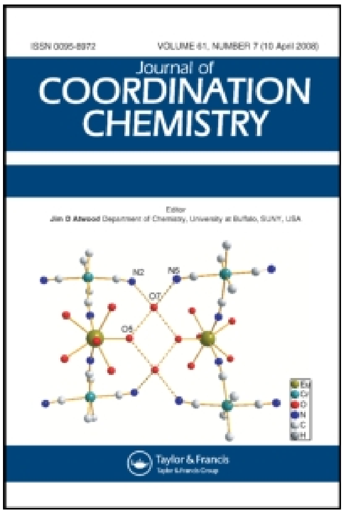

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Synthesis and crystal structure of a copper(II) complex of the tridentate ligand di-(2-benzimidazolylmethyl)imine

Weibing Lu[a]; Xiaohai Zhou[a]
[a] College of Chemistry and Molecular Science, Wuhan University, Wuhan, P. R., China

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Synthesis and crystal structure of a copper(II) complex of the tridentate ligand di-(2-benzimidazolylmethyl)imine

WEIBING LU and XIAOHAI ZHOU*

College of Chemistry and Molecular Science, Wuhan University,
Wuhan, 430072, P. R. China

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A copper complex $[Cu(IDB)Cl] \cdot 0.5[CuCl_4] \cdot H_2O$ (**1**) (IDB = di(2-benzimidazolylmethyl)imine) was synthesized and its structure was determined by X-ray single crystal diffraction. In this complex, the central copper(II) ion is four-coordinate, IDB serves as a neutral tridentate chelating ligand for the tetragonal copper ion. The cyclic voltammogram of complex **1** in CH_3CN gave two reversible redox waves ($E_{1/2,1} = -0.14\,V$ and $E_{1/2,2} = 0.08\,V$ *versus* SCE) which correspond to the Cu(II, II)/Cu(I, II) and Cu(II, II)/Cu(II, I) redox processes, respectively.

Keywords: Di(2-benzimidazolylmethyl)imine; Crystal structure; Electrochemistry

1. Introduction

Histidine plays a role in the coordination chemistry of many metalloproteins [1]. Complexes of imidazole and benzimidazole ligands have received much attention as they serve as functional models for the active sites of metalloproteins. The ligands tris(2-benzimidazolylmethyl)amine (NTB) and di(2-benzimidazolylmethyl)imine (IDB) have proven to be appropriate model compounds of histidine. Complexes of the former ligand and its analogues have been extensively studied [2–27], but reports on complexes of the latter ligand are rare. Liao *et al.* reported a diiron(III) complex [28] and a nickel(II) complex [29] of this ligand. In this article, we report the synthesis and crystal structure of a copper(II) complex of this ligand $[Cu(IDB)Cl] \cdot 0.5[CuCl_4] \cdot H_2O$ (**1**).

2. Experimental

2.1. *Apparatus and reagents*

All starting materials were purchased from commercial sources with highest purity. An IR spectrum was measured on a Shimadzu FT-IR-8100 spectrometer as a

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*Corresponding author. Email: lwblqy@163.com

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KBr pellet. Elemental analysis (C, H and N) was determined by a Vario EL III elemental analyzer. UV-vis spectroscopy was performed with a Varian CARY 300 UV-Visible spectrophotometer. Redox potentials of complex 1 in dry CH_3CN containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as supporting electrolyte were determined at room temperature by cyclic voltammetry using a three-electrode system in the absence of air on a CHI 660A electrochemical workstation. A platinum plate, platinum wire and saturated calomel electrode (SCE) were used as the working electrode, the counter electrode and the reference electrode, respectively.

The ligand IDB [di(2-benzimidazolylmethyl)imine] was prepared according to the literature procedure [30].

2.2. *Synthesis*

2.2.1. Synthesis of the complex. A solution of di(2-benzimidazolylmethyl)imine (69 mg, 0.25 mmol) in ethanol (30 mL) was heated to 50°C, then a solution of copper dichloride dihydrate (172 mg, 1.0 mmol) in the same solvent (20 mL) was added. The resultant 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.

IR(cm^{-1}): 3320, 3043, 2920, 2851, 1600, 1549, 1453, 1448; Anal. Found C, 38.43; H, 3.65; N, 13.92%, this result is in agreement with: $[IDBCuCl \cdot H_2O]_2[CuCl_4] \cdot 4H_2O$: Calcd C, 38.22; H, 4.02; N, 13.40%.

2.3. *Crystallographic measurements and structure determination*

A single crystal with dimensions $0.6 \times 0.5 \times 0.5\,mm^3$ was mounted onto a glass fibre. Data were collected on a Rigaku RAXIS RAPID IP device with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. The total number of reflections collected was 8216 in the range $2.45 < \theta < 27.48°$, of which 4157 were unique, 2960 of the reflections were included in the refinement [$I > 2\sigma(I)$]. Final $R = 0.0393$, $wR = 0.0903$. Refinement was carried out by full-matrix least-squares on F^2 using SHELXL-97 software package [31]. A summary of crystal parameters and refinement details is given in table 1.

3. Results and discussion

3.1. *Structure description*

Complex **1** can be described as $[Cu(IDB)Cl] \cdot 0.5[CuCl_4] \cdot H_2O$, consisting of the cation $[Cu(IDB)Cl]^+$ and the anion $[CuCl_4]^{2-}$ with one solvated water molecule. The molecular structure and the molecular packing of this complex are shown in figures 1 and 2, respectively.

As shown in figure 1, the central copper(II) (Cu1) in this complex is four coordinate in a tetragonal geometry. The three nitrogen atoms (N1, N3, N5) of IDB and a chloride anion (Cl1) form the tetragonal geometry. The bond angle of N(5)–Cu(1)–Cl(1) is 177.21(8)°. The copper(II) (Cu2) in the counter anion $[CuCl_4]^{2-}$ is in a square planar

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

Empirical formula	$C_{16}H_{17}Cl_3Cu_{1.5}N_5O$
Formula weight	497.01
Temperature (K)	293(2)
Measurement method	Oscillation
Wavelength (Å)	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions (Å, °)	$a = 8.3591(17)$, $\alpha = 74.67(3)$ $b = 10.078(2)$, $\beta = 88.99(3)$ $c = 11.619(2)$, $\gamma = 83.37(3)$
Volume (Å^3)	937.7(3)
Reflections no. for cell measurement	8216
θ range for cell measurement (°)	2.45–27.48
Z, D_{Calcd} (mg m^{-3})	2, 1.760
Absorption coefficient (mm^{-1})	2.161
F(000)	501
Crystal shape/Crystal color	Block/Green
Crystal size (mm^3)	$0.6 \times 0.5 \times 0.5$
Reflections collected/unique	8216/4157 [R(int) = 0.0417]
Reflections with $I > 2\sigma(I)$	2960
Completeness to $\theta = 27.48$	97.1%
Absorption correction	Empirical
Max. and min. transmission	0.339 and 0.273
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4157/0/262
Goodness-of-fit on F^2	0.970
Final R indices $I > 2\sigma(I)$	$R_1 = 0.0393$, $wR_2 = 0.0903$
R indices (all data)	$R_1 = 0.0582$, $wR_2 = 0.0943$
Extinction coefficient	0.0359(19)

geometry formed by four identical chloride anions. The bond angles of Cl(3)–Cu(2)–Cl(3)#1 and Cl(2)#1–Cu(2)–Cl(2) are both 180.0°.

Selected bond lengths and angles are listed in table 2. The bond length between the metal center (Cu1) and Cl(1) is about 2.24 Å. The bond distance between the Cu ion and the secondary nitrogen atom (N5) of 2.050 Å is slightly longer (0.087 Å) than those between the copper ion and the nitrogen atoms (N1, N3) of the benzimidazolyl groups (av. 1.963 Å). As shown in figure 1, there exist hydrogen bonds between the noncoordinating nitrogen atom (N4) of the benzimidazolyl group and the solvated water molecules (OW). The noncoordinating nitrogen atom (N4) serves as a hydrogen donor and the solvated water (OW) serves as hydrogen acceptor. As shown in figure 2, there exist hydrogen bonds between the solvated water and the chloride anion in $[CuCl_4]^{2-}$. Furthermore, there also exist hydrogen bonds between the noncoordinating nitrogen atom (N2) and the secondary nitrogen atom (N5) of the benzimidazolyl group with the chloride anion in $[CuCl_4]^{2-}$. The nitrogen atom (N5, N2) serves as hydrogen donor and the chloride anion (Cl2, Cl3) serves as hydrogen acceptor respectively. This complex forms a two-dimensional layer-to-layer structure by intermolecular hydrogen bonds. The data on hydrogen bonds are collected in table 3.

3.2. *UV-Vis spectroscopy*

The ultraviolet and visible spectrum was measured in the 200–900 nm range (figure 3). The spectrum shows three strong absorption bands at 242, 271 and 278 nm

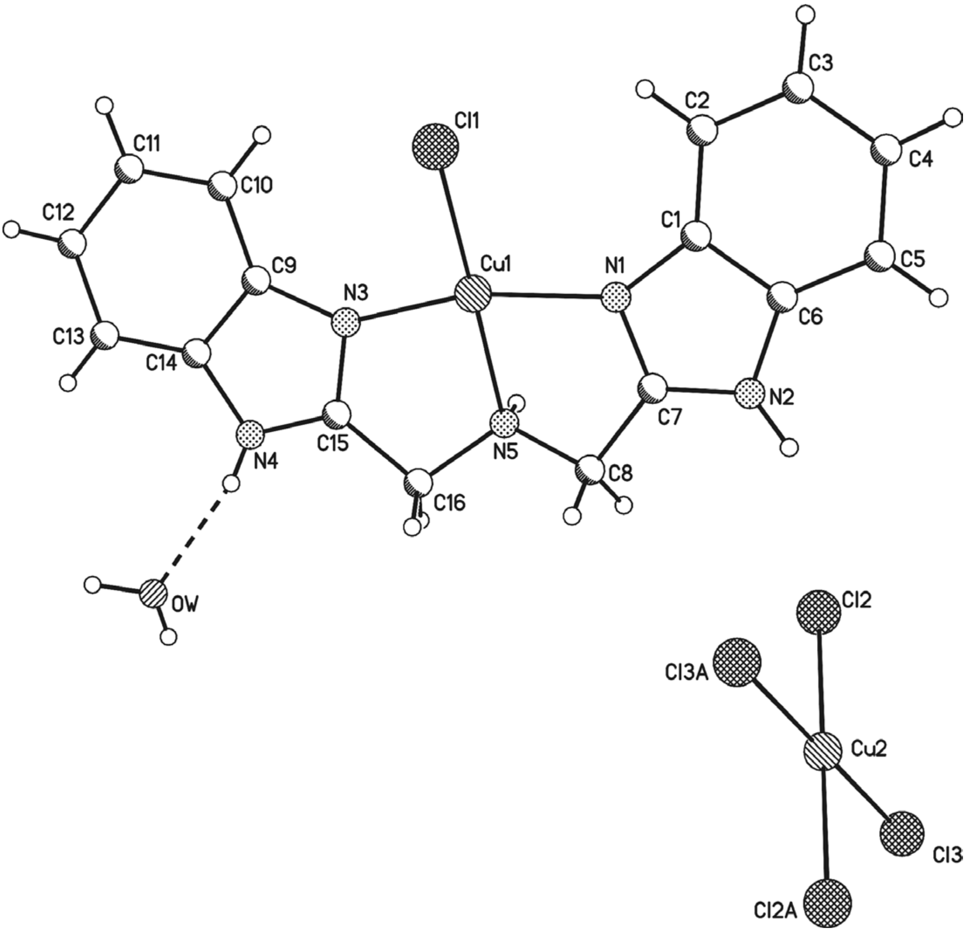


Figure 1. The molecular structure of the $[Cu(IDB)Cl] \cdot 0.5[CuCl_4] \cdot H_2O$ with the atom labeling.

($\varepsilon = 1.39 \times 10^4$, 1.75×10^4 and $1.73 \times 10^4\,M^{-1}\,cm^{-1}$ respectively), which can be attributed to charge transfer and the transition of the ligand itself. In addition, the spectrum indicates a broad d–d band centered at 722 nm ($\varepsilon = 162\,M^{-1}\,cm^{-1}$).

3.3. *Electrochemistry*

Figure 4 shows the cyclic voltammogram of complex **1** in CH_3CN, with two reversible redox waves ($E_{1/2,1} = -0.14\,V$ and $E_{1/2,2} = 0.08\,V$ *vs.* SCE). The first and second reversible waves at $E_{1/2,1}$ and $E_{1/2,\,2}$ correspond to the Cu(II, II)/Cu(I, II) and Cu(II, II)/Cu(II, I) redox couples, respectively. The difference in the $E_{1/2}$ values between the first and second redox processes ($\Delta E_{1/2} = E_{1/2,2} - E_{1/2,1}$) is 0.22 V.

In conclusion, the structure of a copper complex of the tridentate ligand di(2-benzimidazolylmethyl)imine was determined by X-ray single crystal diffraction. There are two copper ions with different geometry. The central copper ion (Cu1) is

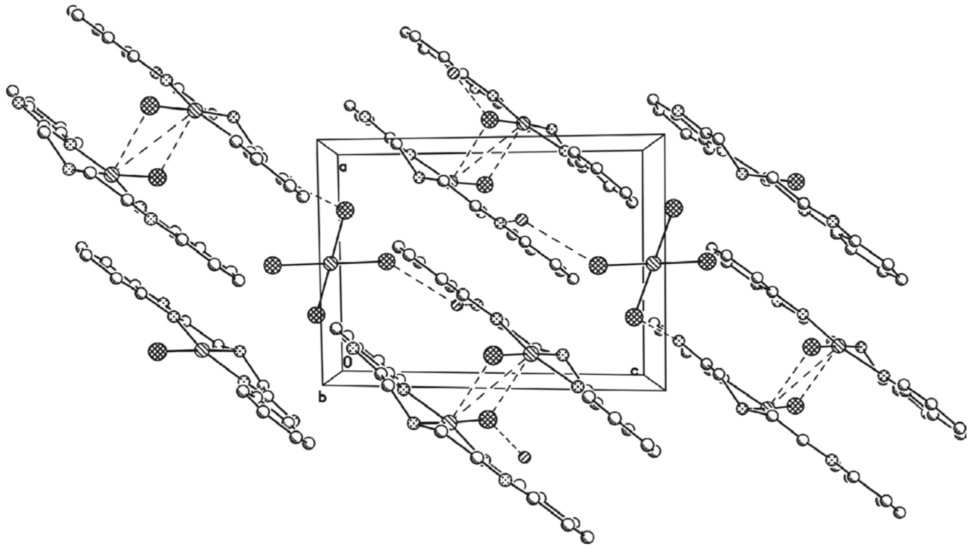


Figure 2. Packing of the molecules of complex **1** showing the intermolecular hydrogen bonds.

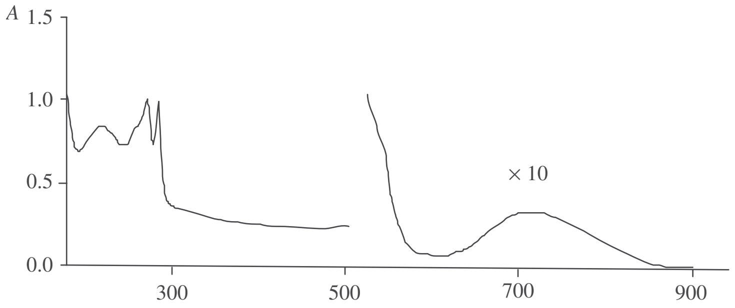
Table 2. Selected bond lengths (Å) and angles (°) of complex **1**.

Bond	Distance
Cu(1)–N(3)	1.961(2)
Cu(1)–N(1)	1.965(2)
Cu(1)–N(5)	2.050(3)
Cu(1)–Cl(1)	2.2429(11)
Cu(2)–Cl(3)	2.2639(12)
Cu(2)–Cl(3)#1	2.2639(12)
Cu(2)–Cl(2)#1	2.2643(10)
Cu(2)–Cl(2)	2.2643(10)
Bond	Angle
N(3)–Cu(1)–N(1)	162.66(10)
N(3)–Cu(1)–N(5)	81.76(10)
N(1)–Cu(1)–N(5)	81.34(10)
N(3)–Cu(1)–Cl(1)	98.59(8)
N(1)–Cu(1)–Cl(1)	98.48(8)
N(5)–Cu(1)–Cl(1)	177.21(8)
Cl(3)–Cu(2)–Cl(3)#1	180.0
Cl(3)–Cu(2)–Cl(2)#1	89.82(4)
Cl(3)#1–Cu(2)–Cl(2)#1	90.18(4)
Cl(3)–Cu(2)–Cl(2)	90.18(4)
Cl(3)#1–Cu(2)–Cl(2)	89.82(4)
Cl(2)#1–Cu(2)–Cl(2)	180.000(1)

four-coordinate in a tetragonal geometry and the other copper ion (Cu2) is in a square planar geometry. The cyclic voltammogram of complex **1** in CH_3CN gives two reversible waves, confirming the existence of two copper ions with different coordination geometry in the same molecule.

Table 3. Hydrogen bonds for complex **1** (Å and °).

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
OW–HOA···Cl(1)#2	0.69(4)	2.44(4)	3.104(3)	163(5)
OW–HOB···Cl(3)#3	0.91(5)	2.26(5)	3.164(4)	173(4)
N(2)–HN2···Cl(2)	0.90(4)	2.46(4)	3.285(3)	153(3)
N(4)–HN4···OW	0.75(3)	1.98(3)	2.723(4)	167(3)
N(5)–HN5···Cl(3)#4	0.86(2)	2.48(2)	3.299(3)	161(2)



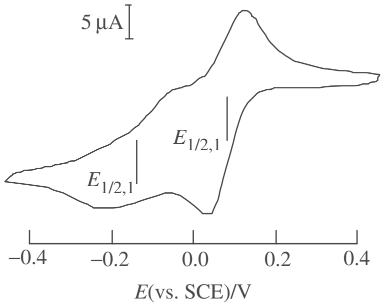


Figure 4. Cyclic voltammogram of complex **1** in CH_3CN.

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 269451. Copy of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB 2 IEZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk).

References

[1] W.R. Scheidt, C.A. Reed. *Chem. Rev.*, **81**, 543 (1981).
[2] B. Kwak, K.W. Cho, M. Pyo, M.S. Lah. *Inorg. Chim. Acta*, **290**, 21 (1999).
[3] C. Su, B. Kang, T. Wen, Y. Tong, X. Yang, C. Zhang, H. Liu, J. Sun. *Polyhedron*, **18**, 1577 (1999).

[4] D. Moon, M.S. Lah. *Inorg. Chem.*, **17**, 3194 (1978).

[5] R.M. Buchanan, R.J. O'Brien, J.F. Richardson, J.-M. Latour. *Inorg. Chim. Acta*, **214**, 33 (1993).

[6] H.M. J. Hendriks, P.J.M.W.L. Briker, G.C. Verschoor, J. Reedijk. *J. Chem. Soc., Dalton Trans.*, **3**, 623 (1982).

[7] H.N. Pandey, Y.S. Sharma, P. Mathur. *Polyhedron*, **11**, 2631 (1992).

[8] Y. Nakao, M. Onoda, T. Sakurai, A. Nakahara, I. Kinoshita, S. Ooi. *Inorg. Chim. Acta*, **151**, 55 (1988).

[9] T. Sakurai, H. Oi, A. Nakahara. *Inorg. Chim. Acta*, **92**, 131 (1984).

[10] L.K. Thompson, B.S. Ramaswamy, R.D. Dawe. *Can. J. Chem.*, **56**, 1311 (1978).

[11] N. Matsumoyo, T. Akui, H. Murakami, J. Kanesaka, A. Ohyoshi, H. Okawa. *J. Chem. Soc., Dalton Trans.*, **4**, 1021 (1988).

[12] J. Liu, S. Wang, L. Wang, F. He, X. Huang. *Polyhedron*, **15**, 3639 (1996).

[13] H.N. Pandey, P. Mathur. *Indian J. Chem. (A)*, **31**, 666 (1992).

[14] N. Matsumoto, T. Akui, A. Ohyoshi, H. Okawa. *Bull. Chem. Soc. Jpn.*, **61**, 2250 (1988).

[15] W. Lu, X. Zhou, *J. Coor. Chem.*, **58**, 1653 (2005).

[16] J. Tian, M. Xie, Z. Liu, S. Yan, D. Liao, Z. Jiang. *J. Coord. Chem.*, **58**, 833 (2005).

[17] J. Tian, M. Xie, S. Yan, D. Liao, Z. Jiang, P. Cheng. *Chin. J. Chem.*, **23**, 525 (2005).

[18] J. Tian, W. Gu, S. Yan, D. Liao, Z. Jiang, P. Cheng. *J. Coord. Chem.*, **56**, 275 (2003).

[19] D. Moon, M.S. Lah, R.E. Del Sesto, J.S. Miller. *Inorg. Chem.*, **41**, 4708 (2002).

[20] S. Ghosh, K.K. Nanda, A.W. Addison, R.J. Butcher. *Inorg. Chem.*, **41**, 2243 (2002).

[21] R. Wietzke, M. Mazzanti, J.-M. Latour, J. Pécaut. *J. Chem. Soc., Dalton Trans.*, **22**, 4167 (2000).

[22] X. Zhang, J. Wang, M. Yu, F. Miao. *Acta Chim. Sinica*, **58**, 1280 (2000).

[23] C. Su, B. Kang, C. Du, Q. Yang, T.C.W. Mak. *Inorg. Chem.*, **39**, 4843 (2000).

[24] A.E. Ceniceros-Gomez, N. Barba-Behrens, M.E. Quiroz-Castro, S. Bernes, H. Noth, S.E. Castillo-Blum. *Polyhedron*, **19**, 1821 (2000).

[25] E. Quiroz-Castro, S. Bernes, N. Barba-Behrens, R. Tapia-Benavides, R. Contreras, H. Noth. *Polyhedron*, **19**, 1479 (2000).

[26] C. Su, B. Kang, Q. Yang, T.C.W. Mak. *J. Chem. Soc., Dalton Trans.*, **12**, 1831 (2000).

[27] C. Su, B. Kang, Q. Yang, T.C.W. Mak. *J. Chem. Soc., Dalton Trans.*, **12**, 1857 (2000).

[28] Z. Liao, D. Xiang, D. Li, F. Sheng, F. Mei, B. Luo, L. Shen. *Synth. React. Inorg. Met.-Org. Chem.*, **30**, 683 (2000).

[29] Y. Chen, Z. Liao, W. Li, D. Li, F. Mei, Y. Wei. *Acta Chim. Sinica*, **58**, 1191 (2000).

[30] H.P. Berends, D.W. Stephan. *Inorg. Chim. Acta*, **93**, 173 (1984).

[31] G. M. Sheldrick. *SHEELXL-97*, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany, 1997.