Synthesis and X-ray diffraction studies of the three metal complexes of the ligand Potassium - N – Anthracene - 9 – Carboxaldehyde Histidine

G. Indiradevi[1], Sabu. P.G[2], Geetha Parameswaran[3]
[1]Associate Professor, Z. G. College, Calicut
[2]Associate Professor, M. A. M. O. College, Mukkam
[3]Professor (Retd), University of Calicut
*Corresponding author: E-Mail: indirasabu@yahoo.com

ABSTRACT

The crystalline systems of Cr(III), Co(II), and Ni(II), complexes of anthracence carboxaldehyde L Histidine is determined and confirm its molecular formula assigned from elemental, spectral and magnetic studies. The complexes having the formula $[CuL_2 (H_2O)_2]$, $[NiL_2 (H_2O)_2]$ and $[CrL_2 (H_2O)Cl]$ were synthesized and characterized by elemental analysis, conductance and spectral data measurements. X-ray diffraction studies were carried out using powder technique. The unit cell dimensions a, b, c number of molecules per unit cell n, and density D has been found out from crystallographic data. The densities of the above complexes have been measured by making pellets under 6.5 ton pressure. 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 in all cases are in good agreement with observed values.

KEY WORDS: crystalline system, complexes, X-ray diffraction, unit cell, orthorhombic.

1. INTRODUCTION

In X-ray crystallographic studies graphical methods have been used by for indexing powder photographs (Hull, 1921; Bunn, 1945). Hesse (1948) and Lipson (1949) introduced easier methods for studying crystallographic pattern. Hentry (1951), introduced equations for studying powder crystallographs. A number of studies on elastic constants of such compounds are already reported. (Hearmon, 1956; Krishnan, 1958 and Suryanarayana, 1956). The synthesis and crystal structure of the Schiff base complex of Cu (II) complexes have been reported by Doman (1990). X-ray powder analysis of complex of Ni (II) with Schiff bases derived from O. Vanillin and Diamines have been reported (Liu, 1993). X-ray analysis of Cu (II) complexes of Schiff base derived from salicylaldehyde and glycine was carried (Nathmala, 1991). Mononuclear and binuclear Cu (II) complexes with Schiff base were prepared and studied by X-ray powder method (Dodwad, 1995).

For analytical diffraction studies the sample is ground to a fine homogeneous powder. Diffraction patterns are obtained by automatic scanning. The identification of a species from its diffraction pattern is based upon position of lines and their relative intensities.

In this study the X-ray diffraction pattern of Ni(II),Cr(III) and Cu(II) complexes of anthracene carboxaldehyde –L histidine is determined. The unit cell dimensions, number of molecules per unit cell and density has been found from crystallographic data. The density measured by making pellets under 6.5 ton pressures. The nature of crystalline systems and constants A, B, C were found out. From A, B, C lattice constants a, b, c and volume were obtained By the X-ray crystallographic studies the determination of unit cell dimensions, lattice type of the crystal, the inter planar spacing of lattice planes and miller indices of the reflection planes are carried out. X-ray powder pattern is used. The application to seven complexes of various ligands carried out .Results shows that all complexes are orthorhombic.

2. MATERIALS AND INSTRUMENTS

Instruments used for studying crystalline nature are Bruker D 5005 AXS X ray diffractometer, Pellitiser, and Densitometer. Diffraction patterns are obtained by automatic scanning. Analar grade chemicals and commercial solvents after purification were used for the preparation of the ligand and complexes.

2.1. Method: Histidine in alcoholic potassium hydroxide was refluxed with ethanolic solution of anthracene carboxaldehyde on a water bath. On cooling the mixture in ice, needle shaped yellow crystals of potassium salt of the ligand were obtained. The ligand obtained is recrystallised from ethanol. (Yield 95 %, melting point 98^0 C). A solution of metal acetate in ethanol/methanol was added drop wise to a refluxing solution of ligand in ethanol/methanol. Sodium acetate in ethanol/methanol was added and refluxed. The precipitate separated was filtered, washed with 50% methanol/ethanol and dried over anhydrous calcium chloride. Cr (III) complex was prepared from its chloride. The diffraction pattern was obtained using Bruker D 5005 AXS X ray diffractometer. The powder lines were recorded for 2θ values from 4^0 to 60^0 at a chart speed of 20 mm / min and a scan speed of 2^0 mm $^{-1}$ with Cu kα (λ - 1. 54184 A^0) radiation. The density of each complex was found out by making pellets at a pressure of 6.5 Ton.

2.2. Data analysis: Even though powder diffraction pattern between 2θ values of 4^0 and 60^0 is recorded for simplicity first few peaks are considered using Lipsons equations[6]. The nature of crystalline systems and constants A, B, C (where A = $\lambda^2 / 4\ a^2$, B = $\lambda^2 / 4\ b^2$ and C = $\lambda^2 / 4\ c^2$) were found out from which the lattice constants a, b, c and hence the volume were obtained. The complexes were made into pellets by applying the 6.5 Ton pressure and density was calculated. The density and number of molecules per unit cell were also found.

3. RESULTS AND CONCLUSION

The complexes were characterized on the basis of elemental analysis, magnetic measurements, electronic and infrared spectral data, conductance measurements and thermal data. The ligand anthracene – 9 – carboxaldehyde – L – histidine was characterized on the basis of elemental analysis and spectral data. Molecular formula of this ligand is suggested as $C_{21} H_{17} N_3 O_2$ and the complexes as $[CuL_2 (H_2O)_2]$, $[NiCuL_2 (H_2O)_2]$ and $[CrL_2 (H_2O)Cl]$.The UV and IR spectra of the ligand and complexes showed the characteristic bands. The infrared spectroscopic results provide support for the molecular constitution of these complexes. The structure of acidic form of ligand assigned is given below.
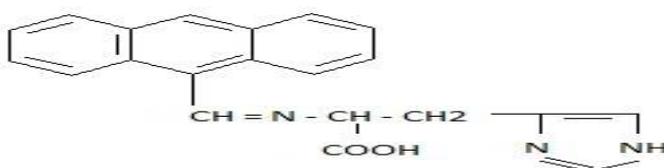
The assignments are made on the basis of comparison with the spectra of similar type of compounds. A broad feature at 3443 – 3350 cm^{-1} in the spectra of these complexes is attributed to the hydroxyl-stretching mode of water molecules. In addition a medium band approximately at 870 – 900 cm^{-1} suggests that water molecules are coordinated. The other very strong bands are observed in the 1700 – 1380 cm^{-1} region, one at ≈1660 cm^{-1} and the other at ≈1407 cm^{-1}. These are attributed to the asymmetric and symmetric stretching vibration respectively of carboxylate ion. Further the separation value, Δγ COO$^-$ (γasy COO$^-$ - γsy COO$^-$) of ≈ 250 cm^{-1} rules out the possibility of a bridged or coordinated carboxylate group. A strong band approximately at 1546 cm^{-1} in the spectrum of the ligand anthracene carboxaldehyde – L histidine may be assigned to γ C = N stretch. This band shows a downward shift by about 19 – 39 cm^{-1} in the spectra of all the metal complexes, indicating the participation of the azomethine nitrogen in coordination with metal ions. The shifted band in many cases is coincident with the C = C band, which then shows greater intensity or broadening. Only tentative assignments are made on the basis of information available in literature. Spectra of all complexes prepared in this investigation showed intense broad bands at 598 – 530 cm^{-1} and 505 - 499 cm^{-1} assignable to γ M – N and γ M – O. The aromatic out of plane vibration is seen near 810 cm^{-1} and in plane vibration at 770 cm^{-1} and 720 cm^{-1}. Molar conductance values indicate nonelectrolyte nature of these complexes. Magnetic moment values suggest octahedral geometry to these complexes. Electronic spectra of the ligand anthracene carboxaldehyde –L- histidine is characterised by two bands lying around 32365cm-1 and 24270cm^{-1}.These bands assigned to n σ * and n π* transitions. During complex formation a red shift is detected for these bands indicate the involvement of Schiff base in coordination. The electronic spectrum of Cu (II) complex showed absorption maximum at 15380cm^{-1}, Ni(II) exhibit two d-d transitions at 16,700cm^{-1} and 22500cm^{-1}. Cr(II) complex show a weak band at 17930cm^{-1}due to transition of $^4A_{2g}$ $^4T_{1g}$ in the spectrum and hence the octahedral geometry to the complex is suggested.

The values of sin^{2}θ for each peak have been calculated and corresponding h, k l are in good agreement with observed values. All the reflections have been indexed for h, k, l values using methods reported in literature. All the three complexes have been found to be orthorhombic. The values of Sin^{2}θ for each peak have been calculated with the help of the cell parameters and the corresponding h, k, l in all cases are in good agreement with observed values. The calculated density of each complex was in good agreement with that of experimental value found out. This confirms the molecular structure. In all the three complexes there occur 1:2 stoichiometry between metal ion and ligand.

Table.1. Micro analytical magnetic moment and molar conductance of Metal Complexes

Metal Complexes	color	Melting Point	Metal Percentage		μ_{eff}	Ω_m^{-1}
			Observed	Calculated		
$[CrL_2(H_2O)Cl]$	Greenishyellow	176	6.73	6.58	4.1	4.27
$[Ni\ L_2(H_2O)_2]$	Pale Yellow	194	7.3	7.53	3.36	8.63
$[CuL_2(H_2O)_2]$	BluishGreen	185	7.4	8.09	1.54	9.23
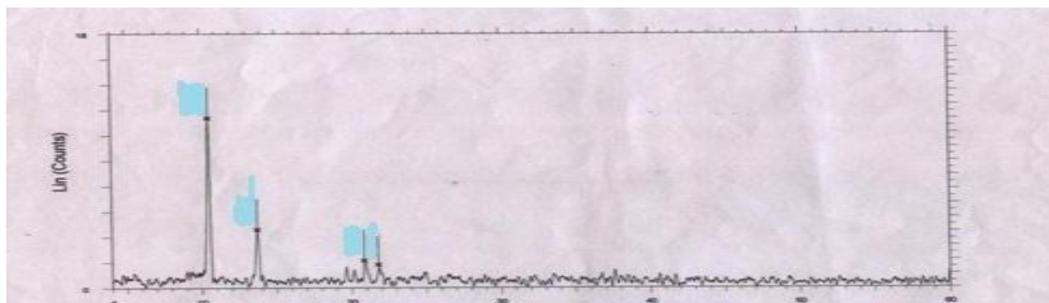
Fig.1.X ray Diffraction pattern of Ni Complex

Table.2. X Ray data of Ni [ACH]$_2$ [H$_2$O]$_2$ Crystal System : Ortho rhombic

Peak no	d spacing	Relative intensity	Sin θ		h k l
			Observed	Calculated	
1	8.4255	100	0.008372	0.008372	100
2	6.3691	39	0.014851	0.014871	111
3	4.6736	12	0.028678	0.027209	121
4	4.3509	7	0.030903	0.033488	113
5	4.2127	17	0.033208	0.033488	200
6	4.08696	14	0.035755	0.035581	201
7	3.59261	9	0.046475	0.046046	212
8	3.370192	8	0.05253	0.052325	221
9	2.97886	7	0.066113	0.066976	204
10	2.77028	7	0.077132	0.077441	301
11	2.6643716	8	0.08426	0.08372	302
12	2.4322	8	0099629	0.100464	323
13	2.4073	10	0.103317	0.102557	241
14	2.2126	8	0.121211	0.121394	333
15	2.1575	7	0.126964	0.127673	305

A = 0.008372, B =0.004186 C =0.002096, a = 8.425481, b= 11.91543, c = 16.85096

Cell Volume = 1691.72 A, Density = 1.435 gm/ cm ^{3}, No of molecules per unit cell = 2

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