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THERMAL DEHYDRATION AND *K*-X-RAY ABSORPTION STUDIES ON COPPER(II) CHELATES OF SOME PHENOLIC LIGANDS

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ABSTRACT

The thermal dehydration of copper(II) chelates of salicylhydrazide (SH), 5-bromo-salicylhydrazide (5BSH), salicylhydroxamic acid (SHA), salicylic (SA), 4-amino-salicyclic (4ASA) and 5-sulpho-salicylic (5SSA) acids has been investigated from the analysis of kinetic data obtained from thermal techniques (TG, DTG, DTA). The statistical analysis of activation energy (E^*) and of log Z values shows the validity of a linear compensation law.

The change in stereochemistry as a consequence of dehydration has been investigated from *K*-X-ray absorption spectra.

INTRODUCTION

In view of our continuing interest in the thermal behaviour of metal chelates of carboxylic, α-hydroxy and phenolic acids [1–8], we thought it worthwhile to study the thermal dehydration of copper(II) chelates of salicylhydrazide (SH), 5-bromo-salicylhydrazide (5BSH), salicylhydroxamic (SHA), salicylic (SA), 4-aminosalicylic (4ASA) and 5-sulphosalicylic (5SSA) acids, with particular interest in investigating the applicability of a linear kinetic compensation law.

Although, in thermogravimetric literature, pre-exponential factor data derived from TG curves are very scarce, the compensation effect seems to be very general [9,10]. In the present paper the relationship between log Z and E values has been studied in the case of the thermal dehydration of copper(II) chelates with the aforementioned ligands.

The change in stereochemistry as a consequence of dehydration has been studied by investigation of the *K*-X-ray absorption spectra of hydrated and dehydrated chelates.

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EXPERIMENTAL

Chemicals

BDH and AR grade ligands (except SH, 5BSH and SHA) mentioned above were used as supplied. SH, 5BSH and SHA were prepared as reported previously [11,12].

Preparation of copper(II) chelates

The copper(II) chelates of SH, 5BSH, SHA, SA, 4ASA and 5SSA were prepared as described elsewhere [13]. The hot aqueous solution of copper(II) perchlorate is mixed with an ethanolic solution of the ligand in 1 : 2 (M : L) ratio by taking ligand in slight excess. The mixture was refluxed for 4–5 h and the volume of the solution was reduced by one half. The products, which separated either immediately or when the reaction mixture was set aside for some hours, were washed with hot water, ethanol and dried in vacuo over silica gel (yields ca. 75–80%).

Analytical procedures

Microanalyses for carbon, hydrogen and nitrogen were performed on a Colemann CHN analyser 29. Copper was estimated by a standard iodometric procedure [14]. Analytical data are given in Table 1.

TABLE 1

Abbreviated names, colour, percentage yield and elemental analysis of copper(II) chelates of phenolic ligands

Chelate [a]	Colour	% yield	Elemental analysis, observed (calculated) (%)			
			C	H	N	Cu
$Cu(SH)_2 \cdot 2H_2O$	Bluish green	80	41.54(41.63)	4.85(4.96)	13.74(13.88)	15.82(15.74)
$Cu(SH)_2$ [b]	Grey	–	45.55(45.71)	4.27(4.35)	15.16(15.24)	17.15(17.29)
$Cu(5BSH)_2 \cdot 2H_2O$	Olive green	70	29.35(29.94)	3.05(3.21)	9.85(9.98)	11.16(11.35)
$Cu(5BSH)_2$ [b]	Dark green	–	31.26(31.98)	2.43(2.66)	10.62(10.66)	11.98(12.10)
$Cu(SA)_2 \cdot 2H_2O$	Green	70	44.97(45.10)	3.74(3.59)	–	17.01(16.90)
$Cu(SA)_2$ [b]	Dark green	–	49.72(49.22)	2.90(3.00)	–	18.80(17.87)
$Cu(4ASA)_2 \cdot 2H_2O$	Dark green	85	41.63(42.10)	3.96(4.10)	6.94(7.16)	15.76(15.88)
$Cu(4ASA)_2$ [b]	Grey	–	46.00(45.71)	3.30(3.27)	7.55(7.62)	17.20(17.38)
$Cu(5SSA)_2 \cdot 2H_2O$	Green	75	31.60(30.98)	2.25(2.31)	–	11.95(12.25)
$Cu(5SSA)_2$ [b]	Dark green	–	34.00(33.77)	1.92(2.01)	–	12.82(12.76)
$Cu(SHA)_2 \cdot 2H_2O$	Olive green	80	41.63(41.95)	3.96(4.10)	6.93(6.00)	15.75(15.62)
$Cu(SHA)_2$ [b]	Green	–	45.12(45.43)	3.68(3.79)	7.16(7.50)	16.95(17.18)

[a] SH = salicylhydrazide, 5BSH = 5-bromosalicylhydrazide, SA = salicylic acid, 4ASA = 4-aminosalicylic acid, 5SSA = 5-sulphosalicylic acid, SHA = salicylhydroxamic acid.

[b] Decomposition products.

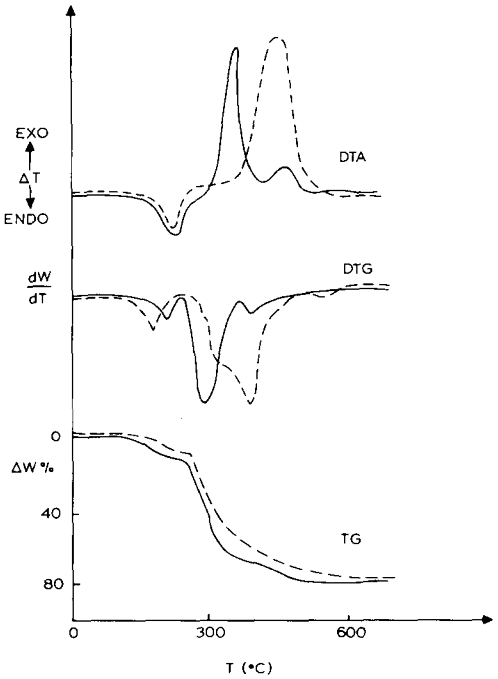

Fig. 1. TG, DTA and DTG curves for copper(II) chelates of phenolic ligands: (———) Cu(II)–SA, (— — —) Cu(II)–4ASA.

Thermal measurements

Thermogravimetry (TG) was carried out on a Stanton-Redcroft recording thermobalance (HT-model) of 1 mg sensitivity in static air with a heating rate of 4°C min^{-1}. The chart speed was maintained at 3 in. h^{-1}. The sample (100 mg) was homogenised by sieving below 100 mesh and was packed as uniformly as possible in a platinum crucible of appropriate size. The same platinum crucible was used throughout all the experiments.

A differential thermal analysis (DTA) assembly with an F and M Scientific 240 Hewlett-Packard temperature programmer, and a Platinet-II thermocouple (Engelhard, U.S.A.) were used. DTA curves for 40-mg samples were recorded by a Rikadenki Kogyo recorder in static air at a heating rate of 4°C min^{-1}. Alumina was used as a standard reference material.

The TG, DTG and DTA results are shown in Figs. 1–3.

IR spectra

The presence of water molecules in the chelates and the composition of the residue were identified by IR spectroscopy, using a Perkin-Elmer Model 377 spectrophotometer (4000–400 cm^{-1}) in KBr matrix.

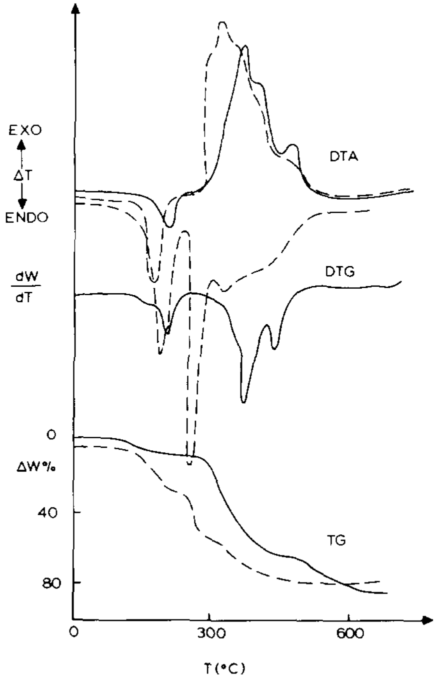

Fig. 2. TG, DTA and DTG curves for copper(II) chelates of phenolic ligands: (———) Cu(II)-5SSA, (— — —) Cu(II)-SHA.

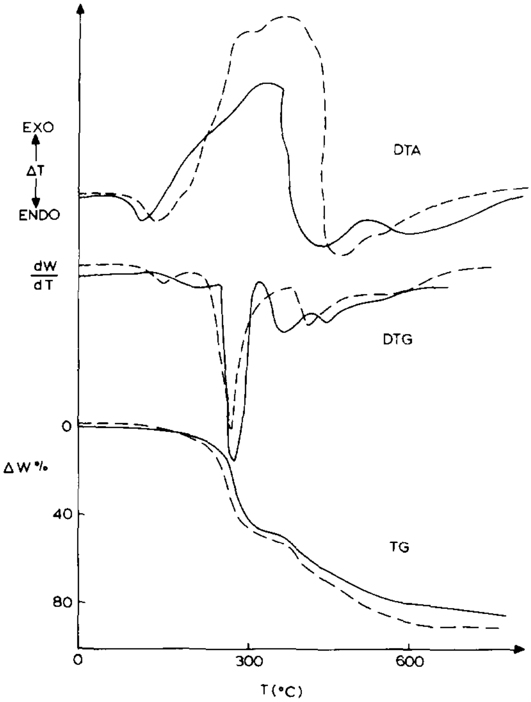

Fig. 3. TG, DTA and DTG curves for copper(II) chelates of phenolic ligands: (———) Cu(II)-SH, (— — —) Cu(II)-5BrSH.

TABLE 2

K-X-ray absorption parameters for hydrous and anhydrous copper(II) chelates of phenolic ligands

Absorber	Energy of *K* edge E (eV)±0.2 eV	Edge shift E (eV)±0.2 eV	Edge-width (eV)±0.2 eV	Type of Van Nordstrand curve
Copper (metal)	8979.30 [a]	–	–	–
$Cu(SH)_2 \cdot 2H_2O$	8988.39	9.07	8.75	Ia
$Cu(5BSH)_2 \cdot 2H_2O$	8957.75	8.45	9.87	Ia
$Cu(SA)_2 \cdot 2H_2O$	8986.90	7.60	9.12	Ia
$Cu(4ASA)_2 \cdot 2H_2O$	8986.50	7.20	9.65	Ia
$Cu(5SSA)_2 \cdot 2H_2O$	8985.80	6.50	6.08	Ia
$Cu(SHA)_2 \cdot 2H_2O$	8987.43	8.13	10.15	Ia
$Cu(SH)_2$	8983.35	4.05	12.05	IVb
$Cu(5BSH)_2$	8983.47	4.17	11.25	IVb
$Cu(SA)_2$	8983.76	4.46	11.40	IVb
$Cu(4ASA)_2$	8983.61	4.31	13.16	IVb
$Cu(5SSA)_2$	8982.88	3.58	8.35	IVb
$Cu(SHA)_2$	8983.83	4.53	10.15	IVb

[a] 8979.13 eV, reported by Bearden [47].

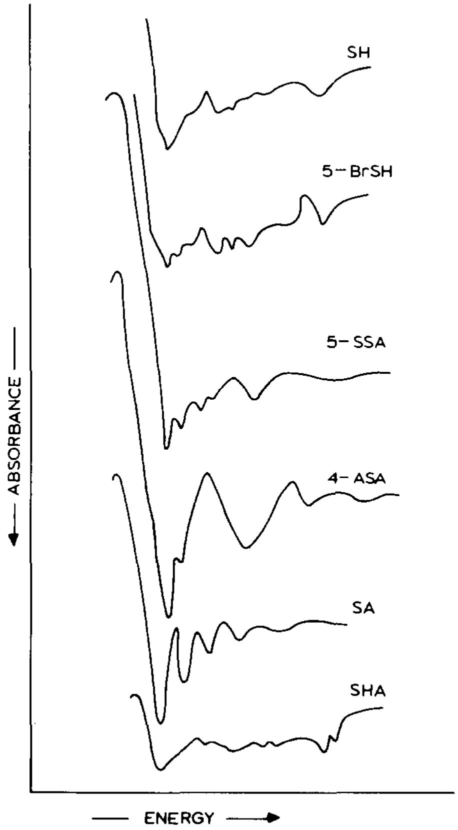

Fig. 4. *K*-X-ray absorption spectra for hydrous copper(II) chelates of phenolic ligands.

Far-IR spectra (650–50 cm^{-1}) were recorded employing a Polytec FTR-30 Fourier far-IR spectrometer.

K-*X-ray absorption spectra*

A molybdenum target X-ray tube was employed to supply continuous radiation at 30 kV and 10–12 mA. A 40 cm transmission type curved crystal spectrograph was used to record the spectra photographically. The ($\bar{2}01$) planes of mica, reflecting in the second order gave a dispersion of about 12.4 XU mm^{-1} in the region of the Cu edge. Absorption screens were prepared from the sample following the method described by Sandstrom [15].

The *K*-X-ray absorption parameters are reported in Table 2 and the spectra given in Figs. 4 and 5.

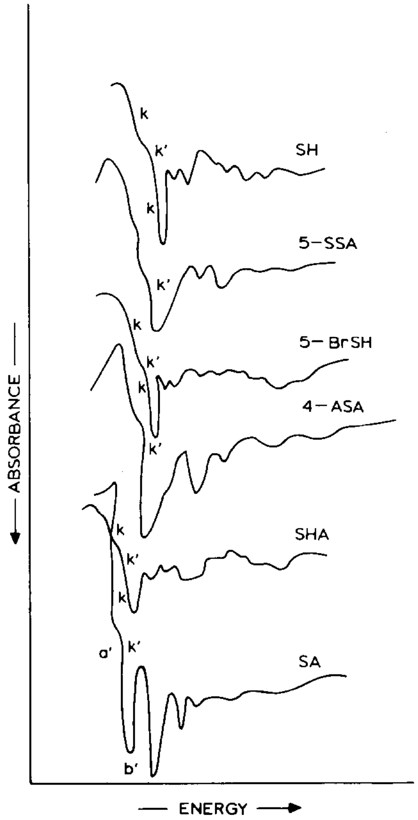

Fig. 5. *K*-X-ray absorption spectra of anhydrous copper(II) chelates of phenolic ligands.

RESULTS AND DISCUSSION.

Stoichiometry and stereochemistry

The elemental analysis reveals 1 : 2 metal–ligand stoichiometry for all complexes which are nonelectrolytes in nitromethane and nitrobenzene. The analysis has also indicated that the chelates contain two molecules of water. The appearance of IR bands in the 1615–1620, 795–810 and 515–545 cm^{-1} regions indicates the presence of coordinated water [16]. The bands are assigned to $\delta(OH)$, $\delta r(H_2O)$ and $\delta w(H_2O)$ modes of coordinated water [16–21]. This is further borne out by the thermal decomposition data (Figs. 1–3).

The study of *K*-X-ray absorption of spectra (Fig. 4) of hydrated chelates of copper(II) with ligands used resemble the type Ia curve of Van Nordstrand [22] indicating octahedral stereochemistry. It should, however, be noted that the curves given by Van Nordstrand are absorption coefficient versus energy curves, whereas our curves show the variation of transmitted intensity with energy. The observed stereochemistry is consistent with earlier reported data on magnetic susceptibility and electronic spectra [23,24]. The thermal decomposition would appear to be consistent with this type of structure and would suggest that the water molecules are directly bonded to the metal ion along with two ligand moieties to give a coordination number of six for the copper(II) ions.

Kinetics of thermal dehydration

By using the TG curves (Figs. 1–3), a kinetic study has been made of the dehydration process. The methods of Horowitz and Metzger [25] and Fuoss et al. [26] were found to be suitable for this purpose.

Various kinetic parameters for the thermal dehydration reaction were evaluated, and are presented in Table 3 along with log *Z* values.

Determination of order of reaction

The Horowitz–Metzger equation [25]

$$C_S = (n)^{1/1-n} = W_s - W_f/W_0 - W_f \tag{1}$$

was used for estimating the values of reaction order. Here, W_s stands for the weight fraction at T_s, i.e., the DTG peak temperature, W_0 and W_f are the initial and the final weights of the substance, respectively. The order of dehydration of the copper(II) chelates is obtained by comparing the C_S value yielded by the above method with the values given in Horowitz and Metzger's table [25]. The order, in each case, is calculated to be one, showing that the dehydration follows first-order kinetics.

Evaluation of other kinetic parameters

The Fuoss method [26] is employed to evaluate the activation energy, E^*, and the frequency factor, Z, for the first-order kinetics of dehydration. The following equations (2 and 3) are used for this purpose.

$$E^* = \frac{R/T_i^2}{W_i}\left(\frac{\mathrm{d}W}{\mathrm{d}T}\right)_i \tag{2}$$

$$Z = \frac{a}{W_i}\left(\frac{\mathrm{d}W}{\mathrm{d}T}\right)\exp(E^*/RT_i) \tag{3}$$

where the terms have their usual meanings [26].

The activation entropy, S^*, the free energy of activation, G^*, and the specific reaction rate constant, K_r, were calculated using the relationships [27] given in eqns. (4), (5) and (6)

$$S^* = (\log Zh/kT)R \tag{4}$$

$$G^* = E^* - T_i S^* \tag{5}$$

$$K_r = Z\exp(-E^*/RT_i) \tag{6}$$

In eqn. (4), k and h are the Boltzmann and Planck constants, respectively.

The kinetic parameters thus obtained are presented in Table 3.

A perusal of Table 3 shows that the activation energy for the splitting of H_2O–Cu bonds lies around 20.0 kcal mol^{-1}, with an estimated uncertainty of ± 0.5 kcal mol^{-1}. These values are comparable to the generally accepted values of the activation energy of the dehydration reaction [28] and are also consistent with those reported by us [29].

Dependence of S^* on G^*

It may be useful to compare the thermodynamic functions, S^* and G^*, obtained for the dehydration reaction of the copper(II) chelates of phenolic ligands which fulfil a mutual linear relation [30,31]. This can be expressed for our purposes as

$$S^* = \alpha + \beta G^* \tag{7}$$

The coefficients of eqn. (7) were computed by the method of least squares. The value of the correlation coefficient (0.987) indicates that the method of least squares is applicable and that the correlation between S^* and G^* is genuine (Fig. 6).

It is interesting to compare the thermodynamic functions for the two slightly different ligands, SH and 5BSH. These ligands have a longer side-chain in the vicinity of phenolic group as compared to other ligands and have exhibited greater free energy of activation for thermal dehydration. The increase is due to a slightly lower value of H^* and especially to a higher value of S^*.

TABLE 3

Kinetic parameters for thermal dehydration of copper(II) chelates of phenolic ligands [a]

Chelate	T_i (K)	E^* (kcal mol^{-1})	S^* (mol^{-1} °C^{-1})	G^* (kcal mol^{-1})	H^* (kcal mol^{-1})	log Z (s^{-1})	K_r (s^{-1})
$Cu(SH)_2 \cdot 2H_2O$	523	19.939	−14.31	27.55	17.535	5.8426	4.68×10^{-3}
$Cu(5BSH)_2 \cdot 2H_2O$	833	18.991	−15.11	27.04	16.697	5.439	4.48×10^{-3}
$Cu(SA)_2 \cdot 2H_2O$	833	18.522	−13.89	25.09	17.586	6.000	2.77×10^{-3}
$Cu(4ASA)_2 \cdot 2H_2O$	833	20.206	−12.27	26.00	19.292	6.818	3.03×10^{-3}
$Cu(5SSA)_2 \cdot 2H_2O$	833	22.227	−10.33	27.11	21.313	7.793	3.37×10^{-3}
$Cu(SHA) \cdot 2H_2O$	833	18.570	−14.31	24.39	17.666	5.762	3.97×10^{-4}

[a] E^* = activation energy, S^* = activation entropy, G^* = free energy of activation, H^* = activation enthalpy, Z = frequency factor, K_r = specific reaction rate.

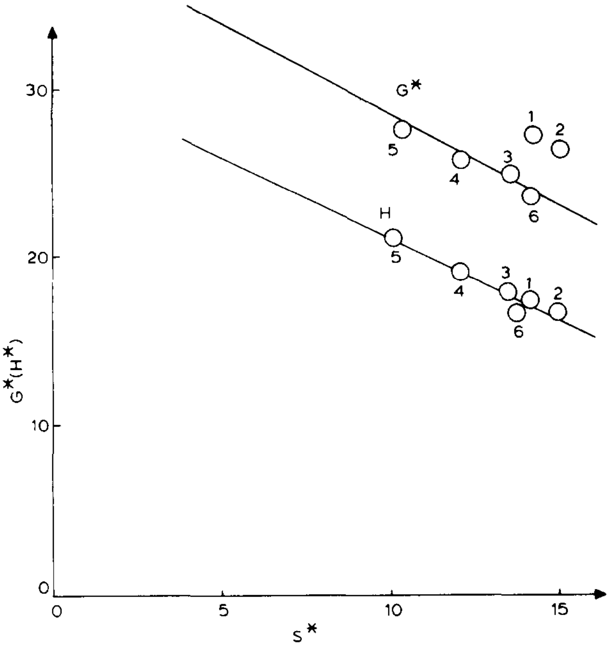

Fig. 6. Correlation of S^* with $G^*(H^*)$ for copper(II) chelates of phenolic ligands: (1) Cu(II)-SH, (2) Cu(II)-5BrSH, (3) Cu(II)-SA, (4) Cu(II)-4ASA, (5) Cu(II)-5ASA, (6) Cu(II)-SHA.

It is interesting to note that S^* values for the thermal dehydration of Cu(II)-SH and Cu(II)-SHA are the same, thereby indicating a mutual secondary steric influence of the side-chain in the vicinity of the phenolic group on dehydration. Generally, the S^* values for the dehydration of salicylhydrazides and salicylhydroxamic acids are much higher than those for salicylic acids.

The negative value of the activation entropy suggests that the thermal dehydration reaction is slower. This is clearly borne out from the shape of the corresponding TG curve.

Estimation of isokinetic temperature, β

An attempt has also been made to calculate the isokinetic temperature, β, from the relationship (8)

$$H^* = H_0^* + \beta S^* \tag{8}$$

The enthalpy of activation, H^*, needed for this purpose has been evaluated from the equation (9)

$$H^* = E^* - RT_i \tag{9}$$

The values of H^*, as recorded in Table 3, indicate that they differ from

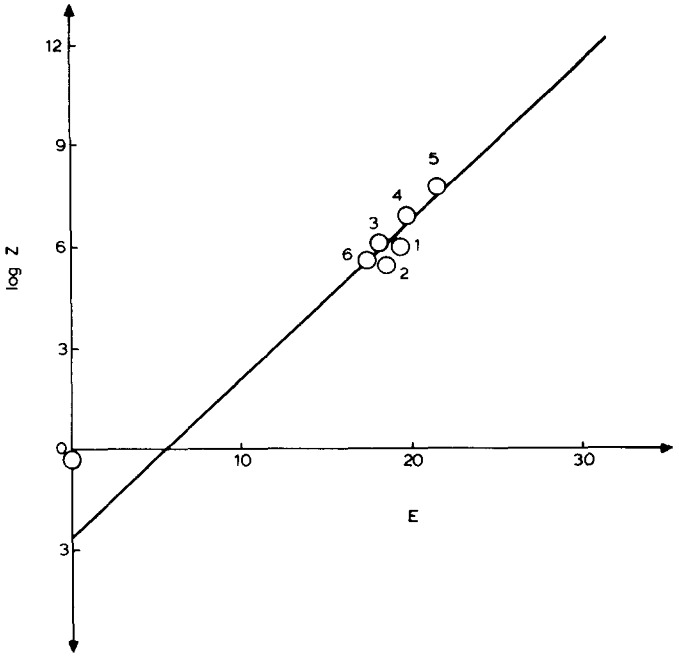

Fig. 7. Linear kinetic compensation effect for dehydration of copper(II) chelates of phenolic ligands: (1) Cu(II)–SH, (2) Cu(II)–5BrSH, (3) Cu(II)–SA, (4) Cu(II)–4ASA, (5) Cu(II)–5SSA, (6) Cu(II)–SHA.

the values of E^* by an average of 1.0 kcal mol^{-1}. This small difference could not be differentiated experimentally and thus we can safely say that E^* and H^* are equivalent. The error limit in the values of H^* is ±0.5 kcal mol^{-1}.

A straight line graph (Fig. 6) obtained between H^* and S^* indicates that the correlation between H^* and S^* as represented by eqn. (8) is genuine. From the graph the isokinetic temperature was estimated to be -0.469.

The values of all the other kinetic parameters (Table 3) obtained are within the range usually observed for a first-order reaction [28,32,33]. Thus, it can be concluded that the thermal dehydration of these copper(II) complexes is a first-order reaction.

Validity of a linear kinetic compensation law

Very frequently the relation between Z and E^* takes the form

$$\log Z = aE^* + b \qquad (10)$$

One can observe the log Z values to vary in parallel with the E^* values, indicating a "kinetic compensation effect" [34].

The graphical plot of log Z vs. E^* for all the above complexes is shown in Fig. 7. It is apparent from the figure that the same linear compensation law (Fig. 7) operates for the loss of coordinated water throughout the whole class of complex compounds studied.

We have carried out a statistical analysis of the data and, by means of the least-squares method, determined the constants a (8.928) and b (-2.75). The value of Jaffe's [35] correlation coefficient (0.997) indicates good linearity between log Z and E^*.

As far as the slope of the straight line obtained is concerned, the a value for the loss of coordinated water is slightly more than that obtained for the loss of crystallization water [36].

Analysis of intermediate products

In order to isolate the intermediate products formed due to thermal dehydration, the samples were withdrawn from the furnace at appropriate temperatures and the residues were analysed. Mean results of three determinations are listed in Table 1. All intermediate products of the decomposition steps could not be isolated and identified owing to the lack of a clear-cut horizontal on the TG curves. An attempt has been made to obtain the IR spectra of the decomposition products of all the six chelates. The disappearance of characteristic bands of coordination water indicates the loss of coordinated water to form an anhydrous complex. This further confirms the dehydration.

Finally, the far-IR spectra of the final residue exhibit bands at ~ 610(m), 500(s) and 410(m) cm^{-1} indicating the formation of CuO as the end product [37]. These results are in agreement with the predicted composition and structure of the complexes.

Evidence for change in stereochemistry

The study of K-X-ray absorption spectra of anhydrous chelates (Fig. 5) indicated that they resemble type IVb curves of Van Nordstrand [22], i.e., the curves for tetrahedrally surrounded metal ions. The curves show splitting of the principal absorption edge into two components, K and K^1. According to Sinha and Mande [38–42]. The minima at the markings a′ and b′ in Fig. 5 represent the limit of the X-ray absorption transitions $1S \rightarrow 4p$ and $1S \rightarrow p$, respectively. The form of these discontinuities suggest that the copper(II) ion is octahedrally surrounded in the hydrous complexes, while in the anhydrous complexes the surrounding of the ion is tetrahedral. Thus, X-ray absorption spectroscopy provides a method of distinguishing between octahedral and tetrahedral surroundings of the metal ion in chelates.

The edge-widths of the dehydrated copper(II) chelates are greater than that of the chelates containing coordinated water molecules. This result reveals a lowering of stereochemistry from octahedral to tetrahedral [41].

Glend and Dodd [43] argued that lowering of symmetry is generally favoured by an increase in the covalent character of the metal-donor bond. The chemical (edge) shift should be smaller in the case of compounds with lower symmetry features. Obviously, the chelates with octahedral coordination will have more shifts compared with those having tetrahedral coordination. The observed results, in the present case, are in fair agreement with these findings. Similar results were obtained by Cotton and Hanson [44], Shrivastawa and Nigam [45] and Mande and Chetal [46].

On the basis of changes in edge structure, edge width and edge shift (Table 2), it can be concluded that on thermal dehydration of the copper(II) chelates, octahedral symmetry changes to tetrahedral as a consequence of elimination of the two coordinated water molecules from the chelates.

CONCLUSIONS

(1) Thermal dehydration of copper(II) chelates of phenolic ligands follow first-order kinetics and is governed by a linear kinetic compensation law.

(2) The high free energy of activation for the dehydration of copper(II) chelates of hydrazides (SH and 5BSH) is attributed to the longer side-chain nearer to the phenolic group.

(3) *K*-X-ray absorption spectra indicate a change from octahedral to tetrahedral stereochemistry as a consequence of dehydration.

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