

Synthesis and Characterization of Copper(II) Complexes with Tetraazadiphenol Macrocyclic Ligand Having Cyclohexane Rings

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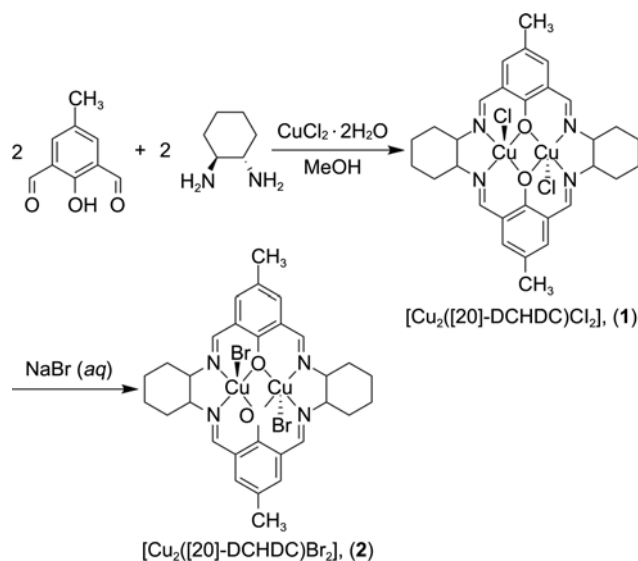
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Over the years the design and construction of compartment ligands has become a fascinating investigation field of coordination chemistry since metal complexes of these ligands have been used for the generation of compounds with specific spectroscopic and magnetic properties and thus of interesting potential applications.¹⁻³ Of the many metallo-enzymes, approximately one third of all enzymatic proteins, there is a group of copper proteins which possess functionalities ranging from electron transfer to hydrocarbon oxidation in many forms of lives.⁴⁻⁷

Our research has focused on the synthesis of optically active metal complexes based on chiral diamine skeletons.^{8,9} Schiff base Robson-type macrocycles containing two bridging phenol groups have been widely used to synthesize homo- and hetero-dinuclear complexes.^{10,11} Typically, Robson-type macrocyclic complexes like tetraazadiphenol macrocyclic transition metal complexes have been derived from the template condensation of achiral diamines such as ethyl-

enediamine or diethylenetriamine and 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde.¹⁰ However, the use of chiral diamines such as 1*R*,2*R*-diaminocyclohexane, 1*R*,2*R*-diphenylethylenediamine, and *R*-1,1-binaphthalenyl-2,2-diamine in the construction of chiral Schiff base Robson-type macrocycles has received only limited study.¹²

The advantages of chiral ligands are enantioselectivity in catalysis based on stereo-specific coordination geometry, thus regulating stereo-selectivity. In order to better understand some aspects of different molecular topologies, we explore in the current paper the synthesis, optical properties and crystal structures of two tetraazadiphenol macrocyclic dinuclear copper(II) complexes, [Cu₂([20]-DCHDC)Cl₂]-H₂O (**1**) and [Cu₂([20]-DCHDC)Br₂]-0.5H₂O (**2**) {H₂[20]-DCHDC = 14,29-dimethyl-3,10,18,25-tetraazapentacyclo-[25,3,1,0^{4,9},1^{12,16},0^{19,24}]ditriacontane-2,10,12,14,16(32),17,25,27(31),28,30-decene-31,32-diol}. The copper(II) complex **1** was prepared by the reaction of *trans*-1,2-diaminocyclohexane with cupric chloride dihydrate in methanol in the presence of 2,6-diformyl-*p*-cresol (DFPC). When [Cu₂([20]-DCHDC)Cl₂]-6H₂O (**1**) was treated with sodium bromide, as depicted in Scheme 1, the dinuclear Cu(II) bromo complex **2** was formed as pale green precipitate.



Scheme 1. Synthetic route of the dinuclear tetraazadiphenol macrocycles.

Results and Discussion

General Properties. The chloro complex **1** is soluble in water, methanol, hot DMSO and hot DMF. The bromo complex **2** is soluble in hot methanol and hot DMSO. The molar conductances of complex **1** ($\lambda_{M(\text{methanol})} = 65 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) and complex **2** ($\lambda_{M(\text{methanol})} = 49 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$) are consistent with a non-electrolytic behavior. The visible spectra of chloro and bromo complexes show a characteristic band near 650 nm. In general typical Cu(II) complexes of square pyramidal (SP) or distorted SP geometries exhibit a band over the 550-650 nm range.^{15,16} The broad bands centered at 540 nm (**1**) and 570 nm (**2**) arise from ²E_g → ²T_{2g} (*O_h*) transition, owing to characteristic Jahn-Teller effects of Cu(II) centers. The formation of dinuclear Cu(II) complexes

Table 1. Crystallographic Data and Structure Refinement for Complex **1** and **2**

Identification code	1	2
Empirical formula	C ₃₀ H ₄₆ Cl ₂ Cu ₂ N ₄ O ₈	C ₃₀ H ₄₆ Br ₂ Cu ₂ N ₄ O ₈
Formula weight	788.69	877.61
Temperature (K)	173(2)	173(2)
Crystal system	Orthorhombic	Orthorhombic
Space group	Cmca	Cmca
<i>a</i> (Å)	16.8306(7)	16.8510(7)
<i>b</i> (Å)	7.9928(3)	8.0835(3)
<i>c</i> (Å)	24.5686(10)	24.7963(11)
Volume (Å ³)	3305.1(2)	3377.6(2)
<i>Z</i>	4	4
Absorption coefficient (mm ⁻¹)	1.504	3.680
Theta range for data collection	2.42 to 26.99°	2.42 to 26.98°
Reflections collected	9675	9931
Data / restraints / parameters	1865 / 0 / 129	1905 / 0 / 129
Goodness-of-fit on <i>F</i> ²	1.082	1.129
Final <i>R</i> 1 and <i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)]	0.0294, 0.0789	0.0276, 0.0710
<i>R</i> 1 and <i>wR</i> 2 indices (all data)	0.0353, 0.0830	0.0374, 0.0795

confirmed by elemental analyses, molar conductances and electronic absorption spectra of the **1** and **2**, as well as characteristic IR absorption bands and FAB mass spectra.

For complexes **1** and **2**, strong evidence that aldehyde groups had been completely converted into imine groups in Schiff base was provided by the disappearance of the aldehydic C=O stretching band at 1728 cm⁻¹ and the appearance of a strong band at 1627 cm⁻¹ assigned as a ν(C=N) stretching band. The bands that appear near 3020–2850 cm⁻¹ and 1550–1540 cm⁻¹ are due to C–H and aromatic ring C=C stretching vibrations, respectively. The sharp absorption bands near 1240–1230 cm⁻¹ are attributed to phenolic C–O vibration. The IR spectra of **1** and **2** exhibit a weak band at 503 cm⁻¹ attributed to the Cu–N (macrocyclic) vibration.¹⁷

The FAB mass spectra of complexes **1** and **2** show the molecular ion peaks centered around *m/z* 643 and 687, which are ascribed to the [Cu₂([20]-DCHDC)Cl]⁺ and [Cu₂([20]-DCHDC)Br]⁺ species, respectively, supporting strongly the presence of dinuclear active sites in the macrocyclic complexes.

Description of Crystal Structures. Complex **2** is isostructural with complex **1**, which is confirmed by the single crystal X-ray crystallographic determination (Table 1 and 2). Therefore only the structure of complex **1** is described here in detail. Selected bond lengths and angles relevant to the coordination geometries for both complexes **1** and **2** are listed in Table 2.

The chloro complex **1** crystallizes in the orthorhombic space group *Cmca* with *a* = 16.8306(7) Å, *b* = 7.9928(3) Å, *c* = 24.5686(10) Å. The crystal structure of complex **1** is composed of a neutral [Cu₂([20]-DCHDC)Cl₂] unit and six lattice water molecules as shown in Figure 1. The dinuclear complex **1** with two Cu(II) ions has a crystallographically imposed *C*_{2*v*} symmetry with the 2-fold axis, passed through O1 and C5 atoms, perpendicular to the plane containing the

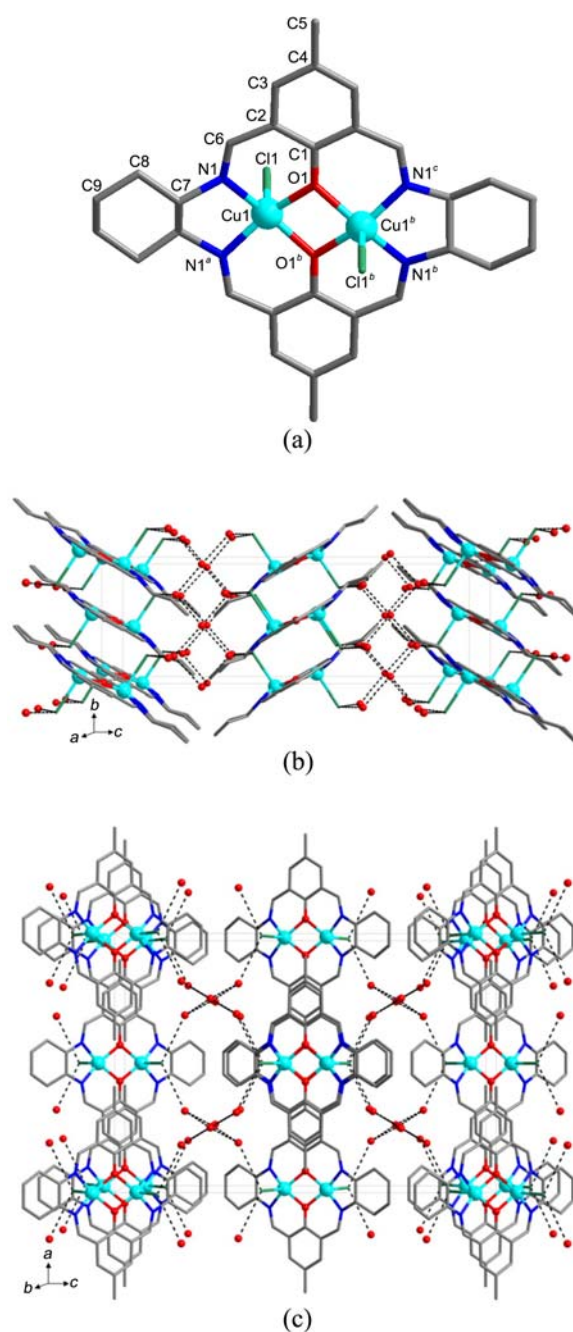


Figure 1. (a) Coordination geometry of complex **1**. (b) and (c) Perspective views of the unit cell with hydrogen bonds shown as dashed lines along the *a*- and *b*-axis, respectively. Hydrogen and disordered atoms are omitted for clarity. [Symmetry codes: ^a*x*+1, *y*, *z*; ^b*x*+1, *-y*, *-z*+1; ^c*x*, *-y*, *-z*+1.]

two Cu(II) ions and two coordinated chloride anions. Thus the asymmetric unit of **1** consists of a half of copper(II) ion, a quarter of [20]-DCHDC macrocyclic ligand, a half of chloride anion and one and a half of lattice water molecules.

In crystal structure of **1**, each copper(II) ion has a five-coordinated square-pyramidal geometry. The N₂O₂-type of macrocycle [20]-DCHDC tetradentate ligand occupies basal positions and an axial position is bonded with a chloride anion. To the best of our knowledge, complexes **1** and **2**

Table 2. Selected Bond Lengths (Å) and Angles (°) for **1** and **2**

Complex 1			
Cu1-N1	1.9142(17)	Cu1-O1	1.9187(13)
Cu1-Cl1	2.5217(9)	Cu1...Cu1B	2.9703(7)
N1-Cu1-N1 ^a	88.86(10)	N1-Cu1-O1	92.41(7)
N1-Cu1-O1 ^b	158.21(6)	N1-Cu1-Cl1	97.11(6)
N1A-Cu1-O1 ^b	92.41(7)	N1A-Cu1-Cl1	97.11(6)
O1-Cu1-N1 ^a	158.21(6)	O1-Cu1-O1B	78.57(9)
O1-Cu1-Cl1	104.30(2)	O1B-Cu1-Cl1	104.30(2)
Complex 2			
Cu1-N1	1.904(2)	Cu1-O1	1.9131(15)
Cu1-Br1	2.6822(6)	Cu1...Cu1B	2.9547(8)
N1-Cu1-N1 ^a	89.30(12)	N1-Cu1-O1	92.90(8)
N1-Cu1-O1 ^b	160.66(8)	N1-Cu1-Br1	96.25(7)
N1A-Cu1-O1 ^b	92.90(8)	N1A-Cu1-Br1	96.25(7)
O1-Cu1-N1 ^a	160.66(8)	O1-Cu1-O1B	78.89(10)
O1-Cu1-Br1	102.60(2)	O1B-Cu1-Br1	102.60(2)

Symmetry codes: ^a-x+1, y, z; ^b-x+1, -y, -z+1.

represents the first structurally characterized examples of a macrocyclic dinuclear chloro or bromo Cu(II) complex containing two monodentate anions.

The macrocyclic dinuclear complex **1** adopts a non-flat structure with the two square pyramidal copper centers bridged by the two phenoxide oxygen atoms, with the angle Cu-O-Cu of 129.28(5)°. The basal Cu-ligand bond lengths [Cu1-N1 1.9142(17) Å, Cu1-O1 1.9187(17) Å] are similar with those of azido cupric complex with the [20]-DCHDC macrocyclic ligand.⁸ Two chloride ions occupy apical positions in a trans arrangement with somewhat longer contacts [Cu-Cl 2.5217(9) Å] owing to the Jahn-Teller effect in *d*⁹ electronic configuration. Both the copper centers are displaced toward the chloride ions by 0.352(1) Å from the mean N₂O₂ basal plane. The Cu...Cu separation distance of 2.9703(7) Å is slightly longer than the sum of van der Waals radius of Cu atoms (2.86 Å).¹⁹

As shown in Figure 1(b), (c) and Table 3, there are two

Table 3. Hydrogen Bonds (Å and deg) for Complexes **1** and **2**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
Cl complex				
O1W-H1WA...Cl1	0.84	2.61	3.435(2)	166.8
O1W-H1WB...O2W	0.87	2.09	2.922(3)	158.2
O1W-H1WC...O2W ⁱ	0.85	2.12	2.890(3)	150.9
O2W-H2WA...O1W ⁱⁱ	0.85	2.06	2.890(3)	166.4
O2W-H2WB...O1W ⁱⁱⁱ	0.84	2.14	2.922(3)	154.1
Br complex				
O1W-H1WA...Br1	0.84	2.69	3.518(2)	167.1
O1W-H1WB...O2W	0.88	2.05	2.894(3)	159.8
O1W-H1WC...O2W ⁱ	0.86	2.08	2.871(3)	152.8
O2W-H2WA...O1W ⁱⁱ	0.85	2.04	2.871(3)	164.8
O2W-H2WB...O1W ⁱⁱⁱ	0.85	2.12	2.894(3)	152.4

Symmetry codes: ⁱx, y-1/2, -z+3/2; ⁱⁱ-x+3/2, y+1/2, z; ⁱⁱⁱ-x+3/2, y, -z+3/2.

types of intermolecular hydrogen bonds in crystal packing structure of **1**. One is O-H...Cl type of hydrogen bonds between lattice water molecules and the coordinated chloride atoms (O1W-H1WA...Cl1 3.435(2) Å). The other is O-H...O fashion of hydrogen bonds formed by the lattice water molecules, where the separation distances between hydrogen donor and acceptor atoms are 2.922(3) and 2.890(3) Å. The lattice water molecules are connected with each other by hydrogen bonds propagating like an infinite 1D chain (Fig. 1(b)). The 1D chain is further connected by hydrogen bonds between chloride atoms and water molecules to construct a 3D structure. Moreover the 3D structure is stabilized by intermolecular π ... π interaction between the parallel aromatic rings with a centroid-to-centroid distance of 4.03 Å and a distance between the aromatic planes of 3.46(2) Å.

In summary, the one-pot reaction of *trans*-1,2-diaminocyclohexane and cupric chloride dihydrate with DFPC afforded a dinuclear Cu(II) complex **1** of macrocyclic ligand [20]-DCHDC. By replacing the coordinated chloride ions in complex **1** with bromide ions, an isostructural dinuclear Cu(II) complex **2** was isolated. Both complexes have been fully characterized by element analysis, conductance, electronic and IR spectra as well as FAB-MS method. The crystal structures of both complexes determined by X-ray crystallography reveal the two square pyramidal copper(II) centers bridged by the two phenoxide oxygen atoms of [20]-DCHDC macrocyclic ligand. Furthermore, both complexes exhibit the 3D supramolecular network by the O-H...Cl and O-H...O hydrogen bonds as well as the π ... π interaction.

Experimental

General Methods. All chemicals were commercial analytical reagents and were used without further purification. Solvents used for electrochemical and spectroscopic studies were purified by standard procedures. 2,6-Diformyl-*p*-cresol (DFPC) was prepared with high yields by an improved oxidation method using active manganese(IV) dioxide.¹⁷

Measurements. Microanalyses of C, H, and N were carried out using LECO CHN-900 analyzer. Conductance measurements of the complexes were performed in CH₃OH or DMSO at 25 ± 1 °C using an ORION 162 conductivity temperature meter. IR spectra were recorded with a Bruker FSS66 FT-IR spectrometer. FAB-MS spectra were obtained on a JEOL JMS-700 Mass Spectrometer using argon (6 kV, 10 mA) as the FAB gas. The accelerating voltage was 10 kV and glycerol was used as the matrix. The mass spectrometer was operated in positive ion mode and mass spectra were calibrated by Alkali-CsI positive.

Synthesis of [Cu₂([20]-DCHDC)Cl₂·6H₂O (1). A methanolic solution (50 mL) of 2,6-diformyl-*p*-cresol (3.280 g, 20 mmol) was added to a suspension of the *trans*-1,2-diaminocyclohexane (2.400 g, 20 mmol) and cupric chloride dihydrate (3.410 g, 20 mmol) in methanol (30 mL). The mixture was refluxed for 2 h, forming a deep blue solution. The solution was concentrated until a dark precipitates were just resulted. Tetrahydrofuran (200 mL) was added to the

mixture, and the resulted pale green products were filtered, thoroughly washed with water, and dried at 150 °C *in vacuo*. Yield: 64%. Anal. Calcd (Found) % for C₃₀H₃₄N₄O₂Cl₂Cu₂: C, 52.94 (52.62); H, 5.04 (5.01); N, 8.23 (8.15). IR (KBr pellet, cm⁻¹) 3454, 3022, 2929, 2858, 1627, 1548, 1448, 1382, 1348, 1311, 1240, 862, 819, 769, 503. λ_M(methanol): 65 ohm⁻¹cm²mol⁻¹.

Synthesis of [Cu₂([20]-DCHDC)Br₂]6H₂O (2). To an aqueous solution (150 mL) of [Cu₂([20]-DCHDC)Cl₂]·H₂O (0.6986 g, 1 mmol), sodium bromide (0.5145 g, 5 mmol) in water (20 mL) was added dropwise with stirring. The resulting mixture was refluxed for 2 h, and then resulting pale green precipitates were collected by filtration, thoroughly washed with water, and dried *in vacuo*. Yield 80%. Anal. Calcd (Found) % for C₃₀H₃₄N₄O₂Br₂Cu₂: C, 46.82 (46.55); H, 4.45 (4.31); N, 7.28 (7.16). IR (KBr pellet, cm⁻¹) 3429, 3001, 2933, 2860, 1627, 1544, 1444, 1382, 1346, 1301, 1236, 864, 817, 769, 503. λ_M(DMSO): 49 ohm⁻¹cm²mol⁻¹.

X-ray Crystallography of Complexes. Green crystals of [Cu₂([20]-DCHDC)Cl₂]·6H₂O (**1**) suitable for X-ray diffraction study were obtained by slow evaporation of H₂O-CH₃OH (1:1) solution of complex **1**. Pale green crystals of [Cu₂([20]-DCHDC)Br₂]·6H₂O (**2**) with X-ray quality were obtained by recrystallization of the complex **2** from warm methanol. The single crystal of complexes **1** and **2** were attached to glass fibers and mounted on a Bruker SMART diffractometer equipped with a graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation, and a CCD detector; 50 frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. All data collections were performed at 173 K. Decay was monitored by 50 standard data frames measured at the beginning and end of data collection. The program SAINTPLUS¹³ was used for integration of the diffraction profiles. All of the calculations for the structure determination were carried out using the SHELXTL package.¹⁴ In all cases, all nonhydrogen atoms were refined anisotropically and all hydrogen atoms, except all water molecules for both complexes **1** and **2**, were placed in idealized positions and refined isotropically in a riding manner along with the their respective parent atoms. In the case of water molecules, the initial positions of the hydrogen atoms of water molecule were obtained from difference electron density maps. Their positional parameters were then refined using a riding model. In both complexes, two carbon atoms (C7 and C9) of cyclohexane moiety were disordered over two sites with site occupancy factor of 0.50.

The summary of the crystal data, experimental details and refinement results for complexes **1** and **2** is listed in Table 1.

Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC-296788 for **1** and 296787 for **2**). These data can be obtained free of charge *via* <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk (or FIZ, D-76344, Eggenstein-Leopoldshafen, Germany, E-mail: crysdata@fiz-karlsruhe.de).

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