X-RAY DIFFRACTION STUDIES OF SOME TRANSITION METAL COMPLEXES OF AMINO ACID SCHIFF BASES OF ANTHRACENE CARBOXALDEHYDE

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ABSTRACT

X- ray diffraction studies of anthracene carboxaldehyde -amino acid - metal complexes were carried out. The arrangement of atoms and its spacing can be accurately determined using the results of these studies. The diffraction pattern was obtained using Bruker D5005 AXS X-ray diffractometer. Powder lines were recorded for 2θ values from 4° to 60° . The four complexes studied were found to be orthorhombic in nature. The density values of each complexes were calculated and found to be in good agreement with values obtained using experiments. The metal ion and ligand show a stoichiometry of 1 : 2, except Ag (I) complex. In the case of silver complex metal to ligand ratio was 1:1.

KEYWORDS: X-Ray Diffraction, Crystalline Materials, Ligand, Stoichiometry & Powder

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INTRODUCTION

X-Ray diffraction was discovered by Von Laue in 1912. Comparing to other techniques, X ray diffraction is very simple to use. This technique is useful to study the arrangement of atoms in a crystal and also the spacing between atoms.

The structure of metal complexes can be easily determined by X-ray diffraction method. Usually, powder method is used for the studies of materials, which are not having single crystalline form. The X -ray diffraction pattern is different for different crystalline substances. So X-ray powder method is very use full in this study. The quantitative property and the qualitative property of compounds in a solid sample can be studied by analytical method. X - ray method is the only one available now for this study. A fine homogeneous powder of the sample is prepared for the analytical study. The particles of this sample will be oriented in a specified pattern, when an X-ray beam passes through this powder. This orientation is based on conditions of Bragg law. This pattern of orientation can be studied using scanning. The position of lines is one of the factors for the identification of a species. The relative intensity of these lines is another factor which decides the species.

Now days, X ray diffraction method is widely used in the study of coordination compound structure. Structure of such compounds explained by Werner's theory can be well confirmed by this study. Bjurstrom and Bunn used graphical methods of X ray diffraction studies for indexing powder photographs. Hesse and Lipson, Lipson and Wooster, and Henry suggested equations, as well as easier methods for the study of these patterns.

For the complete determination of molecular structure, X-ray diffraction is a widely used physical procedure. Crystallographic study of the nature of crystals such as crystal faces and the intercepts of these faces on

crystal axes are use full for the classification of crystals. Using this type of study, the crystals are classified in to seven types, based on their axial angles and axial lengths. The classifications are cubic, tetragonal, orthorhombic, trigonal, hexagonal, monoclinic and triclinic. A study on the elastic constants of these compounds was made by Bhagavantam, Hearmon, Krishnan and Suryanarayana. The miller indices of the reflection planes of the crystal, the lattice type of the crystal, the inter planar lattice spacing and the dimension of unit cell can be determined using these studies. This is possible by studying the interference pattern created by the crystal, when X ray with specified wavelength scattered through the crystal. This diffraction clearly obeys Bragg's law and hence by knowing the angle of diffraction θ , the distance between planes d , can be calculated. Hence an X-ray crystallographic pattern between 2θ and intensity of diffraction is used for the analysis of the crystalline data.

Crystal System Determination

From theoretical methods of study of crystalline systems there is a relationship between the Miller indices h, k, l and the distance between planes d . This relationship decides the nature of crystal structure. In cubic crystal system, the axial lengths $a = b = c$ and the axial angles $\alpha = \beta = \gamma = 90^\circ$. In this case, the relation between h, k, l and distance between the planes d is $1/d^2 = (h^2 + k^2 + l^2) / a^2$

In the above case, if one of the distance is not equal, that is $a = b \neq c$, the system is tetragonal system. If all of them are different in each other, that is $a \neq b \neq c$, it is called orthorhombic crystal. In orthorhombic crystal the axial angles will be the same. For such a crystal system the equation is

$$1/d^2 = (h/a)^2 + (k/b)^2 + (l/c)^2$$

Hexagonal system is another one, in which $a = b \neq c$ and $\alpha = \beta = 90^\circ, \gamma = 120^\circ, a = b = c, \alpha = \beta = \gamma \neq 90^\circ$ for rhombohedral system, $a = b \neq c, \alpha = \gamma = 90^\circ$, and $\beta \neq 90^\circ$, and for triclinic system, $a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$.

Doman et al studied the synthesis of the Schiff base complex of Cu (II) complexes and its crystal structure is reported. Nathmala reported the studies of salicylaldehyde and glycine Schiff bases of Mononuclear and binuclear Cu (II) complexes using X-ray powder method. Garcia Raso et al studied the X-ray diffraction structure of two N- salicyclidene tryptophanato diaquo Cu (II) complexes. Mahmood Saleem et al published a study of X-ray crystal structure of salicylaldehyde and diamino acids Schiff base. Cavaco Isabel et al used the X –ray diffraction analysis deduce the structure of N salicylidene amino acidate complexes of oxovanadium (IV) in which complexes are formed from glycine and alanine This study suggested that both the tridentate Schiff base ligands occupy equatorial positions and possess an octahedral geometry.

Anthranilic acid and 5- bromoanthranilic acid Schiff bases are used to prepare Cd (II) complexes and its X ray studies were reported. Laly Thomas Kotturan discussed the X-ray diffraction studies of complexes of Fe(II), Ni(II) and Cu(II) of o-vanillin L – histidine. Castineiras et al studied the crystal and molecular structure of neutral Cu (II) complexes of Schiff bases formed from 2- aminopyridine and substituted salicylaldehydes by X-ray diffraction method.

In this study Fe (III), Cu (II), Zn (II) and Ag (I) complexes of anthracence carboxaldehyde amino acids were synthesized, characterized and their crystalline systems were studied. These studies include the number of molecules per unit cell, unit cell dimensions, and the density.

MATERIALS, METHODS AND INSTRUMENTS

The solvents collected commercially were purified by distillation. The ligand anthracene carboxaldehyde – tyrosine (ACT), anthracene carboxaldehyde – glycine (ACG), anthracene carboxaldehyde alanine (ACA) and anthracene carboxaldehyde - phenyl alanine were synthesized and characterized.

Experimental

The reagents used for the preparation of complexes were of analar grade. The diffraction pattern was obtained using Bruker D 5005 AXS X ray diffractometer. The powder lines were recorded for 2θ values from 4° to 60° at a chart speed of 20 mm / min and a scan speed of 2° min^{-1} with $\text{Cu K}\alpha$ ($\lambda = 1.54184 \text{ \AA}$) radiation. The density of each complex was found out by making pellets at a pressure of 6.5 Ton

Treatment of data

Powder diffraction pattern is recorded for a range of 2θ values from 4° to 60° . In this study, the first few peaks are selected and studied using Lipson's equations. The 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. Hence the value of lattice constants a, b, c is determined. This will be helpful to calculate the volume and hence the density. The number of molecules per unit cell was also found out.

RESULTS AND DISCUSSIONS

The X-ray diffraction pattern of, Ag (I), Fe (III) complexes of anthracene carboxaldehyde –glycine, Zn (II) complex of anthracene carboxaldehyde –tyrosine, and Cu (II) complex of anthracene carboxaldehyde phenyl alanine were recorded and studied. 15 peaks between 4° to 51° were used for the study. All the reflections have been indexed for h, k, l values using methods reported in literature. In this work complexes of different amino acids and metal ions of anthracene carboxaldehyde were used. It was observed that the complexes studied were orthorhombic in nature. Results show that the values of $\text{Sin}^2 \theta$ for each peak have been calculated using the cell parameter values and the corresponding h, k, l values are in good agreement with the observed values.

The number of molecules per unit cell, lattice constants a, b, and c for each unit cell and the density of each complex are calculated and presented in Tables. When comparing with the values obtained in experiments it is in good agreement with theoretical values. This confirms the molecular structure. Except Ag (I) complex there occur 1:2 stoichiometry between ligand and metal ion. In the case of Ag (I) complex metal to ligand ratio was 1:1. The x-ray application to four complexes of anthracene carboxaldehyde - amino acids shows that all are orthorhombic.

X Ray Data of [Ag (ACG) (H_2O)]

Name of Crystal system : orthorhombic

A = 0.008372, B = 0.004186 C = 0.002093

a = $8425481 \text{ \AA}$ b = $1191543 \text{ \AA}$ c = $16.85096 \text{ \AA}$

Cell Volume : $1691.72 \text{ \AA}^3$

Density : 1.507 g/cm^3

Number of molecules per unit cell = 4

Table 1

Peak No	d Spacing $\text{\AA}^0$	Relative Intensity	$\sin^2 \theta$		h k l
			Observed	Calculated	
1	8.43	100	0.00837	0.00837	1 0 0
2	7.5380	14	0.01004	0.01047	1 0 1
3	6.8794	17	0.01281	0.01256	1 1 0
4	6.3691	32	0.01443	0.01465	1 1 1
5	4.6736	17	0.02752	0.02721	1 2 1
6	4.3509	38	0.03166	0.03140	1 1 3
7	4.0870	14	0.03543	0.03558	2 0 1
8	3.8659	14	0.03975	0.03977	2 1 1
9	3.5137	13	0.04777	0.04814	1 3 1
10	3.3047	17	0.05430	0.05442	1 3 2
11	2.6644	16	0.08354	0.08372	3 0 2
12	2.4580	13	0.09807	0.09837	3 1 3
13	2.3368	34	0.10869	0.10884	3 0 4
14	2.18	35	0.12552	0.12558	3 2 4
15	2.08	14	0.13851	0.13814	4 1 0

Figure 1: Thermal Spectra of [Zc (ACT)2]

Figure 2: Thermal Spectra of [Cu (ACPA)2 (H2O)2]

(ACT is Anthracene Carboxaldehyde Tyrosine, and ACPA is Anthracene Carboxaldehyde Phenyl alanine)

Experimental Values of X Ray of [Zn (ACT)₂]

Name of Crystal system: orthorhombic

A = 0.008372, B = 0.003805 C = 0.002262

a = 8.425481Å⁰ b = 12.49701Å⁰ c = 16.20674Å⁰

Cell Volume : 1706.46Å³

Density : 1.313g/cm³

Number of molecules per unit cell = 4

Table 2

Peak No	d Spacing Å ⁰	Relative Intensity	sin ² θ		h k l
			Observed	Calculated	
1	8.4255	100	0.00837	0.00837	1 0 0
2	6.4154	18	0.01443	0.01440	1 1 1
3	4.9482	9	0.02474	0.02427	0 2 2
4	4.5477	7	0.02912	0.02874	1 0 3
5	4.2127	16	0.03321	0.03349	2 0 0
6	4.0345	8	0.03641	0.03651	0 3 1
7	3.6514	11	0.04412	0.04458	1 0 4
8	3.3996	9	0.05156	0.05143	0 2 4
9	3.1526	7	0.05955	0.05980	1 2 4
10	3.0718	6	0.06269	0.06299	1 3 3
11	2.7673	5	0.07713	0.07761	3 0 1
12	2.6536	7	0.08426	0.08438	3 0 2
13	2.5973	6	0.08793	0.08810	2 3 3
14	2.5095	5	0.09421	0.09438	2 4 0
15	2.2765	5	0.11418	0.11468	0 1 7

CONCLUSIONS

In this study, the colored complexes of anthracene carboxaldehyde with glycine, alanine, phenyl alanine and tyrosine were synthesized. A detailed study of these complexes using X ray powder method shows that they are orthorhombic in nature and possess 1:2 metal to ligand ratio except silver complex which possess 1:1 metal to ligand ratio. Hence a structure of [Ml₂ (H₂O)₂] and [Ag(H₂O)₂] respectively is assigned to these complexes.

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