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THERMAL STUDIES ON COPPER(II) CHELATES OF SOME O-/N-DONOR LIGANDS

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ABSTRACT

The thermal dehydration of copper(II) chelates of O-/N-donor ligands, viz. salicylhydrazide (SH), 5-bromo-salicylhydrazide (5BSH), salicylamide (SAM), nicotinamide (NIA) and gallic acid (GA) has been investigated from the analysis of kinetic data obtained from thermal techniques (TG, DTG, DTA). The statistical analysis of activation energy ($E^\star$) and of log Z values shows the validity of a linear compensation law. The change in the stereochemistry as a consequence of dehydration has been investigated from X-ray K-absorption spectra. The final residue was identified by far-IR as well as X-ray K-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 some C-/N-donor ligands, viz. salicylhydrazide (SH), 5-bromosalicylhydrazide (5BSH), salicylamide (SAM), nicotinamide (NIA) and gallic acid (GA), with a special interest in the investigation of the applicability of a linear kinetic compensation law and the change in stereochemistry of the complexes due to thermal dehydration.

Although in the thermogravimetric literature preexponential 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 $E^\star$ values has been studied in the case of thermal dehydration of copper(II) chelates with the afore-mentioned ligands. The change in stereochemistry as a consequence of dehydration has been studied by investigation of the X-ray K-absorption spectra of hydrated and dehydrated chelates. The end product was identified by far-IR as well as X-ray K-absorption spectra.

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EXPERIMENTAL

Chemicals

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

Preparation of copper(II) chelates

The copper(II) chelates of SH, 5BSH, SAM, GA and NIA 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, then 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 standard iodometric procedure [14]. Analytical data are given in Table 1.

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 Platinel-II thermocouple (Engelhard, USA) 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.

TABLE 1

Abbreviated names, colour, % yield and elemental analysis of copper(II) chelates of O-/N-ligands

S.No.	Chelate [a]	Colour	Yield (%)	Elemental analysis; observed (calculated)			
				C (%)	H (%)	N (%)	Cu (%)
1.	$Cu(SH)_2 \cdot 2H_2O$	Bluish-green	80	41.54(41.64)	4.85(4.96)	13.74(13.88)	15.82(15.74)
2.	$Cu(SH)_2$ [b]	Grey	–	45.55(45.71)	4.27(4.35)	15.16(15.24)	17.15(17.29)
3.	$Cu(5BSH)_2 \cdot 2H_2O$	Olive green	75	29.35(29.94)	3.05(3.21)	9.85(9.98)	11.16(11.35)
4.	$Cu(5BSH)_2$ [b]	Dark green	–	31.26(31.98)	2.43(2.66)	10.62(10.66)	11.98(12.10)
5.	$Cu(SAM)_2$	Green	70	45.21(45.18)	4.34(4.28)	7.22(7.53)	16.89(17.01)
6.	$Cu(SAM)_2$ [b]	Dark green	–	–	–	–	–
7.	$Cu(NIA)_2(SO_4) \cdot 2H_2O$	Green	82	27.92(27.82)	2.76(2.70)	10.70(10.82)	12.32(12.22)
8.	$Cu(NIA)_2$ [b]	Dark grey	–	–	–	–	–
9.	$Cu(GA)_2 \cdot 2H_2O$	Grey	80	38.62(38.57)	2.82(2.75)	–	14.49(14.58)
10.	$Cu(GA)_2$ [b]	Dark grey	–	–	–	–	–

[a] SH, salicylhydrazide; 5BSH, 5-bromosalicylhydrazide; SAM, salicylamide; NIA, nicotinamide; GA, gallic acid moiety.

[b] Thermal dehydration product.

TABLE 2

Kinetic parameters for the thermal decomposition of copper(II) chelates of O-/N-donor ligands [a]

S.No.	Chelate	T_i (K)	$E^\star$ (kcal mol^{-1})	$S^\star$ (cal mol^{-1} °C^{-1})	$G^\star$ (kcal mol^{-1})	$H^\star$ (kcal mol^{-1})	log Z (s^{-1})	$-\log K_r$ (s^{-1})
1.	$Cu(SH)_2 \cdot 2H_2O$	523	19.94	−18.19	9.39	18.90	5.842	2.328
2.	$Cu(5BSH)_2 \cdot 2H_2O$	533	18.99	−18.60	8.02	17.94	5.439	2.348
3.	$Cu(SAM)_2 \cdot 2H_2O$	607	21.94	−17.62	10.04	20.74	6.480	2.724
4.	$Cu(NIA) \cdot 2H_2O$	585	27.32	−15.44	17.13	26.16	8.646	2.565
5.	$Cu(GA)_2 \cdot 2H_2O$	526	31.96	−13.08	20.04	30.92	10.962	1.966

[a] $E^\star$, energy of activation (kcal mol^{-1}); $S^\star$, entropy of activation (cal mol^{-1} °C^{-1}); $G^\star$, free energy of activation (kcal mol^{-1}); $H^\star$, enthalpy of activation (kcal mol^{-1}); Z, frequency factor (s^{-1}); K_r, specific rate constant (s^{-1}).

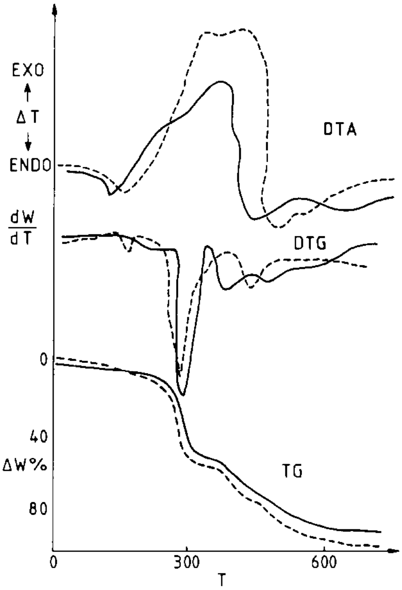

Fig. 1. ——— TG, DTG and DTA for copper(II) chelate of salicylhydrazide. ------ TG, DTG and DTA for copper(II) chelate of 5-bromosalicylhydrazide.

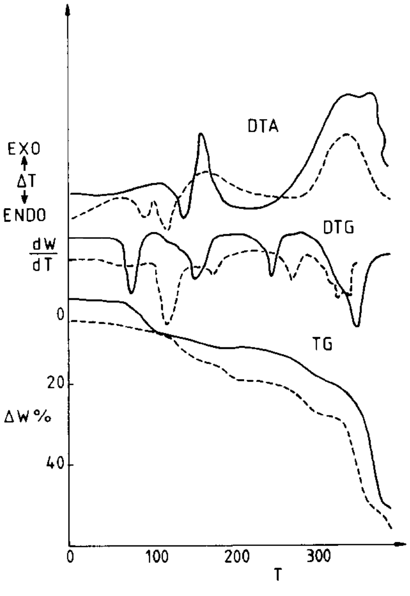

Fig. 2. ——— TG, DTG and DTA for copper(II) chelate of nicotinamide. ------ TG, DTG and DTA for copper(II) chelate of salicylamide.

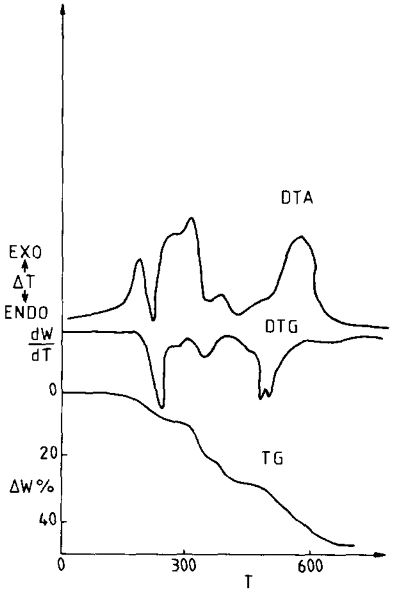

Fig. 3. TG, DTG and DTA for copper(II) chelate of gallic acid.

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

X-ray K*-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

TABLE 3

X-ray *K*-absorption parameters for thermal dehydration/decomposition products of copper(II) chelates of O-/N-donor ligands [a]

S.No.	Absorber	Energy of K-edge E (eV) ± 0.2 eV	Edge-shift E (eV) ± 0.2 eV	Edge-width ΔE (eV) ± 0.2 eV	Type of Van Nordstrand curves
1.	Copper (metal)	8979.30 [b]	–	–	–
2.	Copper oxide	8982.18 [c]	3.88	–	–
3.	$Cu(SH)_2$	8983.35	4.05(9.07)	12.05(8.75)	IVb (Ia)
4.	$Cu(5BSH)_2$	8983.47	4.17(8.45)	11.25(9.87)	IVb (Ia)
5.	$Cu(SAM)_2$	8983.28	3.98(6.75)	11.23(9.65)	IVb (Ia)
6.	$Cu(NIA)_2$	8983.51	4.21(6.92)	10.75(8.75)	IVb (Ia)
7.	$Cu(GA)_2$	8983.30	4.00(7.22)	11.40(9.47)	IVb (Ia)

[a] Values in parentheses are for the chelates before thermal dehydration/decomposition.
[b] 8979.13 eV, reported by Bearden [43].
[c] 8982.1 eV, reported by Agrawal [51].

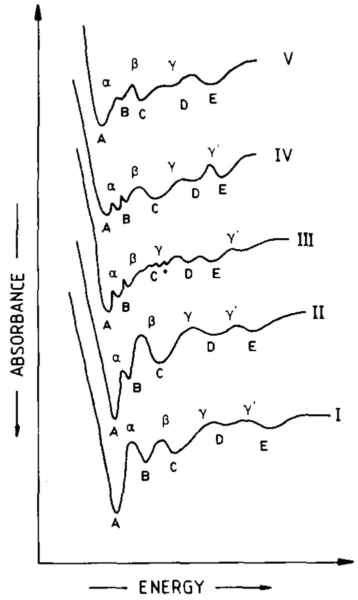

Fig. 4. X-ray *K*-absorption spectra for hydrated copper(II) chelate: I, Cu–SH; II, Cu–5BSH; III, Cu–SAM; IV, Cu–NIA; V, Cu–GA.

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 μ mm^{-1} in the region of Cu-edge. Absorption screens were prepared from the sample following the method described by Sandstrom [15].

The X-ray *K*-absorption parameters are reported in Table 3 and the spectra given in Figs. 4 and 7.

RESULTS AND DISCUSSION

Stoichiometry and stereochemistry

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

X-ray *K*-absorption spectra (Fig. 4) of hydrated chelates of copper(II) with the ligands used resemble type IA curves of Van Nordstrand [22–24], indicating octahedral stereochemistry. It should, however, be noted that the curves given by Van Nordstrand are absorption coefficient vs. energy curves, whereas our curves show the variation of transmitted intensity with energy. 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 as presented in Table 2. The same table contains the log Z values.

Determination of order of reaction

The Horowitz–Metzger equation [25] $C_s = (n)^{1/1-n}$ where C_s is the weight fraction of the substance present at the DTG peak temperature T_s and is given by

$$C_s = W_s - W_f / W_0 - W_f \tag{1}$$

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. The order of reaction for dehydration of the copper(II) chelates is obtained by comparing the C_S value yielded by the above method with the values given in the Horowitz and Metzger [25] table. 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 $E^\star$ and the frequency factor Z for the first order kinetics of dehydration. The following equations are used for this purpose

$$E^\star = \frac{R/T_i^2}{W_i}\left(\frac{dW}{dT}\right)_i \tag{2}$$

$$Z = \frac{a}{W_i}\left(\frac{dW}{dT}\right)\exp(E^\star/RT_i) \tag{3}$$

where R = the gas constant, T_i = inflection temperature (K), W_i = weight at the point on the TG curve where it goes from concave-down to concave-up,

$(dW/dT)_i$ = rate of change of weight at the point of inflection, and a = heating rate.

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

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

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

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

where k and h are the Boltzmann and Planck constants, respectively.

The kinetic parameters thus obtained are presented in Table 2.

A perusal of Table 2 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 ±0.55 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 Khadikar et al. [29].

Dependance of $S^\star$ *on* $G^\star$

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

$$S^\star = \alpha + cG^\star \tag{7}$$

The coefficients of eqn. (7) were computed by the method of least-squares. The value of the correlation coefficient (0.996) indicates that the method of least-squares is applicable, and that the correlation between $S^\star$ and $G^\star$ is genuine (Fig. 5).

It is interesting to compare the thermodynamic functions for the slightly different ligand NIC whose coordination character is different from the other ligands used. Unlike the others, NIC acts as a monodentate ligand [13] and does not possess phenolic OH groups for coordination. It has exhibited greater free energy of activation for thermal dehydration. The increase may be due to a slightly higher negative entropy of activation and may be attributed to the fact that in the Cu–NIC complex the adjacent nicotinamide moieties are linked by hydrogen bonding [13].

It is worth noting that the $S^\star$ value for the thermal dehydration of Cu(II)–SH is the same as the one reported earlier [50] for copper(II) chelates of salicylhydroxamic acid [Cu(II)–SHA] indicating thereby a mutual secondary steric influence of the side-chain in the vicinity of phenolic group on dehydration. Generally, the $S^\star$ values for the dehydration of salicylhydrazides and salicylhydroxamic acids are much higher than those for salicylic acid [50].

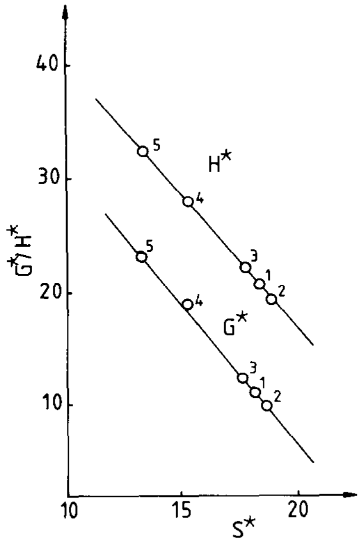

Fig. 5. Correlation of $S^\star$ ($\mathrm{mol}^{-1}\ \mathrm{C}^{-1}$) with $G^\star/H^\star$ (kcal mol^{-1}) for copper chelates; 1, Cu–SH; 2, Cu–5BSH; 3, Cu–SAM; 4, Cu–NIA; 5, Cu–GA.

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

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

The enthalpy of activation, $H^\star$, needed for this purpose, has been evaluated from the equation

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

The values of $H^\star$ as recorded in Table 2 indicate that they differ from the values of $E^\star$ by an average of 0.87 kcal mol^{-1}. This small difference could not be differentiated experimentally and thus we can safely say that $E^\star$ and $H^\star$ are equivalent. The error limit in the values of $H^\star$ is 1.0 kcal mol^{-1}.

A straight line graph (Fig. 5) obtained between $H^\star$ and $S^\star$ indicates that the correlation between $H^\star$ and $S^\star$ 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 2) obtained are within the range usually observed for a first-order reaction.

Validity of a linear kinetic compensation law

Procedural variables have a considerable influence on the kinetic parameters of thermal decomposition reactions. Variations of these parameters are not independent of each other and certain general correlations exist between them [33]. Of these correlations only the so-called kinetic compensation effect is well known.

Very frequently the relation between Z and $E^\star$ takes the form

$$\log Z = aE^\star + b \tag{10}$$

One can observe that the log Z values vary in parallel with the $E^\star$ values, indicating a "kinetic compensation effect" [33].

The graphical plot of log Z vs. $E^\star$ for all the above complexes is shown in Fig. 6. It is apparent from the figure that the same linear compensation law (Fig. 7) operates for the loss of coordinated water in 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 (0.8095) and b (-2.85). The value of Jaffe's [34] correlation coefficient (0.997) indicates good linearity between log Z and $E^\star$.

As far as the slope of the straight line obtained is concerned, the a value for the loss of coordinated water is in practice more than that obtained for the loss of water of crystallisation [35].

Analysis of intermediate products

In order to isolate the intermediate products formed due to the thermal dehydration, the samples were withdrawn from the furnace at appropriate

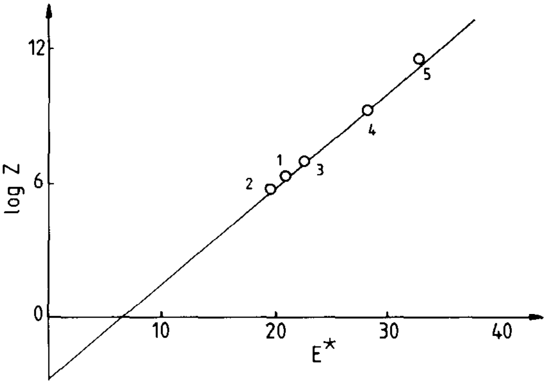

Fig. 6. Linear compensation law (log Z vs. $E^\star$) for copper(II) chelates; 1, Cu–SH; 2, Cu–5BSH; 3, Cu–SAM; 4, Cu–NIA; 5, Cu–GA.

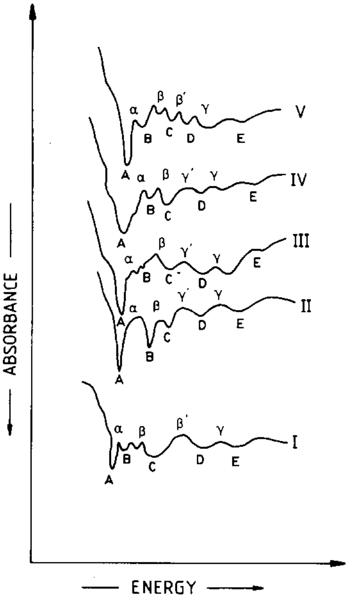

Fig. 7. X-ray K-absorption spectra for thermal dehydrated product for copper(II) complexes; I, Cu–SH; II, Cu–5BSH; III, Cu–SAM; IV, Cu–NIA; V, Cu–GA.

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 in the TG curves. Attempts were made to obtain the IR spectra of the decomposition products of all the six chelates. The disappearance of characteristic bands of coordination water upon dehydration indicates the loss of coordinated water forming anhydrous complexes. This further confirms the dehydration.

Finally, the X-ray K-absorption of the final residue is found to be identical with that observed for CuO [43,51]. Far-IR spectra of the final residue exhibit bands at 610(m), 500(s) and 410(m) cm^{-1}, supporting further the formation of CuO as the end product [41]. These results are in agreement with the predicted composition and structure of the chelates.

Evidence for change in stereochemistry

The study of X-ray K-absorption spectra of anhydrous chelates (Fig. 7) indicated that they resemble type IVb curves of Van Nordstrand [22], i.e. the curves for the tetrahedrally surrounded metal ions. The curves show the splitting of the principal absorption edge into two components K and K_1. According to Sinha and Mande [36] and others [37–40] the minima at the positions marked ‘A’ and ‘B’ in Fig. 7 represent the X-ray absorption transitions *1s* → *4p* and *1s* → *5p* limit respectively. The forms of these discontinuities suggest that the copper(II) ion is octahedrally surrounded in the hydrous complexes, while in the anhydrous complexes the ion is in a tetrahedral environment. Thus, X-ray absorption spectroscopy provides a method of estimating the change from octahedral to tetrahedral surroundings of metal ion in chelates due to thermal dehydration.

The edge-widths of the dehydrated copper(II) chelates are greater than those of the chelates containing coordinated water molecules. This result further reveals the lowering of stereochemistry from octahedral to tetrahedral [39] due to thermal dehydration. Remarkable changes in the electronic spectra of the chelates upon heating also supported the idea of change in the stereochemistry on thermal dehydration.

Glen and Dodd [44] 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 less in 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 (Table 3), in the present case, are in fair agreement with this concept. Similar results were obtained by Cotton and Hanson [45], Shrivastawa and Nigam [46], Mande and Chetal [47] and by Khadikar and Anikhindi [48].

On the basis of changes in edge-structure, edge-width and edge-shift (Table 3), it can be concluded that on thermal dehydration of the copper(II) chelates, octahedral stereochemistry changes to tetrahedral as a consequence of the elimination of the two coordinated water molecules from the chelates.

Shape of the DTA peaks

The recorded DTA curves (Figs. 1–3) are observed to have unusually shaped exothermal peaks; however, we have compared them with those reported by Khadikar and coworkers [2–8] for similar organic compounds. Such abnormal shapes have also been reported in some malato-aquo- [50] and EDTA-chelates [49]. The abnormality is probably due to the various gaseous combustion products which escape as a consequence of the decomposition of the organic skeleton. A large broad exothermal peak in a wide temperature range on the DTA curve for decomposition of the dehydrated chelates indicates oxidation and combustion processes as well as the decomposition.

Binding strength of water molecules

The order of the strength of binding of the water molecules to the copper ion is borne out clearly in the temperature range over which these chelates are dehydrated. A close look at Figs. 1 and 2 indicates that, in general, the dehydration temperatures are found in the order Cu–GA > Cu–NIA > Cu–SAM > Cu–SH > Cu–5BSH.

It is also noteworthy that for the dehydration of the copper(II) chelates there is very little difference in the inception temperatures. However, the final temperatures are markedly different. This variation in the internal reaction is reflected in the values of activation energy. Thus more quantitative evidence for the binding strength of water molecules in the chelates is obtained from the corresponding values of activation energy, which further are found to vary in the order given above.

CONCLUSIONS

1. Thermal dehydration of copper(II) chelates of O-/N-donor ligands follows 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. The X-ray *K*-absorption and optical spectra indicate the change from octahedral to tetrahedral stereochemistry as a consequence of dehydration.
4. The binding strength of water molecules is found to be in the order CU–GA > Cu–NIA > Cu–SAM > Cu–SH > Cu–5BSH, which is also the order of activation energy.

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