

Synthesis and characterisation of a novel copper(II) complex of the tridentate Schiff base derived from salicylaldehyde and valine

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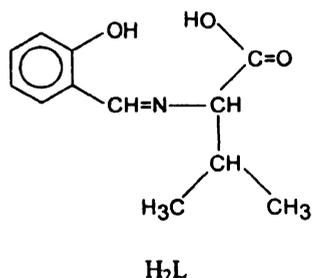
Abstract : Reactions of bis-salicylaldehydato copper(II) with valine are found to produce the corresponding aminoacid Schiff base complex $\text{Cu(L)(H}_2\text{O)}$ (H_2L = tridentate Schiff base derived from salicylaldehyde and valine). The compound is characterized by elemental analysis, spectroscopic, electrochemical properties and ESR data. Crystal structure analysis of the copper(II) complex confirms square planar environment comprising of NO_3 framework of ligands (orthorhombic, $P2_12_12_1$, $Z = 4$, $a = 7.3835(3)$ Å, $b = 12.8846(7)$ Å, $c = 27.3973(10)$ Å, $\alpha = \beta = \gamma = 90^\circ$).

Keywords : Salicylaldehyde, valine, copper(II), Schiff base, synthesis.

Introduction

Transition metal complexes with the tridentate Schiff base ligands derived from salicylaldehyde and aminoacids are found to be the objects of considerable attention in various fields of bioinorganic chemistry such as their importance as intermediates in many metabolic reactions of aminoacids catalysed by enzymes^{1,2}, their antibacterial and anticancer activities³⁻⁵.

Synthetic and structural investigations performed on copper(II) complexes of salicylaldiminato aminoacid Schiff bases have drawn much interests⁶⁻¹². No report is however available on the stabilization of valine based Schiff base complexes. The synthesis and characterisation of the copper(II) complex of the tridentate Schiff base derived from salicylaldehyde and valine including the crystal structure analysis of the copper(II) complex are described here.



Results and discussion

The plausible synthesis of tridentate Schiff base deriv-

able from the condensation between salicylaldehyde and valine in 1 : 1 molar ratio has been attempted in ethanol-water (10 : 1) medium at refluxing temperature. However, no such condensation product can be isolated and instead unreacted valine separated out from the reaction mixture in nearly quantitative amount indicative of no reaction. Thus the studies on the synthetic prospect of the copper(II) complex of the expected Schiff base ligand H_2L cannot be performed by the usual method of reaction between the Schiff base and the metal(II) salts i.e. metal(II) acetate hydrates. However the reaction of bis-salicylaldehydato copper(II) dihydrate with valine in 1 : 2 molar ratio in ethanol : water (2 : 1, v/v) yielded the corresponding copper(II) complex of molecular composition $\text{Cu(L)(H}_2\text{O)}$ (1). The product on purification by washing with ethanol : ether (1 : 5, v/v) and ether and after drying were isolated as dark green powdery solid.

The coordination geometry of the ligands around the central metal ion is indicated by the magnetic moment value of the complex. The magnetic moment value of 1.94 B.M. observed for $\text{Cu(L)(H}_2\text{O)}$ (1) suggests the presence of square planar environment of ligands around the copper(II) ion^{13,14}.

The electronic spectra of the copper(II) complex showed bands at 240(4.10), 320(sh), 420(sh), 535(3.40), 670(sh) nm and the values are found to be in good agreement with those expected for the copper(II) ion bonded via

ketimino group (=C=N-) and O atoms in a square planar coordination environment.

The band observed at 670 nm is assigned as due to the $d_{xy} \rightarrow d_{x^2-y^2}$ and the band at 530 nm is assignable to (d_{xz} , d_{yz}) $\rightarrow d_{x^2-y^2}$ transition whereas the band at 320 nm may be assigned as the intraligand $\pi \rightarrow \pi^*$ transition and the high frequency band at 235 nm is possibly due to the ligand (σ_L) \rightarrow metal (e_g) transition¹⁵.

The infrared spectra of the complex **1** show strong but broad bands at 3350 cm^{-1} along with very strong bands at 1645 cm^{-1} which may be assigned as due to the presence of coordinated water molecule¹⁶. The medium to weak but sharp bands appear at ~ 2960 and ~ 2930 cm^{-1} support the presence of aliphatic hydrocarbons,

-CH-
|
H₃C-CH-CH₃¹⁷.

The strong band at 1602 cm^{-1} is the characteristic $\nu(\text{C}=\text{N})$ band, suggestive of binding with the copper(II) ion through imino (=C=N-) nitrogen of the Schiff base¹⁸. Strong bands at 1635 cm^{-1} [$\nu_{\text{as}}(\text{COO}^-)$] and 1345 cm^{-1} [$\nu_{\text{s}}(\text{COO}^-)$] and the large difference of $\Delta\nu$ value at 290 cm^{-1} observed for **1** suggest monodentate carboxylate coordination with the copper ion¹⁹. The medium but sharp bands at 1310 cm^{-1} are the $\nu(\text{C}-\text{O})$ (phenolic) bands²⁰. The "out-of-plane" $\delta(\text{C}-\text{H})$ (phenyl) of the disubstituted benzene rings appear at ~ 759 cm^{-1} ²¹. The metal-nitrogen and metal-oxygen stretching frequency bands appear at $\nu(\text{M}-\text{N})$, 588 cm^{-1} (m) and at $\nu(\text{M}-\text{O})$, 465 cm^{-1} (m) respectively.

Cyclic voltammetric study²² performed on complex **1** shows the presence of an irreversible reductive potential at -0.44 V assignable to Cu^{II} to Cu^{I} reduction. The irreversible oxidation potential at $+0.92$ V may be due to the oxidation of the ligand part. ESR spectrum of **1** showed a single signal with $g_{\parallel} = 2.10$ and $g_{\perp} = 2.05$ and no half-filled signal was observed for a possible dimerisation which however is in agreement with the crystal structure determination described latter.

Description of the crystal structure of $\text{Cu}(\text{L})(\text{H}_2\text{O})$ (**1**) :

Crystal data collection, structure solution and refinement details are presented in Table 1. A selection of bond angles and bond lengths are recorded in Table 2. Data for hydrogen bonds are presented in Table 3. The molecular structure of **1** alongwith atom numbering scheme is pre-

Table 1. Crystal data and structure refinement for $\text{Cu}(\text{L})(\text{H}_2\text{O})$ (**1**)^a

Empirical formula	$\text{C}_{12}\text{H}_{13}\text{CuNO}_4$
Formula weight	298.77
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Unit cell dimensions	$a = 7.3835(3)$ Å $b = 12.8846(7)$ Å $c = 27.3973(10)$ Å $\alpha = \beta = \gamma = 90^\circ$
Volume	2606.4(2) Å ³
Z, Calculated density	8, 1.523 mg/m^3
Absorption coefficient	1.681 mm^{-1}
$F(000)$	1224
Crystal size	0.3 × 0.3 × 0.2 mm
Theta range for data collection	1.75 to 20.90°
Limiting indices	$-5 < h < 7$, $-12 < k < 10$, $-26 < l < 27$
Reflections collected/unique	9185/2701 [$R(\text{int}) = 0.0461$]
Completeness to $\theta = 20.90$	97.7%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2701/0/327
Goodness-of-fit on F^2	1.015
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0351$, $wR2 = 0.0864$
R indices (all data)	$R1 = 0.0454$, $wR2 = 0.0921$
Absolute structure parameter	0.01(2)
Largest diff. peak and hole	0.654 and -0.393 e.Å ⁻³

^aEsd values are in parentheses.

Table 2. Selected bond lengths (Å) and angles (°) for $\text{Cu}(\text{L})(\text{H}_2\text{O})$ (**1**)^a

O(1)-Cu(1)	1.894(4)	O(1)-Cu(1)-N(1)	95.61(19)
O(3)-Cu(1)	1.912(4)	O(1)-Cu(1)-O(3)	179.5(2)
O(4)-Cu(1)	1.939(4)	N(1)-Cu(1)-O(3)	84.11(19)
N(1)-Cu(1)	1.909(5)	O(1)-Cu(1)-O(4)	93.04(18)
C(9)-O(2)	1.241(7)	N(1)-Cu(1)-O(4)	167.5(2)
C(9)-O(3)	1.250(7)	O(3)-Cu(1)-O(4)	87.17(18)
C(1)-O(1)	1.318(7)	C(7)-N(1)-C(8)	120.5(5)
C(6)-C(7)	1.435(9)	O(2)-C(9)-O(3)	123.0(6)
C(7)-N(1)	1.284(8)	N(1)-C(8)-C(10)	109.9(5)
C(8)-N(1)	1.468(7)	N(1)-C(8)-C(9)	105.3(5)
C(8)-C(10)	1.530(9)	C(10)-C(8)-C(9)	112.6(5)
C(8)-C(9)	1.546(8)		

^aEsd values are in parentheses.

sented in Figs. 1 and 2 illustrates the stereoview of the unit cell of **1**. The structure of **1** contains two indepen-

Table 3. Hydrogen bonds for [Cu(L)(H₂O)] (1) [Å and (°)]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4')...O(2)#1	0.82	1.96	2.729(6)	156.5
O(8)-H(8')...O(6)#1	0.82	1.92	2.615(6)	141.9

Symmetry transformations used to generate equivalent atoms :
#1 x-1, y, z.

dent Cu(L)(H₂O) (1) complexes per asymmetric unit. Each copper atom is four coordinated by an NO₃ donor set from one tridentate ligand and one water molecule where the phenolate O atom and the carboxylic O atom are deprotonated. The independent molecules A and B differ in the conformation of the six membered chelate rings

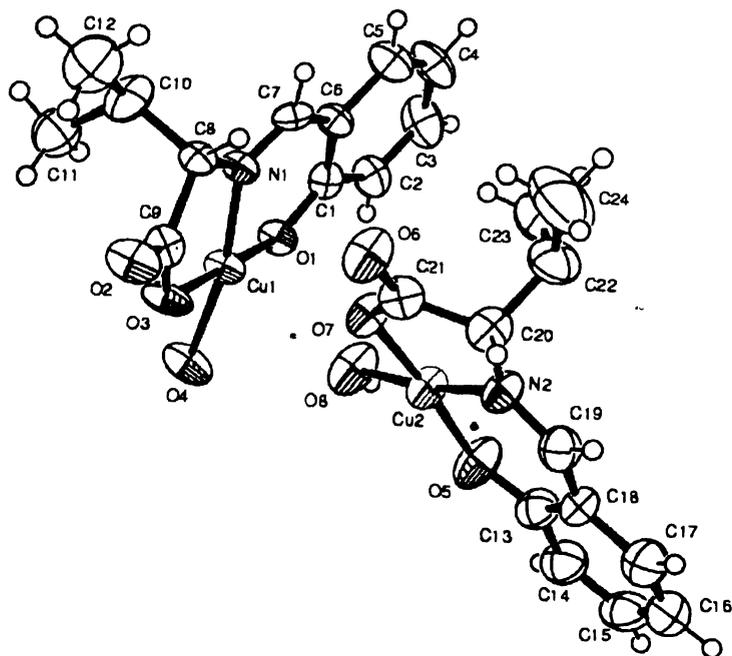


Fig. 1. ORTEP plot of Cu(L)(H₂O) (1) with atom numbering scheme.

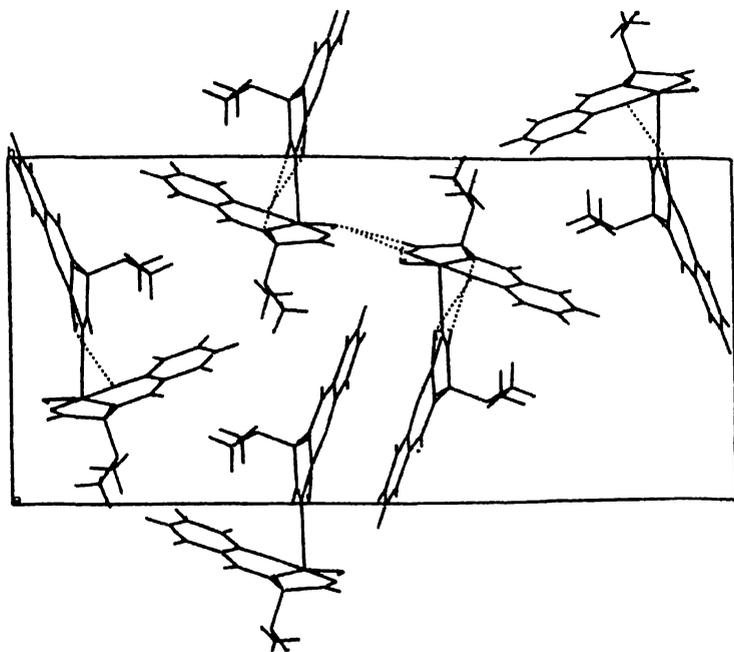


Fig. 2. Stereoview of Cu(L)(H₂O) (1).

which adopt a twist-boat form in A and is essentially planar in B (r.m.s deviation, 0.028 Å). This is also reflected by the significant differences in the torsion angles of the two molecules. N(1)–Cu(1)–O(1)–C(1), 19.5(8)°; N(2)–Cu(2)–O(5)–C(13), 9.4(9)°; N(1)–C(8)–C(10)–C(11), 70.4(7)° and N(2)–C(19)–C(18)–C(17), 0.4(12)° in the solid state. The Cu–N, 1.909(4) Å and Cu–O, 1.894(4) Å, 1.912(4) Å and 1.939(4) Å bond distances are well within the expected range^{23,24}. The N(1)–C(7), 1.284(8) Å and N(2)–C(19), 1.297(9) Å bond lengths are typical as known for C=N bond²⁵.

All the H atoms are found in a difference map and refined (C–H, 0.96 Å). The molecules are linked by O–H...O hydrogen bonds into infinite chains with the sequence A...B...A...B (Table 3).

Experimental

Salicylaldehyde (Aldrich), valine (Aldrich) and copper(II) acetate monohydrate (E. Merck) were of GR grade and used as purchased. The bis(salicylaldehydato)-copper(II) was prepared by the literature method²⁶.

Microanalysis of C, H, N were performed on a Perkin-Elmer 2400 Series II CHN analyzer. Metal content was determined on a Perkin-Elmer Atomic absorption Spectrometer. The electronic absorption spectra was recorded on a Shimadzu MPS-2000 UV-Vis spectrophotometer. The IR spectra (KBr pellet) was recorded on a Perkin-Elmer Paragon 1000 FTIR spectrometer. Room temperature magnetic susceptibility was measured on a EG and G par vibrating sample magnetometer with Hg[Co(SCN)₄] used as standard. Mass spectra (Electrospray) was recorded on a MICROMASS QUARTRO II quadrupole mass spectrometer. The electrochemical measurement was made using a par mode 273 potentiostat with a platinum wire as auxiliary electrode and an aqueous saturated calomel electrode as the reference electrode in a three electrode configurations. A REOO74 x-y recorder was used to trace the voltammograms. Electrochemical measurement was performed under nitrogen atmosphere at 298 K and were uncorrected for junction potentials. ESR spectra was recorded in DMF solution.

Crystal structure of Cu(L)(H₂O) :

Good quality crystals suitable for the X-ray diffraction study was obtained on slow cooling of a near saturated solution of Cu(L)(H₂O) (1) in methanol and keep-

ing at ~5 °C.

Three dimensional X-ray data were collected on a Enraf Nonius CAD 4 MACH 3 diffractometer by the θ -2 θ method using graphite monochromarised MoK α radiation ($\lambda = 0.71073$ Å). The structures were solved by the direct methods and refined by full matrix least squares calculations (SHELXL-97)²⁷. Neutral atom scattering factors and anomalous scattering factors were taken from the International Tables for X-Ray Crystallography²⁸ and from SHELXL-97.

Synthesis of Cu(L)(H₂O) (1) :

Valine (0.47 g, 4 mmol) in 20 ml ethanol was mixed with bis-salicylaldehydato copper(II) (0.61 g, 2 mmol) in 20 ml ethanol and on addition of 10 ml water the mixture was refluxed for 3 h. Filtered off when hot, the filtrate on reduction of volume to ~20 ml was kept cooled at 5 °C. Some pasty mass separated out, the mother liquor was removed by decantation. The pasty product was then stirred thoroughly with 10 ml portions of ethanol : ether (1 : 5, v/v) thrice and then with 5 ml portions of ether twice and each time the washings were removed by decantation. The product obtained as dark green powdery solid was dried in air and *in vacuo*.

Yield, 63%; m.p. 165–167 °C (dec.); paramagnetic, μ_{eff} , 1.94 B.M. (298 K). Found : C, 48.24; H, 4.54; N, 4.48; Cu, 20.89. Calcd. for C₁₂H₁₅NO₄Cu : C, 47.92; H, 5.03; N, 4.66; Cu, 21.13%. FTIR (cm⁻¹) : ν (C–H, aromatic), ν (O–H), 3350 (s, br); ν (C–H, aliphatic), 2961–2929 (mw); ν_{as} (COO⁻), 1635(s); δ (HOH), 1645(vs); ν (C=N), 1602(ν_{s}); ν_{s} (COO⁻), 1345(m); ν (C–O, phenolic), 1310 (m); δ (C–H, aromatic “out-of-plane”), 759(s); ν (Cu–N), 588(m); ν (Cu–O), 465(m). UV-Vis (λ_{max} , nm) (log ϵ) : 240(4.10), 320(sh), 420(sh), 535(3.40), 670(sh). MS : m/z , 301(=M⁺).

Supplementary materials :

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 669600. Copies of this information may be obtained free of charge from the Director, CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK (Fax : +44-1223-336-033; E-mail : deposit@ccdc.cam.ac.uk).

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