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The Copper(II) Complexes with Tetradentate Schiff Base Ligands: Synthesis, Crystal Structures, and Computational Studies[1]

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Abstract—Mononuclear copper(II) Schiff base complexes, Cu($BrSal_2Pn$) (**I**) and Cu($BrSal_2MePn$) (**II**), where $BrSal_2Pn$ = N,N'-bis(5-bromo-2-hydroxybenzylidene)propane-1,3-diamine and $BrSal_2MePn$ = N,N'-bis(5-bromo-2-hydroxybenzylidene)-2,2-dimethylpropane-1,3-diamine, have been synthesized and characterized by elemental analyses and single-crystal X-ray diffraction. Also, the optimized geometries of them have been calculated using density functional theory method (B3LYP/6-31g). Obtained structural parameters are in agreement with the experimental data. The geometry around the copper atoms display a distorted square-planner structure by coordinating with two oxygen atoms from the phenols moieties and two nitrogen atoms from the imino groups of ligands and thus established three 6-membered rings.

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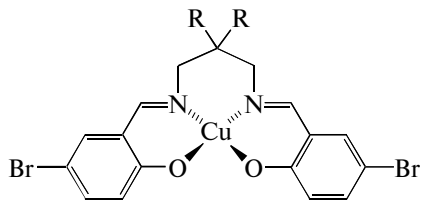
INTRODUCTION

During recent years transition metal complexes of tetradentate Schiff base ligands have received much attention [1–5]. Schiff base ligands played important role in the development of coordination chemistry of transition metals, such as Zn(II), Ni(II), Mn(III) and etc. [1–10]. The coordination geometry of the complexes depends upon the chemical structure of ligand chosen [1–10], the coordination geometry preferred by transition metal [11, 12], metal-to-ligand ratio [13, 14], reaction temperature [15, 16], the coordination ability of counteranion and bridging ligands [17–21]. The study of copper(II) tetradentate Schiff base complexes has come from different areas of interest which include magnetic properties [1, 22, 23], catalytic activity [24], chemical structure [22, 25–27] and DFT calculation [28]. However, the structure of some other mononuclear copper(II) complexes with tetradentate Schiff base ligands have been reported [28–32]. In this paper, we reported synthesis, crystal structures and computational studies of two mononuclear copper(II) Schiff base complexes, Cu($BrSal_2Pn$) (**I**) and Cu($BrSal_2MePn$) (**II**):



R = H: Cu($BrSal_2Pn$) (**I**); R = Me: Cu($BrSal_2MePn$) (**II**)

[1] The article is published in the original.

EXPERIMENTAL

Material and methods. All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer.

Synthesis of the Schiff bases $BrSal_2PnH_2$ and $BrSal_2MePnH_2$. These ligands were prepared by reaction of 5-bromo-2-hydroxybenzaldehyde with 1,3-diaminopropane or 2,2-dimethylpropylenediamine, respectively, based on the reported method [33]. The yield was 93 and 91%, respectively.

Synthesis of Cu($BrSal_2Pn$) (I) and Cu($BrSal_2MePn$) (II). To a solution of $BrSal_2Pn$ or $BrSal_2MePn$ (2 mmol in 20 mL acetone) was added methanolic solution of Et_3N (2 mmol in 5 mL). The mixture was stirred for a few minutes. Then methanolic solution of $Cu(NO_3)_2 \cdot 3H_2O$ (1 mmol in 15 mL) was added to the mixture slowly. The mixture was stirred for about 30 min. The dark green crystals obtained by slow evaporation of solvent at room temperature after 3 days. The yields of **I** and **II** were 88%.

For $C_{17}H_{14}Br_2CuN_2O_2$ (**I**)			
anal. calcd., %:	C, 40.70;	H, 2.81;	N, 5.58.
Found, %:	C, 40.76;	H, 2.92;	N, 5.61.
For $C_{19}H_{18}Br_2CuN_2O_2$ (**II**)			
anal. calcd., %:	C, 43.08;	H, 3.42;	N, 5.29.
Found, %:	C, 43.06;	H, 3.49;	N, 5.30.

Table 1. Crystallographic data and structure refinement parameters for **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	1003.32	1059.43
Crystal system; space group	Monoclinic; $C2/c$	Monoclinic; $I2/a$
T, K	170	170
a, Å	21.1683(7)	7.7353(8)
b, Å	8.1151(3)	10.6176(8)
c, Å	9.4891(3)	22.7645(15)
β, deg	92.365(3)	92.600(8)
V, Å^3	1628.68(10)	1867.7(3)
Z	2	2
F(000)	980	1044
μ, mm^{-1}	6.26	5.46
ρ_{calcd}, mg m^{-3}	2.046	1.884
Crystal size, deg	0.36 × 0.24 × 0.07	0.25 × 0.31 × 0.11
Index ranges h, k, l	$-29 \le h \le 30$, $-11 \le k \le 11$, $-8 \le l \le 13$	$-7 \le h \le 11$, $-15 \le k \le 15$, $-31 \le l \le 31$
θ Range, deg	2.7–31.6	3.3–31.8
Measured reflections	7665	7872
Independent reflections (R_{int})	2552 (0.028)	2858 (0.025)
Reflection with $I > 2\sigma(I)$	1697	1958
S	1.09	0.97
R ($F^2 > 2\sigma(F^2)$)	0.029	0.030
wR (F^2)	0.090	0.080
Parameters	113	119
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	0.61, –0.49	0.71, –0.34
$(\Delta/\sigma)_{max}$	0.001	0.001

X-ray structure determination. A dark green single crystals of **I** and **II** were placed at the top of a glass fiber with silicone grease and mounted on an Xcalibur 2 CCD diffractometer (Oxford Diffraction) fitted with a graphite-monochromated MoK_α radiation (λ = 0.71073 Å). Data were collected at 170 K. The structure was solved by direct methods and successive Fourier difference syntheses and refined on F^2 by weighed anisotropic full-matrix least-squares methods [34]. All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were calculated and, therefore, included as isotropic fixed contributors to F_c. Data collection and data reduction were done with the CRYSALIS-CCD and CRYSALIS-RED programs [35]. All other calculations were performed with standard procedures (WINGX) [36]. Crystal data, structure refinement, and collection parameters for **I** and **II** are listed in Table 1. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 892992 for **I** and 892993 for **II**; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Computational details. The geometry of **I** and **II** has been optimized by using HF model with the method at B3LYP/6-31g basis set. All HF calculations were performed using the Gaussian 98 R-A.9 package [37].

RESULTS AND DISCUSSION

As shown in Fig. 1, our results demonstrate that the Cu^{2+} ion is coordinated with one Schiff base ligand, forming a four-coordination number and monomeric, crystallized in the monoclinic space group $C2/c$ for **I** and $I2/a$ for **II**. Molecular site symmetry for **I** and **II** is $C2$. Selected bond distances and angles to described coordination environment of **I** and **II** are given in Table 2.

Depending on the substituent effects, coordination geometry of the copper(II) complexes containing tetradentate Schiff base ligands is varied from a square planar to a tetrahedral and shows structural phase transitions by heating [38, 39]. In the presence of tetradentate N_2O_2 Schiff base ligand, coordination geometry around the Cu^{2+} ion adopts a distorted square-planar rather than the tetrahedron [28–32].

The geometry around the Cu^{2+} ion of complexes **I** and **II** is established by two phenolato oxygen atoms (O(1) and O(1)^i) and two imino nitrogen atoms (N(1) and N(1)^i). The structures also show that the oxygen atoms of phenolic groups (O(1) and O(1)^i) and nitrogen atoms of imine moiety (N(1) and N(1)^i) adopt a *cis*-configuration around the copper atom. Examination of the copper-ligand distances of copper(II) tetradentate Schiff base complexes [29–32, 40, 41] shows that the Cu–N distances are longer than those of Cu–O bonds as the title complexes are. The Cu–N bond distances are 1.955(2) Å in **I** and 1.9419(17) Å in **II**, while the Cu–O distances have 1.9126(19) Å in **I**

Table 2. Selected bond distances and bond angles for **I** and **II***

Bond (exp./theor.)	*d*, Å (exp./theor.)	
	I	**II**
Br–C(4)/C(6)–Br(9)	1.901(3)/1.876	1.897(2)/1.882
Cu–O(1)^{i}/Cu(24)–O(23)	1.9126(19)/1.896	1.8896(15)/1.881
Cu–O(1)/Cu(24)–O(10)	1.9126(19)/1.886	1.8896(15)/1.878
Cu–N(1)^{i}/Cu(24)–N(14)	1.955(2)/1.947	1.9419(17)/1.947
Cu–N(1)/Cu(24)–N(1)	1.955(2)/1.945	1.9419(17)/1.931
O(1)–C(1)/O(10)–C(5)	1.297(3)/1.296	1.296(3)/1.303
C(6)–C(1)/C(3)–C(5)	1.412(4)/1.447	1.419(3)/1.442
C(6)–C(7)/C(3)–C(2)	1.431(4)/1.444	1.431(3)/1.439
N(1)–C(7)/N(1)–C(2)	1.303(4)/1.302	1.276(3)/1.304
N(1)–C(8*A*)/N(1)–C(11)	1.485(7)/1.487	
N(1)–C(8*B*)/N(1)–C(11)	1.508(7)/1.487	
N(1)–N(8)/N(1)–C(11)		1.460(3)/1.493
Angle (exp./theor.)	ω, deg (exp./theor.)	
	I	**II**
O(1)^{i}CuO(1)/O(10)Cu(24)O(23)	87.53(12)/89.6	88.13(9)/91.1
O(1)CuN(1)/O(10)Cu(24)N(1)	93.38(9)/92.8	93.54(7)/94.3
O(1)CuN(1)^{i}/O(10)Cu(24)N(14)	153.77(9)/152.8	160.80(7)/159.1
N(1)^{i}CuN(1)/N(1)Cu(24)N(14)	97.12(14)/99.2	91.12(10)/92.6
C(7)N(1)C(8*A*)/C(2)N(1)C(11)	110.2(3)/111.8	
C(7)N(1)C(8*B*)/C(2)N(1)C(11)	119.3(3)/118.8	
C(7)N(1)C(8)/C(2)N(1)C(11)		118.66(18)/117.8
C(7)N(1)Cu/C(2)N(1)Cu(24)	122.64(19)/124.6	125.06(14)/124.9
C(8*A*)N(1)Cu/C(11)N(1)Cu(24)	126.7(3)/125.5	
C(8*B*)N(1)Cu/C(11)N(1)Cu(24)	117.3(3)/116.5	
C(8)N(1)Cu/C(11)N(1)Cu(24)		115.65(13)/117.0
N(1)C(7)C(6)/N(1)C(2)C(3)	127.5(3)/126.9	126.5(2)/126.5

* Symmetry codes: ^{i} $-x + 1, y, -z + 1/2$.

and 1.8896(15) Å in **II**, and are similar to those bonds in related copper(II) Schiff base complexes [30–32]. The C(7)=N(1) bond distances in **I** and **II** are 1.303(4) and 1.276(3) Å, respectively, conform to the value for a double C=N bond. The N(1)–C(8*A*) and N(1)–C(8*B*) bond distances in **I** and N(1)–C(8) bond distance in **II** are 1.485(7), 1.4508(7), and 1.460(3) Å, respectively, conform to the value for a single C–N bond [29–32, 40, 41].

It is worth noting the angular deviations of the coordination environment from ideal *trans*-square planar geometry (Table 2). These deviations reflect the chelating ring strain in the place of the imine nitrogens and phenolato oxygens [40].

Only some structural information is available for copper(II) complexes with tetradentate Schiff base ligands [28, 42]. The geometry optimizations of complexes **I** and **II** with labaling of the atoms were performed by DFT, computations utilizing B3LYP hybrid method are shown in Fig. 2. There is a very well agreement between the theoretically determined parameters, bond distances and angles of **I** and **II** with the experimental values are available in Table 2.

Carried out analysis from DFT on a number of bond distances and angles of complexes **I** and **II** shown the coordination geometry around the Cu^{2+} ion is distorted square planar with oxygen atoms (O(10) and O(23)) and two nitrogen atoms (N(1) and N(14)) from

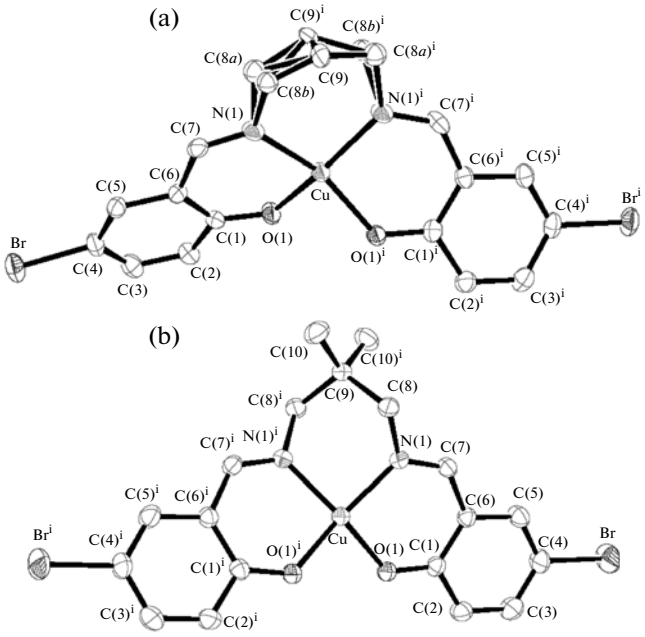


Fig. 1. Molecular structures of **I** (a) and **II** (b) with thermal ellipsoid of 50%.

the Schiff base ligands $BrSal_2Pn$ and $BrSal_2MePn$. The average calculated values of Cu–N (1.955 Å in **I** and 1.942 Å in **II**) and Cu–O (1.912 Å in **I** and 1.889 Å in **II**) bond distances are in the expected range and good agreement with the experimental values (Table 2).

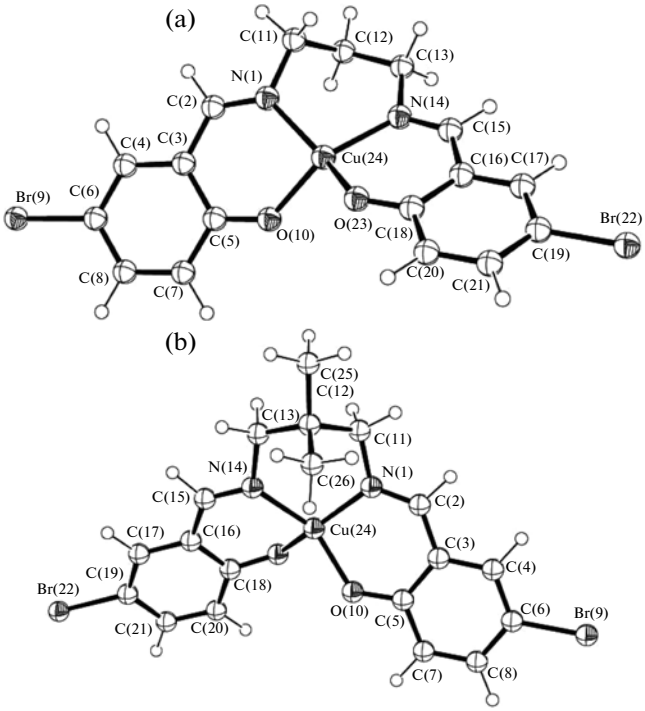


Fig. 2. Molecular structure of **I** (a) and **II** (b) from computational calculation.

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