Research Article

Synthesis, Crystal Structure, and Characterization of Ternary Copper(II) Complex Derived from N-(salicylidene)-L-valine

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Ternary Schiff base copper(II) complex [CuL(tmpda)] (where H₂L is N-(salicylidene)-L-valine; tmpda is N,N,N',N'-tetramethyl-1,3-propanediamine) has been characterized by UV-Vis., FTIR, and single crystal XRD. The crystal structure displays a distorted square pyramidal geometry in which Schiff base is bonded to the Cu(II) ion via phenolate oxygen, imine nitrogen, and an oxygen atom of the carboxylate group through the basal plane and the chelating diamine, N,N,N',N'-tetramethyl-1,3-propanediamine, displays an axial and equatorial mode of binding via NN-donor atoms.

1. Introduction

Transition metal complexes derived from Schiff bases have attracted attention of the researchers for their extensive application in the field of industry and biology [1]. The Schiff bases derived from amino acids and *o*-hydroxy aldehydes or ketones are found to be tridentate [2, 3]. The metal complexes derived from N-alkylidene or N-arylidene alkanoate have attracted much attention owing to their interest in several fields of biological systems, as well as due to their electrochemical properties. Schiff base amino acids are very good chelating agents. The transition metal complexes derived from salicylaldehyde and amino acids can serve as nonenzymatic models for the more complicated metal-pyridoxal (vitamin B6) amino acid Schiff base systems and are the key intermediates for many metabolic reactions of amino acids catalyzed by enzymes [4, 5]. Transition metal complexes derived from amino acid Schiff bases were reported to exhibit antimicrobial, antitumor, and antilarval activities and also act as mimetic systems of enzyme models [6–9].

Herein, we report the synthesis, crystal structure, and spectroscopic studies of Schiff base copper(II) complex derived from N-(salicylidene)-L-valine and, an aliphatic chelating diamine, tmpda.

2. Experimental

2.1. Materials and Physical Measurements. All the reagents and chemicals were procured from commercial sources and were used without purification. Copper(II) acetate monohydrate, salicylaldehyde, and N,N,N',N'-tetramethyl-1,3-propanediamine were purchased from Sigma Aldrich.

Molar conductance of the complex was measured in DMF (10^{−3} M) using a direct digital conductometer. Elemental analyses of the Cu(II) complex were performed with a Perkin-Elmer model 2400 series II CHN analyzer. FTIR spectrum of solid complex was recorded using KBr pellet in the region of 4000–400 cm^{−1} on AVATAR 330 spectrophotometer. UV-Visible spectrum of the complex in DMF was recorded in the region of 200–800 nm using a Hitachi U-2800 spectrophotometer.

2.2. Synthesis. The procedure for the synthesis of Schiff base copper(II) complex is given below and the structure of the Schiff base is depicted in Figure 1.

L-valine (0.351 g, 3 mmol) and KOH (0.336 g, 6 mmol) were dissolved in water. To this an ethanolic solution (25 mL) of salicylaldehyde (0.3 mL, 3 mmol) was added. The reaction mixture was stirred for about 1 h at 333 K. The solution

FIGURE 1: Structure of Schiff base ligand (H_2L).

turned yellow. To the above solution, copper(II) acetate monohydrate (0.61 g, 3 mmol) was added and the reaction mixture was stirred for 1 h, followed by addition of tmpda (0.3 mL, 3 mmol). The mixture was stirred for another 2 h at the same temperature. The resultant green colored solution was filtered and kept at room temperature. Green colored crystals were obtained after the evaporation of the mother liquor. Finally, it was filtered and dried.

Analytical data of Schiff base Cu(II) complex are given below:

MF: $C_{19}H_{31}O_3N_3Cu$; $\Lambda_M = 2.3 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$;

Elemental analyses found (calculated) %: C: 55.26 (55.25); H: 7.63 (7.57); N: 10.18 (10.17).

2.3. X-Ray Crystallography. Single crystal X-ray diffraction data of the Schiff base ternary copper(II) complex was used for data collected on a Bruker single crystal Kappa Apex II diffractometer. Single crystals of Cu(II) complex suitable for X-ray diffraction study were obtained from slow evaporation of the mother liquor at room temperature. A green colored crystal of the Cu(II) complex having the dimensions $0.13 \times 0.22 \times 0.25$ mm was used for the X-ray crystallographic analysis. Crystal data were collected using graphite monochromatized Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$).

The structure of Cu(II) complex was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares techniques against F^2 using SHELXL-2014/7 [10, 11]. All the nonhydrogen atoms were refined anisotropically. A summary of pertinent crystal data along with further details of structure determination and refinement is given in Table 1.

3. Results and Discussion

3.1. Solubility. The Cu(II) complex was found to be freely soluble in DMSO, DMF, and ethanol at room temperature, whereas it is partially soluble in water and chloroform. The lower molar conductivity value ($2.3 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$) of the complex in DMF (10^{-3} M) indicated the nonelectrolytic nature [12].

3.2. Crystal Structure of $[CuL(tmpda)]$. The selected bond lengths and bond angles of the Schiff base Cu(II) complex are listed in Table 2. The Cu(II) complex crystallizes in the tetragonal system, with the space group $P4_3$ and with the values $a = 10.7750(6) \text{ \AA}$, $b = 10.7750(6) \text{ \AA}$, and

TABLE 1: Crystal data and structure refinement for $[CuL(tmpda)]$.

CCDC deposition number	1406394
Empirical formula	$C_{19}H_{31}CuN_3O_3$
Formula weight (g/mol)	413.01
Temperature (K)	296(2)
Wavelength ($\text{\AA}$)	0.71073
Crystal system, space group	Tetragonal, $P4_3$
Unit cell dimensions	
a, b, c ($\text{\AA}$)	10.7750(6), 10.7750(6), 17.8722(10)
α, β, γ ($^\circ$)	90, 90, 90
Volume ($\text{\AA}^3$)	2075.0(3)
Z , calculated density (g/cm^3)	4, 1.322
Absorption coefficient (mm^{-1})	1.075
$F(000)$	876
Crystal size (mm)	$0.130 \times 0.220 \times 0.250$
θ range for data collection ($^\circ$)	1.89 to 24.98
Limiting indices	$-12 \leq h \leq 7, -10 \leq k \leq 12, -20 \leq l \leq 21$
Reflections collected/unique	7583/4920
Independent reflections	3452 [$R(\text{int}) = 0.0298$]
Completeness to $\theta = 25.00^\circ$	100%
Absorption correction none	< 41
Max. and min. transmission	0.8730 and 0.7750
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data/restraints/parameters	3452/1/241
Goodness of fit on F^2	1.026
$\Delta/\sigma_{\text{max}}$	0.073
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0529, wR2 = 0.1290$
R indices (all data)	$R1 = 0.0640, wR2 = 0.1361$
Absolute structure parameter	1.0(0)
Largest diff. peak and hole ($\text{e-\AA}^{-3}$)	0.307 and -0.280
RMS deviation from mean	$0.053 \text{ e-\AA}^{-3}$

$c = 17.8722(10) \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, and $\gamma = 90^\circ$, $V = 2075.0(3) \text{ \AA}^3$, and $Z = 4$. An ORTEP view of copper(II) complex along with the atom numbering scheme is shown in Figure 2.

Five coordinated Cu(II) complexes exist with square pyramidal (sp) or trigonal bipyramidal (tbp) geometry. In order to distinguish between sp and tbp geometries in case of five coordinated complexes, Addison et al. [13] introduced trigonality index τ (where $\tau = (\beta - \alpha)/60$, in which α and β are the two largest coordination angles). In general, for an ideal square pyramidal $\tau = 0$ and for ideal tbp geometry, $\tau = 1$. In the present case, taking the angles N(3)–Cu(1)–N(2) 167.0° as α and O(1)–Cu(1)–O(2) 171.9° as β , the τ value is calculated. For Cu(II) complex the τ value is 0.0816,

TABLE 2: Selected bond lengths (Å) and angles (°) for the [CuL(tmpda)].

Cu(1)–O(1)	1.923(6)	O(1)–Cu(1)–N(3)	92.1(3)
Cu(1)–O(2)	1.959(6)	N(3)–Cu(1)–O(2)	83.0(3)
Cu(1)–N(1)	2.445(8)	N(3)–Cu(1)–N(2)	167.0(3)
Cu(1)–N(3)	1.954(7)	O(1)–Cu(1)–N(1)	95.4(3)
Cu(1)–N(2)	2.058(7)	O(2)–Cu(1)–N(1)	91.9(3)
		O(1)–Cu(1)–O(2)	171.9(3)
		O(1)–Cu(1)–N(2)	89.3(3)
		O(2)–Cu(1)–N(2)	94.1(3)
		N(3)–Cu(1)–N(1)	100.6(3)
		N(2)–Cu(1)–N(1)	92.2(3)

FIGURE 2: An ORTEP view of [CuL(tmpda)] along with the numbering scheme.

which indicates nearly an ideal square pyramidal geometry around Cu(II) ion. The basal plane is occupied by imine nitrogen atom N(3), phenolate oxygen atom O(1), and one of the oxygen atoms O(2) of carboxylate group of Schiff base and one of the nitrogen atoms N(2). The axial site is occupied by another nitrogen atom N(1) of tmpda. The Cu(1)–N(3), Cu(1)–N(2), Cu(1)–O(1), and Cu(1)–O(2) distances are 1.954(7) Å, 2.058(7) Å, 1.923(6) Å, and 1.959(6) Å, respectively, and the Cu(1)–N(1) bond length 2.445(8) Å is significantly longer than the equatorial bonds.

The equatorial O(1)–Cu(1)–N(3), N(3)–Cu(1)–O(2), O(2)–Cu(1)–N(2), and O(1)–Cu(1)–N(2) bond angles are 92.1(3)°, 83.0(3)°, 94.1(3)°, and 89.3(3)°, respectively. The sum of the angles around copper(II) ion is 358.5°, close to 360°. Hence, the atoms O(1), O(2), N(3), N(2), and Cu(1) lie in one plane with the slight deviation of copper(II) ion from the basal plane. The apical N(2)–Cu(1)–N(1), N(3)–Cu(1)–N(1), O(1)–Cu(1)–N(1), and O(2)–Cu(1)–N(1) bond angles are 92.2(3)°, 100.6(3)°, 95.4(3)°, and 91.9(3)°,

FIGURE 3: The unit cell packing diagram of the [CuL(tmpda)] viewed along *b*-axis.

respectively. The diagonal bond angles for O(1)–Cu(1)–O(2) and N(3)–Cu(1)–N(2) are 171.9(3)° and 167.0(3)°, respectively.

3.3. Crystal Packing. The crystal packing of the Cu(II) complex is shown in Figure 3. No notable hydrogen bonding was found and van der Waals force is the main intermolecular interaction. The two-dimensional chain formed by van der Waals forces between hydrogen atoms (H14 and H5A) and the noncoordinated carboxylate oxygen atoms (O(3)) of the Schiff bases [14] ligand.

FTIR spectrum of [CuL(tmpda)] exhibited an intense band at 1627 cm^{−1}, corresponding to a coordinated imine group with Cu(II) ion. The band appeared at 1284 cm^{−1}, indicating the coordination of the Schiff base ligand with the copper(II) ion, via deprotonation. The asymmetric (ν_{as} COO[−]) and symmetric stretching were observed at 1533 and 1340 cm^{−1}, respectively. The separation between asymmetric and symmetric bands $\Delta\nu = [\nu_{as} \text{COO}^- - \nu_s \text{COO}^-]$ of the complex is greater than that of free carboxylate anion (145 cm^{−1}). This confirms the monodentate coordination of the carboxylate ion present in the Schiff base ligand [15]. The appearance of bands at 466 and 557 cm^{−1} is assigned to $\nu(\text{Cu}–\text{O})$ and $\nu(\text{Cu}–\text{N})$, respectively [16].

The electronic absorption spectrum of Cu(II) recorded in DMF (10^{−3} M) showed an absorption band at 280 nm and 365 nm can be assigned to $\pi\text{--}\pi^*$ transition of aromatic chromophore and $n\text{--}\pi^*$ transition of imine moiety, respectively. A broad band observed at 650 nm corresponds to d-d transition.

4. Conclusion

A ternary Schiff base copper(II) complex [CuL(tmpda)] was synthesized and characterized by UV-Vis. and FTIR spectroscopy. The structure of the complex was unambiguously studied by single crystal XRD. Molar conductance measurement confirmed the nonelectrolytic nature of the complex.

The XRD studies revealed square pyramidal geometry for the complex. Cu(II) ion was coordinated via phenolic oxygen, imine nitrogen, and oxygen atom of carboxylate group of Schiff base ligand occupying the basal plane, whereas nitrogen atoms of tmpda occupy axial as well as equatorial sites.

Competing Interests

The authors declare that there are no competing interests regarding the publication of this paper.

Acknowledgments

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