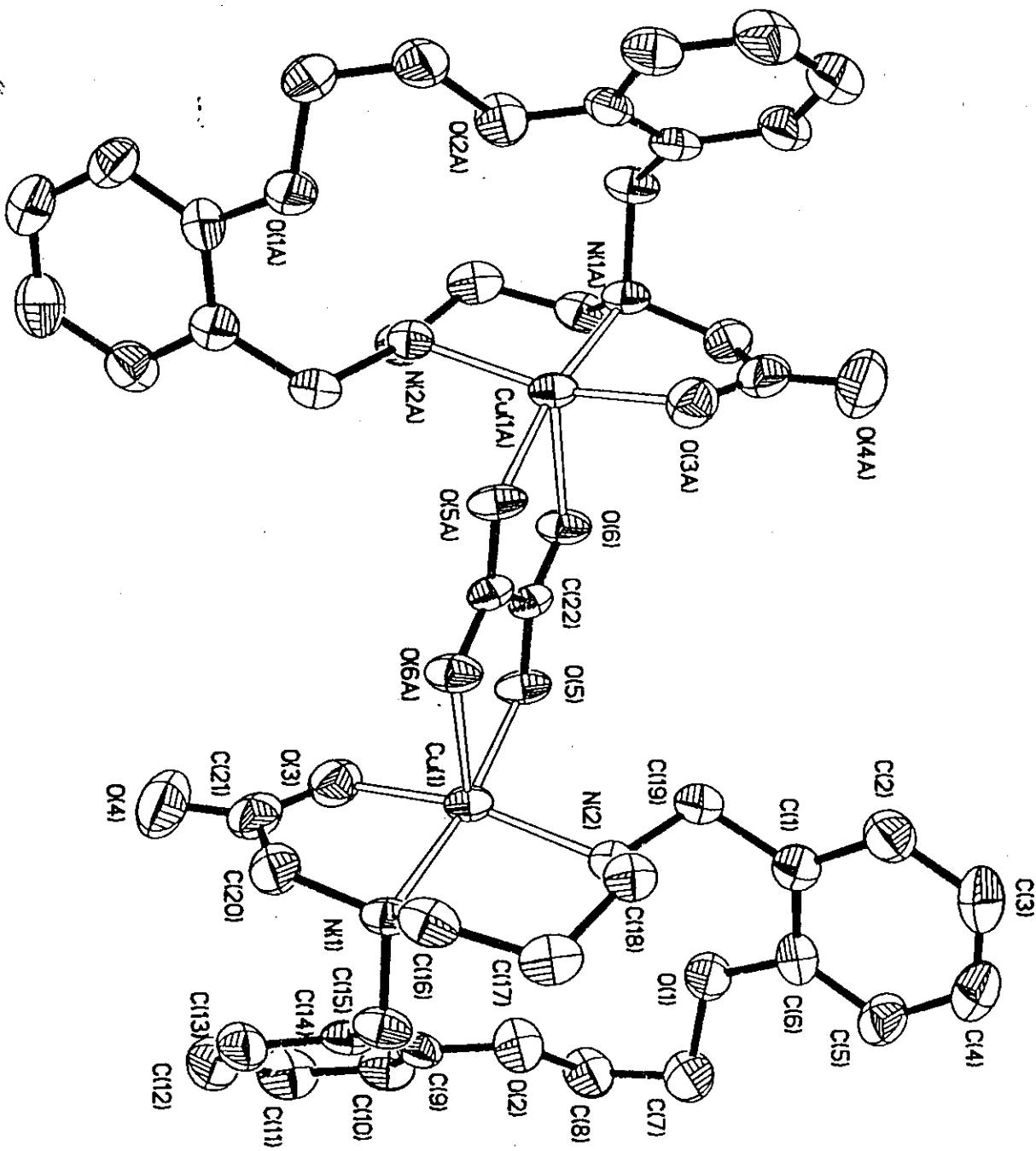


Fig. 3 Molecular Structure of the copper complex

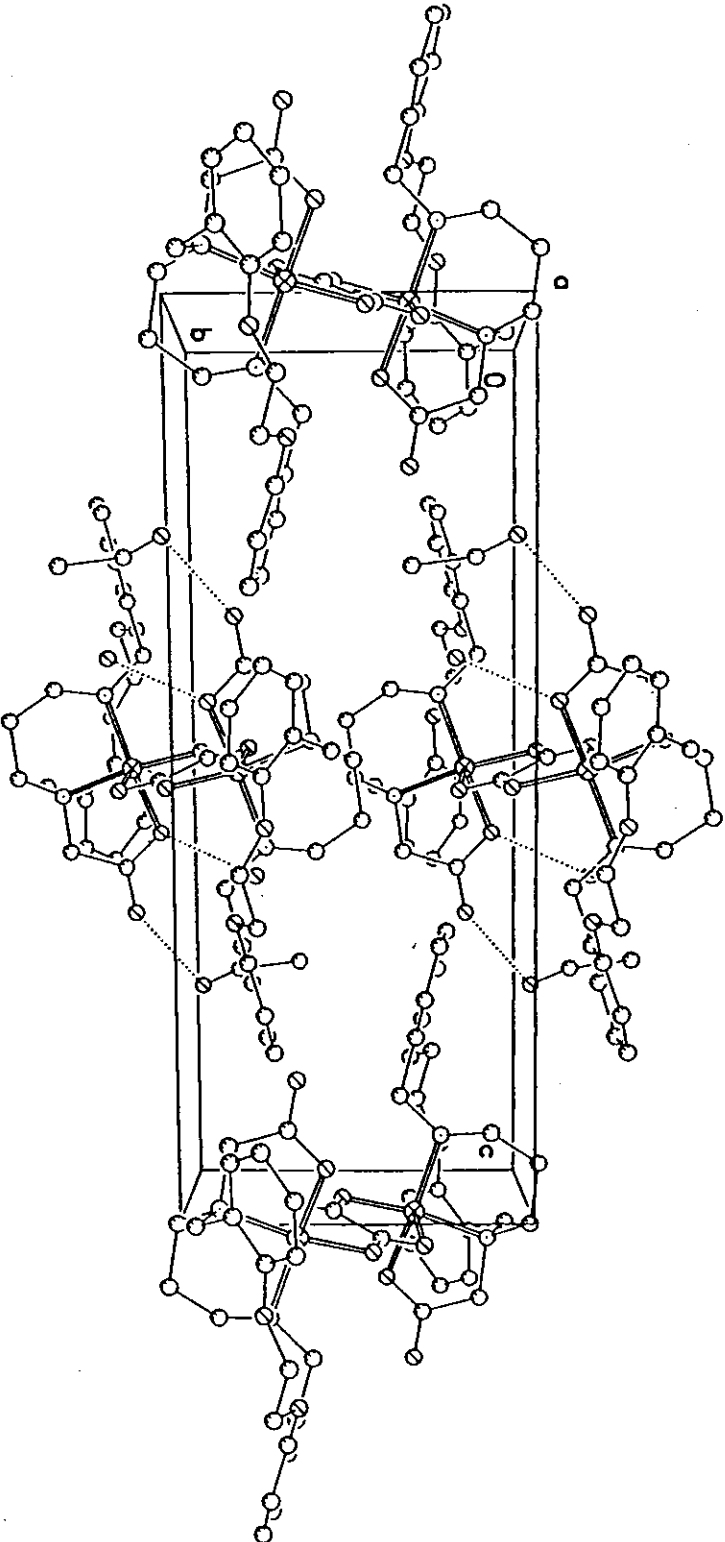


Fig. 4 Packing diagram of molecules in unit cell viewed down C axis