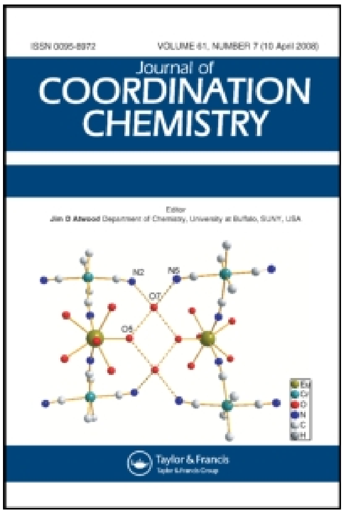

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Synthesis, structure and spectroscopic properties of CuL(MeOH), H_2L = (*E*)-N^1-(2-((2-aminocyclohexydiimino)(phenyl)methyl)-4-chlorophenyl)-N^2-(2-benzyl-4-chlorophenyl)oxalamide

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A new kind of copper(II) complex, CuL(MeOH) (H_2L = (*E*)-N^1-(2-((2-aminocyclohexydiimino)(phenyl)methyl)-4-chlorophenyl)-N^2-(2-benzyl-4-chlorophenyl)oxalamide) has been synthesized and its structure determined by single-crystal X-ray methods. Copper(II) ion is five-coordinate, bonding to four nitrogen atoms from H_2L and one oxygen atom from MeOH. Hydrogen bonds in the crystal result in the formation of a one-dimensional structure. EPR spectra are discussed. Computer simulation gave $g_{\|} = 2.200$, $g_{\perp} = 2.002$. On the basis of the synthesis and the crystal structure, the mechanism of the metal template reaction involved in the formation of the complex was verified.

Keywords: Copper(II); Crystal structure; Metal template; Hydrogen bonding; EPR

1. Introduction

Metal complexes of macrocyclic ligands are of great interest in coordination chemistry because of their special structures, properties and functionalities [1–3]. For example, many copper(II) complexes of tetraazamacrocyclic ligands, which are also of great biological importance, have been electrochemically investigated [1,4–15]. At the same time, it has been found that the oxamide group is an efficient bridging mediator of magnetic exchange between neighbouring metal ions, the type and magnitude of coupling depending on the metal ions used and their coordination environments [16]. However, only a limited number of copper(II) complexes of macrocyclic ligands incorporating oxamide groups has been synthesized [17,18]. Since these mononuclear

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complexes contain unbridged oxamido groups, they can be used as precursors for heteropolynuclear complexes, as has been reported recently [18].

With these facts in mind, we have synthesized a new oxamide ligand, 2,2′-(oxalyldiimino)*bis*(chlorobenzaldehyde) (L′), and a mononuclear copper(II) complex CuL(MeOH) based on its condensation with *trans*-1,2-diaminocyclohexane. An X-ray investigation shows that O–H···O hydrogen bonds exist in the crystal, resulting in a one-dimensional structure.

2. Experimental

2.1. *Materials and physical measurements*

All starting chemicals were of AR grade and used as received. IR spectra were recorded using KBr discs on a Shimadzu IR-408 spectrophotometer in the $4000-600\,\mathrm{cm}^{-1}$ region. Electronic spectra were measured on a JASCO V-570 spectrophotometer using dimethylformamide as solvent. X-band EPR spectra of a crystalline sample were recorded on a Bruker EMX-6/1 D-SPC spectrometer at room temperature.

2.2. *Synthesis of ligand L′ and complex CuL(MeOH)*

Oxalyl chloride (1.27 g, 0.01 mol) was added slowly to a benzene solution containing 2-amino-5-chlorobenzophenone (4.63 g, 0.02 mol). The mixture was stirred at room temperature for 1 h. The product (L′) was filtered off, washed with benzene, saturated with $NaHCO_3$ and dried under vacuum.

CuL(MeOH) was prepared by refluxing L′ (2.96 g, 5.73 m mol), *trans*-1,2-diaminocyclohexane (1.96 g, 17.18 m mol) and $Cu(Ac)_2 \cdot H_2O$ (1.14 g, 5.73 m mol) for 10 h in $50\,\mathrm{cm}^3$ of MeOH, in the presence of $6.0\,\mathrm{cm}^3$ of 2 M NaOH. After the mixture was cooled and filtered, the precipitate obtained was washed with water and dried under vacuum. The deep gray filtrate, kept at room temperature for several days, gave grayish crystals suitable for X-ray analysis.

2.3. *Crystallographic data collection and structure determination*

A crystal of dimensions *ca* $0.24 \times 0.20 \times 0.14$ mm was mounted on a Bruker Smart 1000 diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Diffaction data were collected using ω–2θ scans at room temperature (293 K). An LP correction was applied to the data. The structure was solved by direct methods using SHELXS-97 and refinement on F^2 was performed using SHELXLÙ-97 by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms [19,20]. All hydrogen atom positions were located in calculated positions and refined isotropically. Crystal data and refinement details are summarized in table 1.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 238356.

Table 1. Crystal data and structure refinement details for the complex.

Empirical formula	$C_{35}H_{32}Cl_2CuN_4O_4$
Formula weight	707.09
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	
a (Å)	21.191(11)
b (Å)	13.995(7)
c (Å)	11.210(6)
V	3325(3) $Å^3$
Calculated density (Z)	4, 1.413 $mg\,m^{-3}$
Absorption coefficient	0.862 mm^{-1}
$F(000)$	1460
Crystal size	0.24 × 0.20 × 0.14 mm
θ range for data collection	1.74–25.01°
Limiting indices	$-22 \le h \le 25$, $-14 \le k \le 16$, $-13 \le l \le 12$
Reflections collected/unique	16904/5855 [$R_{int} = 0.0867$]
Max. and min. transmission	1.000 and 0.617
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5855/0/416
Goodness-of-fit on F^2	1.020
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0514$, $wR2 = 0.1105$
R indices (all data)	$R1 = 0.0875$, $wR2 = 0.1279$
Largest diff. peak and hole	1.307 and −0.576 e $Å^{-3}$

3. Results and discussion

3.1. *Crystal structure of CuL(MeOH)*

A perspective view of CuL(MeOH) with the atom numbering scheme is shown in figure 1 and selected bond lengths and angles are listed in table 2. The copper(II) ion is five-coordinate and has a distorted square pyramidal configuration. For Cu1, four nitrogens (N1, N2, N3, N4) from H_2L form the basal plane, and an oxygen atom of an MeOH molecule occupies the apical position. Distances between Cu and N are 1.941 (N1), 1.962 (N2), 1.976 (N3) and 2.019 Å (N4), respectively (average 1.975 Å); the Cu–O bond distance is 2.355 Å. Copper(II) ion is displaced from the N4 least-squares plane by some 0.13 Å, while deviations of the four nitrogen donors from the plane are from 0.124 to 0.134 Å. In the crystal, H-bonds between O(2B) and N(4A) of 1,2-diaminocyclohexane with a distance of 3.027 Å are evident. A second kind of H-bond exists between O(1B) and coordinated MeOH (O(4A)) molecules (O(1B)···O(4A) 2.713 Å). These link adjacent CuL(MeOH) together to form a one-dimensional structure.

There are three possible reactions as the first step in the formation of the complex, the reaction of diamine with metal salt, the reaction of diamine with the oxamide ligand and the reaction of metal salt with oxamide ligand. From the structure and the Cu–N bond distances, we note that the Cu–N4 bond distance is longer than the other Cu–N bond distances. This indicates that reaction of the diamine with the metal salt is possibly the first to take place, as has been previously suggested [17c].

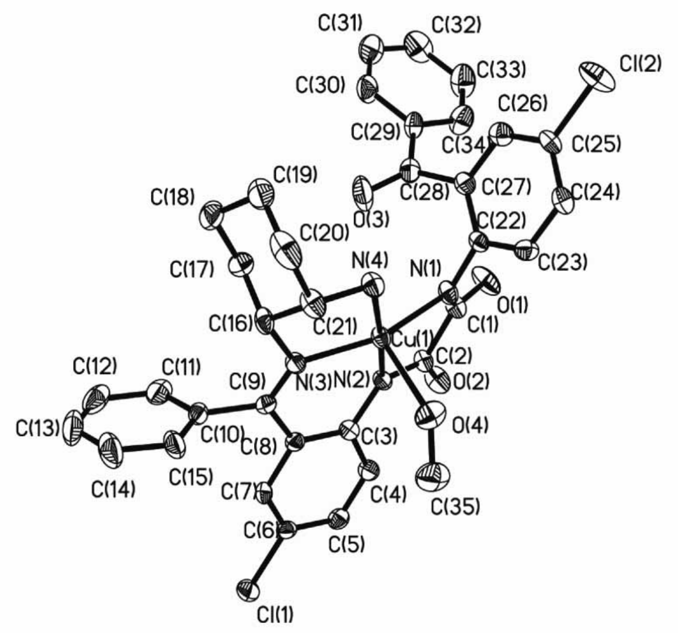

Figure 1. A perspective view of the complex showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for the complex.

Cu(1)–N(2)	1.941(4)	N(1)–C(1)	1.312(7)
Cu(1)–N(1)	1.962(4)	N(1)–C(22)	1.420(7)
Cu(1)–N(3)	1.976(4)	N(2)–C(2)	1.352(6)
Cu(1)–N(4)	2.019(4)	N(2)–C(3)	1.407(7)
Cu(1)–O(4)	2.355(4)	N(3)–C(9)	1.289(6)
Cl(1)–C(6)	1.750(5)	N(3)–C(16)	1.483(7)
O(1)–C(1)	1.243(6)	N(4)–C(21)	1.483(7)
O(2)–C(2)	1.229(6)	C(1)–C(2)	1.546(7)
O(3)–C(28)	1.220(7)	O(4)–C(35)	1.395(8)
N(2)–Cu(1)–N(1)	84.78(18)	C(22)–N(1)–Cu(1)	126.5(3)
N(2)–Cu(1)–N(3)	92.19(18)	C(2)–N(2)–C(3)	122.2(4)
N(1)–Cu(1)–N(3)	160.02(19)	C(2)–N(2)–Cu(1)	113.4(3)
N(2)–Cu(1)–N(4)	175.1(2)	C(3)–N(2)–Cu(1)	123.9(3)
N(1)–Cu(1)–N(4)	95.96(18)	C(9)–N(3)–C(16)	121.9(4)
N(3)–Cu(1)–N(4)	85.45(19)	C(9)–N(3)–Cu(1)	127.6(4)
N(2)–Cu(1)–O(4)	96.53(17)	C(16)–N(3)–Cu(1)	110.1(3)
N(1)–Cu(1)–O(4)	103.30(19)	C(21)–N(4)–Cu(1)	108.4(3)
N(3)–Cu(1)–O(4)	96.66(18)	H(4A)–N(4)–H(4B)	108.4
N(4)–Cu(1)–O(4)	88.06(18)	O(1)–C(1)–N(1)	126.7(5)
C(1)–N(1)–C(22)	119.6(4)	O(1)–C(1)–C(2)	118.6(5)
C(1)–N(1)–Cu(1)	112.8(4)	N(1)–C(1C(2)	114.7(5)

3.2. *Spectroscopic studies*

Infrared spectra of CuL(MeOH) display an oxamide carbonyl stretch at 1660 cm^{-1}. Bands at 1610 and 1595 cm^{-1} may be assigned to the C=N absorptions [18a,b,17c]. Absorption at 3200–3400 cm^{-1} may be assigned to N–H stretching and O–H stretching

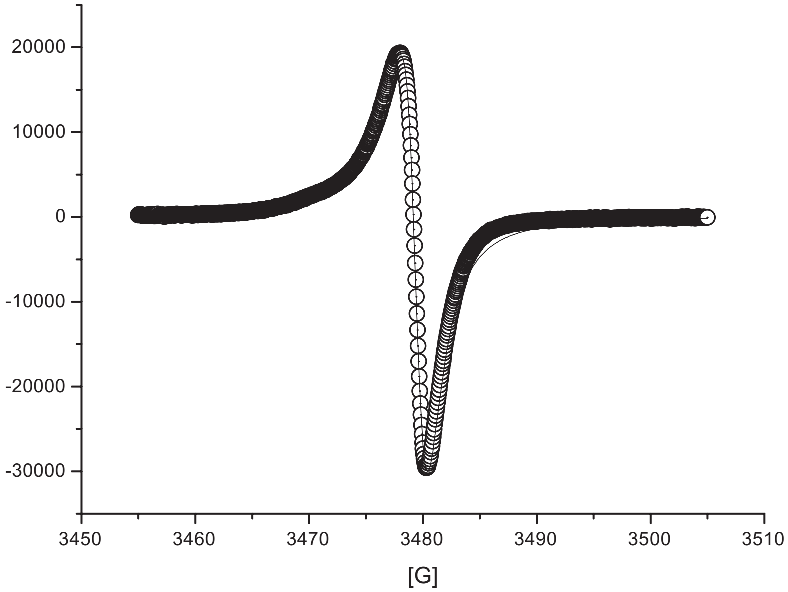

Figure 2. Experimental (⊙) and simulated (solid line) X-band EPR spectrum of the complex.

in H_2O or MeOH [21]. Electronic spectra displayed a strong absorption band in the 400–260 nm region and a weak absorption at 510 nm. The former may be attributed to charge transfer and/or a ligand transition. The latter may be assigned to d–d transitions of copper(II) in a distorted square pyramid configuration. EPR spectra of CuL(MeOH) measured on a polycrystalline power at room temperature show an isotropic signal. EPR data were simulated by the WINEPR program to give $g_{||} = 2.200$, $g_{\perp} = 2.002$. As shown in figure 2, the simulated curve reproduces very well the experimental data over the whole magnetic field range investigated.

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