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Structure and electrochemical behaviour of Bis[N-(4-methylphenyl)salicylaldimine]copper(II) N,N-dimethylformamide solvate

The molecular model of mononuclear complex formed, through a reaction between N-(4-methylphenyl)salicylaldimine and Cu^{II} ion was determined using x-ray diffraction method. The Cu^{II} coordination was found to have a distorted square-planar structure and a *cis* coordination geometry was observed within the surrounding of the copper. The electro chemical behaviour of the mononuclear copper complex was studied with cyclic voltammetry.

Keywords: crystal structure, mononuclear Cu complex, Schiff base, element analysis, thermal analysis, IR, cyclic voltammetry

Introduction

Schiff bases were used in coordination chemistry by P. Pfeiffer [1]. Co and Cu Schiff base complexes were of the first complexes whose crystallographic structure was determined using ancient methods [2]. In recent years research on many newly synthesized Cu Schiff base complexes continues [3,4,5,6,7,8]. It has been reported in literature that the structure of the R-group bonded to the imine nitrogen severely effects the coordination for complexes formed between ON type Schiff bases and transition metals [9, 10, 11, 12].
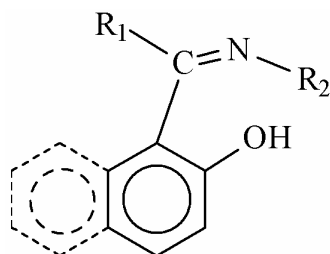

Fig. 1: ON type Schiff base.

Fig. 1 is a general scheme of an ON type Schiff base. It is reported in literature that the steric structure of the R_2-group effects the coordination geometry. It has been stated that when the

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R$_2$-group is a large group like t-butyl, then a tetrahedral complex is formed with Ni^{II} and Cu^{II}. On the other hand if the R$_2$-group is small or planar then a square-planar coordination with *trans*-structure can be formed [12]. X-ray studies have revealed the complexes to posses a *trans*-structures (Fig. 2) [3, 4, 5, 6, 7, 8].
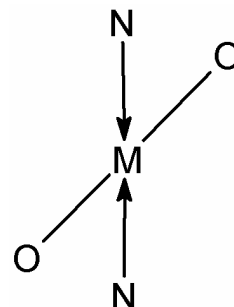

Fig. 2: Diagram of a *trans*-structure.

In this study a complex was prepared from a simple ON type Schiff base, N-(4-methylphenyl)salicylaldimin and Cu^{II} ion in dmf (dimethylformamide) media. The molecular structure of the complex was determined by x-ray diffraction. The mononuclear complex was seen to be of a distorted-square planar structure and *cis* coordination geometry.
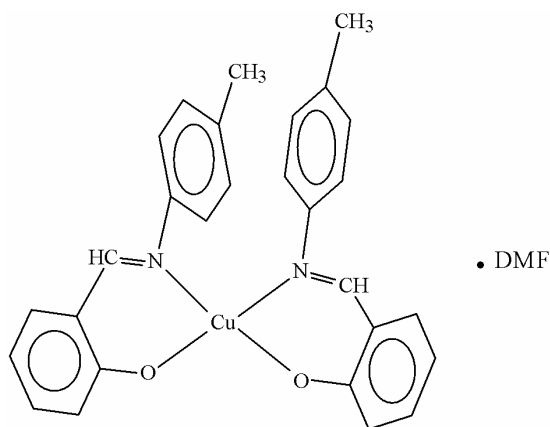

Fig. 3: Chemical diagram of the title compound.

Experimental

Synthesis

The ligand N-(4-methylphenyl)salicylaldimine was prepared by the condensation reaction of equimolar amounts of salicylaldehyde and 4-methylaniline in EtOH (ethanol) media. 0.422 g (0.002 mol) N-(4-methylphenyl)salicylaldimine was dissolved in 50 ml of hot dmf. To this solution was added 1.00 ml Et$_3$N and 0.341 g (0.002 mol) CuCl$_2$.H$_2$O dissolved in 20 ml hot dmf. The resulting solution was left to stand at atmospheric conditions for 12 hours. The precipitate crystals were filtered and dried in air. [C$_{31}$H$_{31}$N$_3$O$_3$Cu]

Element analysis

Calculation %: C: 66.83, H: 5.61, N: 7.54, Cu: 11.40
Found %: C: 66.79, H: 5.90, N: 7.39, Cu: 11.63

Thermal Analysis

dmf loss at 170°C, calculated %: 13.10, found %: 12.66

IR data (cm^{-1})

ν_{C-H} (Ar): 3052, ν_{C-H} (Aliph): 2914-2860, $\nu_{C=O}$ (dmf): 1676, $\nu_{C=N}$: 1620, $\nu_{C=C}$ (Ar): 1600, δ_{C-H} (Aliph): 1472

Cyclic Voltammetry (CV)

Cyclic voltammetry experiments were carried out using a conventional three electrode cell having a Pt foil electrode with an area of 1 cm^2 as the working electrode. Prior to the experiments the electrode was cleaned and polished with 0.05 micron alumina, wiped washed with acetone and finally with distilled water. The counter electrode consisted of a piece of platinum wire. The reference electrode to which all potentials are referred was a saturated Ag/AgCl electrode isolated from the main cell by a Haber-Luggin Capillary. The test solutions were deoxygenated with argon for 30 minutes. All measurements were carried out at room temperature. The working media consisted of dmf and Bu$_4$NBr as supporting electrolyte in the potential range –2V to +0.2V with a scan rate of 100 mV/s. All measurements were carried out on a VoltaLab 40 system connected to a PC. The software used was VoltaLab 40 Electrochemical software.

The cyclic voltammograms of {N,N′-bis(salicylidene)-1,3-propanediaminato} copper(II) and {N-(2-methylphenyl)salicylidiminato}copper(II) complexes were recorded for comparison. The voltammogram of the complex is in Fig.4. Although demetalization was not observed as stated in literature [4] the Cu^{2+}/Cu$^+$ and Cu$^+$/Cu^0 reduction processes can be observed at –1.05 and –1.78V, respectively.
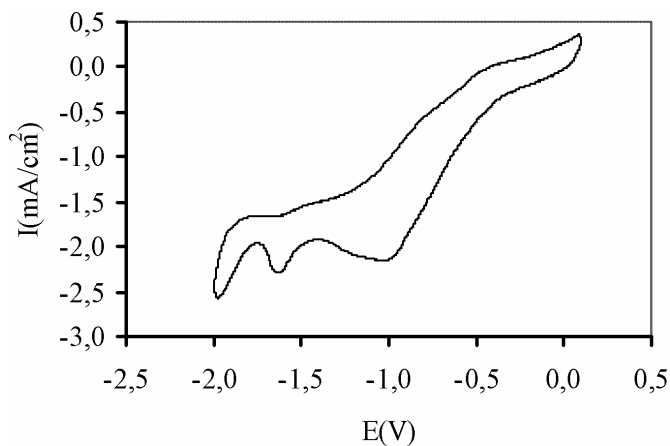

Fig. 4: The voltammogram of the complex.

The most important feature observed in the voltammogram is the intensity of the Cu^+/Cu^0 reduction which is large with respect to the other complexes and literature (Fig. 4). Moreover the reduction potential of Cu^+/Cu^0 is seen to shift to more negative potential with respect to {N-(2-methylphenyl) salicylaldimino} copper(II) and {N,N′-bis(salicylidene)-1,3-propan-ediaminato} copper(II).

X-ray crystal structure analysis

X-ray diffraction data of single crystal were collected at room temperature with graphite-monochromated MoK_α radiation on an Enraf-Nonius CAD4 diffractometer [13] operating in $\omega/2\theta$ scan mode. The cell parameters were determined from a least-squares refinement of 25 centred reflections in the range of $9.94 \leq \theta \leq 18.02°$. Cell refinement was carried out using CAD-4 EXPRESS [13]. During data collection, three standard reflections were periodically measured for every 120 minutes, showed no significant intensity variation. 5819 reflections were collected of which 5537 symmetry-independent reflections and 3391 had $I \geq 2\sigma(I)$. Absorption correction (*y*-scan) was applied to intensity values (T_{max} = 0.9198, T_{min} = 0.8735). Data reduction was carried out using SHELXL97 [14].

The structure was solved by direct method using the program SHELXS97 [14] in the WinGX package [15] and a full-matrix least-squares refinement on F^2 was done. For all non-hydrogen atoms anisotropic displacement parameters have been refined. Hydrogen atoms of the aromatic rings and the methyl groups were placed geometrically and refined as riding with $U_{eq}(H)=1.2\ U_{iso}(C)$. H7, H21 and H29 atoms were taken from a difference Fourier map and refined with isotropic thermal parameters. A chemical diagram of the title compound is given Figure 3. The ORTEP drawing [16] of the molecule is shown in Figure 5. Selected crystal and experimental data are given in Table 1 and the final atomic parameters are presented in Table 2. Selected bond lengths and angles are given in Table 3 and Table 4.

Table 1: Crystal and experimental data

Empirical formula	$C_{28}H_{24}CuN_2O_2 \cdot C_3H_7NO$
Formula weight	557.13
Temperature (K)	295(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions: (Å, º)	
a = 12.087(2)	$\alpha = 90$
b = 20.079(2)	$\beta = 76.25(2)$
c = 11.609(3)	$\gamma = 90$
Volume (Å^3)	2737.0(8)
Z	4
Calculated density (g.cm^{-3})	1.352
Absorption coefficient (mm^{-1})	0.835
F(000)	1164
Crystal colour and shape	yellow-prism
Crystal size (mm)	0.40x0.15x0.10
Theta range for data collection (º)	2.41 - 26.29

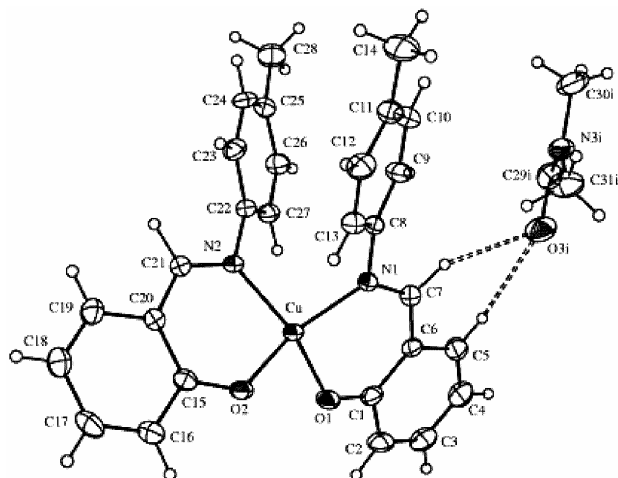| Index range	$-15 \leq h \leq 14$, $0 \leq k \leq 25$, $-14 \leq l \leq 0$
Number of reflections used	5537
Number of parameters	350
R [for I>2σ(I)]	R1 = 0.0485, wR2 = 0.1150
R [for all reflections]	R1 = 0.1208, wR2 = 0.1371
Goodness of fit	1.026
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	-0.60, 0.55

Fig. 5: ORTEP drawing of the title compound with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. (i) = x, -y+3/2, z-1/2

Table 2: Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for non-hydrogen atoms. $U_{eq} = (\frac{1}{3})\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$

Atom	X	y	Z	U_{eq}
Cu	-0.35716(4)	0.84780(2)	0.64177(3)	0.03411(15)
N1	-0.2946(2)	0.92947(13)	0.5578(2)	0.0320(6)
N2	-0.3372(2)	0.78852(14)	0.5037(2)	0.0314(6)
N3	-0.1572(3)	0.35393(17)	0.8312(3)	0.0504(9)
O1	-0.3170(2)	0.87339(13)	0.7844(2)	0.0477(7)
O2	-0.4813(2)	0.79907(12)	0.7339(2)	0.0406(6)
O3	-0.0913(3)	0.38538(17)	0.9887(3)	0.0738(9)
C1	-0.2376(3)	0.91552(19)	0.7929(3)	0.0391(9)
C2	-0.1964(4)	0.9162(2)	0.8970(3)	0.0551(11)
C3	-0.1123(4)	0.9593(2)	0.9098(4)	0.0589(12)
C4	-0.0664(4)	1.0053(2)	0.8239(4)	0.0550(11)
C5	-0.1061(3)	1.0074(2)	0.7222(3)	0.0456(10)
C6	-0.1902(3)	0.96278(17)	0.7042(3)	0.0348(8)
C7	-0.2263(3)	0.96955(18)	0.5957(3)	0.0366(8)
C8	-0.3221(3)	0.94534(16)	0.4472(3)	0.0340(8)
C9	-0.2438(3)	0.9713(2)	0.3522(3)	0.0461(10)

C10	-0.2770(4)	0.9886(2)	0.2496(3)	0.0550(11)
C11	-0.3874(4)	0.9794(2)	0.2391(3)	0.0509(10)
C12	-0.4634(4)	0.9501(2)	0.3330(4)	0.0526(11)
C13	-0.4318(3)	0.93323(19)	0.4359(3)	0.0426(9)
C14	-0.4253(5)	1.0005(3)	0.1286(4)	0.0825(16)
C15	-0.5325(3)	0.74754(18)	0.7021(3)	0.0352(8)
C16	-0.6246(3)	0.7184(2)	0.7848(3)	0.0442(9)
C17	-0.6837(3)	0.6658(2)	0.7544(4)	0.0541(11)
C18	-0.6546(4)	0.6382(2)	0.6414(4)	0.0561(11)
C19	-0.5656(3)	0.66440(18)	0.5606(4)	0.0495(10)
C20	-0.5021(3)	0.71894(17)	0.5872(3)	0.0353(8)
C21	-0.4066(3)	0.73997(18)	0.4975(3)	0.0358(8)
C22	-0.2434(3)	0.79809(17)	0.4016(3)	0.0336(8)
C23	-0.2590(3)	0.79560(19)	0.2866(3)	0.0425(9)
C24	-0.1669(4)	0.8020(2)	0.1922(3)	0.0462(10)
C25	-0.0580(4)	0.8111(2)	0.2069(3)	0.0465(10)
C26	-0.0449(3)	0.8170(2)	0.3221(3)	0.0445(9)
C27	-0.1358(3)	0.81018(18)	0.4181(3)	0.0386(9)
C28	0.0427(4)	0.8146(3)	0.1011(4)	0.0675(13)
C29	-0.0772(4)	0.3715(2)	0.8846(4)	0.0557(11)
C30	-0.1329(5)	0.3371(3)	0.7068(4)	0.0797(16)
C31	-0.2743(4)	0.3489(3)	0.8967(4)	0.0721(14)

Table 3: Selected bond lengths (Å).

Cu - O2	1.895(2)	N3 - C29	1.315(6)
Cu - O1	1.903(2)	N3 - C30	1.443(5)
Cu - N2	1.965(3)	N3 - C31	1.444(5)
Cu - N1	1.965(3)	O1 - C1	1.301(4)
N1 - C7	1.302(4)	O2 - C15	1.304(4)
N1 - C8	1.436(4)	O3 - C29	1.212(5)
N2 - C21	1.299(4)	C11 – C14	1.521(5)
N2 - C22	1.445(4)	C25 – C28	1.511(5)

Table 4: Selected bond angles (°).

O2 - Cu – O1	88.84(11)	C7 - N1 – Cu	123.2(2)
N2 - Cu – N1	98.18(11)	C8 - N1 – Cu	119.0(2)
O1 - Cu – N1	93.38(11)	C21 - N2 – Cu	123.0(2)
O2 - Cu – N2	94.30(11)	C22 - N2 – Cu	120.6(2)
O1 - Cu – N2	149.98(12)	C29 - N3 – C31	120.6(4)
O2 - Cu – N1	150.56(11)	C29 – N3 – C30	122.5(4)
C15 - O2 – Cu	128.0(2)	C30 - N3 – C31	116.9(4)
C1 - O1 – Cu	125.9(2)	O3 - C29 – N3	126.0(5)

Results and Discussion

Table 3 and Table 4 shows the coordination in the vicinity of the Cu ion to be distorted square-planar. Two ligands are twisted according to Cu atom. The dihedral angle between the coordination planes O1/Cu/N1 and O2/Cu/N2 is 40.50(10)º. The distances of the contributing atoms from the basal plane through the atoms O1, O2, N1, N2 are -0.564(3), 0.439(3), 0.469(3) and -0.477(3) Å, respectively. The Cu atom is located -0.0257(5) Å from this plane. If the distance of the basal plane and Cu are taken into consideration the coordination can be tend as a tetrahedral coordination. On the other hand the angles are in consistency with a square square-planar structure rather than a tetrahedron. If a tetrahedral coordination was seen then *cis* or *trans* isomerism could not be discussed. These structures are frequently observed for Schiff base complexes with Cu^{II} ion [12]. Values, which show high distortion, have also been encountered [4]. Square-planar and square-pyramidal structures are the most frequently seen coordinations for the Cu^{II} complexes. These most important features observed in this complex is that it posses a *cis* isomeric structure.

Intermolecular hydrogen bonds link the Cu-complex and the DMF molecule in three-dimensional. Hydrogen bonds were calculated with PARST [17] and details are given in Table 5. To get information about the conformation of the title complex, dihedral angles between the neighbouring least square planes in the molecule were calculated with PARST [17]. Some dihedral angles between the planes around the coordination sphere are given in Table 6. The title molecule is not planar but the phenyl rings are essentially planar. The C8···C13 and C22···C27 rings are almost parallel to each other. The dihedral angle between these two rings is 21.71(12) and the distance between the ring centroids is 3.933(2) Å

Table 5: Hydrogen-bonding geometry (Å,º) for the title compound.

D - H ... A	D – H	H … A	D ... A	D – H ... A
C5 – H5 … O3i	0.93	2.58	3.433(5)	152.3
C7 – H7 … O3i	0.98(3)	2.49(3)	3.425(5)	160(3)

Symmetry code: (i) = x, -y+3/2, z-1/2

Table 6: Selected dihedral angles (α) in the title compound.

Plane 1	Plane 2	α (º)
O1 – Cu - N1	O2 – Cu – N2	40.50(10)
O1 – Cu - N1	O1 – C1 – C6 – C7 – N1	16.52(10)
O2 – Cu – N2	O2 – C15 – C20 – C21 – N2	4.93(10)
O1 – C1 – C6 – C7 – N1	C8 – C9 – C10 – C11 – C12 – C13	31.47(11)
O2 – C15 – C20 – C21 – N2	C22- C23 – C24 – C25 – C26 – C27	42.86(11)
C8 – C9 – C10 – C11 – C12 – C13	C22- C23 – C24 – C25 – C26 – C27	21.71(12)

The geometric structure effects the oxidation/reduction potentials of the complex. It has been stated in the literature [4,18] that these structures effect the reduction of the groups attached to the imine nitrogen. But all studies refer to complexes with a *trans* isomer structure. Best

examples of distorted square-planar complex given in literature are ONNO type tetradentate Schiff base complexes. The Cu^{2+}/Cu^+ and Cu^+/Cu^0 reduction potentials, for the *cis* structures, are more negative with respect to the *trans* structure [3]. The same is true for the title complex. The reduction potentials obtained for the Cu^{2+}/Cu^+ and Cu^+/Cu^0 reactions are in consistency with those obtained for the tetradentate *cis* Schiff base complexes.

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