Asian Journal of Chemistry Vol. 17, No. 2 (2005), 929–933

Synthesis and Crystal Structure of N,N′-1,2-Phenylene-bis(salicylideneiminato)Copper(II) monohydrate

SHU-SHENG ZHANG*, BO YANG†, YAN-FANG WANG, XUE-MEI LI and KUI JIAO
College of Chemistry and Molecular Engineering
Qingdao University of Science and Technology
266 042 Qingdao, Shandong, China
E-mail: zhangshush@public.qd.sd.cn; Tel: (86)(532)4022750; Fax: (86)(532)4023927

In the title compound ($C_{20}H_{14}N_2O_2Cu$)·H_2O, the space group is R-3 with a = b = 31.676(7), c = 9.040(6) Å, α = β = 90, γ = 120°, belonging to none of the seven crystal systems. The crystal used to collect the present data was twinned. The complex is formed with *cis*-N,N′-1,2-phenylene-bis(salicylidene-iminato) ligand and shows nearly planar geometry. The Cu atom is coordinated by the O and N atoms of the ligand and has a distorted square-planar geometry. The water molecule is bonded to both acceptor O atoms, *viz.*, O1W-H1W1 . . . O1 and O1W-H2W1 . . . O2 intermolecular interactions. The packing is stabilizied by the *n-n* interactions.

Key Words: Salicylideneiminato-copper(II) complex, Crystal structure, Twinned crystal.

INTRODUCTION

Schiff base and its complex have been investigated bacause of function group (C=N) with potential reaction and electro-effect factor[1]. The complexes of transition metal ions with Schiff bases provide a large class of compounds of both stereochemical and magnetochemical interest due to their preparative accessibility, diversity and structure variability. Metal derivatives of Schiff bases have been studied extensively, and copper(II) and nickel(II) complexes play a major role in both synthetic and structural research[2]. In recent years, special attention has been given to the group of copper(II) complexes containing Schiff bases derived from salicylaldehyde and various amino acids and O- or N-donor neutral ligands. Ligands derived from substituted salicylaldimine have played an important part in revealing the preferred coordination geometries of metal complexes. Of particular interest have been those involving copper(II) since they reveal surprising molecular diversity not only in coordination geometry but in more subtle changes in the ligands. Thus complexes with four, five or six donors or with marked tetrahedral distortions are accompanied by bond length changes and deviations from expected ligand geometry[3–5]. In this paper, a different structure in crystal system of the title compound has been reported.

---

†College of Chemistry and Chemical Engineering, Ocean University of China, 266 003 Qingdao, Shandong, China.

EXPERIMENTAL

All chemicals were of analytical reagent grade and used directly without further purification. Elemental analysis was performed by Perkin-Elmer 240. The melting point was determined on an X-4 microscopic melting apparatus and uncorrected.

Preparation of N,N′-1,2-phenylene-bis(salicylideneiminato) ($C_{20}H_{16}N_2O_2$): A solution of 3.6 g salicylaldehyde (30 mmol) in ethanol (50 mL) was added dropwise to boiling ethanol (100 mL) solution of 1.6 g *o*-phenylene diamine (15 mmol). After stirring for 2 h under reflux, the solution was filtered and concentrated *in vacuo*. The yellow crystals (3.8 g) were obtained by recrystallization from acetone.

Preparation of the title compound ($C_{20}H_{16}N_2O_2Cu$)·H_2O: To the boiling ethanol solution (100 mL) of 3.16 g N,N′-1,2-phenylene-bis(salicylidene-iminato) (10 mmol), 1.82 g copper(II) acetate (10 mmol) in ethanol (50 mL) was added dropwise. The solution was stirred for 4 h under reflux. After concentration *in vacuo*, dark purple deposits were obtained. Anal. Calcd. (%) for ($C_{20}H_{14}N_2O_2Cu$)·H_2O: C 60.67, H 4.08, N 7.08; Found (%): C 60.66, H 4.07, N 7.05. The title compound dissolved in chloroform/ethyl acetate (1/1). After filtration, the brown filtrate stood at room temperature. Single crystals suitable for X-ray crystallographic analysis were obtained form the mixed solvent by natural evaporation of 6 d.

Crystallographic data and structure determination[6]: A summary of the key crystallographic information is given in Table-1.

TABLE-1
SUMMARY OF CRYSTALLOGRAPHIC RESULTS FOR COMPOUND (I)

Formula	$C_{20}H_{16}N_5O_3Cu$
Formula weight	385.44
Color/shape	brown/black
Space group	R-3
a (Å)	31.677 (5)
b (Å)	31.677 (5)
c (Å)	9.0406 (18)
V (Å^3)	7856 (2)
Z value	18
$D_{(calcd.)}$ (g cm^{-3})	1.506
μ (mm^{-1})	1.27
Crystal size/mm	0.34 × 0.32 × 0.28
Temp. (K)	293 (2)
θ ranges (°)	2.55–24.97
h/k/l	–32, 0/–32, 0/–10, 10
Reflections collected	3051
Independent reflections	2296
Absorption correction	Empirical
Final R indices [I > 2σ(I)]	R_1 = 0.0679, wR = 0.2619

A suitable crystal of the title compound was mounted on a Nonius CAD4 diffractometer. Reflection data were measured at 20°C using Mo-K_α radiation ($\lambda = 0.71073$ Å) with a graphite monochromator[7]. The technique used was ω-scan with θ limits $3.84 < \theta < 24.97°$. Empirical absorption corrections were carried out by using the SADABS program[8]. Selected bond lengths and angles are presented in Table-2.

TABLE-2
SELECTED GEOMETRIC PARAMETERS (Å, °)

Cu1-O1	1.895 (5)	O2-C20	1.301 (7)
Cu1-O2	1.899 (4)	N1-C7	1.290 (8)
Cu1-N2	1.930 (5)	N1-C8	1.418 (8)
Cu1-N1	1.941 (5)	N2-C14	1.302 (7)
O1-C1	1.302 (8)	N2-C13	1.419 (7)
O1-Cu1-O2	87.280 (19)	O1-Cu1-N1	94.100 (2)
O1-Cu1-N2	176.000 (2)	O2-Cu1-N1	176.100 (2)
O2-Cu1-N2	94.970 (19)	N2-Cu1-N1	83.900 (2)

The structure of the title compound was solved by direct methods and refined by least squares on F^2 by using the SHELXTL software package[9]. All non-H atoms were anisotropically refined. All H atoms were fixed geometrically and treated as riding, with C—H distances = 0.93 Å and U_{iso} (H) = $1.2U_{eq.(C)}$. The final conventional R(F) = 0.0679 and wR(F^2) = 0.1836 for $I > 2\sigma(I)$ with weighting scheme, $\omega = 1/[\sigma^2(F_0^2) + (0.11761P)^2 + 44.7851P]$, where $P = (F_0^2 + 2F_c^2)/3$. The molecular graphics were plotted using SHELXTL. Atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography[10]. Software used to prepare material for publication: SHELXTL, PARST[11] and PLATON[12].

RESULTS AND DISCUSSION

Marinovich *et al.*[13] have reported the structures of N,N′-1,2-phenylene-bis(salicylidene-iminato)copper(II) from chloroform and pyridine. The structure from chloroform shows two crystallographically distinct square-planar molecules per asymmetric unit in an orthorhombic cell, a = 20.159(2), b = 14.918(1), c = 13.329(1) Å; space group $Pna2_1$. Two different stereochemistries are observed when pyridine is the solvent. One has square-planar geometry and the other square-pyramidal with a pyridine molecule bound in the fifth coordination site. The space group is P-1 with a = 8.748 (4), b = 14.499 (4), c = 18.725(5) Å, α 109.93 (3), β = 91.99 (2), γ = 101.64 (3)°. In our work, water has been used as the solvent instead of chloroform and pyridine. What is surprising is that the crystallographic result of the title compound is quite different from the former. The space group is R-3 with a = b = 31.676 (7), c = 9.040 (6) Å, α = β = 90, γ = 120°, belonging to none of the seven crystal systems. The crystal used to collect the present data was twinned. There are two orientational domains, with a and b lattice parameters interchanged. The origin of the twinning is due to the unit-cell a and b axes being equal in length within experimental error. While introduction of the twin command TWIN (010/100/001) in the refinement did not reduce R and wR.

The complex is formed with *cis*-N,N′-1,2-phenylene-bis(salicylidene-iminato) ligand and shows nearly planar geometry (Fig. 1). The Cu atom is coordinated by the O and N atoms of the ligand and has a distorted square-planar geometry. The distortion consists of a reduction of the O1-Cu1-N2 and O2-Cu1-N1 angles with the chelate rings from the ideal value of 180° to 176.0(2) and 176.1(2)°, respectively. A two-fold of symmetry passes through the Cu atom, such that all other atoms are symmetry-related in pairs.

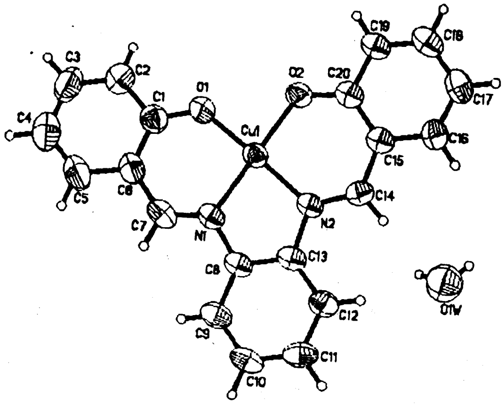

Fig. 1. The structure of the title compound showing 50% probability displacement ellipsoids and the atom numbering scheme

The Cu—O and Cu—N bond lengths are within experimental error. However, the N1-C7 bond length [1.290(8) Å] is significant longer than [1.270(3) Å] in the related chloroform compound[13], while the C6-C7 [1.412(10) Å] and O1-C1 [1.302(8) Å] bond lengths are shorter than those corresponding to values in reference 13 [1.457(4) and 1.345(3) Å]. The dihedral angles between the mean planes of the two six-membered rings formed by Cu and their fused benzene rings are 0.9(2) and 4.3(3)°, respectively, comparable with the corresponding values 0.6 and 2.7° in the previously reported chloroform compound.

The water molecule is bonded to both acceptor O atoms, *viz*., O1W-H1W1...O1 and O1W-H2W1...O2 intermolecular interactions (Fig. 2 and

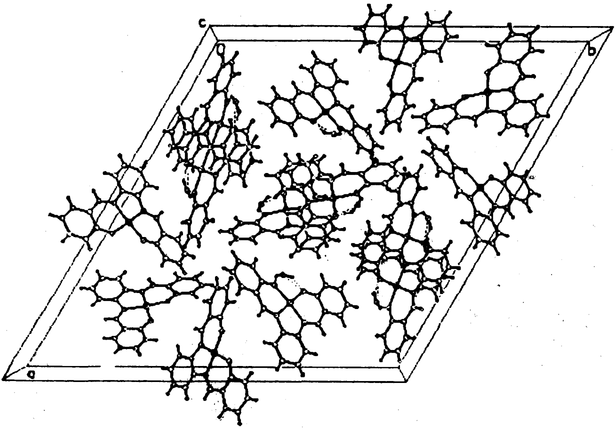

Fig. 2. Packing diagram of the title compound

Table-3). The packing is stabilized by the Cg1...Cg5 (–x, 1 – y, 1 – z) 3.55 Å, Cg1...Cg6 (–x, 1 – y, –z) 3.46 Å, Cg3...Cg5 (–x, 1 – y, 1 – z) 3.62 Å and Cg3...Cg6 (–x, 1 – y, 1 – z) 3.66 Å (where Cg1 is the centroid of the five-membered chelate ring, Cg3 is the centroid of the six-membered chelate ring containing O2, while Cg5 and Cg6 denote the centroids of the C8-C13 and C15-C20 rings, respectively) interactions.

TABLE-3
HYDROGEN-BONDING GEOMETRY (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O1W-H1W1···O1[i]	0.85	2.41	3.13(9)	142
O1W-H2W1···O2[i]	0.85	2.18	2.87(1)	138

Symmetry code: (i) – x, 1 – y, –z.

ACKNOWLEDGEMENTS

We thank the National Natural Science Foundation of China (No. 20275020) and the Outstanding Adult-young Scientific Research Encouraging Foundation of Shandong Province (No. 03BS081) for financial support.

REFERENCES

1. E. Yalcin, K. Mehmet and E. Ayhan, *Anal. Sci.*, **19**, 331 (2003).
2. S. Tero-Kubata, K. Akijama and T. Ikoma, *J. Phys. Chem.*, **95**, 766 (1991).
3. L. Sacconi, *Coord. Chem. Rev.*, **31**, 126 (1996).
4. M. Calligaris, G. Nardian and L. Randaccio, *Coord. Chem. Rev.*, **7**, 385 (1972).
5. N. Waters, *God. Jugosl. Centr. Kristalogr. (Ann. Yugosl. Centre Crystallogr.)*, **17**, 25 (1982).
6. CCDC 226277 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).
7. Siemens, SMART and SAINT, Area Detector Control and Integration Software, Siemens Analytical X-ray Systems, Inc., Madison, Wisconsin, USA (1996).
8. SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen, Germany (1996).
9. G.M. Sheldrick, SHELXTL, v5 Reference Manual, Siemens Analytical X-ray Systems, Inc., Madison, Wisconsin, USA (1996).
10. A.J.C. Wilson, International Table for X-ray Crystallography, Volume C, Kluwer Academic Publishers, Dordrecht, Tables 6.1.1.4 (pp. 500–502) and 4.2.6.8 (pp. 219–222) respectively (1992).
11. M. Nardelli, *J. Appl. Cryst.*, **28**, 659 (1995).
12. A.L. Spek, *Acta Cryst.*, **A46**, C-34 (1990).
13. A.F. Marinovich, R.S. O'Mahony, J.M. Waters and T.N.M. Waters, *Croatica Chim. Acta*, **72**, 685 (1999).

(*Received*: 5 June 2004; *Accepted*: 24 December 2004) AJC-4028