Structural and Spectroscopic Studies on $[Cu(DACH)_2(H_2O)]Cl_2$ (DACH = 1,4-Diazacycloheptane)

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A penta-coordinated Cu(II) complex with 1,4-diazacycloheptane (DACH), $[Cu(DACH)_2(H_2O)]Cl_2$ (1), has been synthesized and characterized by X-ray diffraction, IR spectra, elemental analyses, thermal analyses, UV-Vis and ESR techniques. Complex 1 crystallizes in orthorhombic crystal system, *Pbcn* space group with $a = 1.6075(4)$, $b = 1.0539(3)$, $c = 0.9195(3)$ nm, $V = 1.5578(7)$ nm^3, $M_r = 352.79$, $Z = 4$, $D_c = 1.487$ g/cm^3, final $R = 0.0451$ and $wR = 0.1294$. The structure of 1 indicates that the central Cu(II) atom is penta-coordinated by four nitrogen atoms of two DACH moieties at the equatorial positions and a water molecule at the axis position. The coordination geometry of Cu(II) could be considered as an approximately ideal square-pyramidal environment. Both DACH rings arrange in *cis*-form and are predominantly in the boat-boat conformation (80%) with some disorder to the chair-chair conformation (20%). The Cl^- anions are hydrogen bonded with the nitrogen donors of the DACH rings and the oxygen donor of the coordinated H_2O molecule to form a one-dimensional zigzag linear structure. The solution behaviors of 1 are also discussed in detail by Uv-vis and ESR technique.

Keywords crystal structure, 1,4-diazacyclohepane (DACH), Cu(II) complex, electronic spectra, ESR

Introduction

Mesocyclic ligands (molecules contain seven- to ten-membered rings) occupy an important place between acyclic and macrocyclic ligands which offer several attractive features as a framework for ligand development: an exceptionally strong ligand field, unique conformational requirements and the potential for further functionalzation.[1,2] 1,5-Diazacyclooctane (DACO) and 1,4-diazacycloheptane (DACH) are the most important examples of diazamesocyclic ligands and have been studied on the spectral properties because these saturated ligands can essentially avoid of the effects arising from π-bonding and the metal atom orbitals are subject solely to effects arising from the apical and/or equatorial ligation.[3-6]

However, to our knowledge, the study on the crystal structure of the metal complexes with DACH is still quite rare.[7-9] In contrast to the symmetric disposition of DACO moieties around the metal atom in bis-DACO metal complexes, the DACH may be attached to the metal atom in two different ways since it has both a dimethylene and trimethylene group spanning the two nitrogen atoms: *cis*-form[7] and *trans*-form.[8] As a continuous of our work of this interesting project,[10-12] It is reported that herein the synthesis, crystal structure and solution behaviors of a new Cu(II) complex of DACH, $[Cu(DACH)_2H_2O]Cl_2$ (**1**, Chart 1), assembling into a zigzag chain through hydrogen bonds.

Experimental

Materials and general methods

All the reagents for syntheses and analyses were of

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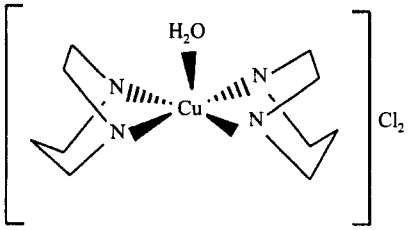
analytical grade and used without further purification. FT-IR spectrum (KBr pellets) was taken on a FT-IR 170SX (Nicolet) spectrometer and electronic absorption spectrum on a Hitachi UV-3010 spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. Thermal stability (TG-DTA) studies were carried out on a Dupont thermal analyzer. ESR spectra (X-band) in both solid state and solution were recorded on a Bruker ER-200-DSRC10 spectrometer.

Chart 1



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Synthesis of the title complex **1**

A mixture of $CuCl_2 \cdot 2H_2O$ (138 mg, 0.8 mmol) and 1,4-diazacycloheptane (160 mg, 1.6 mmol) was dissolved in methanol (10 mL) at room temperature. Violet powders precipitated immediately. The complex was filtered and washed several times with anhydrous ether. Yield 240 mg (85%). Block-shaped single crystals suitable for X-ray diffraction were recrystallized from CH_3COCH_3/CH_3OH ($V/V = 10/1$). FT-IR (KBr) ν: 3426 (b), 3225 (vs), 3133 (vs), 2957 (m), 2882 (s), 1665 (m), 1477 (m), 1456 (m), 1445 (m), 1436 (m), 1427 (m), 1384 (w), 1365 (w), 1323 (m), 1291 (w), 1248 (w), 1128 (s), 1075 (w), 974 (vs), 886 (m), 783 (w), 684 (w) cm^{-1}; Anal. calcd for $C_{10}H_{26}Cl_2CuN_4O$: C 34.04, H 7.43, N 15.88; found C 33.97, H 7.66, N 15.76.

X-Ray crystallography

Single-crystal X-ray diffraction measurement of **1** was carried out with a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection. The determination of unit cell parameters and data collections were performed with Mo K_α radiation (λ = 0.071073 nm). Unit cell dimensions were obtained with least-squares refinements and the structure was solved by direct methods using SHELXL-97 program.[13] A total of 1597 independent reflections were collected in the range of $2.31 < \theta < 26.39°$ with $R_{int} = 0.0354$ by ω scan mode at room temperature. All data were corrected using SADABS method with $T_{max} = 0.8542$ and $T_{min} = 0.7222$.

Cu(II) atoms were located from E-maps and the other non-hydrogen atoms and the hydrogen atoms of the coordinated water were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms of the ligand were added theoretically, and riding on the concerned atoms and refined with fixed thermal factors. Crystallographic data and experimental details for structural analyses are summarized in Table 1.

Table 1 Crystallographic data and structure refinement summary for complex **1**

Formula	$C_{10}H_{26}Cl_2N_4CuO$
M_r	352.79
Crystal system	orthorhombic
Space group	*Pbcn*
Temp. (K)	298 ± 2
a (nm)	1.6075(4)
b (nm)	1.0539(3)
c (nm)	0.9195(3)
V (nm^3)	1.5578(7)
D_x (g/cm^3)	1.604
Z	4
w^{-1}	$\sigma^2(F_o^2) + (0.0656P)^2 + 2.5550P$
R	0.0451
R_w	0.1294
Δ/σ_{max} and Δ/σ_{min}	0.065 and 0.011
Max. and Min. Res. Peak (e/nm^3)	523 and −498

Results and discussion

Synthesis and general characterization

The reaction of DACH with $CuCl_2 \cdot 2H_2O$ in 2:1 ratio in CH_3OH gives the powder having the formula C_{10}-

$H_{26}Cl_2CuN_4O$, which is dissolvable in H_2O and normal organic solvents (such as CH_3OH, C_2H_5OH, CH_3CN, DMF and $MeNO_2$), and difficultly solvable in CH_3COCH_3 and $PhNO_2$. Complex **1** is air stable at room temperature and without melting point before decomposition. A significant feature observed in the IR spectrum of the complex is a broad band at *ca*. 3400 cm^{-1} due to the OH stretch of the coordinated H_2O molecule. Thermal analyses (from room temperature to 800 ℃) show that the decomposition starts when it is heated at above 273 ℃ and stops at above 594 ℃. The TGA data indicate that the total weight loss (4.85% at 90—110 ℃) is consistent with the loss for one coordinated water molecule (the theoretical weight loss is 5.10%).

Description of the crystal structure

The ORTEP structure of $[Cu(DACH)_2(H_2O)]^{2+}$ cation in complex **1** with atom labeling is shown in Fig. 1. The atomic coordinates and thermal parameters are listed in Table 2, and the selected bond distances and angles are given in Table 3.

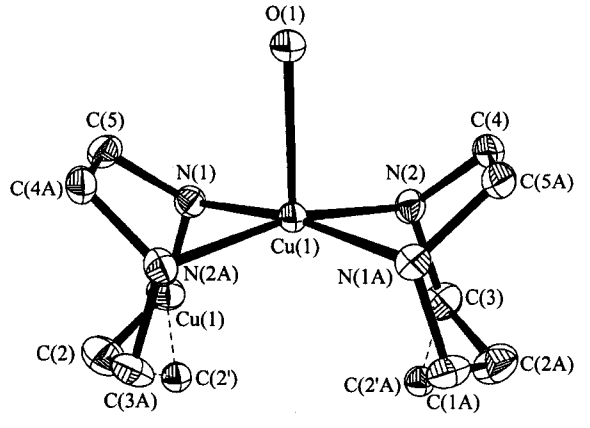

Fig. 1 ORTEP drawing of the $[Cu(DACH)_2(H_2O)]^{2+}$ cation in **1** with 30% probability thermal ellipsoids.

The structure of the title complex **1** comprises a discrete $[Cu(DACH)_2(H_2O)]^{2+}$ cation and two non-coordinated Cl^- anions. The Cu(II) ion lies on a crystallographic two-fold rotation axis. The Cu(II) center is coordinated by four nitrogen atoms of the DACH moieties and the oxygen donor of the coordinated H_2O molecule completes the coordination polyhedron. The coordination geometry of the penta-coordinated Cu(II) ion (CuN_4O) could be best described as a square-pyramid with the oxygen anion occupying the axial position, which is reflected by the τ value (0.07) defined by Addison *et al* ($\tau = 0$ for an ideal square-pyramid, and $\tau = 1$ for an ideal trigonal bipyramid).[14] The central Cu(II) ion is 0.02097 nm above the basal least-squares plane defined by N(1), N(2), N(1A) and N(2A), towards the apical O(1) atom. The Cl^- anions have not a close contact to the Cu(II) centers since the shortest Cu···Cl distance is 0.4198 nm.

Table 2 Atomic coordinates ($\times 10^4$) and thermal parameters ($nm^2 \times 10$) of non-hydrogen atoms

Atom	*x*	*y*	*z*	*U*(eq)
Cu(1)	5000	2980(1)	2500	29(1)
N(1)	4461(2)	2815(3)	523(4)	35(1)
C(1)	4234(3)	1461(4)	247(5)	47(1)
C(2')	4070(13)	777(18)	1680(20)	29(7)
C(4)	6674(3)	3631(4)	2935(5)	42(1)
Cl(1)	8755(1)	2181(1)	3492(1)	44(1)
O(1)	5000	5151(5)	2500	56(1)
N(2)	6214(2)	2743(3)	1992(4)	37(1)
C(2)	3516(5)	1040(7)	1156(8)	59(3)
C(3)	6464(3)	1394(5)	2233(6)	48(1)
C(5)	3726(3)	3658(4)	550(5)	45(1)

The two independent Cu—N_{DACH} bond distances are nearly the same [0.2021(3) vs. 0.2022(3) nm], both being normal Cu—N coordination bonds. The C—C bond distances in the methylene groups of DACH are in the range of 0.1471(19)—0.1534(7) nm, which are normal aliphatic C—C bonds with sp^3 hybrid. Both DACH moieties arrange in *cis*-form as observed in the previous report on Cu(II) complex of DACH.[8] However, the disorder of C(2) was found in this crystal. The site occupation factor for C(2) was refined to 80%, and for C(2') to 20%. That is, the DACH ring is predominantly in the boat-boat conformation with some disorder to the chair-chair conformation.

An important feature of **1** to note is that the uncoordinated Cl^- anions bridge the complex cations to form a one-dimensional zigzag chain along the *a*-axis through N—H···Cl and O—H···Cl hydrogen bonds as shown in Fig. 2. The uncoordinated chloride anion accepts the hydrogen atoms of the nitrogen atoms of the DACH ring, forming two inter-molecule hydrogen bond N(1)—H(1A)···Cl(1) ($-x+3/2$, $-y+1/2$, $z-1/2$)

and N(2)—H(2A)···Cl(1) ($-x+3/2$, $-y+1/2$, $z-1/2$). Each chloride anion also forms acceptor of hydrogen bond, O(1)—H(1)···Cl(1) ($-x+3/2$, $y+1/2$, z), with the water molecule of another adjacent cation. Therefore, the Cl^- anions bridge the cation units to form a one-dimensional zigzag linear structure.

Table 3 Selected bond lengths (10^{-1} nm) and angles (°) for complex **1**

Bond length (10^{-1} nm)			
Cu(1)—N(1)	2.021(3)	Cu(1)—N(2)	2.022(3)
Cu(1)—O(1)	2.288(5)	N(1)—C(5)	1.479(5)
N(1)—C(1)	1.494(6)	N(2)—C(4)	1.476(6)
N(2)—C(3)	1.493(6)		
Bond angle (°)			
N(1)-Cu(1)-N(1A)	170.1(2)	N(1)-Cu(1)-N(2A)	77.50(15)
N(1)-Cu(1)-N(2)	101.25(15)	N(2A)-Cu(1)-N(2)	165.8(2)
N(1)-Cu(1)-O(1)	94.96(10)	N(2)-Cu(1)-O(1)	97.12(11)

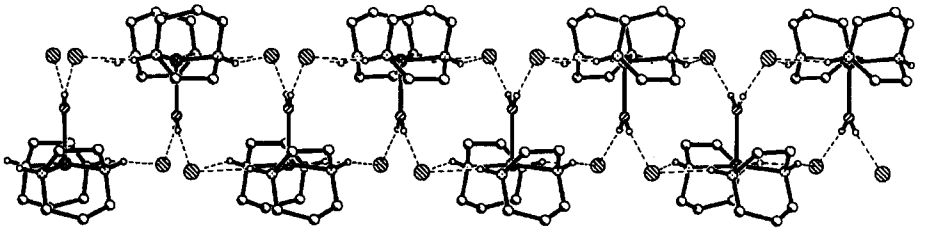

Fig. 2 View of the one-dimensional zigzag chain in the title complex. Important hydrogen bond distances (10^{-1} nm) and angles (°): N(1)···Cl(1) 3.422, N(2)···Cl(1) 3.220, O(1)···Cl(1) 3.068; N(1)-H(1A)···Cl(1) 148.90, N(2)-H(2A)···Cl(1) 159.39, O(1)-H(1)···Cl(1) 161.82.

Electronic spectra

Visible absorption spectra for complex **1** in various solvents are shown in Fig. 3. The UV-Vis spectral data for complex **1** in diffenent solution show absorption maxima at 560, 604, 616, 606, 617 and 609 nm, respectively. This spectral feature is typical of penta-coordinated Cu(II) complexes with square-pyramidal geometry which generally exhibits a band in the 550—650 nm range (d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$).[15,16] It exhibits one strong ligand-to-metal charge transfer (LMCT) band toward higher energy at 370 nm in $MeNO_2$,[17] which is also observed in that of $[Cu(DACH)_2Br_2]$.[6] In additon, the electronic spectra in other solution all display characteristic absorptions at 250—280 nm assigned to the ligand transition.

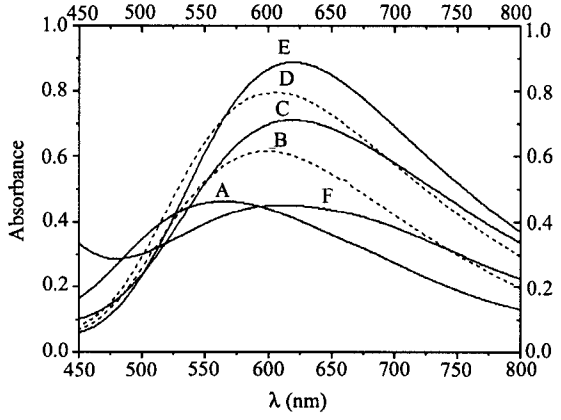

Fig. 3 Electronic absorption maxima for **1** in (A) H_2O, (B) CH_3OH, (C) CH_3CN, (D) C_2H_5OH, (E) DMF and (F) $MeNO_2$.

Electron spin resonance spectra

The X-band ESR spectra of **1** were measured in the polycrystalline state and in methanol solution, at room temperature and 110 K. The room-temperature ESR spectrum is characterized by one broad line of width 55 G centered at $g_{iso} = 2.12$ (Fig. 4a). This kind of behavior is very common in many Cu(II) complexes. These isotropic ESR spectra are most commonly due to dipolar broading and enhanced spin-lattice relaxation of

the chloride anion.[18] At 110 K, the spectrum of **1** is almost the same as that at room temperature, indicating a similar situation.

The room-temperature solution spectrum is spilt into four equally spaced absorptions (Fig. 4b) by the interaction with the Cu(II) nucleus (I = 3/2). The hyperfine splitting lines characteristic of Cu(II) is also observed for the frozen solution of **1** (Fig. 4c). The approximate ESR parameters are obtained as $g_{iso} = 2.16$ ($A_{iso} = 107$ G), $g_{\parallel} = 2.25$ ($A_{\parallel} = 192$ G) and $g_{\perp} = 2.11$ ($A_{\perp} = 65$ G), where $g_{\perp} = (3g_{iso} - g_{\parallel})/2$ and $A_{\perp} = (3A_{iso} - A_{\parallel})/2$.[19] It has the relation $g_{\parallel} > g_{\perp} > g_e$, and larger $A_{\parallel}$ value, indicating slighter distortion in the coordination geometry of the Cu(II) center away from the square-pyramid in solution,[20] which is similar to the geometry in the solid state.

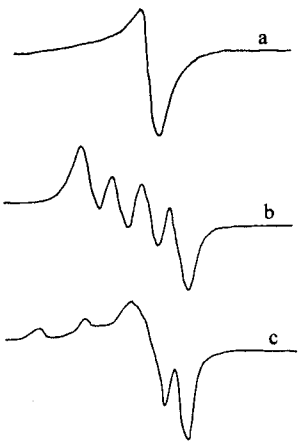

Fig. 4 X-band ESR spectra of **1** in (a) solid state at R.T., (b) CH_3OH at R.T. and (c) CH_3OH at 110 K.

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