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X-Ray Diffraction Studies of Iron(II), Nickel(II) and Copper(II) Complexes of *o*-Vanillin-L-Histidine

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o-Vanillin-L-histidine was synthesized by refluxing *o*-vanillin with L-histidine. This *o*-vanillin-L-histidine (*o*-VALH) was used to synthesize iron(II), nickel(II) and copper(II) complexes having metal to ligand stoichiometry 1 : 1. The ligand and metal complexes were characterized by elemental analysis, molar conductivity, electronic absorption and IR absorption spectra. The magnetic nature of the complexes was established using Gouy's balance method. The XRD data was used to index the compound for orthorhombic system.

Key Words: XRD, Fe(II), Ni(II), Cu(II), Complexes, *o*-Vanillin-L-histidine.

INTRODUCTION

Many transition metal complexes have been synthesized for their analytical and commercial applications[1,2]. Literature survey also reveals that transition metal complexes generally crystallize with octahedral, tetrahedral or square-planar geometry[3-5]. But the systematic studies on determination of lattice parameters are the shortcomings for most of these complexes. In continuation of our work for synthesizing and characterizing Fe(II), Ni(II) and Cu(II) complexes of *o*-vanillin-L-histidine, an attempt was made to evaluate lattice parameters. It is also interesting to note that the above complexes exhibit very good antibacterial properties[6].

EXPERIMENTAL

All the chemicals used for the synthesis were of AR grade. *o*-Vanillin-L-histidine (*o*-VALH) was prepared from *o*-vanillin and L-histidine following the reported procedure by Schiff. Samples of iron(II), nickel(II) and copper(II) chelates of *o*-vanillin-L-histidine were synthesized by adding the metal salt solution in appropriate solvent to the boiling solution of the ligand. The mixture was refluxed and the separated nickel(II) and copper(II) chelate were filtered. Iron(II) complex was formed only after adding the refluxed solution to distilled water with constant stirring. All the three complexes were collected washed with 1 : 1 alcohol and dried in vacuum desiccator. The elemental analyses of ligand and complexes were carried out using reported methods[7]. The complexes were tested for solubility using various pclar and non-polar solvents. Mclar conductivity of the ligand and complexes were recorded using 10^{-4} molar solution on a Toshniwal conductivity meter. The electronic absorption spectra of complexes were recorded from their aqueous solution in the UV-visible region on Shimadzu UV-1601 spectrophotometer. Infrared spectra were recorded on Shimadzu FTIR-8101 spectrophotometer using KBr pellets. The X-ray diffractograms were recorded on Philips PW-712 X-ray diffractometer using CuK_α radiations (CuK_α, $\lambda = 1.5418$ Å). The X-ray diffractograms were scanned in the 2θ range of 5°–60°.

RESULTS AND DISCUSSION

The results of elemental and spectral analysis are summarized in Table-1 and 2, respectively. The complexes are anhydrous in nature and stable at room temperature. The observed values of the elemental analysis are in close agreement with the calculated values for the metal complexes. All these complexes have metal-to-ligand stoichiometry 1 : 1. The complexes are sparingly soluble in common organic solvents but are sufficiently soluble in hot distilled water. The low values of the molar conductance suggest the non-electrolytic behaviour of these complexes. The Gouy's balance method indicates that all these complexes are paramagnetic in nature and suggests an octahedral geometry for iron(II), nickel(II) and copper(II) complexes.

The infirared spectra of the chelate indicate the absence of characteristic absorption for the —OH group and a shift in ν(C═N) shows that —OH group and C═N are involved in coordination. The chelation of the carbonyl oxygen is confirmed by the shift of carbonyl stretching frequency of the carboxylate group to lower frequencies. The asymmetric and symmetric stretching vibrations of the carboxylate groups occur at *ca.* 1600 and 1400 cm^{-1} respectively showing a difference of about 200 cm^{-1}. This indicates the monodentate behaviour of the carboxylate group[8,9]. All the three complexes show broad absorption bands between 3500–3100 cm^{-1} due to the presence of coordinated water molecules which is further supported by the appearance of rocking mode of medium intensity bands at *ca.* 860 cm^{-1},[10]. The weak bands in the 515–512 cm^{-1} and 410–405 cm^{-1} regions exhibited by the complexes are tentatively assigned to ν(M—N) and ν(M—O) respectively[11].

The complexes were characterized with respect to various electronic transitions associated with it in the UV-visible spectral region. The ligand spectrum showed two characteristic bands near 38000 and 27500 cm^{-1}. The shift of these bands exhibited in the spectra of complexes can be taken as a proof of coordination of the ligand to metal ions. The expected $^5T_{2g} \rightarrow {}^5E_g$ electronic transition in the octahedral Fe(II) complex[12] has been recorded at about 18400 cm^{-1}. The two electronic absorption bands at 10482 and 22600 cm^{-1} present in Ni(II) complex are due to $^3A_{2g}$ (F) → $^3T_{1g}$(P) transitions. The octahedral geometry of Cu(II) complex is clear from the absorption bands at 17123 and 23420 cm^{-1}.

The good quality of X-ray diffractograms of iron(II) and copper(II) complexes

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TABLE-1
MICRO-ANALYTICAL, MAGNETIC AND CONDUCTANCE DATA OF METAL CHELATES OF *o*-VANILLIN-L-HISTIDINE

Complex (Colour)	Analysis (%), Found (Calcd.)				μ_{eff} (B.M.)	Ω_m (ohm^{-2} cm^2 mol^{-1})
	M	C	H	N		
[FeL(H_2O)$_3$] (Brown)	14.93 (14.06)	42.78 (42.30)	4.31 (4.78)	11.21 (10.58)	4.94	2.86
[NiL(H_2O)$_3$] (Violet)	14.86 (14.68)	42.89 (42.00)	4.99 (4.75)	11.24 (10.50)	2.86	3.45
[CuL(H_2O)$_3$] (Green)	15.52 (15.68)	42.50 (41.50)	4.04 (4.69)	10.31 (10.38)	2.08	1.28

TABLE-2
CHARACTERISTIC INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF METAL CHELATES OF *o*-VANILLIN-L-HISTIDINE

Compound	ν(H_2O)	ν_{asym}(COO^-)	ν(C═N) azomethine	ν(C═N) (in ring)	ν_{sym}(COO^-)	ν(C—O) Phenolic	In-plane deformation	Out-of -plane deformation	ν(M—N)	ν(M—O)
LH_2		1720 s	1480 m	1440 m	1400 s	1280 m	830 m	760 m, 738 m	—	—
[FeL(H_2O)$_3$]	3500–3100 br	1630 s	1530 m	1443 m	1370 s	1300 m	830 m	780 m, 744 m	512 w	405 w
[NiL(H_2O)$_3$]		1628 s	1520 m	1440 m	1390 s	1320 m	820 m	770 m, 713 m	515 w	410 w
[CuL(H_2O)$_3$]		1635 s	1525 m	1442 m	1330 s	1320 m	830 m	780 m, 744 m	510 w	410 w

indicates high crystallinity of these complexes. The powder diffraction pattern of Fe(II) complex of *o*-VALH exhibited 15 peaks between 5–23° 2θ values. [Ni(o-VALH)$(H_2O)_3$] recorded 16 peaks up to 28° of 2θ while [Cu(o-VALH) $H_2O)_3$] exhibited the same number of peaks when charted up to 27°. All the reflections have been indexed for h, k, *l* values using methods reported in literature[13]. The 'd' values of refluxes were obtained using Bragg's equation ($n\lambda = 2d \sin \theta$). All the three complexes have been found to be orthorhombic. The values of $\sin^2 \theta$ for each peak have been calculated with the help of the cell parameters and the corresponding h, k, *l* values. In all cases they are in good agreement with observed $\sin^2 \theta$ values as shown in Tables 3–5. The lattice constants a, b and c for each unit cell have been found out and are given in Tables 3–5, along with the density and number of molecules per unit cell.

TABLE-3

X-RAY POWDER DIFFRACTION DATA OF [FeL$(H_2O)_3$]

Crystal system : orthorhombic

A = 0.002971; B = 0.001980; C = 0.000990; a = 14.1335 Å; b = 17.3245 Å; c = 24.5006 Å;

Cell volume V = 5999.1145 Å; Density D = 1.7398 gm/cm^3; n = 16

Peak No.	d spacing (Å)	Relative intensity ($I/I_0 \times 100$)	$\sin^2 \theta$ Observed	$\sin^2 \theta$ Calculated	h k l
1	14.1450	31	0.00297	0.00297	100
2	11.0444	69	0.00486	0.00495	110
3	10.2787	28	0.00562	0.00594	012
4	8.2273	52	0.00877	0.00890	021
5	7.6936	21	0.01003	0.01080	013
6	7.0780	29	0.01185	0.01188	200
7	6.8101	35	0.01281	0.01287	201
8	6.6802	25	0.01331	0.01386	210
9	6.3256	18	0.01485	0.01485	211
10	5.1404	38	0.02249	0.02178	131
11	4.9008	28	0.02474	0.02475	132
12	4.4846	24	0.02955	0.02970	311
13	4.2709	28	0.03258	0.03260	041
14	4.0404	35	0.03640	0.03564	141
15	3.9513	32	0.03806	0.03861	142

TABLE-4
X RAY POWDER DIFFRACTION DATA OF $[NiL(H_2O)_3]$

Crystal system : orthorhombic.
A = 0.00885; B = 0.00177; C = 0.000885; a = 8.1945 Å; b = 18.3234 Å; c = 25.9133 Å;
Cell Volume V = 3890.9105 Å Density D = 1.7401 gm/cm^3; n = 10

Peak No.	d spacing (Å)	Relative intensity ($I/I_0 \times 100$)	$\sin^2\theta$		h k l
			Observed	Calculated	
1	8.1923	53	0.00885	0.00885	100
2	7.5283	39	0.01048	0.01062	110
3	6.5110	31	0.01401	0.01416	012
4	5.9073	82	0.01703	0.01680	021
5	5.0124	62	0.02366	0.02301	104
6	4.8729	33	0.02501	0.02560	131
7	4.5534	34	0.02867	0.02830	040
8	4.0767	26	0.03575	0.03540	200
9	3.9352	28	0.03839	0.03805	211
10	3.8182	32	0.04077	0.04070	202
11	3.7532	28	0.04216	0.04240	212
12	3.6622	25	0.04459	0.04425	050
13	3.5073	26	0.04833	0.04690	135
14	3.4141	31	0.05098	0.05130	204
15	3.2902	28	0.05489	0.05398	151
16	3.2041	43	0.05791	0.05750	205

TABLE-5
X-RAY POWDER DIFFRACTION DATA OF $[CuL(H_2O)_3]$

Crystal system : orthorhombic;
A = 0.007596; B = 0.001519; C = 0.000844; a = 8.8427 Å ; b = 19.7795 Å; c = 26.5352 Å;
Cell volume V = 4641.1175 Å Density D = 1.7508 gm/cm^3 n = 12

Peak No.	d spacing (Å)	Relative intensity ($I/I_0 \times 100$)	$\sin^2\theta$		h k l
			Observed	Calculated	
1	8.8406	100	0.00759	0.00759	100
2	7.6936	20	0.01003	0.00995	111
3	7.3140	26	0.01110	0.01360	030
4	6.1086	40	0.01592	0.01500	014
5	5.6106	51	0.01889	0.01704	032
6	5.2158	52	0.02184	0.02120	130
7	5.1565	17	0.02314	0.02430	040
8	4.9290	28	0.02447	0.02457	132
9	4.6217	38	0.02781	0.02767	042
10	4.4407	67	0.03015	0.03030	200
11	4.0767	27	0.03575	0.03526	142
12	3.9513	32	0.03806	0.03798	106
13	3.7080	28	0.04322	0.04390	036
14	3.6040	52	0.04574	0.04557	150
15	3.3634	32	0.05253	0.05310	153
16	3.2029	32	0.05449	0.05460	060

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