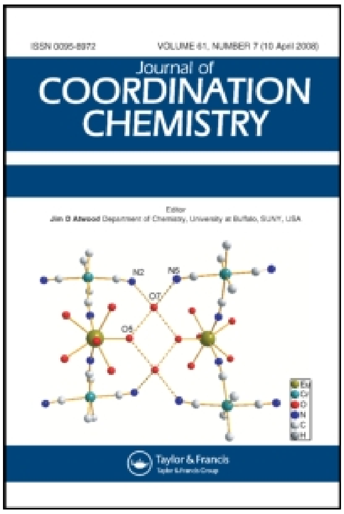

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Lu, Weibing and Zhou, Xiaohai(2005) 'Synthesis and crystal structure of a copper(II) complex of the tripodal tetradentate ligand tris(2-benzimidazolylmethyl)amine', Journal of Coordination Chemistry, 58: 18, 1653 — 1658
To link to this Article: DOI: 10.1080/00958970500148487
URL: http://dx.doi.org/10.1080/00958970500148487

Journal of Coordination Chemistry
Vol. 58, No. 18, December 2005, 1653–1658

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Synthesis and crystal structure of a copper(II) complex of the tripodal tetradentate ligand tris(2-benzimidazolylmethyl)amine

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(*Received 1 June 2004; in final form 18 April 2005*)

A mononuclear copper complex [Cu(NTB)Cl]Cl · $3CH_3CH_2OH$ (**1**) (NTB = tris(2-benzimidazolylmethyl)amine) was synthesized and its structure was determined by single crystal X-ray diffraction. In this complex, copper(II) is five-coordinate with NTB serving as a neutral tetradentate ligand. Three tertiary nitrogen atoms of benzimidazole groups of NTB formed the base of the trigonal bipyramidal geometry. One axial position was occupied by the apical nitrogen atom of NTB and the other was occupied by chloride. The ESR spectrum of complex **1** in ethanol at 101 K was recorded and the well-defined ESR parameters ($g_{\|} = 2.02$, $g_{\perp} = 2.16$ and $A_{\|} = 109\,\mathrm{G}$) indicated that the Cu(II) has a distorted trigonal-bipyramidal environment, in good agreement with crystal structure determination for complex **1**.

Keywords: Tris(2-benzimidazolylmethyl)amine; Crystal structure; ESR

1. Introduction

Histidine plays a key role in the coordination chemistry of many metalloproteins [1]. Complexes of imidazole and benzimidazole ligands have received attention as functional models for the active sites of metalloproteins. The ligand tris(2-benzimidazolylmethyl)amine (NTB) has proven to be an appropriate model of histidine. Complexes of this ligand and its analogues have been extensively studied [2–14]. In this article, we report the synthesis and crystal structure of copper(II) complex of this ligand [Cu(NTB)Cl]Cl · $3CH_3CH_2OH$ (**1**).

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Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2005 Taylor & Francis
DOI: 10.1080/00958970500148487

2. Experimental

2.1. *Apparatus and reagents*

All starting materials were purchased from commercial sources with highest purity. IR spectra was performed on a Shimadzu FT-IR-8100 spectrometer as a KBr pellet. Elemental analysis (C, H and N) was determined on a Perkin-Elmer 240B elemental analyzer. Copper was determined by a HP 7500a ICP-MS (Agilent) System. A mass spectrum with glycerol as matrix was performed on a ZAB-HF-3F MS instrument. An X band ESR spectrum was recorded on an ER 200-D-SRC 1012 spectrometer.

2.2. *Synthesis of the complex*

A solution of tris(2-benzimidazolylmethyl)amine (102 mg, 0.25 mmol) in absolute ethanol (50 mL) was heated to 50°C, then a solution of copper dichloride dihydrate (43 mg, 0.25 mmol) in the same solvent (15 mL) was added. The mixture was stirred at 50°C for another 30 min, cooled and kept at room temperature. Upon slow evaporation of the solvent for several days, green block crystals of the copper complex formed. The crystals were filtered and easily effloresced, with loss of the solvated ethanol molecules.[1]

IR(cm^{-1}): 3320, 3043, 2920, 2851, 1600, 1549, 1453, 1448; MS: 505 (M–Cl); Anal. Calcd for $\mathrm{CuC_{24}H_{21}N_7Cl_2}$: C, 53.09; H, 3.87; N, 18.06; Cu, 11.89. Found: C, 53.40; H, 3.31; N, 18.44; Cu, 12.41%.

2.3. *Crystallographic measurements and structure determination*

Because a crystal of complex **1** loses its solvents of crystallization, it was mounted in a glass capillary with the mother liquor to prevent the loss of the structural solvents during data collection. A single crystal with dimensions $0.5 \times 0.4 \times 0.2\,\mathrm{mm}^3$ was used for the structure analysis. The data were collected on a Rigaku RAXIS RAPID IP device with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073\,\text{Å}$) at 293(2) K. The total number of reflections collected was 15033 in the range of $2.19 < \theta < 27.48°$, of which 7462 were unique, 2997 of the reflections were included in the refinement [$I > 2\sigma(I)$]. Final $R = 0.0569$, $wR = 0.1436$. Refinement was carried out by full-matrix least-squares on F^2. The SHELXL-97 software package was used. A summary of crystal parameters and refinement details is given in table 1.

3. Results and discussion

3.1. *Mass spectroscopy*

The FAB mass spectrum of complex **1** gave a peak at m/z 505, this peak corresponding to the five-coordinate metal complex ion, $[\mathrm{Cu(NTB)Cl}]^+$.

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[1] The ligand NTB [tris(2-benzimidazolylmethyl)amine] was prepared according to the literature procedure [15].

Table 1. Crystal data and structure refinement for complex **1**.

Empirical formula	$C_{30}H_{39}Cl_2CuN_7O_3$
Formula weight	680.12
Temperature	293(2) K
Measurement method	Oscillation
Wavelength (Å)	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	$a = 11.052(2)$ Å, $\alpha = 114.73(3)^\circ$ $b = 12.895(3)$ Å, $\beta = 92.62(3)^\circ$ $c = 13.828(3)$ Å, $\gamma = 107.12(3)^\circ$
Volume (Å^3)	1677.9(6)
Reflections no. for cell measurement	15033
θ range for cell measurement (°)	2.19–27.48
Z, D_{cal}	2, 1.346 mg m^{-3}
Absorption coefficient (mm^{-1})	0.851
$F(000)$	710
Crystal shape/crystal color	Block/green
Crystal size (mm^3)	$0.5 \times 0.4 \times 0.2$
Reflections collected/unique	15033/7462 [R(int) = 0.0373]
Reflections with $I > 2\sigma(I)$	2997
Completeness to $\theta = 27.48$	96.9%
Absorption correction	Empirical
Max. and min. transmission	0.843 and 0.514
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7462/0/401
Goodness-of-fit on F^2	0.851
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0569$, $wR2 = 0.1436$
R indices (all data)	$R1 = 0.1465$, $wR2 = 0.1649$
Extinction coefficient	0.0005(9)

3.2. *Structure description*

Complex **1** consists of the cation [Cu(NTB)Cl]$^+$ and the anion Cl$^-$ with three solvated ethanol molecules. The molecular structure and the molecular packing of this complex are shown in figures 1 and 2, respectively.

As shown in figure 1, the copper(II) ion has a trigonal bipyramidal geometry. Three nitrogen atoms (N2, N4, N6) of benzimidazole groups form the base of the trigonal bipyramidal geometry. The apical nitrogen atom (N1) of NTB occupies one axial site, while a chloride anion (Cl1) occupies the other. The apical nitrogen atom and the chloride anion are in a *trans* position. The N(1)–Cu(1)–Cl(1) bond angle is 173.09(9)°.

Selected bond lengths and bond angles are listed in table 2. The Cu–Cl(1) bond length is about 2.27 Å. The bond distance between the Cu(II) and the tertiary apical nitrogen atom (N1) of 2.242 Å is approximately 0.21 Å longer than those between the copper ion and the basal nitrogen atoms of the benzimidazolyl groups (av. 2.036 Å). A similar elongation is also observed in other copper [3], iron [5, 16] and cobalt [17, 18] complexes of tripodal tetradentate ligands containing a benzimidazolylmethyl group.

As shown in figure 1, there exist hydrogen bonds between the non-coordinating nitrogen atoms (N3, N5, N7) of the benzimidazolyl groups and the solvated ethanol molecules (O1, O2, O3), respectively. The non-coordinating nitrogen atoms (N3, N5, N7) serves as hydrogen donors and the solvated ethanols (O1, O2, O3) serve as hydrogen acceptors. At the same time, there also exist hydrogen bonds between the

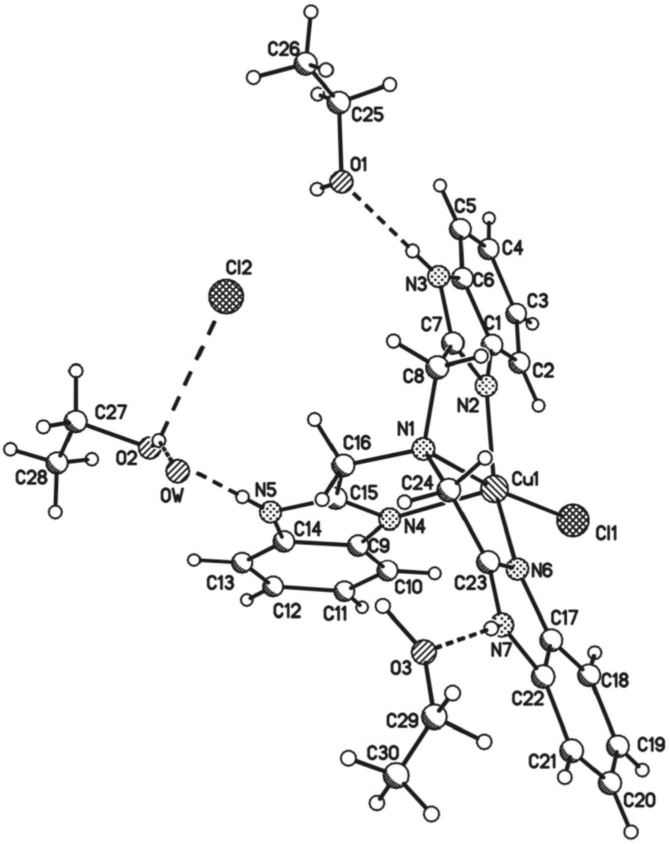

Figure 1. The molecular structure of the $[Cu(NTB)Cl]Cl \cdot 3CH_3CH_2OH$ with the atom labeling.

solvated ethanol (O2, O3) and the chloride anion (Cl2). As shown in figure 2, this complex forms a one-dimensional chain structure by intermolecular hydrogen bonds. The data of hydrogen bonds are collected in table 3.

3.3. *ESR spectroscopy*

Figure 3 demonstrates the ESR spectrum of complex **1** in ethanol at 101 K, from which the well-defined ESR parameters ($g_{\parallel} = 2.02$, $g_{\perp} = 2.16$ and $A_{\parallel} = 109\,\mathrm{G}$) were obtained. Such parameters strongly indicate that the Cu(II) ion in complex **1** has a distorted trigonal-bipyramidal environment following the criteria given by Bencini *et al*. [19], in good agreement with the crystal structure **1**.

4. Conclusion

In conclusion, the structure of a mononuclear copper complex of the tetradentate ligand tris(2-benzimidazolylmethyl)amine was determined by single crystal X-ray diffraction. The crystal data as well as the ESR parameters of this complex indicated that the Cu(II) ion in this complex has a distorted trigonal-bipyramidal environment.

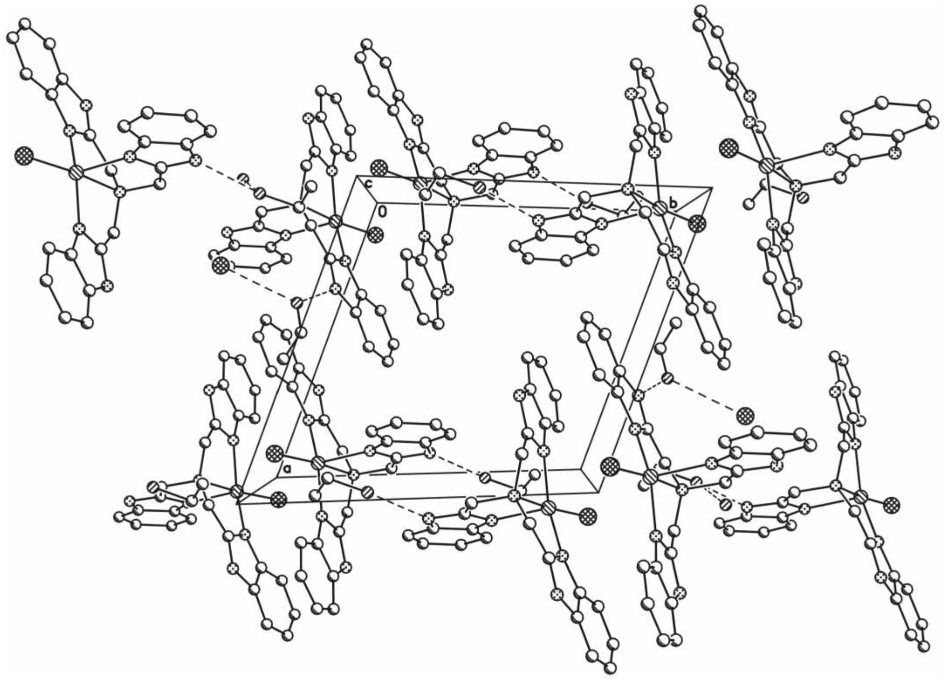

Figure 2. Packing of the molecules of complex **1** showing the intermolecular hydrogen bonds.

Table 2. Selected bond lengths (Å) and angles (°) of complex **1**.

Bond	
Distance	
Cu(1)–N(6)	1.978(4)
Cu(1)–N(2)	1.980(4)
Cu(1)–N(4)	2.150(3)
Cu(1)–N(1)	2.242(3)
Cu(1)–Cl(1)	2.2688(14)
Angle	
N(6)–Cu(1)–N(2)	150.92(15)
N(6)–Cu(1)–N(4)	102.13(13)
N(2)–Cu(1)–N(4)	96.16(13)
N(6)–Cu(1)–N(1)	81.09(14)
N(2)–Cu(1)–N(1)	80.11(14)
N(4)–Cu(1)–N(1)	79.89(13)
N(6)–Cu(1)–Cl(1)	98.11(11)
N(2)–Cu(1)–Cl(1)	97.91(12)
N(4)–Cu(1)–Cl(1)	106.95(11)
N(1)–Cu(1)–Cl(1)	173.09(9)

Supplementary materials

X-ray crystallographic file in CIF format for the complex **1** has been deposited at the Cambridge Crystallographic Data Center with the deposition number CCDC 205875. Copy of this information may be obtained free of charge from The Director, CCDC,

Table 3. Hydrogen bonds for A [Å and °].

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N(3)–HN3···O(1)	0.79(4)	1.98(4)	2.759(6)	174(5)
N(5)–HN5···O(2)	0.731(4)	2.102(5)	2.824(6)	170.0(3)
N(7)–HN7···O(3)	0.84(4)	1.98(4)	2.775(5)	157(4)
O(2)–HO2···OW	0.764(5)	1.771(13)	2.473(13)	152.3(7)
O(2)–HO2···Cl(2)	0.764(5)	2.9544(17)	3.435(7)	123.5(5)
O(3)–HO3···Cl(2)#1	1.02(4)	2.17(4)	3.078(5)	148(3)

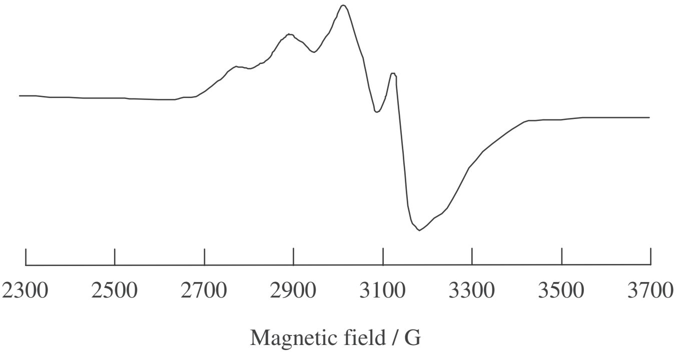

Figure 3. ESR spectrum of complex **1** at 101 K in CH_3CH_2OH. Operation condition: microwave frequency: 9.45 GHz, modulation width: 2 Gauss, microwave power: 1 mW.

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