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POWDER X-RAY DIFFRACTION AND THERMAL STUDIES OF SOME METAL COMPLEXES DERIVED FROM BENZOFURAN SCHIFF BASE

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ABSTRACT Powder X-ray diffraction and thermogravimetric studies of metal(II) complexes derived from 3-(2-hydroxybenzylideneamino)-5-bromobenzofuran-2-carboxamide Schiff base have been carried out in the current investigation. With the continuation of our previous research here, we report important structural information, geometry, and thermal stability of the synthesized compounds. The trend of the recorded data gives precise information about the crystallinity of the metal complexes.

KEYWORDS : Benzofuran, Schiff base, X-ray diffraction, Thermal studies.

INTRODUCTION

William Lawrence Bragg and *William Henry Bragg* in 1913 proposed and express the necessary conditions for diffraction successfully and given simple mathematical form and is also called *Bragg's Law (Cullity, 1956; Cullity & Stock, 2001)*. In the powder method, the crystalline material is subjected to very fine powder or in the form of loose or consolidated microscopic grains. Each particle of the powder is a tiny crystal, or assemblage of smaller crystals, oriented at random with respect to the incident beam. The powder is equivalent in fact, to a single crystal rotated, not about one axis, but also about all possible axis(CHATTERJEE, 2010; Nuffield et al., 1966).

Gavali et. al.(Gavali & Hankarep, 2007) have reported the powder X-ray diffraction (PXRD) pattern of the ligand HSTACB and its Cd(II) complex. The diffraction of HSTACB ligand consists of nine reflections between 10-80° (2θ) with maximum reflection at θ = 18.26° which corresponds to d = 4.8531Å. The diffractogram of the coordination Cd (II) complex records ten reflections between 10-80° (θ) with maximum reflection at θ = 14.84° which corresponds to d = 5.9646Å. The observed values for HSTACB and Cd2 $[HSTACB]_2Cl_2$ are a good fit for the tetragonal system to give a lattice constant that has been found to be the tetragonal type. *Zhu et. al.(Zhu & Gu, 2006)*, have repeated the X-ray powder lines observed in the Co (II) complex and showed satisfactorily on the basis of a unit-lattice for the metal complex. *Khare et. al.(Singh & Gautam, 1987)*, have reported the X-ray diffraction data of tris (2, 2'-bipyridyl) nickel(II) tungstate and tungstatoquo bis(2,2'-bipyridyl) cobalt(II) monohydrate. The unit cell parameter calculations have been done for the tetragonal symmetry of the nickel complex–(Fankuchen, 1955; Woolfson et al., 1997; "X-Ray Crystallography. M. J. Buerger," 1945). The cell parameters have been calculated by using the equation, $Sin^2\theta = \lambda^2/4a^2 \; x(h^2+k^2+l^2)$, Where $\lambda^2/4a^2$ is a common factor.

Thermogravimetric analysis (TGA) is one of the very useful tools in chemical sciences and can provide much information about the physical and chemical phenomena of a compound. During thermal analysis, compounds can undergo various phases like second-order phase transitions which include absorption, adsorption, vaporization, sublimation, and desorption, including chemisorptions, desolvation (especially dehydration), decomposition, and solid-gas reactions (e.g., oxidation or reduction) respectively(Coats & Redfern, 1963). Duval studies over the thousand gravimetric precipitates by this method –(De Clercq & Duval, 1951; Keer, 1993; Rao et al., 1970; Wendlandt, 1960). The TG data to estimate kinetic parameters of solid-state reactions involving weight loss (or gain) has been studied by a number of researchers—(Becker, 1965). *Freeman and Carroll* et. al. (Freeman & Carroll, 1958) have identified some of the advantages of this method over traditional isothermal studies. However, the significance of technical particulars, such as container geometry, degree of heating, pre-history of the sample, and unit size, on the factors has yet to be completely explored. It is also essential to confirm precise temperature extent, both for accuracy and also to detect any exit from a direct heating rate owing to endo or exothermic reactions. A novel mathematical explanation of TG suggestions allows one to define appropriately the kinetic factors of the pyrolysis curve (Blaedel & Knight, 1954). The slope of the straight line, plot of a function of the weight fraction left vs. the temperature gives the activation energy of pyrolysis(Abou-Melha & Faruk, 2008).

EXPERIMENTAL:

Benzofuran-2-carboxamide was synthesized according to the literature procedure(Kawase et al., 1962). The metal and the chloride content were determined according to the *Vogel's* procedure(Vogel, 1954). The total synthesis of our ligand and metal complexes can be found in our earlier publications–(Sadu Suryakant S., 2014a, 2014b). Extending from the previous work, here we report the PXRD and TG studies of metal complexes of the ligand 3-(2-hydroxybenzylideneamino)-5-bromobenzofuran-2-carboxamide[L].

Thermogravimetric (TG) studies of the complexes were carried on the Perkin Elmer thermal analysis instrument at a heating rate of 10C per minute in nitrogen atmosphere from 40 - 450C. The range of temperature and the experimental and calculated weight losses of decomposition is shown in figure -4 & 5.

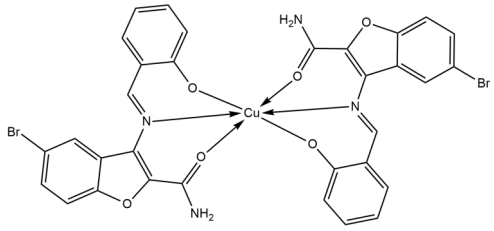


Figure 1: Structure of Copper(II) complex

RESULTS AND DISCUSSION: PXRD STUDIES OF THE LIGAND [L] AND IT'S COPPER (II) COMPLEX.

The PXRD pattern of ligand [L] and it's Copper(II) complex has been recorded with Cu-Kα X-ray source in the range 3-80°. The PXRD pattern of the ligand [L] is depicted in Figure-2, shows seventeen reflections in the range 15-50º listed in Table-1. The 2θ value with maximum intensity peak for the ligand was found to be 23.526º corresponding to interplanar distance 3.77857 *Å*. All the main peaks have been indexed by trial and error methods(Cullity, 1956). The interplanar distance '*d*' calculated from the positions of the intense peaks using *Bragg's* relationship $n\pi = 2d\sin\theta$, (Cu-Kα= 1.54056 Å).

The interplanar distance values obtained have been compared with calculated values. The comparison of these values revealed a good agreement between calculated and observed *d* values. The unit cell calculations have been made for the cubic symmetry of the ligand. There is an absence of forbidden peaks indicates the non-cubic system of the ligand [L].

TABLE – 1
PXRD DATA OF LIGAND [L]

2θ	Sin θ	hkl	a (A°)	d-spacing(A°)	
				Obs.	Obs.
15.400	0.1340	100	5.749	5.749	5.748
16.251	0.1413	100	5.449	5.449	5.449
18.825	0.1635	110	6.661	4.710	4.710
22.949	0.1989	110	5.475	3.872	3.872
23.526	0.2039	110	5.343	3.778	3.778
25.787	0.2231	111	5.979	3.452	3.452
27.642	0.2389	111	5.584	3.224	3.224

30.061	0.2593	200	5.940	2.970	2.970
31.122	0.2683	200	5.742	2.871	2.871
32.390	0.2789	200	5.523	2.761	2.761
34.251	0.2945	210	5.849	2.615	2.615
35.950	0.3086	210	5.581	2.496	2.496
37.315	0.3199	211	5.897	2.407	2.407
39.982	0.3419	211	5.961	2.253	2.253
41.633	0.3554	220	5.734	2.167	2.167
44.492	0.3786	220	5.754	2.034	2.034
49.610	0.4195	310	5.806	1.836	1.836

TABLE – 2
PXRD DATA OF LIGAND [L]

2θ	Sin θ	hkl	a (A˚)	d-spacing(A˚)	
				Obs.	Obs.
4.17	0.0727	100	10.5930	10.593	10.593
09.4840	0.1648	210	10.4532	4.6749	4.6748
11.6740	0.2023	220	10.7673	3.8069	3.8068
12.0630	0.2089	220	10.4250	3.6858	3.6857
13.4300	0.2323	310	10.4877	3.3165	3.3165
14.0560	0.2429	311	10.5189	3.1716	3.1715
15.7535	0.2715	321	10.6156	2.8372	2.8371
16.3600	0.2817	----	10.5913	2.7347	2.7346
16.7200	0.2877	400	10.7097	2.6770	2.6774
17.7560	0.3049	411	10.7161	2.5258	2.5258
19.4745	0.3334	421	10.5879	2.3105	2.3104
20.4885	0.3500	----	10.5541	2.2007	2.2006
22.2170	0.3781	----	10.5854	2.0372	2.0371
26.9155	0.4527	----	10.6266	1.7016	1.7016
28.0635	0.4704	541	10.6111	1.6373	1.6373
4.1700	0.0727	100	10.5930	10.593	10.593
09.4840	0.1648	210	10.4532	4.6749	4.6748

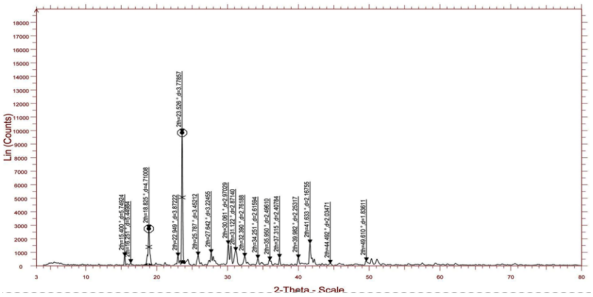


Figure 2: The PXRD pattern of ligand [L]

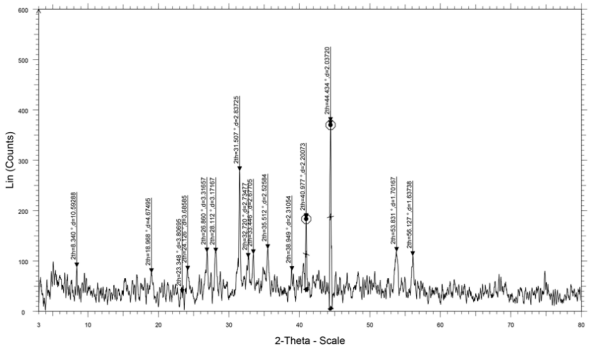


Figure 3: The PXRD pattern of Copper(II) complex

TGA AND DTA STUDIES OF Cd(II) AND Hg(II) COMPLEXES.

The $[Cd(C_{16}H_{10}BrN_2O_3)Cl]$ complex is thermally decomposed in two successive decomposition steps. The first estimated weight loss of one halide species at a temperature of 273.99°C. This practical weight loss of 18.94% is in accordance with the theoretical weight loss of 15.81%. The complex underwent further decomposition and gave another break at 327.53°C with a weight loss of 63.36% which corresponds to the decomposition of complex to expel $(C_{16}H_{10}N_2O_3)$ and (-Cl) species[17-19]. This observed weight loss 63.36% is in accordance with the theoretical weight loss of 61.75%. The complex showed a gradual degradation up to 340.3°C and onwards. The weight of the residue 24.38% corresponds to the formation of the CdO (Blaedel & Knight, 1954).

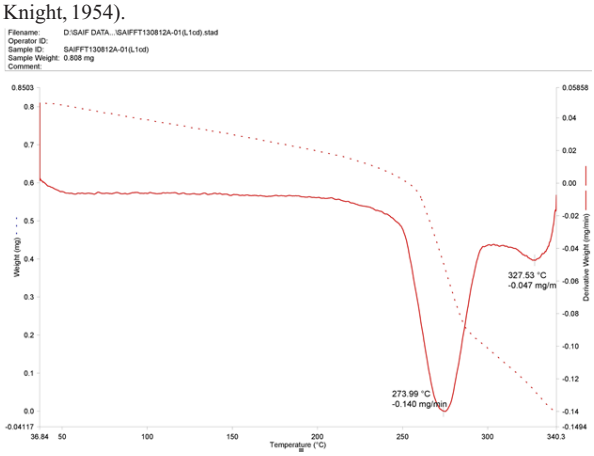
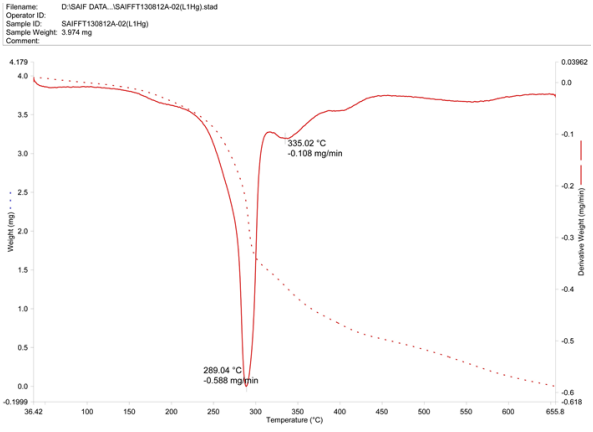


Figure 4: TG-DTA spectrum of Cd(II) complex of the ligand [L]

The $[Hg(L)Cl]$ complex with the general formula $[Hg(C_{16}H_{10}BrN_2O_3)Cl]$ is thermally decomposed in three successive decomposition steps. The first estimated weight loss of one $-(C_7H_6)$ species at the temperature 289.04C. This practical weight loss of 14.55% is in accordance with the theoretical weight loss of 14.98%. At the second decomposition, the spectrum gave another break at 335.02C with weight loss of 32.36% which corresponds to the decomposition of $-(C_8H_4NO)$ and –Cl species. This observed weight loss of 32.36% is in accordance with the theoretical weight loss of 32.49%. The complex showed a gradual degradation of up to 655.8C. The weight of the residue 2.61% corresponds to the formation of the HgO(Abou-Melha & Faruk, 2008).

Figure 5: TG-DTA spectrum of Hg(II) complex of the ligand [L]



CONCLUSION:

The PXRD data analysis shows an absence of forbidden peaks which indicates the non-cubic system of the ligand and the presence of forbidden peaks reveal the cubic system of the complex. The range of temperature and the experimental and calculated weight losses of decomposition with probable assignment support the proposed structures of the ligand and complexes.

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