



of Cu(II). The complex was characterised by analytical, electronic, infrared spectral, thermal and magnetic studies.

### EXPERIMENTAL

The ligand was prepared from citronellal and thiosemicarbazide. Citronellal (1.8 mL 0.01 M) in 10 mL ethanol was mixed with thiosemicarbazide (0.91 g, 0.01 M) in 10 mL ethanol and 2 to 3 drops of conc. HCl, and was refluxed for 0.5 h. The solution was cooled and neutralised by using 0.1 N NaOH, when light yellow crystals were separated (yield 60%). These crystals were further purified by recrystallisation from ethanol and characterised on the basis of analytical and spectral data, m.p. 120°C.

C<sub>11</sub>H<sub>20</sub>N<sub>3</sub>S: Found (Calcd.)%: C 58.23 (58.41), H 8.36 (8.89), N 17.94 (18.54), S 13.58 (14.15).

Copper(II) complex was prepared by the general method. An aqueous solution of copper(II) acetate (0.01 M) was mixed with 0.01 M solution of ligand in ethanol and 5 g of sodium acetate. Brown precipitate formed was filtered and dried. The complex was characterised by elemental analysis, conductance, magnetic measurements, IR and TG studies.

#### Mathematical analysis of data

The TG curve for [CuL(Ac)(H<sub>2</sub>O)]<sub>2</sub> exhibited a three stage decomposition pattern (Fig. 2). The first stage corresponds to the loss of one water molecule.

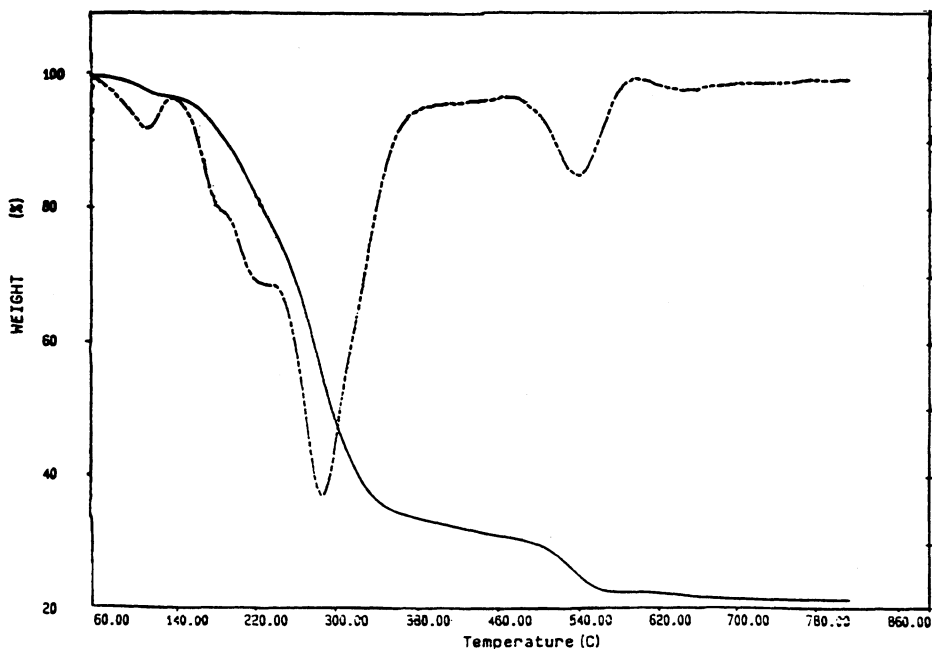


Fig. 2. TG and DTG traces of [CuL(Ac)(H<sub>2</sub>O)]<sub>2</sub>

The second stage represents the major decomposition step and the third stage represents the loss of acetate part.

The second stage was subjected to kinetic analysis. Evaluation of the reaction mechanism by nonisothermal methods has been discussed by Sestak and Berggren<sup>9</sup> and Satava<sup>10</sup>. The procedure is based on the assumption that the non-isothermal reaction proceeds isothermally in an infinitesimal time interval, so that the rate can be expressed by an Arrhenius type equation,

$$d\alpha/dt = Ae^{-E/RT}(f\alpha) \quad (1)$$

where A is the pre-exponential factor, t is the time and  $f(\alpha)$  depends on the mechanism of the process. For a linear heating rate,  $\phi$ ,  $dT/dt = \phi$  and substitution into equation (1) gives

$$d\alpha/dt = \int_0^T A/\phi e^{-E/RT} dt \quad (2)$$

Integration of the left hand side of equation (2) gives

$$d\alpha/f(\alpha) = g(\alpha) = A/\phi e^{-E/RT} dt \quad (3)$$

where  $g(\alpha)$  is the integrated form of  $f(\alpha)$ . A series of  $f(\alpha)$  forms are proposed and the mechanism is obtained from that which gives the best representation of the experimental data. For evaluating kinetic parameters from the mechanistic equations given by Satava, Coats and Redfern, the equation was used in the general form

$$\ln g(\alpha)/T^2 = \ln \frac{AR}{\phi E} - \frac{E}{RT} \quad (4)$$

and the various  $g(\alpha)$  forms were substituted. This has been recommended to be one of the best solutions by several authors<sup>12, 13</sup>.

Along with the mechanistic equations, two non mechanistic methods suggested by Coats and Redfern and Horowitz and Metzger<sup>14</sup> were also used for comparison. The reaction order can easily be estimated by comparing the values using  $n = 0.33, 0.5$  and  $0.66$  and  $1$  in equations (5) and (6)

$$1 - (1 - \alpha)^{1-n}/(1 - n)T^2 \text{ vs } 1/T \text{ for } n = 1 \quad (5)$$

$$\log [-\log (1 - \alpha)/T^2] \text{ vs } 1/T \text{ for } n = 1 \quad (6)$$

### Master Curve Method<sup>15</sup>

Recently a graphical method was suggested for the evaluation of  $n$  using the above equation  $C_s = n^{1/(1-n)}$  where  $C_s = (1 - \alpha_s)/\alpha_s$  is the fraction decomposed at the DTG peak temperature  $T_s$ . A master curve was drawn by calculating  $C_s$  values for values of  $n$  starting from  $n = 0.2$  to  $n = 3$ . Knowing the values of  $C_s$  from the TG curve, the values of  $n$  can be read off from the graph.

## RESULTS AND DISCUSSION

The structure of the copper chelate was found to be  $[\text{CuL}(\text{Ac})(\text{H}_2\text{O})]_2$  based on analytical, conductance and susceptibility data (Fig. 3).

Empirical formula,  $\text{CuC}_{13}\text{H}_{25}\text{N}_3\text{SO}_3$  Found (Calcd.)%: C 42.80 (42.55), H 6.50 (6.86), N 11.12 (11.45), S 7.98 (8.73).

IR spectrum of the ligands shows strong bands in the region between  $3270$  and  $3250\text{ cm}^{-1}$  which may be assigned to  $\nu\text{NH}_2$  and  $\nu\text{NH}$ .<sup>16</sup> The broad band near  $3500$  indicates the presence of lattice water.<sup>17</sup> The shifting of the band at  $1580\text{ cm}^{-1}$  ( $\nu\text{C}=\text{N}$ ) to lower wave numbers in the complexes indicates the participation of N(3) in coordination.<sup>18</sup> The absence of bands in the region  $2650\text{--}2500\text{ cm}^{-1}$  in the free ligand indicates that it exists in the thioketo form in the solid state. However during the complex formation it must exist in the enol form. This is indicated by the absence of the band due to  $\text{C}-\text{S}$  of the ligand in the complex and the appearance of a new band on complexation around  $660\text{ cm}^{-1}$  which can be attributed to  $\nu\text{C}-\text{S}$ .

The electronic spectrum of the complex in ethanol shows no (d—d) bands in the visible region suggesting a strong metal-metal interaction. This is supported by the very low magnetic susceptibility value (0.23 BM), recorded by the Guoy balance. But a broad band in the visible region is exhibited by solution of DMSO, pyridine and DMF and  $20408$ ,  $22720$  and  $23800\text{ cm}^{-1}$  respectively. This effect may be due to the change of strength and symmetry of the ligand field associated with formation of monometric adducts.

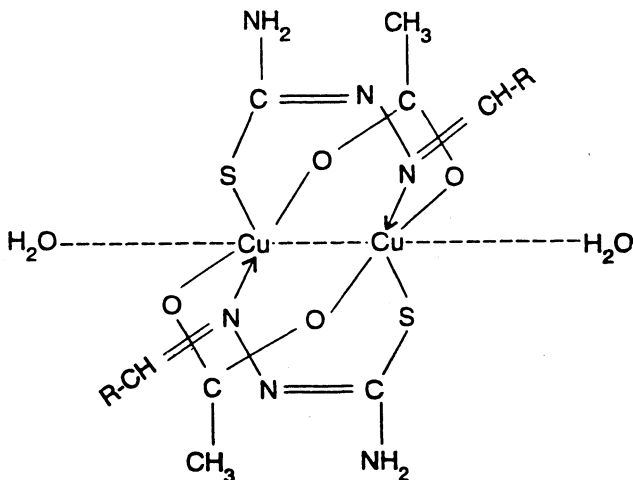


Fig. 3

On the basis of above evidences, a dimeric structure has been assigned to the above complex (Fig. 3). The TG curve for copper(II) chelate gives a three stage decomposition pattern. The first stage represents the loss of one molecule of  $\text{H}_2\text{O}$  at about  $120^\circ\text{C}$  and this can be considered as coordinated water. The E value obtained for this step by various nonmechanistic methods (Coats Redfern eqn. =  $6.17\text{ kcal/mol}$ , Horowitz Metzger eqn =  $7.3\text{ kcal/mol}$ ) is comparable to that for other similar hydrated complexes of transition metals.<sup>19, 20</sup> The second

stage represents the loss of the ligand molecule and DTG gives a well defined peak in the appropriate region. The third stage shows the loss of acetate part. The overall loss of mass from the curve is 74.9% while the theoretical loss in mass for the conversion of  $[\text{CuL}(\text{Ac})(\text{H}_2\text{O})_2]$  to  $\text{CuO}$  is 78.3%. The X-ray diffraction data of the residue is given in Table 1.

TABLE-1  
X-RAY DIFFRACTION DATA FOR THE DECOMPOSITION RESIDUE  $[\text{CuL}(\text{Ac})(\text{H}_2\text{O})_2]$

d-spacing (observed) Å	Intensity order (observed)	Substance	d-spacing from ASTM data file	Intensity grading from ASTM data file
2.50	1		2.52	100
2.30	2	CuO	2.32	96
1.86	3		1.87	25

The thermal data are given in Table 2. Data from independent pyrolytic experiments are also included in this table. The kinetic parameters calculated from TG for the nine mechanistic equations are given in Table 3. The corresponding values of  $E$ ,  $A$  and  $\Delta S$  and  $r$  from nonmechanistic equations and Mampell's equations are given in Table 4.

TABLE-2  
THERMAL DECOMPOSITION DATA FOR  $[\text{CuL}(\text{Ac})(\text{H}_2\text{O})_2]$

Stage	Peak temp in DTG, °C	Temp range in TG, °C	% loss of mass		Probable Assignemnt
			From TG	Theoretical	
1	110	80-140	4.40	4.40	Loss of water
2	280	140-420	65.55	65.93	Loss of L
3	540	420-620	9.50	10.42	Loss of acetate

### Decomposition Kinetics

From Tables 3 and 4 it can be seen that more than one equation gives good linear curves with high values of correlation coefficients. So that it may become difficult to assign the reaction mechanisms unequivocally from the linearity of the curve alone. In such cases some authors have chosen the function  $g(\alpha)$  which gives the kinetic parameters in agreement with those obtained by the numerical method. In the present case, it is observed that for the second stage of decomposition,  $E$ ,  $A$  and  $\Delta S$  values obtained from the Coats Redfern method with  $n = 1$  are in good agreement with the  $E$ ,  $A$  and  $\Delta S$  values from the Mampell equation which is based on random nucleation.

We can thus infer in the above case that the rate controlling process for the reaction is random nucleation with the formation of one nucleus on each particle and is independent of the thermal techniques used.

The  $E$ ,  $A$  and  $\Delta S$  values obtained by different nonmechanistic methods show good agreement.

TABLE-3  
KINETIC PARAMETERS FOR THE DECOMPOSITION OF  $[\text{CuL}(\text{Ac})(\text{H}_2\text{O})_2]$  FROM TG USING MECHANISTIC EQUATIONS

Parameter	1	2	3	4	5	6	7	8	9
E	1.2133	1.4697	1.7462	1.5635	9.714	3.781	1.828	7.151	8.011
A	$1.15 \times 10^2$	$9.37 \times 10^2$	$4.257 \times 10^3$	$5.68 \times 10^2$	$2.9 \times 10^1$	$5.8 \times 10^{-2}$	4.93	$8.49 \times 10^{-1}$	1.494
$\Delta S$	-50.33	-46.17	-43.16	-47.16	-53.02	-65.42	-70.32	-60.09	-58.97
r	0.9835	0.9903	0.9853	0.9913	0.9962	0.9949	0.9924	0.9921	0.9950

E in kcal mol<sup>-1</sup>, A in S<sup>-1</sup>,  $\Delta S$  in e.u.

TABLE-4  
KINETIC PARAMETERS FOR THE DECOMPOSITION OF  $[\text{CuL}(\text{Ac})(\text{H}_2\text{O})_2]$ -STAGE II— FROM TG USING NON-METHANISTIC AND MECHANISTIC EQUATIONS

Parameters	Coats-Redfern	Horowitz-Metzger	Mampell	Order n	
				Coats Redfern	Master curve
E	9.714	11.64	9.714	1	1
A	$2.97 \times 10^1$	$2.53 \times 10^2$	$2.97 \times 10^1$		
$\Delta S$	-53.02	-48.77	-53.02		
r	0.9962	0.9952	0.9962		

E in kcal mol<sup>-1</sup>, A in S<sup>-1</sup>,  $\Delta S$  in e.u.

### ACKNOWLEDGEMENT

The authors are thankful to the UGC, New Delhi, for financial help.

### REFERENCES

1. N.N. Orlova, V.A. Aksevova, V.A. Seliolovkin, N.S. Bogdanova and G.N. Pershin, *Russ. Pharm. Toxicol.*, **348** (1988).
2. G. Dognagk, R. Behnisch, F. Mietzsch and H. Schmidt, *Naturwissen Schaftefn*, **33**, 315 (1946).
3. U. Srivastava, R.B. Pathak and S.C. Bahel, *J. Indian Chem. Soc.*, **58**, 822 (1981).
4. V.K. Pandey and A.K. Agarwal, *Acta Cienc. Indica*, **6**, 166 (1980).
5. S. Laly and Geetha Parameshwaran, *Bull. Chem. Soc. (Jpn.)*, **62**, 3763 (1980).
6. \_\_\_\_\_, *Thermochim. Acta*, **43**, 168 (1990).
7. N.L. Mary and Geetha Parmeshwaran, *Synth. and Reac. Inorg. and Metal-Org. Chem.*, **23**, 1209 (1993).
8. V. Indira and Geetha Parameshwaran, *J. Therm. Anal.*, **39**, 1417 (1993).
9. J. Sestak, *Thermochim. Acta*, **3** (1971).
10. V. Satava, *Thermochim. Acta*, **2**, 2 (1971).
11. A.W. Coats and J.P. Redfern, *Nature (London)*, **68**, 201 (1964).
12. M.D. Judd and M.T. Pope, *J. Therm. Anal.*, **4**, 31 (1972).
13. J. Zsako, *J. Therm. Anal.*, **8**, 349 (1975).
14. H.H. Horowitz and G. Metzger, *Anal. Chem.*, **35**, 1464 (1963).
15. P.M. Madhusoodanan, P.N.K. Nambissan and C.G.R. Nair, *Thermochim. Acta*, **9**, 149 (1974).
16. V.A. Hernes and K.K.W. Sunk, *Can. J. Chem.*, **46**, 3241 (1968).
17. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, p. 22 (1963).
18. S.N. Poddar and Nityananda Saha, *J. Indian Chem. Soc.*, **52**, 57 (1975).
19. K. Singh and Saniran Mitra, *Proceedings of the Sixth National Symposium on Thermal Analysis, ITAS, Delhi 8*.
20. L.S. Prabhu, Mirashi, S.R. Naik and J.K. Khoje, *Proceedings of the Seventh National Symposium on Thermal Analysis, ITAS, Srinagar*, 16, 92 (1989).

(Received: 8 March 1994; Accepted: 22 June 1994)

AJC-836