Asian Journal of Chemistry Vol. 13, No. 4 (2001), 1482–1488

Thermal and Powder X-ray Diffraction Studies of Copper(II) Complexes of Schiff Bases

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Copper(II) complexes (CuL_2) of the Schiff bases (LH) derived from 4-phenyl-2-aminothiazole and *o*-hydroxyaldehydes have been characterized by thermogravimetric analysis and powder X-ray diffraction studies. The TG curves are critically analysed to evaluate the various methods such as Freeman-Carroll, Coats-Redfern, MacCallum-Tanner, Horowitz-Metzger and Zsako. The values of kinetic parameters calculated by these methods are in good mutual agreement. A tetragonal crystal system is proposed on the basis of X-ray diffraction studies. Various X-ray parameters (lattice parameters, volume of unit cell and particle size) are calculated.

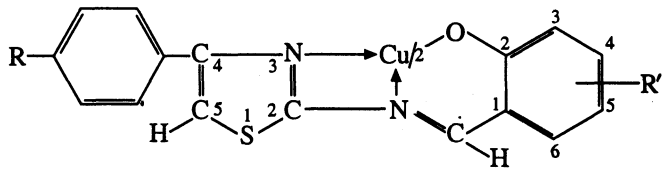
INTRODUCTION

Schiff bases derived from *o*-hydroxyaldehydes have strong ability to form transition metal complexes. Thermogravimetry is being employed presently in the investigation of chemical reactions in the liquids and solids at high temperatures. It involves the continuous measurements of change in weight as the sample temperature is increased. Calculation of various kinetic parameters from the TG curves by various methods has created a huge interest among the researchers. Now-a-days powder XRD is used as one of the important tools for structural determination because it is a non-destructive, fast and sensitive technique.

In our earlier communication,[1-3] we reported synthesis and characterization of metal complexes of the type ML_2 [M = Co(II), Ni(II), Cu(II) and Zn(II), LH = Schiff bases derived from 4-aryl-2-aminothiazole (aryl = C_6H_5, *p*-ClC_6H_4, *p*-$CH_3OC_6H_4$, *p*-$CH_3C_6H_4$ etc.) and substituted salicylaldehyde or 2-hydroxy-1-naphthaldehyde]. The complexes possess 1 : 2 metal : ligand stoichiometry and octahedral geometry. Coordination to the central metal atom takes place through the oxygen of the phenolic OH group, nitrogen of the azomethine group and nitrogen of the thiazole ring. The complexes are non-electrolytic in nature.

In the present communication we report thermogravimetric and powder XRD studies of copper(II) complexes (I) of Schiff base derived from 4-phenyl-2-aminothiazole and salicylaldehyde or 2-hydroxy-1-naphthaldehyde. Various kinetic parameters such as order of reaction (n), energy of activation (E), pre-exponential factor (z), entropy of activation (ΔS) and change in free energy (G) by methods such as Freeman-Carroll (FC)[4], Coats-Redfern (CR)[5], MacCallum-

Tanner (MT)[6], Horowitz-Metzger (HM)[7] and Zsako[8]. X-ray parameters such as lattice parameters, volume of unit cell and particle size etc. are calculated.



R = H R′ = H : $(C_{16}H_{11}N_2OS)_2Cu$

R = H R′ = 4-CH_3, $(C_{17}H_{13}N_2OS)_2Cu$

R = H, R′ =  : $(C_{20}H_{13}N_2OS)_2Cu$

EXPERIMENTAL

The ligands and the complexes were prepared as reported in our earlier communication[1]. AR grade chemicals and solvents were used.

Thermal measurements were performed by using Metler TA 4000 system. The furnace heating rate was 10°C/minute in nitrogen atmosphere. XRD spectra were run in the range 10–100° on a Philips PW 1710 diffractometer attached with computer along with graphical assembly in which CuKα radiation source connected with the tube of Cu-NF 2 kV/20 mA was used.

RESULTS AND DISCUSSION

All the complexes are crystalline solids, non-electrolytic in nature and possess 1 : 2 (M : L) stoichiometry (theoretical and experimental values of elemental analysis are in good mutual agreement).

The TG curves of two complexes $(C_{20}H_{13}N_2OS)_2Cu$ and $(C_{16}H_{11}N_2OS)_2Cu$ indicate that the analysis of thermal decomposition took place in two stages. The TG curves were analysed for the calculation of the kinetic parameters (n, E, Z, ΔS and G). The complexes do not show any loss in weight when heated up to 200°C and this indicates the absence of water of crystallization or coordinated water in the complexes.

The copper(II) complex $(C_{20}H_{13}N_2OS)_2Cu$ shows 53.20% weight loss in the temperature range 256–542°C in the initial stage and 30.94% weight loss (542–678°C) in the final stage. The final stable decomposition product (8.75% residue) analysed may be due to copper oxide.

The copper(II) complex $(C_{16}H_{11}N_2OS)_2Cu$ shows 34.24% weight loss in the temperature range 227–546°C in the initial stage and 49.17% weight loss (546–769°C) in the final stage. The final stage decomposition product (11.5% residue) analysed may be due to copper oxide.

Kinetic parameters were calculated by using various methods as under:

Freeman-Carroll method[4]

$$\frac{(E/2.303\ R)\Delta T^{-1}}{\log W_r} = -b + \frac{\Delta \log dw/dt}{\Delta \log W_r}$$

$$E = -2.303 \times R \times \text{slope},\ z = \frac{E \times q \times e^{E/RT_s^2}}{RT_s^2}$$

Gangadevi *et al.*[9] made some modification in Freeman-Carroll method, the equation is applicable for 1st order reaction,

$$\ln \frac{dw/dt}{W_r} = \frac{-E}{RT} + \ln Z$$

We modified the first order rate expression suggested by Gangadevi *et al.*[9] a under

$$\ln\left[\frac{dw/dt}{wr^n}\right] = \frac{-E}{RT} + \ln Z$$

By using different values of order of reaction, n, straight line is fitted by regression. The highest value of r, correlation coefficient, gives the correct value of n. Slope and intercept of this line is used to find E and Z.

Coats-Redfern method[5]

$$\log \frac{1-(1-\alpha)^{1-n}}{(1-n)T^2} = \log \frac{ZR}{Eq}\left(1 - \frac{2RT}{E}\right) - \frac{E}{2.303R} \times \frac{1}{T}$$

$$E = 2.303 \times \text{slope} \times R$$

For calculation of Z values, average value of intercept is taken (by substituting all values of temperature T).

MacCallum-Tanner method[6]

$$\log\left(\frac{1-(1-\alpha)^{1-n}}{(1-n)}\right) = \log \frac{ZE}{Rq} - 0.485\ E^{0.435} - \frac{(0.449 + 0.217E)}{T} \times 10^3$$

$$E = \left(\frac{\text{Slope}}{10^3} - 0.449\right) \Big/ (0.217)$$

Horowitz-Metzger method[7]

$$\log\left(\frac{1-(1-\alpha)^{1-n}}{(1-n)}\right) = \log \frac{ZRT_s^2}{qE} - \frac{E}{2.303RT_s} + \frac{E\theta}{2.303RT_s^2}$$

$$E = 2.303 \times \text{slope} \times R \times T_s^2$$

$$Z = E/RT_s^2 \times q \times e^{E/RT_s}$$

Zsako method[8]

Doyle's trial and error method[10] was simplified by a statistical approach as reported by Zsako[8]. Several researchers used alternative forms of p(x) functions[5, 10–12] for calculating kinetic parameters from TG curve by Zsako method.

We have calculated kinetic parameters such as n, E, Z and ΔS by Zsako method by using five different forms of p(x) function as under:

$$X = E/RT$$

Method I[5]: $p(x) = \frac{(x-2)}{x^3} e^{-x}$

Method II[11]: $p(x) = \frac{e^{-x}}{(x+2)(x-d)}$ where $d = \frac{16}{x^2 - 4x + 84}$

Method III[12]: $p(x) = \frac{e^{-x}(x^3 + 18x^2 + 88x + 96)}{(x^4 + 20x^3 + 120x^2 + 240x + 120)}$

Method IV[11]: $p(x) = \frac{1}{x(x-2)} e^{-x}$

Method V[10]: $p(x) = 2.315 - 0.4567x$

The values of ΔS and G were calculated by using the following equations:

$$\Delta S = 2.303 \log \frac{Zh}{KT_s}, \quad G = E - T_s \Delta S$$

We calculated *standard deviation/average B*, instead of standard deviation as a parameter for testing the constancy of difference in B values as per modification suggested by Zsako and Zsako (Jr)[13] for the calculation of E and n values. Z, ΔS and G were calculated by the usual way.

The values of kinetic parameters (n, E, Z, ΔS, G) calculated by F.C., C.R., M.T., H.M. and Zsako methods are in good mutual agreement.

In all the above methods, $W_r = W_c - W$ (W_c = weight loss at completion of reaction and W = total weight loss up to time t), R = gas constant, T = absolute temperature, T_s = temperature at half weight loss, $\theta = T - T_s$, α = conversion degree or fraction decomposed, q = heating rate, dw/dt = weight loss with time t, Z = pre-exponential factor, h = Planck's constant, K = Boltzmann factor, ΔS = entropy of activation and G = free energy change.

X-ray diffraction studies: A representative complex $(C_{17}H_{13}N_2OS)_2Cu$ (R^1 = 4-CH_3) has been studied by powder XRD. The XRD data for the complex is given in Table-2. There are 22 reflections (2θ) between 11.245° to 47.945° with maximum at 2θ = 11.245° and d = 7.8621 Å. The general procedure and methods of calculation are based on the published work[14–16]. The observed and calculated values of d and q are in good mutual agreement. The lattice parameters (a, b, c) of unit cell and cell volume were calculated by assuming a tetragonal structure for the complex. The cell parameters such as

$$a = b \neq c \ (a = b = 19.2444 \text{ Å}, c = 37.7976 \text{ Å}) \quad \text{and} \quad \alpha = \beta = \gamma = 90°$$

required for a tetragonal crystal system are found to be quite satisfactory[17] and therefore a tetragonal system is proposed for the complex.

TABLE-1
KINETIC PARAMETERS OBTAINED BY USING FREEMAN-CARROLL, COATS-REDFERN, MacCALLUM-TANNER, HOROWITZ-METZGER AND ZSAKO METHODS

Compound	Step	Kinetic parameters	F.C.	C.R.	M.T.	H.M.	Zsako				
							I	II	III	IV	V
$(C_{20}H_{13}N_2OS)_2Cu$	I	n	1.35	1.142	1.05	1.35	1.05	1.05	1.142	1.05	0.95
		E_a	13.67	10.20	10.26	13.27	10.20	10.00	12.00	10.00	11.00
		Z	2.98×10^2	2.47×10^5	6.04	78.00	4.78	3.68	2.27	3.75	30.36
		ΔS	–24.53	–17.81	–28.43	–25.87	–28.66	–28.93	–29.41	–28.91	–26.82
		G	29.60	21.76	28.71	30.06	28.8	28.77	31.08	28.75	28.40
	II	n	2.7	2.451	2.451	2.7	2.4	2.4	2.4	2.4	2.4
		E_A	132.54	100.3	102.48	110.94	100	100	102	100	98
		Z	2.07×10^{31}	1.00×10^{23}	9.28×10^{23}	4.49×10^{25}	8.16×10^{22}	8.15×10^{22}	4.46×10^{21}	8.15×10^{22}	2.92×10^{22}
		ΔS	41.57	22.42	24.65	28.52	22.21	22.21	19.31	22.21	21.19
		G	95.98	80.58	80.80	85.85	80.46	80.46	85.01	80.06	79.36
$(C_{16}H_{11}N_2OS)_2Cu$	I	n	1.4	1.704	1.6	2.0	1.704	1.704	1.7	1.704	1.6
		E_a	13.35	15.36	15.41	21.10	16	16	17	16	17
		Z	1.97×10^2	6.339×10^3	3.79×10^2	3.08×10^4	6.26×10^2	6.05×10^2	1.05×10^{92}	6.09×10^2	2.7×10^3
		ΔS	–24.98	–21.51	–24.32	–19.92	–23.82	–23.85	–25.6	–23.85	–22.36
		G	30.07	29.75	31.69	34.43	31.94	31.96	34.13	31.95	31.96
	II	n	2.2	2.2	2.187	2.4	2.187	2.187	2.1	2.187	2.1
		Ea	50.93	48.83	50.61	56.60	50	50	51	50	50
		Z	2.23×10^{10}	1.44×10^9	5.75×10^9	8.76×10^{10}	2.79×10^9	2.77×10^9	1.66×10^8	2.77×10^9	2.80×10^9
		ΔS	–6.77	–9.5	–8.12	–5.4	–8.85	–8.85	–11.66	–8.85	–8.84
		G	57.27	57.7	58.23	61.66	58.28	58.29	61.92	58.29	58.28

TABLE-2
X-RAY DATA OF $(C_{17}H_{13}N_2OS)_2Cu$ (R = H, R′ = 4-CH_3)

Peak No.	2θ	d (obs.)	d (cal.)	Q (obs.)	Q. (cal.)	dQ ($\times 10^4$)	I/I max (%)	hkl
1.	11.245	7.8621	7.833	0.0162	0.0163	1	100	122
2.	12.410	7.1265	7.107	0.0197	0.0198	2	16.22	123
3.	13.005	6.8018	6.804	0.0216	0.0216	2	23.63	220
4.	13.795	6.4140	6.415	0.0243	0.0243	2	28.59	030
5.	15.340	5.7713	5.793	0.0300	0.0298	2	11.11	132
6.	16.025	5.5261	5.522	0.0327	0.0328	2	6.96	224
7.	17.145	5.1676	5.199	0.0374	0.0370	2	30.86	017
8.	18.425	4.8113	4.811	0.0432	0.0432	2	19.75	040
9.	20.615	4.3049	4.303	0.0540	0.0540	3	70.61	240
10.	22.090	4.0207	4.013	0.0619	0.0621	3	38.20	119
11.	23.270	3.8194	3.824	0.0686	0.0684	3	38.20	046
12.	25.570	3.4808	3.473	0.0825	0.0829	3	75.35	337
13.	27.735	3.2138	3.211	0.0968	0.0970	3	41.71	1310
14.	29.065	3.0697	3.069	0.1061	0.1062	4	50.17	163
15.	31.080	2.8751	2.878	0.1210	0.1207	4	33.22	447
16.	32.980	2.7137	2.713	0.1358	0.1359	4	16.22	456
17.	35.035	2.5591	2.558	0.1527	0.1528	4	23.63	268
18.	38.105	2.3597	2.358	0.1796	0.1798	5	16.22	178
19.	40.075	2.2481	2.247	0.1979	0.1980	5	33.22	086
20.	42.570	2.1219	2.121	0.2221	0.2223	5	28.59	483
21.	44.790	2.0218	2.022	0.2446	0.2446	5	44.44	578
22.	47.925	1.8958	1.986	0.2782	0.2781	5	21.65	199
23.	53.785	1.7030		0.3448		6	35.67	
24.	63.025	1.4737		0.4604		7	25.70	
25.	68.400	1.3704		0.5325		7	28.59	
26.	86.095	1.1284		0.7853		7	50.17	

Refined calculated cell parameters for tetragonal crystal system a = b = 19.2444 Å, c = 37.7976 Å, Volume of unit cell = 13398.225 $Å^3$, Particle size = 246.3528 Å

ACKNOWLEDGEMENTS

The authors are thankful to authorities of Shivaji University, Kolhapur for providing research facilities and to Dr. P.P. Wadagaonkar and Dr. S.C. Pattar for useful discussions.

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(*Received:* 14 May 2001; *Accepted:* 11 August 2001) AJC-2401