X-Ray Crystal Structure of [*N, N'*-bis(4-Methoxysalicylidene) -2, 3-Dimethylaminopropane] Copper(II) Ethanol Solvate

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Abstract

   The crystal structure of the title Schiff base complex is obtained by single-crystal X-ray diffraction data. The solid state structure determination reveals that the coordination geometry around the copper(II) center is tetrahedrally distorted square-planar. The crystal packing shows one dimensional infinite chains which arises from the intermolecular interaction and stabilize the crystal packing.

Keywords: Schiff base , crystal structure

Introduction

   Mixed donor ligands comprise a vast area of coordination chemistry. The prerequisite is bi- or polydentate capability, and the variety of donor atoms is overwhelming, including the commonly found N, O, S, and P [1]. Among the different coordinating ligands in the field of coordination chemistry, Schiff bases are one of the most prevalent and important of the mixed donor systems which play important rule in coordination chemistry. They result from the condensation of primary amines with ketones or aldehydes to give imines containing a C=N bond which called Schiff base after Schiff [2]. Metal derivatives of Schiff bases have been extensively studied, and Ni (II) and Cu (II) complexes play a major role in both synthesis and structural research. Several complexes of salicylaldehyde and its derivatives have been studied. Encouragement for the syntheses of the symmetrical Schiff base metal complexes

and the study of their physical and chemical properties is provided by their potential abilities in biological modeling application, e.g. to mimic the N4 donor set of Cu (II) in superoxide dismutase (SOD), a Cu (II)–Zn (II) enzyme which destroys the toxic superoxide by catalyzing its disproportionation into peroxide and oxygen and also their oxygen transfer ability as artificial model of Cytochrome P-450 [3-9].

The molecular and crystal structures determined by X-ray and /or neutron diffraction are integral to the research, especially the description and classification of intermolecular in terms of derived interatomic distances and other geometric criteria. Structural information by single-crystal X-ray diffraction provides valuable information about the function and mechanisms of these complexes in the desired reaction. Also, intermolecular interactions play a key role *in vivo* in many biological transformations.

Herein, we report the crystal structure of the title compound in order to obtain clear

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information about all intermolecular interactions involved in the crystal structure.

Experimental Section
Synthesis of the Complex

The ethanolic solution of the Schiff base ligand (1 mmol) was added to a methanolic solution of $CuCl_2 \cdot 4H_2O$ (1.1 mmol) in a round-bottomed flask and refluxed for 1 h. A green crystalline compound was separated out on cooling. It was recrystallized from ethanol to obtain block shaped single crystals suitable for X-ray diffraction.

X-Ray Crystallography

The data were collected on a Bruker SMART APEXII CCD area detector diffractometer with Mo Kα radiation (λ = 0.71073 Å) equipped with an Oxford cryosystem Cobra low temperature attachment. Cell parameters were retrieved using SMART [10] software and refined using SAINT [11] on all observed reflections. Data reduction and correction for Lp and decay were performed using SAINT Plus software. Absorption corrections were applied using SADABS [12]. The structure was solved by direct methods and refined by the least squares method on F^2 using the SHELXTL program package [13]. All calculations were performed by PLATON [14]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and refined with a riding model approximation with their parameters constrained to the parent atom with U_{iso} (H) = 1.2 or 1.5 U_{eq} (C or O).

Results and Discussion
Description of the structure

The perspective drawing of complex **1** and its packing diagram is shown in Fig. 2. The crystal data and refinement details of the title complex are given in Table 1. The selected bond lengths and angles are given in Table 2. The hydrogen bond information is given in Table 3. The bond lengths [15] and angles are within the normal ranges and are comparable to the related structures [16]. The asymmetric unit of the title compound comprises a unit of the complex and an ethanol solvent of crystallization. The copper atom has a distorted square-planar geometry which is coordinated by the N_2O_2 donor atoms of the Schiff base ligand. The intermolecular O−H···O hydrogen bonds between the solvent of crystallization and the complex [O5−H5···O1 and C11−H11A···O5], link neighboring molecules into individual dimers (Fig. 3). These dimers are connected together by intermolecular π···π interactions, forming one-dimensional (1-D) infinite chains along the a-axis (Fig. 3). The intermolecular π···π interactions are involved between the $Cg1$···$Cg1^{(i)}$ [(i) 2 − x, 1 − y, 3 − z] and $Cg2$···$Cg2^{(ii)}$ [1 − x, 1 − y, 3 − z] of the neighboring complexes in which $Cg1$ and $Cg2$ are the centroids of the six-membered Cu(1)/O(1)/C(1)/C(6)/C(7)/N(7) and Cu(1)/O(2)/C(17)/C(12)/C(11)/N(2) rings with the distances of 3.7562(6) and 3.6169(6) Å, respectively (Fig. 3). The crystal structure is further stabilized by the intermolecular C10−H10A···$Cg3$ interactions [$Cg3$ is the centroid of the C(12)/C(13)/C(14)/C(15)/C(16)/C(17) benzene ring]. The dihedral angle between the coordination planes involving Cu(1)/O(1)/C(1)/C(6)/C(7)/N(1) and Cu(1)/O(2)/C(17)/C(12)/C(11)/N(2) is 37.47(03) ° which confirms significant deviation from the square-planar geometry around copper. The dihedral angle between the mean planes of the two benzene rings is 43.78(6) °. The interesting features of the crystal structure are the short intermolecular O(2)···C(7) [3.0724(14) Å; (i) 2 − x, 1 − y, 3 − z] and C(10)···C17 [3.2465(16) Å ; (ii) 1 − x, 1 − y, 3 − z] contacts which are shorter than the sum of the van der Waals (vdW) radii of these atoms. The crystal structure is further stabilized by C−H···π interactions.

Conclusion

The title Schiff base complex was prepared and its solid state structure was obtained by single-crystal X-ray diffraction data. The crystal and molecular structure show interesting intermolecular interactions which stabilize the packing of the complex. The interesting feature of the crystal packing is forming 1-D infinite chains which arises from the intermolecular π···π interactions.

Table 1. The crystal data and refinement details of the complex.

Empirical formula	$C_{21}H_{24}N_2O_4Cu \cdot C_2H_6O$
Formula mass	478.04
Crystal size (mm)	$0.415 \times 0.233 \times 0.143$
Colour	green
Crystal system	Monoclinic
Space group	$P2_1/c$
θ_{max} (°)	32.5
a (Å)	9.6422(3)
b (Å)	17.1635(5)
c (Å)	13.7236(4)
β (°)	93.132(1)
V (Å^3)	2267.78(12)
Z	4
D_{calc} (Mg/m^3)	1.400
μ (mm^{-1})	0.999
F (000)	1004
Index ranges	$-14 \leq h \leq 13$
	$-16 \leq k \leq 25$
	$-20 \leq l \leq 20$
No. of measured reflections	35740
No. of independent reflections/R_{int}	8200/0.029
No. of observed reflections $I > 2\sigma(I)$	6931
No. of parameters	284
Goodness-of-fit (GOF)	1.04
R_1 (observed data)	0.0316
wR_2 (all data)[a]	0.0888
Largest peak and deepest hole (e. Å^{-3})	0.45, -0.96

[a] $w = 1/[\sigma^2(F_o^2) + (0.0464)^2 + 0.8148P]^2$, where $P = (F_o^2 + 2F_c^2)/3$

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

Cu(1)–O(1)	1.9128(8)	O(1)–Cu(1)–O(2)	90.31(4)
Cu(1)–O(1)	1.9070(9)	O(1)–Cu(1)–N(1)	94.29(4)
Cu(1)–N(1)	1.9505(10)	O(1)–Cu(1)–N(2)	152.70(4)
Cu(1)–N(2)	1.9294(10)	O(2)–Cu(1)–N(1)	156.20(4)
O(1)–C(1)	1.3136(15)	O(2)–Cu(1)–N(2)	94.79(4)
O(2)–C(17)	1.3064(14)	N(1)–Cu(1)–N(2)	91.76(4)
N(1)–C(7)	1.2934(15)	O(1)–C(1)–C(6)	123.61(10)
N(2)–C(11)	1.2956(15)	N(1)–C(7)–C(6)	125.63(11)

Table 3. Parameters of hydrogen bonding interactions in the complex.

D–H···A	H···A (Å)	D···A (Å)	D–H···A (°)
O5–H5···O1	1.96	2.7721(13)	163
C11–H11A···O5[i]	2.41	3.3392(15)	167
C19–H19A···O5[ii]	2.51	3.4136(18)	153

(i) $1 - x, 1 - y, 3 - z$, (ii) $1 - x, \frac{1}{2} + y, 5/2 - z$
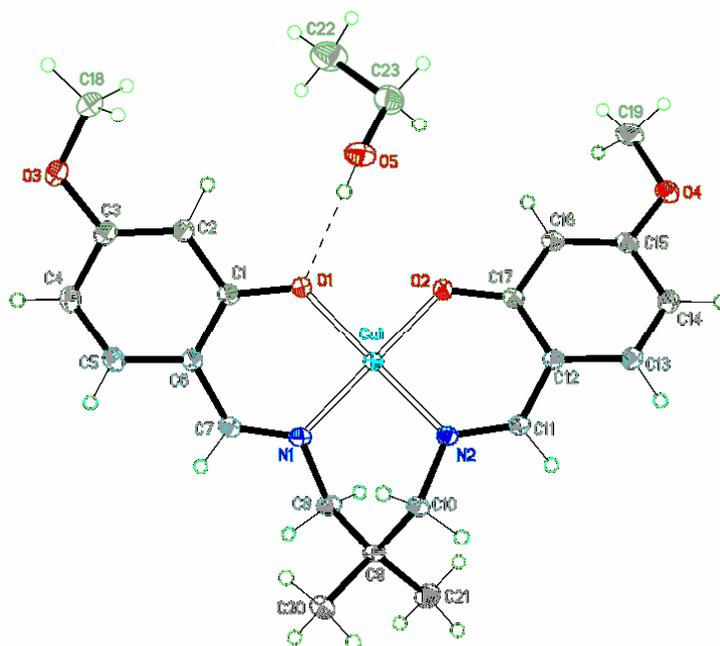
Fig.1. The ORTEP diagram of the complex with 50% thermal ellipsoid probability and atom labels. The dashed lines show intermolecular hydrogen bond.
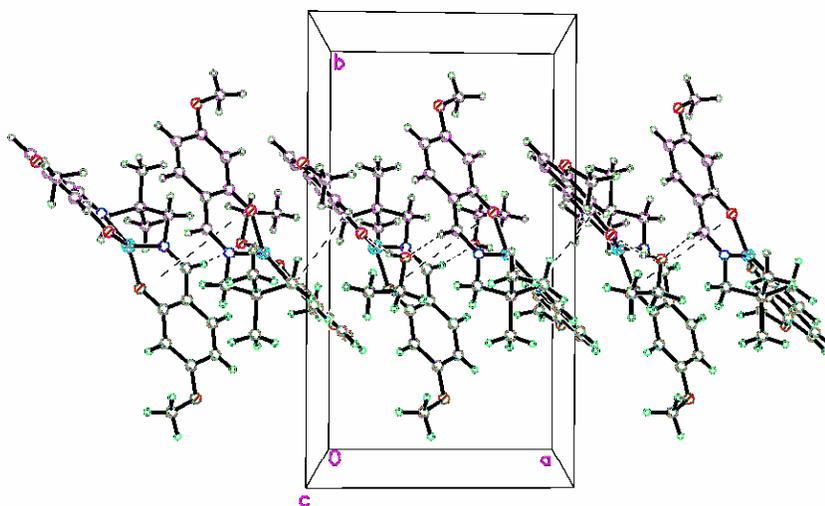

Fig 2. The crystal packing of the complex viewed down the *c*-axis, showing 1-D infinite chains along the *a*-axis by the intermolecular π⋯π interactions.
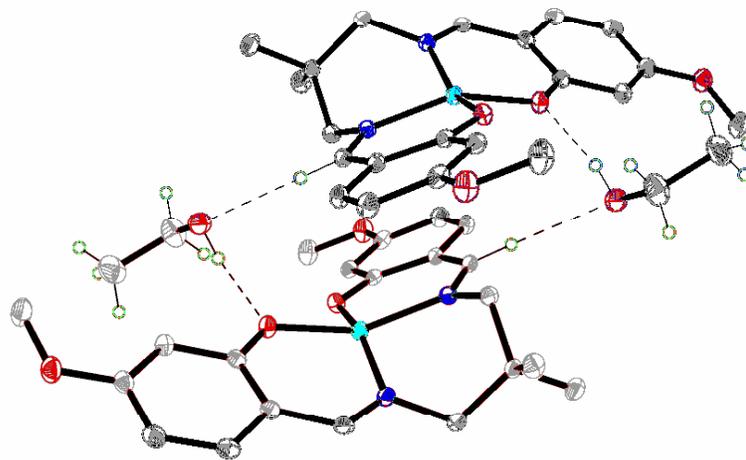
Fig 3. A view of the dimer formation through intermolecular O–H···O hydrogen bonds between the complex and solvent of crystallization.

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