Chemistry Research Journal, 2024, 9(1):147-151
Available online www.chemrj.org

Research Article

ISSN: 2455-8990
CODEN(USA): CRJHA5

A Study on X-ray Diffraction of some newly synthesized copper (II) complexes of Mannich bases derived from Thiazole and Pyridine Moieties

Gayatri Kumari

Associate Professor Department of Chemistry Saraswati P.G. College, Hathras
Email: drgayatri.chem@gmail.com

Abstract
Three new copper (II) complexes of Mannich bases; p-hydroxybenzylidene-2-aminothiazole and p-hydroxybenzylidene-2-amino-6-methylpyridine have been synthesized and characterized by elemental analyses, magnetic measurements, IR, electronic and ESR spectral studies[1]. In the present paper, the X-ray diffraction analysis of these newly synthesized complexes have been investigated for their powder microcrystalline structure. The values of $\sin^2\theta$ (observed and calculated), interplanar spacings (d), relative intensities and hkl values of different lattice planes have been discussed. The X-ray crystal system has been worked out by trial and error method for finding the best fit values between the observed and calculated. The system to which the crystal of complexes belongs has been determined by taking in view the angle α, βand γ on their axis and relative length of the primitive translations a, b and c. The observed and calculated densities of the complexes have been calculated. The studies showed that the calculated and experimental values of complexes and $\sin^2\theta$ were in good agreement and are within the experimental error limits. All the complexes have been crystallized in tetragonal crystal system.

Keywords: copper metal complexes, X-ray studies

1. Introduction

There are various other methods for chemicals analysis, which are also widely applied, but X-ray analysis by diffraction or fluorescence has some special advantage, which can never be provided by non X-ray analysis despite some limitations of X-ray analysis. The added advantage for X-ray analysis is that it can not only identify and estimate the elements but also its compounds in various phases. Hence, diffraction analysis is useful whenever it is necessary to know the state of chemical combination of the elements involved or the particular phases in which they are present and as a result the diffraction method is widely applied for the analysis of materials like different ores, clays, alloys, industrial dusts etc. Many research workers[2-4] have studied the X-ray diffraction analysis of copper (II) metal complexes. X-ray along with electron and neutron beams are the essential tools for the investigation of internal structure of materials. This is because their wavelengths are of the order of distance between the atoms in materials, which act as a diffraction slit. This condition is essential for any wave to create the diffraction pattern and so a crystal is regarded as a three-dimensional diffraction grating.

In the method of X-ray diffraction analysis, copper or molybdenum are bombarded with high-energy electrons, though in principle almost any metal could be used. The emitted X-rays are then filtered or passed through a monochromater to produce Kα radiation from the respective metal. Once the X-rays impinge on the sample, they

diffract off of each of the exposed planar and a detector rotates around the sample recording he intensities of diffraction at each angle.

2. Purpose of the Study

Metals complexes of Mannich bases have been studied extensively in recent years due to the selectivity and sensitivity of the ligands towards various metal ions[5-6]. In the past various methods have been used to understand the coordination behavior of Mannich bases derived from thiazole and pyridine moieties. Therefore, it was thought worthwhile to synthesize some copper(II) complexes of Mannich bases derived from 2-aminothiazole/2-amino-6-methylpyridine with p-hydroxybenzaldehyde and to investigate their bonding characteristics by means of X-ray diffraction method.

3. Materials and Method

All the Mannich bases have been analyzed for C, H, N and S on Thomas CH analyzer-35-Carlo Erba-1106 and some on Coleman-N-analyzer at the Regional Sophisticated Instrumentation Centre, CDRI, Lucknow. The percentage of metal Cu (II) in complexes was determined by AAS methods from Geological survey of India, Lucknow. X-ray analysis of these Cu (II) complexes were recorded on Diffractometer System XPERT-PRO at S.A.I.F., Punjab University, Chandigarh.

4. Result and Discussion

The elemental analyses showed 1:2 (metal : ligand) stoichiometry for all the complexes. The magnetic moment values of all the copper (II) complexes derived from thiazole and pyridine moities were found in the range of 1.79-1.86 B.M., which were very close to the spin only value (1.73 B.M.). In the present work, the X-ray diffraction analysis of three copper (II) complexes [$Cu(C_{10}H_{10}N_2OS)_2.Cl_2$, $Cu(C_{10}H_{10}N_2OS)_2.(NO_3)_2$ and $Cu(C_{13}H_{14}N_2O)_2.(NO_3)_2$] of MB_1 and MB_2 have been investigated for their powder-microcrystalline structure. The data were collected on XPERT-PRO diffractometer using Cukα radiation over a range of 5-69° 2θ and the values $Sin^2\theta$ (observed and calculated), interplanar spacings (d), relative intensities and hkl vaules of different lattice planes have been summarized in Table:- 1, 2 ,3.

X-ray crystal system has been worked out by trial and error method for finding the best fit between the observed and calculated $Sin^2\theta$. The system to which the crystal of complexes belong have been determined by taking in view the angle α, β and γ on their axes and relative length of the primitive translations a, b and c.

- The X-ray diffraction data of Cu(C10H10N2OS)2.Cl2 give 34 reflections between 5o-69o (2θ), which corresponds to d = 17.06886 Ao. The maxima reflection was observed at 2θ = 5.1774 Ao. The observed values fit well in the tetragonal system to give a unit cell with lattice constant a = 24.13901331 Ao , c = 34.13772 Ao and cell volume 19891.77 A03 and n = 32. The cell volume gives the observed value of density, which is 1.4782 g/cm-3 while the calculated value of density has been found to be 1.4569 g/cm-3.
- The diffractogram of Cu(C10H10N2OS)2.(NO3)2 shows 28 reflections between 5o-69o (2θ) with reflection maxima 2θ = 5.1424 Ao, which corresponds to d = 16.41638Ao. A comparison of the value revealed that there is a good agreement between calculated and observed values of Sin2θ. The observed values fit well in the tetragonal system and gives a unit cell with lattice constant a = 24.3034722 Ao, c = 34.3703 Ao and cell volume 20301.11 A03. The number of atoms per unit of cell is 28. The observed and calculated density of the complex comes to be 1.3702 and 1.3728 g/cm-3 respectively.
- The diffraction of Cu(C13H14N2O)2.(NO3)2 consist of 31 reflections between 5o-69o (2θ), which corresponds to d = 17.06886 Ao. The maxima reflection was observed at 2θ = 5.3834 Ao. The observed values fit well in the tetragonal system to give a unit cell lattice constant a = 23.216267 Ao, c = 32.83276 Ao and the cell volume of 17696.69 A03. The number of atoms per unit cell is 24. The observed and calculated density of the complex compound comes to be 1.3507 and 1.38590 g/cm-3.

- On the basis of above discussion it was concluded that the calculated and experimental values of density of complexes and Sin2θ show good agreement and are within the experimental error limits. All the complexes have been crystallized in tetragonal crystal system.

Table 1: X-RAY (POWDER DIFFRACTION) DATA OF COPPER (II) COMPLEXES OF MB_1 $[Cu(C_{10}H_{10}N_2OS)_2.(NO_3)_2]$

S. No.	Interplanar Spacing (dA^0)	Rel. Int.	$Sin^2\theta$(Obs.)	$Sin^2\theta$(Calc.)	hkl
1.	17.18515	6.08	0.0020	0.0020	110
2.	14.9605	6.68	0.0026	0.0025	111
3.	13.3069	6.48	0.0033	0.0331	108
4.	8.93983	1.25	0.0074	0.0070	212
5.	7.51810	1.42	0.0105	0.0100	222
6.	6.86774	100.00	0.0126	0.0125	223
7.	6.56763	7.65	0.0137	0.0135	321
8.	5.70819	1.01	0.0182	0.0180	330
9.	4.79424	2.46	0.0258	0.0256	325
10.	4.59125	1.31	0.0281	0.0281	512
11.	4.37609	1.95	0.0310	0.0311	520
12.	4.10092	5.35	0.0353	0.0356	523
13.	3.87573	3.51	0.0395	0.0391	524
14.	3.69254	1.02	0.0435	0.0436	525
15.	3.61499	3.33	0.0454	0.0452	360
16.	3.44893	45.08	0.0499	0.0497	363
17.	3.20137	5.26	0.0579	0.0577	365
18.	3.03297	96.18	0.0646	0.0632	366
19.	2.79070	13.86	0.0763	0.0763	376
20.	2.66356	19.26	0.0837	0.0833	746
21.	2.52204	7.71	0.0934	0.0934	568
22.	2.45733	17.63	0.0984	0.0981	770
23.	2.30588	10.69	0.1117	0.1110	593
24.	2.25839	6.63	0.1165	0.1165	776
25.	2.15156	3.78	0.1283	0.1285	880
26.	2.07220	8.74	0.1384	0.1386	598
27.	1.89272	2.96	0.1659	0.1647	992
28.	1.77511	2.10	0.1886	0.1863	899

Table 2: X-RAY (POWDER DIFFRACTION) DATA OF COPPER (II) COMPLEXES OF MB_2 $[Cu(C_{13}H_{14}N_2O)_2.(NO_3)_2]$

S. No.	Interplanar Spacing (d A^0)	Rel. Int.	$Sin^2\theta$(Obs.)	$Sin^2\theta$(Calc.)	hkl
1.	16.41638	6.34	0.0022	0.0022	110
2.	14.23837	5.43	0.0029	0.0027	111
3.	10.77760	1.26	0.0051	0.0055	212
4.	8.45153	6.81	0.0083	0.0082	213
5.	6.99204	100.00	0.0121	0.0121	214
6.	6.27954	2.24	0.0150	0.0159	313
7.	5.66280	9.98	0.0185	0.0181	400
8.	5.47643	5.95	0.0198	0.0198	330
9.	5.11224	3.74	0.0227	0.0225	225
10.	4.69632	1.63	0.0269	0.0269	243
11.	4.47788	2.12	0.0296	0.0297	432

12.	4.17833	10.99	0.0340	0.0341	326
13.	3.92798	1.26	0.0385	00385	218
14.	3.63019	6.45	0.0451	0.0451	540
15.	3.48032	32.09	0.0490	0.0495	328
16.	3.36488	3.87	0.0524	0.0528	624
17.	3.19951	30.30	0.0579	0.0577	625
18.	3.05248	22.77	0.0637	0.0638	518
19.	2.81474	7.51	0.0750	0.0753	618
20.	2.68011	23.25	0.0827	0.0825	832
21.	2.58452	4.82	0.0889	0.0886	629
22.	2.47258	12.13	0.0972	0.0968	844
23.	2.31739	4.18	0.1106	0.1106	861
24.	2.26595	3.28	0.1157	0.1155	638
25.	2.15158	1.47	0.1283	0.1288	960
26.	2.08420	5.08	0.1368	0.1370	867
27.	1.95247	1.10	0.1559	0.1546	869
28.	1.90379	2.13	0.1639	0.1629	976
29.	1.77192	1.07	0.1877	0.1876	979
30.	1.73524	1.38	0.1973	0.1981	996
31.	1.71841	2.48	0.2112	0.2053	997

Table 3: X-RAY (POWDER DIFFRACTION) DATA OF COPPER (II) COMPLEXES OF MB_1 $[Cu(C_{10}H_{10}N_2OS)_2.Cl_2]$

S. No.	Interplanar Spacing (d A^0)	Rel. Int.	$Sin^2\theta$(Obs.)	$Sin^2\theta$(Calc.)	hkl
1	5.1774	3.18	0.00203	0.00203	110
2	6.5016	2.06	0.0032	0.0031	102
3	7.3541	3.38	0.0041	0.0041	112
4	8.1315	4.28	0.0050	0.0051	210
5	8.8288	2.12	0.0059	0.0055	211
6	10.0578	2.42	0.0076	0.0071	115
7	11.0735	1.29	0.0093	0.0091	300
8	14.6148	2.35	0.0161	0.0162	400
9	16.0394	11.04	0.0194	0.0193	412
10	17.4284	3.53	0.0229	0.0229	315
11	18.6308	3.07	0.0262	0.0264	334
12	19.5771	4.43	0.0289	0.0285	424
13	21.1161	2.06	0.0335	0.0335	434
14	22.4945	2.62	0.0380	0.0381	505
15	25.8510	3.31	0.0500	0.0509	550
16	26.4339	2.33	0.0522	0.0529	552
17	26.9830	4.68	0.0544	0.0544	545
18	29.3380	5.09	0.0641	0.0641	562
19	31.6318	100.00	0.0742	0.0748	565
20	32.2015	6.67	0.0769	0.0778	805
21	34.3175	3.08	0.0870	0.0870	567
22	35.5656	3.84	0.0932	0.0911	845
23	37.1158	4.21	0.1012	0.1018	828
24	37.8959	2.24	0.1054	0.1033	585

25	39.4976	5.80	0.1141	0.1140	848
26	40.7197	2.14	0.1210	0.1226	849
27	41.4199	4.29	0.1250	0.1232	858
28	42.4116	2.64	0.1308	0.1318	859
29	44.5875	4.26	0.1439	0.1430	869
30	45.3636	1.97	0.1486	0.1481	981
31	47.7174	1.19	0.1636	0.1629	888
32	49.7213	2.92	0.1767	0.1736	979
33	52.3425	3.06	0.1945	0.1975	998
34	53.9011	3.99	0.2054	0.2061	999

5. Conclusion

On the basis of magnetic measurement, electronic spectral studies, electron spin resonance spectral studies and X-ray diffraction analysis, it was concluded that the copper (II) complexes of MB_1 and MB_2 have distorted octahedral geometry.

Acknowledgement

I am very thankful to the Head, Department of Chemistry, Dr. B.R.A. University, Agra for providing laboratory facilities.

References

[1]. Kumari, G., Paliwal, S. and Dhakarey, R., J. Ind. Council Chem., 25, 82-86(2008)
[2]. Koysal, Y., Isik, S.and Aytemir, M.D., Acta Cryst., 60(E), o112(2004)
[3]. Sheldrick, G.M., Acta Cryst., 46(A), 457(1990)
[4]. Jovanovski, G. and Kamenar, B., Cryst. Struct. Comm., 11, 247(1982)
[5]. Haidue, L., Coord. Chem. Rev.,99, 253(1990)
[6]. Cleare, M.J., Coord. Chem. Rev., 12, 349(1974)