

二(桥-氯)-二[氯-(*N,N,N'*-三苄基乙二胺)铜(II)]的晶体结构

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Crystal Structure of Bis(μ -chloro)-bis[chloro (*N,N,N'*-trisbenzylethylenediamine)copper(II)]

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Abstract: The crystal structure of the title complex, $[\text{Cu}(\text{C}_{23}\text{H}_{26}\text{N}_2)\text{Cl}_2]_2 \cdot 2\text{CH}_2\text{Cl}_2$, has been determined by single-crystal, X-ray diffraction techniques. The compound crystallizes as dark-green prisms in space group $P2_1/c$ of the monoclinic system, with $Z=4$ and unit cell dimensions $a=1.710\,9(7)$ nm, $b=2.395\,2(11)$ nm, $c=1.348\,9(6)$ nm and $\beta=110.651(8)^\circ$. The complex consists of two similar but crystallographically independent dimers, of which Cu(II) centers display five-coordinated trigonal-bipyramidal geometry with Cu-Cu separations in two centrosymmetric dimers are 0.345 1 and 0.347 8 nm, respectively, and in each dimer the two copper centers share a common edge formed by two bridging chloride ions, each being equatorial. Solvent molecules of CH_2Cl_2 are packed together in the crystal lattice. CCDC: 253299.

Key words: *N,N,N'*-trisbenzylethylenediamine; copper(II) dimer; dichloro-bridged bond; hydrogen bond

0 Introduction

The copper dimer, bis(μ -hydroxo)-bis[chloro(*N,N,N',N'*-tetramethylethylenediamine) copper(II)] chloride ($\text{Cu}(\text{OH})\text{Cl} \cdot \text{TMEDA}$), prepared from *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and CuCl_2 , exhibited excellent catalytic activity for the preparation of 1,1'-binaphthalene-2,2'-diol (BINOL) by aerobic oxidative coupling of 2-naphthol in the past decade^[1]. Chiral catalysts employed in the preparation of optically active 1,1'-binaphthalene derivatives have attracted much attention, owing to their high chemoselectivity and high

enantioselectivity^[2]. Pan and his coworkers synthesized *N,N,N',N'*-trisbenzylethylenediamine copper(II) complex ($\text{Cu}(\text{TriBEDA})\text{Cl}_2$) by the reaction of copper(II) chloride with *N,N,N',N'*-trisbenzylethylenediamine (TBE-DA)^[3]. Recently, when our group explored the chiral catalysts for the asymmetric synthesis of BINOL, we obtained the crystal of bis(μ -chloro)-bis[chloro(*N,N,N'*-trisbenzylethylenediamine)copper(II)] ($[\text{Cu}(\text{TriBEDA})\text{Cl}_2]_2$) by chance, and its crystal structure was determined. We report herein the synthesis and molecular structure of the copper(II) dimer in order to better understand the coordination behavior.

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1 Experimental

1.1 General procedure

All solvents and other chemicals were of reagent grade and used without further purification. Melting point (uncorrected) was obtained on a Yanagimoto micro melting point apparatus. Infrared spectra were recorded as KBr discs on a BIO-RAD EXALIBUR FTS3000 spectrometer in the $4\,000\sim400\text{ cm}^{-1}$ region, and elemental analyses were measured with Elemental Vario Elrecorder.

1.2 Synthesis of TBEDA

The ligand, TBEDA, was synthesized according to the literature method described earlier^[3]. Heat the mixture of 95% ethanol (40 mL), ethylenediamine (1.19 g, 20 mmol) and saturated sodium hydroxide (6 mL) with continuous stirring at 80 °C for about 20 min, and then add slowly the solution of benzyl chloride (12.17 g, 96 mmol) and absolute ethanol (20 mL) to the above mixture. After stirring the mixture under reflux for 3 h, allow the mixture to cool to the room temperature, filter the mixture to obtain the crude product and wash the crude product with ethanol and water, respectively. Finally, recrystallize the crude product from ethanol to give white needle-shaped product with yield of 70%. m.p. 94~95 °C; IR (KBr, cm^{-1}): 3 079, 3 025, 2 949, 2 896, 1 599, 1 492, 1 451 ($\nu_{\text{C}=\text{C}}$), 1 373 ($\delta_{\text{C-H}}$), 1 243, 1 126, 1 096, 1 068, 1 028, 976 ($\nu_{\text{C-N}}$), 741, 697.

1.3 Preparation of the title complex

Dissolve equimolar quantities of anhydrous CuCl and TBEDA in methanol, stir the mixture overnight at room temperature, and then heat the mixture under reflux for about 30 min. Allow the mixture to cool, filter the mixture, and distill off the solvent to afford a bottle green powder. Dissolve the powder in a small amount of dichloromethane. Finally, allow slow evaporation of dichloromethane from the solution to give rise to dark-green, prismatic crystals after 3 days at ambient temperature. m.p. 133~135 °C; IR (KBr, cm^{-1}): 3 192 ($\nu_{\text{N-H}}$), 3 053, 3 026, 2 952, 2 872, 1 601, 1 496, 1 455 ($\nu_{\text{C}=\text{C}}$), 1 371 ($\delta_{\text{C-H}}$), 1 265, 1 134, 1 093, 1 051, 1 001 ($\nu_{\text{C-N}}$), 971, 756, 730, 706. The C, H and N contents were determined by elemental analysis (calcd for $\text{C}_{48}\text{H}_{56}\text{N}_4\text{Cl}_8\text{Cu}_2$ (%): C 52.43, H 5.13, N 5.09; found (%): C 52.89, H 5.28, N 5.57).

2 Crystal structure determination

A single crystal of the title compound with approximate dimensions of $0.30\text{ mm} \times 0.25\text{ mm} \times 0.20\text{ mm}$ was selected and mounted in a thin capillary. Determination of the unit cell and data collection was performed on a BRUKER SMART-CCD X-ray diffractometer equipped with a graphite monochromatized Mo $K\alpha$ radiation by using the θ - ω scan mode. Experimental data, methods and procedures used to elucidate the structure and other related parameters are given in Table 1. The intensity data were corrected by SADABS for absorption and the structure was solved by direct methods with SHELXS-97 program package^[4,5]. All non-hydrogen atoms were located in successive difference Fourier syntheses. The structure

Table 1 Crystallographic data for the title complex

Empirical formula	$\text{C}_{48}\text{H}_{56}\text{N}_4\text{Cl}_8\text{Cu}_2$
Formula weight	1 099.65
Temperature / K	293(2)
Wavelength / nm	0.071 073
Crystal system	Monoclinic
Space group	$P2_1/c$
<i>a</i> / nm	1.711 0(7)
<i>b</i> / nm	2.395 2(11)
<i>c</i> / nm	1.348 9(6)
β / (°)	110.651(8)
Volume / nm ³	5.173(4)
<i>Z</i>	4
Crystal size / nm	$0.30 \times 0.25 \times 0.20$
Density (calculated) / ($\text{g} \cdot \text{cm}^{-3}$)	1.412
Absorption coefficient / mm^{-1}	1.272
<i>F</i> (000)	2 264
θ Range for data collection / (°)	1.70~25.03
Limiting indices	$-14 \leq h \leq 20$, $-27 \leq k \leq 28$, $-16 \leq l \leq 15$
Reflections collected	21 094
Independent reflections	9 077 [$R(\text{int})=0.115\ 9$]
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000 000 and 0.873 047
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9 077 / 9 / 534
Goodness-of-fit on F^2	0.942
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1=0.066\ 3$, $wR_2=0.145\ 4$
<i>R</i> indices (all data)	$R_1=0.191\ 9$, $wR_2=0.191\ 5$
Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	827 and -983

refinement was performed by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms on F^2 . All hydrogen atoms were added according to theoretical modes.

CCDC: 253299.

Table 2 Selected bond distances (nm) and angles ($^\circ$) for the title complex

Cu(1A)-N(1A)	0.211 0(6)	Cu(2A)-Cl(3A)	0.226 8(2)	C(15A)-C(16A)	0.149 9(10)
Cu(1A)-N(2A)	0.199 4(6)	Cu(2A)-Cl(4A)	0.227 7(2)	C(31A)-C(32A)	0.148 8(10)
Cu(1A)-Cl(1A)	0.226 2(2)	N(1A)-C(15A)	0.150 9(9)	Cu(1A)-Cu(1B)	0.345 1
Cu(1A)-Cl(2A)	0.229 8(2)	N(2A)-C(16A)	0.149 0(9)	Cu(1A)-Cl(2B)	0.27 81
Cu(2A)-N(3A)	0.201 9(6)	N(3A)-C(32A)	0.147 9(9)	Cu(2A)-Cu(2B)	0.347 8
Cu(2A)-N(4A)	0.210 6(6)	N(4A)-C(31A)	0.147 8(9)	Cu(2A)-Cl(4B)	0.280 7
N(2A)-Cu(1A)-N(1A)	84.7(2)	N(4A)-Cu(2A)-Cl(4A)	159.99(19)	Cl(2A)-Cu(1A)-Cl(2B)	94.9
N(2A)-Cu(1A)-Cl(1A)	174.06(18)	Cl(3A)-Cu(2A)-Cl(4A)	93.21(9)	N(1A)-Cu(1A)-Cl(2B)	103.1
N(1A)-Cu(1A)-Cl(1A)	93.48(18)	C(15A)-N(1A)-Cu(1A)	106.4(4)	N(2A)-Cu(1A)-Cl(2B)	83.6
N(2A)-Cu(1A)-Cl(2A)	90.63(18)	C(16A)-C(15A)-N(1A)	108.8(6)	Cu(1A)-Cl(2A)-Cu(1B)	85.1
N(1A)-Cu(1A)-Cl(2A)	160.73(17)	N(2A)-C(16A)-C(15A)	107.5(6)	Cl(4A)-Cu(2A)-Cl(4B)	94.3
Cl(1A)-Cu(1A)-Cl(2A)	92.91(8)	C(16A)-N(2A)-Cu(1A)	105.9(4)	N(3A)-Cu(2A)-Cl(4B)	81.2
N(3A)-Cu(2A)-N(4A)	84.8(3)	C(31A)-N(4A)-Cu(2A)	106.6(5)	N(4A)-Cu(2A)-Cl(4B)	104.2
N(3A)-Cu(2A)-Cl(3A)	172.08(19)	N(4A)-C(31A)-C(32A)	109.4(6)	Cu(2A)-Cl(4A)-Cu(2B)	85.7
N(4A)-Cu(2A)-Cl(3A)	93.81(19)	N(3A)-C(32A)-C(31A)	109.3(6)		
N(3A)-Cu(2A)-Cl(4A)	90.64(19)	C(32A)-N(3A)-Cu(2A)	104.8(5)		

According to Patel^[6], the bulkiness of substituents causes the behavior of the complex in solution and in the solid state to differ from unsubstituted ethylenediamine complex. It is worthy to be noted that in hot solution, ligand containing bulky substituents such as benzyl and ethyl group, tends to bring about an oxidative degradation in the presence of an amount of other than a trace amount of copper halide (CuX_2 , $\text{X} = \text{Cl}, \text{Br}$) as catalyst, so the decomposition of TBEDA leads to the oxidative production of benzaldehyde and the formation of TriBEDA, which stereochemically is more stable in hot solution and then reacts with copper(II) cation to generate the title complex.

It is interesting that copper complex comprises two similar but crystallographically independent dimeric $[\text{Cu}(\text{TriBEDA})\text{Cl}_2]_2$ units that are well separated each other and four solvent molecules of CH_2Cl_2 packed together in the crystal lattice^[7]. A view of the dimers is shown in Fig.1, and the selected bond distances and angles for the two dimers are presented in Tables 2. The two independent dimers have similar configurations but only slightly differences in bond distances and angles. The benzene rings in the dimers

3 Results and discussion

Selected bond lengths and angles are presented in Tables 2.

do not show any unusual features, and all of bond distances and angles are in the normal range with C-C bond distances ranging from 0.135 0(13) to 0.140 2(12) nm and the C-C-C bond angles ranging from 118.3(8) to 122.2 (11) $^\circ$. The geometry around each copper atom

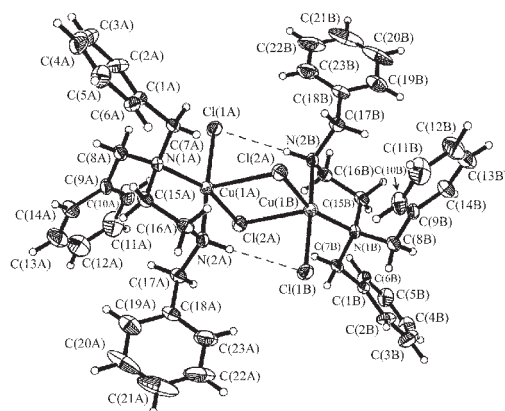


Fig.1 Molecular structure and atom numbering of the title complex with H atoms as circles of arbitrary radii and hydrogen bonds as dashed line

Molecules of CH_2Cl_2 are omitted for clarity and thermal ellipsoids are drawn at the 30% probability level.

can be described as either a distorted trigonal-bipyramidal or a distorted tetragonal-pyramidal arrangement of which two *cis* N atoms from molecule of TriBEDA acting as a didenate ligand and three Cl⁻ anions are coordinated to copper ion with two Cl⁻ anions as the bridging atoms. The Cu₂Cl₂ bridging moiety is constrained to be strictly planar by the presence of the crystallographic inversion centers in the middle of the dimer.

From the viewpoint of trigonal-bipyramidal model, for Cu(1)-dimer, the base plane would consist of the atoms Cl(2A), N(1A), Cl(2B) and Cu(1A) with atoms Cl(1A) and N(2A) occupying the apical sites, and the best least-squares plane through the basal atoms shows the deviations from the plane of 0.003 47, 0.003 87, 0.000 92 and -0.008 26 nm, respectively. The apical atoms, Cl(1A) and N(2A), are located -0.234 47 and 0.190 18 nm, respectively, on either side of this basal plane. For Cu(2)-dimer, the atoms Cl(4A), N(4A), Cl(4B) and Cu(2A) are equatorial with the deviations from the least-squares plane through the equatorial atoms being -0.003 81, -0.004 24, -0.001 03 and 0.009 08 nm, respectively, while Cl(3A) and N(3A) are axial with being displaced 0.235 90 and -0.191 05 nm, respectively, from the equatorial plane.

With use of the tetragonal-pyramidal description, in Cu(1)-dimer, atoms Cl(1A), N(1A), N(2A) and Cl(2A) make up the equatorial plane with deviations from the best least-squares plane being -0.019 65, 0.023 82, -0.024 89 and 0.020 70 nm, respectively, and the Cu(1A) atom sitting -0.012 75 nm from this plane in the direction of the apical atom Cl(2B), which is -0.290 01 nm out of the equatorial plane. In Cu(2)-dimer, atom Cl(4B) occupies the axial site and atoms Cl(3A), N(3A), N(4A) and Cl(4A) form the equatorial plane with deviations from the best least-squares plane being -0.022 03, -0.027 73, 0.026 54 and 0.023 22 nm, respectively, and the atom Cu(2A) is 0.011 22 nm below the plane, i.e., toward the apical atom Cl(4B), which deviates from the equatorial plane by -0.290 39 nm.

Based on the above data, we can arrive at such a conclusion that the distortions from the ideal geometry appear much smaller than those in the ideal tetragonal-pyramidal model, so the geometry at the copper centers is more readily described as trigonal-bipyramidal.

There is clearly no copper-copper bond in the dimers with the Cu(1A)···Cu(1B) and Cu(2A)···Cu(2B) pseudo-bond distances of 0.345 1 and 0.347 8 nm, respectively, being much greater than the values of 0.263~0.299 nm found for the Cu-Cu bonds in other dimers^[7], and with the angle of 53.9° between the two pseudo-bonds and the dihedral angle between the two oblong Cu₂Cl₂ units is 63.3°. The Cu₂Cl₂ bridging units characterized by Cu-Cl distances of 0.229 8(2) and 0.278 1 nm, and Cu(1A)-Cl(2B)-Cu(1B) angle of 85.1° for Cu(1)-dimer and Cu-Cl distances of 0.227 7(2) and 0.280 7 nm, and Cu(2A)-Cl(4B)-Cu(2B) angle of 85.7° for Cu(2)-dimer. Furthermore, the bridging Cu-Cl bonds are of unequal length and the terminal (nonbridging) Cu-Cl distances of 0.226 2(2) and 0.226 8(2) nm are shorter than the bridging Cu-Cl distances [0.229 8(2), 0.278 1, 0.227 6(2) and 0.280 7 nm], falling within values of Cu-Cl distances normally found in other bis(μ -chloral) copper(II) systems^[8-11].

The Cu-N bond distances are relatively stronger coordination bonds and the bond distances are in the range of 0.199 4(6)~0.211 0(6) nm, similar to those of 1,4-bis(3-*tert*-butyl-5-methyl-2-hydroxybenzyl)-1,4-diazacycloheptane copper(II) complex, lying in the range of 0.197 5(9)~0.202 6(7) nm^[12], and those of bis(μ -chloro)-bis[chloro(benzoyltrimethylhydrazino)copper(II)], being 0.212 2(4) nm^[13]. In addition, the Cu-N distance is observed to be considerably different from one another around each copper center with the bond distance of Cu-N of which N atom is benzyl disubstituted, being slightly longer than that of Cu-N of which N atom is benzyl monosubstituted, because of the steric hindrance effect and consequently the enhancement of electron density.

All of Cu-N and Cu-Cl distances are compare well with values Cu-N of 0.200 nm and Cu-Cl of 0.227 nm, which are the sums of the covalent radii for Cu (0.128 nm), N (0.072 nm) and Cl (0.099 nm)^[14]. In addition, contrary to the Cu-Cl-Cu' angles in the other known dihalogen-bridged copper dimers whose copper centers are in a distorted trigonal-bipyramidal environment and in bis[dichloro(*N,N,N',N'*-tetramethylethylenediamine)copper(II)]^[15], the Cu(1A)-Cl(2A)-Cu(1B) and Cu(2A)-Cl(4A)-Cu(2B) angles in the present structure are acute (85.1 and 85.7°).

As can be seen from molecular structure in Fig.1,

there exist two intramolecular hydrogen bonds in all dimer, namely the hydrogen atom attached to the N atom, which is coordinated one copper center and is benzyl monosubstituted, forms a hydrogen bond to the terminal chlorine, which is coordinated the other copper center in each dimer. The weak hydrogen bond interactions and a certain degree of π - π interactions of the phenyl rings play very important rule in the for-

mation, stability and crystallization of the complex^[16] and the two intramolecular hydrogen bonds parameters are listed in Table 3 and are in accordance with those of hydrogen bonds in tris(ethylenediamine)cobalt(III) bis(μ -chloro)-bis(trichlorocuprate(II)) dichloride dihydrate^[8] and in bis(μ -chloro)-bis[chloro(*N,N,N'*-triethylethylenediamine)copper(II)]^[9].

Table 3 Relevant intramolecular hydrogen bonds parameters (distances in nm, angles in degrees)

D-H	<i>d</i> (D-H)	<i>d</i> (H \cdots A)	D-H \cdots A	<i>d</i> (D \cdots A)	A	Symm.
N(2A)-H(2A)	0.091 0	0.253 8	164.63	0.342 3	Cl(1B)	[-x+1, -y+1, -z+1]
N(3A)-H(3A)	0.091 0	0.252 4	161.28	0.339 9	Cl(3B)	[-x, -y+2, -z]

D: Donor; A: Acceptor; Symm.: Symmetry applied in acceptor.

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