

This article was downloaded by:

On: 23 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713455674>

Syntheses and structures of 2,4-dichloro-6-(cyclopropyliminomethyl)phenol and its copper(II) complex

Zhong-Lu You^a; Jing-Yun Chi^a

^a Department of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, P.R. China

To cite this Article You, Zhong-Lu and Chi, Jing-Yun(2006) 'Syntheses and structures of 2,4-dichloro-6-(cyclopropyliminomethyl)phenol and its copper(II) complex', *Journal of Coordination Chemistry*, 59: 17, 1999 – 2004

To link to this Article: DOI: 10.1080/00958970600717827

URL: <http://dx.doi.org/10.1080/00958970600717827>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Syntheses and structures of 2,4-dichloro-6-(cyclopropyliminomethyl)phenol and its copper(II) complex

ZHONG-LU YOU* and JING-YUN CHI

Department of Chemistry and Chemical Engineering, Liaoning Normal University, Huanghe Road 850#, Dalian 116029, P.R. China

(Received in final form 11 January 2006)

A new Schiff base ligand, 2,4-dichloro-6-(cyclopropyliminomethyl)phenol, and a copper(II) complex containing it have been synthesized and characterised. The ligand and complex crystallise in space groups *Cmca* and *C2/c*, respectively. In the complex, the Cu atom is four-coordinate (distorted tetrahedral), bonded to two imine N and two phenolate O atoms from two Schiff base ligands. Bond lengths associated with the donor atoms in the complex are different to those in the ligand. The structure is compatible with spectra of the bulk sample.

Keywords: Schiff base; Copper(II); Crystal structure; IR

1. Introduction

Transition metal compounds containing Schiff base ligands have been of great interest for many years [1–4]. These compounds play an important role in the development of coordination chemistry related to catalysis and enzymatic reactions [5, 6], magnetism and molecular architectures [7, 8]. Schiff base complexes are of particular interest to inorganic chemists as their structural, spectroscopic and chemical properties often strongly depend on detailed ligand structure. Schiff base complexes of copper(II) are specifically of interest in bioinorganic chemistry since they provide models for the active sites of copper proteins [9, 10].

In this study, a new Schiff base ligand, 2,4-dichloro-6-(cyclopropyliminomethyl)phenol (**1**), and a copper(II) complex of it, bis[2,4-dichloro-6-(cyclopropyliminomethyl)phenolato]copper(II) (**2**), are reported. A particular interest was to investigate structural differences between the complex and the free ligand.

*Corresponding author. Email: youzhonglu@yahoo.com.cn

2. Experimental

2.1. Materials and methods

Solvents and reagents were purchased from Aldrich and used without further purification. Elemental analyses for were performed on a Perkin-Elmer 240C instrument. IR spectra were recorded on a Nicolet AVATAR 360 spectrophotometer (KBr pellets) in the 4000–400 cm^{-1} region.

2.2. Synthesis of 2,4-dichloro-6-(cyclopropyliminomethyl)phenol (**1**)

To a MeOH solution (50 cm^3) of 3,5-dichlorosalicylaldehyde (192.2 mg, 1.0 mmol) was added a MeOH solution (30 cm^3) of cyclopropylamine (57.0 mg, 1.0 mmol) with stirring. The mixture was stirred for 10 min at room temperature to give a clear yellow solution. After keeping the solution in air for 15 days, yellow block-shaped crystals of **1**, suitable for X-ray crystal structure determination, formed after about 80% of the solvent had evaporated. The crystals were isolated by filtration, washed three times with cold MeOH and dried in a vacuum desiccator over anhydrous CaCl_2 . Yield, 187.2 mg, 81.36% (based on the 3,5-dichlorosalicylaldehyde), m.p. 137.0–138.5°C. Anal. Calcd for $\text{C}_{10}\text{H}_9\text{Cl}_2\text{NO}$ (%): C, 52.2; H, 3.9; N, 6.1. Found: C, 52.1; H, 4.0; N, 6.1.

2.3. Synthesis of bis[2,4-dichloro-6-(cyclopropyliminomethyl)phenolato]copper(II) (**2**)

To a MeCN solution (20 cm^3) of **1** (115.1 mg, 0.5 mmol) was added a MeOH solution (20 cm^3) of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ (99.8 mg, 0.5 mmol) with stirring. The mixture was stirred for 30 min at room temperature to give a clear blue solution. After keeping the solution in air for 18 days, blue block-shaped crystals of **2**, suitable for X-ray crystal structural determination, were formed by slow evaporation of the solvent. The crystals were isolated, washed three times with cold water/MeOH (1:1, v:v) and dried in a vacuum desiccator over anhydrous CaCl_2 . Yield, 81.3 mg, 62.35% (based on **1**), m.p. 312.5–314.5°C (dec.). Anal. Calcd for $\text{C}_{20}\text{H}_{16}\text{Cl}_4\text{CuN}_2\text{O}_2$ (%): C, 46.0; H, 3.1; N, 5.4. Found: C, 46.3; H, 3.2; N, 5.2.

2.4. X-ray crystallography

Diffraction intensities for compounds **1** and **2** were collected at 298(2) K using a Bruker SMART CCD area detector with Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data were reduced using the SAINT program [11] and empirical absorption corrections were performed using the SADABS program [12]. The structures were solved by direct methods and refined against F^2 by full-matrix least-squares methods using SHELXTL version 5.1 [13]. All non-hydrogen atoms were refined anisotropically. The H1 atom in **1** was located in a difference Fourier map and refined isotropically, with O–H restrained to 0.90(1) Å . All other H atoms were placed at geometrically ideal positions and constrained to ride on their parent atoms. Crystallographic data for the compounds are summarized in table 1. Selected bond lengths and angles are given in table 2.

Table 1. Crystallographical and experimental data for **1** and **2**.

Compound	1	2
Formula	C ₁₀ H ₉ Cl ₂ NO	C ₂₀ H ₁₆ Cl ₄ CuN ₂ O ₂
<i>M</i>	230.08	521.69
<i>T</i> (K)	298(2)	298(2)
Crystal shape/Colour	Block/Yellow	Block/Blue
Crystal size (mm ³)	0.26 × 0.19 × 0.17	0.32 × 0.21 × 0.19
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Cmca</i>	<i>C2/c</i>
<i>a</i> (Å)	6.983(2)	23.594(2)
<i>b</i> (Å)	13.912(3)	7.921(1)
<i>c</i> (Å)	21.593(4)	24.284(2)
β (°)	90.00	110.947(2)
<i>V</i> (Å ³)	2097.7(7)	4238.5(7)
<i>Z</i>	8	8
<i>D</i> _c (g cm ⁻³)	1.457	1.635
μ (Mo-K α) (cm ⁻¹)	0.583	1.555
<i>F</i> (000)	944	2104
<i>R</i> _{int}	0.0232	0.0294
Measured reflections	1292	4826
Observed reflections $I \geq 2\sigma(I)$	1084	3745
Min. and max. transmission	0.8632/0.9074	0.6361/0.7566
Parameters	85	262
Goodness-of-fit on <i>F</i> ²	1.050	1.031
<i>R</i> ₁ , <i>wR</i> ₂ [$I \geq 2\sigma(I)$] ^a	0.0461, 0.1085	0.0383, 0.0879
<i>R</i> ₁ , <i>wR</i> ₂ (all data) ^a	0.0536, 0.1134	0.0545, 0.0948
Large diff. peak and hole (e Å ⁻³)	0.295/−0.299	0.542/−0.454

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

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

		1	
N1–C7	1.266(3)	N1–C8	1.424(4)
O1–C2	1.336(3)		
		2	
Cu1–O1	1.916(2)	Cu1–O2	1.894(2)
Cu1–N1	2.008(2)	Cu1–N2	2.018(2)
N1–C7	1.286(3)	N1–C8	1.440(3)
O1–C2	1.299(3)	N2–C17	1.281(4)
N2–C18	1.450(4)	O2–C12	1.296(3)
O2–Cu1–O1	112.76(8)	O2–Cu1–N1	120.60(9)
O1–Cu1–N1	95.87(8)	O2–Cu1–N2	96.39(8)
O1–Cu1–N2	117.81(9)	N1–Cu1–N2	114.99(9)

3. Results and discussion

Compound **1** is yellow powder, stable in air at room temperature, and soluble in common polar organic solvents such as DMSO, DMF, MeOH, EtOH, MeCN and Me₂CO, but poorly soluble in water and Et₂O. The complex derived from the ligand is a mononuclear copper(II) complex. It was stable in air at room temperature, soluble in DMF, DMSO and MeCN, poorly soluble in water and Et₂O, but slightly soluble in MeOH, EtOH and Me₂CO.

3.1. IR spectra

IR spectra of the Schiff base ligand **1** and its complex **2** provide information about metal–ligand bonding. Assignments are based on typical group frequencies. The weak and broad absorptions (table 3) at about 3431 cm^{-1} substantiate the presence of the phenolic group in **1**. A strong absorption band at 1632 cm^{-1} in **1** is assigned to $\nu(\text{C}=\text{N})$ [14]. This band is shifted to lower wave numbers in the complex, attributed to the coordination of the nitrogen atom. The phenolic $\nu(\text{Ar}-\text{O})$ in **1** gives a strong band at 1203 cm^{-1} [15]. However, in the complex the band appears at 1180 cm^{-1} , a shift found in related species [16–18]. Another weak band at 473 cm^{-1} for the complex can be assigned to $\nu(\text{Cu}-\text{O})$ [19], and provides further evidence for coordination through the deprotonated phenolic oxygen atom.

3.2. Structures of **1** and **2**

Figures 1 and 2 give perspective views of **1** and **2** together with the atomic labelling systems. Ligand **1** possesses mirror symmetry, with atoms C1–C8, H4, H6–H8, O1, H1, C11, C12 and N1 lying on the crystallographic mirror plane. There is an intramolecular O1–H1...N1 hydrogen bond, and the dihedral angle between the phenyl and the cyclopropyl rings is 90.0° . Complex **2** is a mononuclear copper(II) complex. The Cu atom is four-coordinated by two N and two O atoms from two deprotonated ligands of **1**. The angles subtended at the Cu1 atom indicate a distorted tetrahedral geometry. The two ligands in **2** are almost perpendicular to each other, decreasing steric interactions between them. In each ligand, the phenyl and the cyclopropyl rings are nearly perpendicular, with an average dihedral angle of $98.4(2)^\circ$.

Table 3. Characteristic IR data (cm^{-1}) for **1** and **2**.

Compound	$\nu(\text{O}-\text{H})$	$\nu(\text{C}=\text{N})$	$\nu(\text{Ar}-\text{O})$	$\nu(\text{M}-\text{O})$
1	3431w,b	1632s	1203s	
2		1623s	1180s	473m

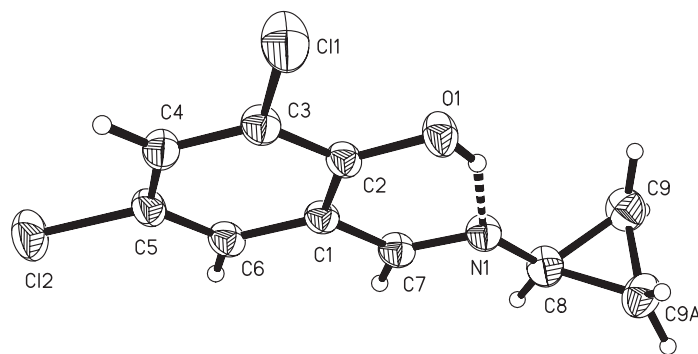


Figure 1. The structure of **1**, showing the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. The intramolecular hydrogen bond is shown as a dashed line.

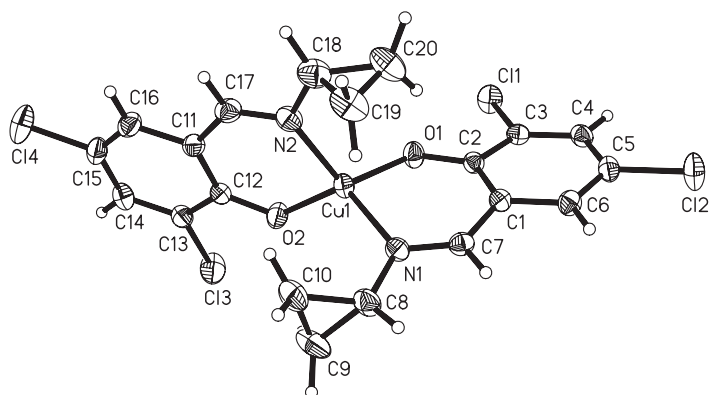


Figure 2. The structure of **2**, showing the atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

The Schiff base ligand **1** can coordinate through the deprotonated form. The bond lengths C7=N1 and C17=N2 in **2** are longer than C7=N1 in **1**, together with C8–N1 and C18–N2 in **2** longer than C8–N1 in **1**, indicating the lone electron pair of the imine N atom is coordinated to copper(II) ion. However, the bonds C2–O1 and C12–O2 in **2** are shorter than C2–O1 in **1**, which is due to the intramolecular O1–H1...N1 hydrogen bond in **1**. In the crystals of **1** and **2**, the molecules are linked through intermolecular C–H...Cl hydrogen bonds, forming chains running along the *b* axis in **1** and the *c* axis in **2**.

Supplementary material

Crystallographic data for **1** and **2** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos CCDC 293612 and 293613. Copies of these data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (20571037).

References

- [1] R.D. Archer, B. Wang. *Inorg. Chem.*, **29**, 39 (1990).
- [2] I. Bertini, H.B. Gray, S.J. Lippard, J.S. Valentine. *Bioinorganic Chemistry*, University Science Books, Mills Valley, CA, USA (1994).
- [3] S.C. Bhatia, J.M. Bindlish, A.R. Saini, P.C. Jain. *J. Chem. Soc., Dalton Trans.*, 1773 (1981).
- [4] S. Chang, L. Jones, C.M. Wang, L.M. Henling, R.H. Grubbs. *Organometallics*, **17**, 3460 (1998).

- [5] P.S. Dixit, K. Srinivasan. *Inorg. Chem.*, **27**, 4507 (1988).
- [6] D.P. Kessissoglou, W.M. Butler, V.L. Pecoraro. *Inorg. Chem.*, **26**, 495 (1987).
- [7] H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo, C. Floriani. *J. Am. Chem. Soc.*, **118**, 981 (1996).
- [8] R. Ramnauth, S. Al-Juaid, M. Motevalli, B.C. Parkin, A.C. Sullivan. *Inorg. Chem.*, **43**, 4072 (2004).
- [9] R. Osterbere. *Coord. Chem. Rev.*, **12**, 309 (1974).
- [10] G.S. Patterson, R.H. Holm. *Bioinorg. Chem.*, **4**, 257 (1975).
- [11] SMART (Version 5.628) and SAINT (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA (1998).
- [12] G.M. Sheldrick. *SADABS. Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany (1996).
- [13] G.M. Sheldrick. *SHELXTL V5.1 Software Reference Manual*, Bruker AXS, Inc., Madison, Wisconsin, USA (1997).
- [14] J.E. Kovacic. *Spectrochim. Acta*, **A23**, 183 (1963).
- [15] G.C. Percy, D.A. Thornton. *J. Inorg. Nucl. Chem.*, **34**, 3357 (1972).
- [16] C. Fukuhara, E. Asato, T. Shimoji, K. Katsura, M. Mori, K. Matsumoto, S. Ooi. *J. Chem. Soc. Dalton Trans.*, 1305 (1987).
- [17] G.E. Batley, D.P. Graddon. *Aust. J. Chem.*, **20**, 877 (1967).
- [18] T. Tokki, Y. Muto, K. Imai, H.B. Janassen. *J. Inorg. Nucl. Chem.*, **35**, 1539 (1973).
- [19] M.M. Bekheit, K.M. Ibrahim. *Synth. React. Inorg. Met.-Org. Chem.*, **16**, 1135 (1986).