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STRUCTURE, THERMAL BEHAVIOUR AND SOLID STATE KINETICS, OF BIS-(5-SULPHOSALICYLATO)-DIAQUO METAL CHELATES OF BIVALENT METAL IONS

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ABSTRACT

Bis-(5-sulphosalicylato)-diaquo complexes of VO(II), Cu(II), Ni(II), Co(II), Fe(II) and Mn(II) have been prepared and the bonding is discussed on the basis of IR studies The kinetic parameters have been evaluated for the thermal dehydration of these complexes Observed kinetic parameters indicate a first order reaction The activation energy of the thermal dehydration decreases in the order VO(II) > Cu(II) > Co(II) > Ni(II) > Fe(II) > Mn(II) which is also the order for the covalency in M–L bond

The statistical analysis of activation energy ($E^\star$) and log Z values shows the validity of a linear compensation law The change in stereochemistry as a consequence of dehydration had 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 recent years there has been considerable interest in the chemistry of salicylic and nuclear substituted salicylic acid ligands and their metal complexes Previous work reported by Khadikar and coworkers concerned with antimicrobiol activity [1–5] and thermal behaviour of transition metal complexes of salicylic, 3,5-dinitrosalicylic and 4-amino-salicylic acids [6–10] A careful survey of literature has shown that no solid state work appears to have been done on the transition metal complexes with 5-sulphosalicylic acid (5SSA) Synthesis, structural and thermal studies on 5SSA complexes of VO(II), Cu(II), Ni(II), Co(II), Fe(II) and Mn(II) have, therefore, been undertaken and the results of these investigations are described in the present communication

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Since most of these complexes are thermally stable, and insensitive to air, they provide an opportunity for studying the kinetics of thermal decomposition The detailed kinetic studies are expected to provide important information supplementing the thermal stability of metal complexes of 5SSA and their decomposition pathways The kinetics of thermal dehydration of aforementioned complexes of 5SSA has, therefore, been carried out employing TG, DTG and DTA techniques

EXPERIMENTAL

The complexes were prepared following the method described elsewhere [11] Equimolar solutions of metal salts and 5SSA were prepared and mixed in the stoichiometric ratio M L = 1 2 (where M stands for the metal ion, viz VO(II), Cu(II), Ni(II), Co(II), Fe(II) and Mn(II), and L for the anion of 5SSA used as ligand), by taking ligand in slight excess The solid complexes obtained were washed thoroughly with ethanol, dried and recrystallized from dimethyl formamide

All the reagents used were of BDH AnalaR grade

Elemental analysis

The metal content was estimated by conventional methods [12] Carbon and hydrogen analyses were carried out on a Colemann CHN Analyser-29

Analytical data of the complexes are given in Table 1

TABLE 1

Analytical data for the bis-(5-sulphosalicylato)-diaquo complexes and their dehydrated products

Complex	Colour	M (%)		O (%)		H (%)	
		Calc	Found	Calc	Found	Calc	Found
Cu(5SSA)$_2$ 2H$_2$O	Green	11 95	12 25	31 60	30 98	2 25	2 31
Cu(5SSA)$_2$ (dp)	Dark Green	12 76	12 82	33 77	34 00	2 01	1 92
Ni(5SSA)$_2$ 2H$_2$O	Light Green	11 14	11 82	31 89	31 27	2 28	2 20
Ni(5SSA)$_2$ (dp)	Green	11 92	12 00	34 09	33 87	2 03	2 10
Co(5SSA)$_2$ 2H$_2$O	Pink	11 18	10 98	31 88	31 16	2 27	2 34
Co(5SSA)$_2$ (dp)	Brown	11 95	12 02	34 08	34 12	2 03	2 09
Mn(5SSA)$_2$ 2H$_2$O	Light buff	10 50	10 41	32 12	31 89	2 29	2 21
Mn(5SSA)$_2$ (dp)	Tan	11 23	11 15	34 37	34 10	2 05	2 13
Fe(5SSA)$_2$ 2H$_2$O	Coffee colour	10 66	11 04	32 07	31 92	2 29	2 23
Fe(5SSA)$_2$ (dp)	Dark brown	11 40	11 36	35 10	35 22	2 04	2 14
VO(5SSA)$_2$ 2H$_2$O	Dark green	12 51	12 41	31 4	32 08	2 24	2 20
VO(5SSA)$_2$ (dp)	Bright green	13 36	13 42	33 54	33 62	2 00	1 92

(dp) means decomposition product

Thermal analyses

Thermogravimetry (TG) was carried out on a Stanton 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 1 in h^{-1}) All the samples were of the same particle size (homogenized by sieving below 100 mesh) and were packed as uniformly as possible in a platinum crucible of appropriate size The same platinum crucible was used throughout the experiments

Differential thermal analysis (DTA) assembly with temperature programmer of F & M Scientific 240 Hewlett Packard and thermocouple platinel II of Engelhard Ltd , U S A were used DTA curves were recorded (Rikadenki Kogyo Co , Ltd) in static air at a heating rate of 4° C min^{-1} Alumina was used as a reference standard

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

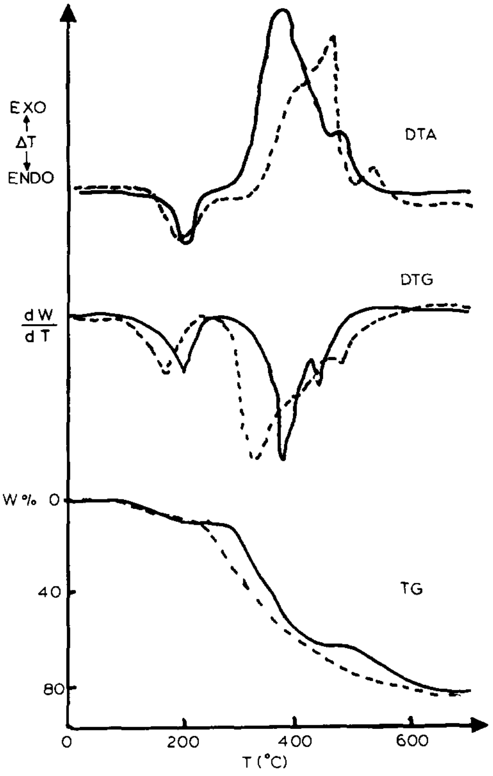

Fig 1 TG, DTG and DTA curves for bis-(5-sulphosalicylato)-diaquo complexes (———) copper(II) complexes, (- - - - -) nickel(II) complexes

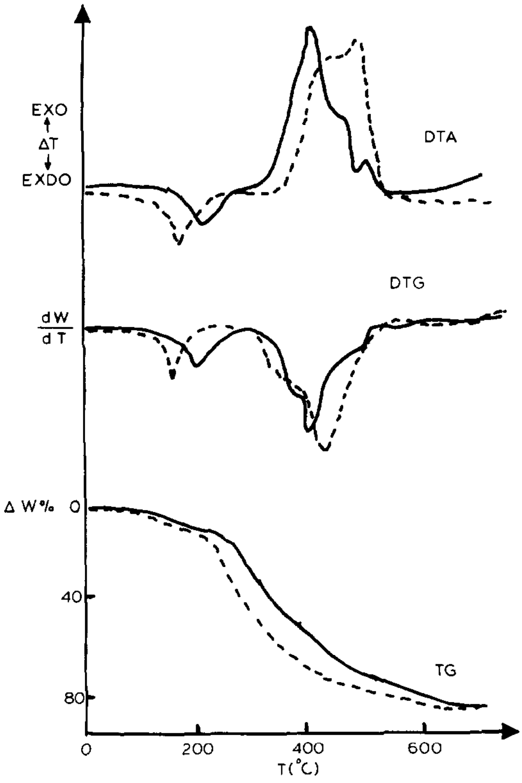

Fig 2 TG, DTG and DTA curves for bis-(5-sulphosalicylato)-diaquo complexes (———) cobalt(II) complex, (- - - - - -) manganese(II) complex

IR spectra

The presence of ligand and the water molecules in the complexes was identified by infrared spectroscopy using a Perkin Elmer Model 377 spectrophotometer using the KBr disc technique

Far-infrared spectra were recorded in the region 500–50 cm^{-1} employing a Polytec FIR 30 Fourier far-infrared spectrometer

The characteristic band positions are given in Table 2

RESULTS AND DISCUSSION

Stoichiometry and behaviour

The results of elemental analyses in Table 1 indicate that the complexes formed have the composition ML_2 $2H_2O$ where M stands for VO(II), Cu(II), Ni(II), Co(II), Fe(II), Mn(II) and L for the anion of 5SSA

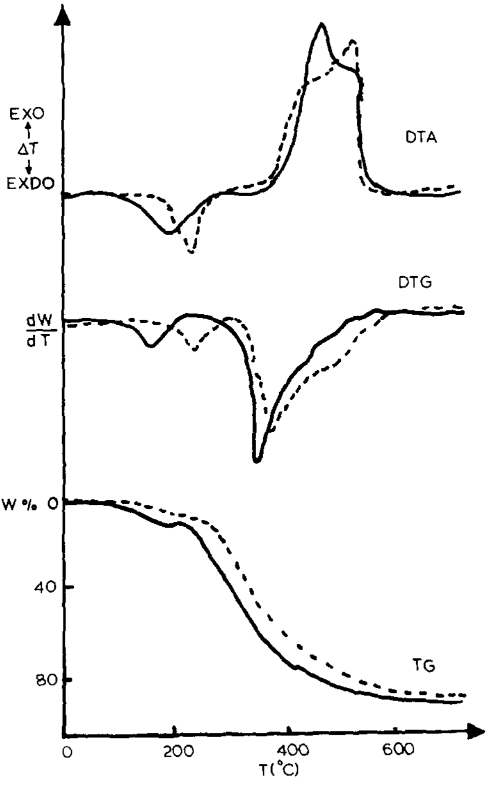

Fig 3 TG, DTG and DTA curves for bis-(5-sulphosalicylato)-diaquo complexes (———) iron(II) complex, (------) oxovanadium(IV) complex

All the complexes are insoluble in water and all common organic solvents except DMF in which they are sparingly soluble, this property being suggestive of polymeric configurations Because of insolubility of the chelate, the extent of polymerization could not be determined

Bonding in complexes

The infrared spectrum of the solid 5SSA is almost identical with that of its complexes in the region 2000–625 cm^{-1} The frequencies of most interest with regard to the structure of the complexes are the C–O and O–H vibrations The $\nu(C{=}O)$ band at 1665 cm^{-1} is shifted to a lower frequency ($\sim$ 1630 cm^{-1}) in all the complexes showing that complexation has taken place through the carboxyl group [13,14] Appearance of the new bands in the neighbourhood of 840 cm^{-1} in all the complexes show that the water molecules are coordinated to the metal ion [15–17] The presence of a band at $\sim$ 315 cm^{-1} confirms the presence of coordinated water [18] The presence of water as coordinated water is further borne out by the thermal

TABLE 2

Characteristic IR frequencies for bis-(5-sulphosalicylato)-diaquo complexes

Assignment	5SSA	Cu(II)-5SSA	Ni(II)-5SSA	Co(II)-5SSA	Mn(II)-5SSA	Fe(II)-5SSA	VO(II)-5SSA
$\nu(COO^-)$(asym)	1665(s)	1648(s)	1650(s)	1640(s)	1630(s)	1635(s)	1650(s)
$\nu(COO^-)$(sym)	1445(s)	1420(s)	1431(s)	1430(s)	1420(s)	1425(s)	1420(s)
ν(O-H)(str)	3600-2400 (3200)(sb)	2800-3750 (3475)(sb)	2900-3690 (3450)(sb)	3000-3715 3510)(sb)	2900-3670 (3400)(sb)	2700-3690 (3480)(sb)	3680-2800 (3520)(sb)
δ(O-H)	1353(s)	1341(s)	1353(s)	1353(s)	1341(s)	1352(s)	1364(s)
$\delta_r(H_2O)$(rocking)	-	850(s)	842(s)	832(s)	830(s)	822(s)	872(s)
ν(M-O)+(C-C)	-	530(w)	520(mb)	495(w)	490(sh)	505(m)	510(w)
$\delta(H_2O)$	-	315(m)	318(mb)	315(w)	320(sh)	310(m)	315(mb)
ν(M-O)+ring deform	-	440(sb)	420(w)	428(m)	405(sh)	425(w)	430(sh)
Δ(C=O)	-	228	219	210	210	210	230

Key s = strong, b = broad, w = weak, m = medium, sh = shoulder Indicates that the decomposition product(s) could not be isolated and identified owing to the lack of a clear-cut horizontal on the TG curve as the intermediate products are not stable to the required extent decomposition data (Figs 1–3) It may also be noted that the O–H (phenolic) bending peak at 1350 cm^{-1} remained almost at the same position for both 5SSA and its complexes This shows that there is no loss of proton by the phenolic OH group on coordination

The increase $\Delta(C=O)$ in the difference between $\nu(COO^-)$(asym) and $\nu(COO^-)$(sym) has been taken as a measure of increasing covalency of the M–O bond The 5SSA, complexes presented a band at ~ 1640 cm^{-1} for $\nu(COO^-)$(asym) and at 1420 cm^{-1} for $\nu(COO^-)$(sym) Thus the covalent character of the M–O bond (Table 2) follows the order Fe(II)–5SSA < Mn(II)–5SSA < Co(II)–5SSA < Ni(II)–5SSA < Cu(II)–5SSA < VO(II)–5SSA

Trends in positions and separation between antisymmetric and symmetric carboxylate stretching band provide a useful observation for assigning the coordination type of carboxylate group Values of $\nu(OCO)$(sym) greater than 1414 cm^{-1} may be assumed as being strongly indicative of bridging bidentate carboxylate, values in the 1414–1400 cm^{-1} spectral range indicate monodentate, and those lower than a 1400 cm^{-1} indicate bidentated carboxylate [20–27].

On the basis of these considerations in all our metal 5-sulphosalicylates I suggest the presence of carboxylate which acts as bridging bidentate This is consistent with the suggested polymeric structure.

Oxovanadium(IV) complexes have a distinct novelty, as they exhibit one additional IR band due to the presence of the multiple covalent V=O bond This band usually occurs at 960 ± 50 cm^{-1} [28] In polymeric complexes with V=O- - -V=O- - - interaction, it is expected that the V=O bond order will be lowered and as a result the V–O stretching frequency would occur at a lower energy The V–O stretching frequency band at 870 cm^{-1} observed in the present case is abnormally low and is found to be coupled with the H_2O rocking mode as indicated by the broadening of the bands This abnormality has been explained earlier [29,30] in terms of the V–O–V–O bridging in polynuclear oxovanadium(IV) complexes

Thermal decomposition

Thermal decomposition curves for all the six isostructural complexes of 5SSA are presented in Figs 1–3, while TG weight loss data and DTA peak temperatures are to be found in Tables 3–5

The TG, DTG and DTA curves reveal that the decomposition of all the six complexes is identical The thermal decomposition starts with loss of coordinated water molecules, followed by pyrolysis of the dehydrated complex, resulting in metal oxide as end product Two decomposition periods, in general, can be distinguished in the TG curves for all the six complexes These two decomposition periods may be explained in accordance with the TG weight loss data, DTG and DTA results as presented in Tables 4 and 5

TABLE 3

Analytical data for the bis-(5-sulphosalicylato)-diaquo complexes [a]

Complex	D P [b]	Temperature range (° C)	Colour	Composition of the residue	Weight loss (%)	
					Calc	Obs
(I) $Cu(5SSA)_2\ 2H_2O$	I	100–240 ± 4	Black	$Cu(5SSA)_2$	6 77	6 50
	II	260–620 ± 2		CuO	85 03	84 75
(II) $Ni(5SSA)_2\ 2H_2O$	I	80–220 ± 4		$Ni(5SSA)_2$	6 83	7 00
	II	230–580 ± 3	Greenish black	NiO	85 81	86 25
(III) $Co(5SSA)_2\ 2H_2O$	I	100–230 ± 3		$Co(5SSA)_2$	6 83	6 75
	II	250–600 ± 2	Dark brown	CoO	85 77	86 50
(IV) $Mn(5SSA)_2\ 2H_2O$	I	80–210 ± 3		$Mn(5SSA)_2$	6 88	7 00
	II	220–570 ± 4	Grey green	MnO [c]	86 43	85 00
(V) $Fe(5SSA)_2\ 2H_2O$	I	90–210 ± 4		$Fe(5SSA)_2$	6 87	6 50
	II	230–640 ± 3	Dark brown	FeO [d]	86 28	85 25
(VI) $VO(5SSA)_2\ 2H_2O$	I	110–260 ± 4		$VO(5SSA)_2$	6 72	6 25
	II	280–620 + 2	Dark blue	O=V=O [e]	84 49	83 00

[a] All the experiments were carried out in air at a heating rate of 4° C min^{-1}

[b] D P = Decomposition period (step)

[c] In the final residue, the possibility of formation of Mn_3O_4 can not be ruled out as the experiments were carried out in air

[d] FeO was the major end product above 600 ° C, however, below this temperature it becomes contaminated with Fe_3O_4, as the metal is characterized by its ability to form such oxide

[e] The end product was expected to be a mixture of vanadium di- and penta-oxides Formation of V_2O_5 may be due to the oxidation of vanadium dioxide in air

In the first decomposition period, as stated earlier, two water molecules escaped and an intermediate of composition $M(5SSA)_2$ is formed

$$M(5SSA)_2\ 2H_2O \rightarrow M(5SSA)_2 + 2H_2O \qquad (1)$$

This period involves a single endothermic step, as shown by the DTA curves

In the second period, the dehydrated complex decomposes finally into metal oxide This period involves one or more steps as evident from one or more exothermic peaks in the DTA curves The thermal decomposition of the dehydrated complex may be represented by the following possible partial reactions

$$\begin{aligned} & && MCO_3 + \text{gaseous combustion products} && \\ & M(5SSA)_2 \rightarrow && H_2, CO, CO_2, H_2O && (2a) \\ & && SO_2 + SO_3 + \text{sulphur} && (2b) \\ & MCO_3 \quad \rightarrow && MO + CO_2 && \end{aligned}$$

Here MO represents the metal oxide formed, and not the composition of the metal oxide

TABLE 4

TG horizontal, maxima and range of DTG and DTA peak of bis-(5-sulphosalicylato)-diaquo complexes

Complex	Decomposition stage	Range of TG horizontal (° C)	Maximum of DTG trace (° C)	Range of DTG effect (° C)	Maxima of DTA trace (° C)	Range of DTA effect (° C)
(I) $Cu(5SSA)_2\ 2H_2O$	I	100–240 ± 4	200	179–226	210 (endo)	146–226
	II	260–620 ± 2	372	353–419	380 (exo)	385–392
		433	433	433–453	480 (exo)	459–485
(II) $Ni(5SSA)_2\ 2H_2O$	I	80–220 ± 4	172	119–185	200 (endo)	152–233
	II	230–580 ± 3	326	285–359	460 (exo)	426–492
			472	472–485	520 (exo)	506–546
(III) $Co(5SSA)_2\ 2H_2O$	I	100–230 ± 3	200	179–219	210 (endo)	166–239
	II	250–600 ± 2	366	366–385	420 (exo)	319–433
			400	385–426	490 (exo)	485–513
(IV) $Mn(5SSA)_2\ 2H_2O$	I	80–210 ± 3	153	133–185	190 (endo)	139–213
	II	220–570 ± 4	433	413–439	480 (exo)	466–533
(V) $Fe(5SSA)_2\ 2H_2O$	I	90–210 ± 4	159	119–192	200 (endo)	172–226
	II	230–640 ± 3	342	300–400	470 (exo)	346–466
(VI) $VO(5SSA)_2\ 2H_2O$	I	110–260 ± 4	219	200–246	220 (endo)	166–233
	II	353	355	319–392	490 (exo)	479–533

TABLE 5

Kinetic data for thermal dehydration of bis-(5-sulphosalicylato)-diaquo complexes

Complex	Dehydration temperature range (° C)	T_i (K)	W [a]	W_i	C_s	$(dw/dT)_i$ (mg ° C^{-1})
(I) $Cu(5SSA)_2$ $2H_2O$	100–240 ± 4	473	6 50	2 50	0 384	0 125
(II) $Ni(5SSA)_2$ $2H_2O$	80–220 ± 4	433	7 00	2 75	0 392	0 125
(III) $Co(5SSA)_2$ $2H_2O$	100–230 ± 3	453	6 75	2 25	0 333	0 100
(IV) $Mn(5SSA)_2$ $2H_2O$	80–210 ± 3	413	7 00	2 25	0 321	0 100
(V) $Fe(5SSA)_2$ $2H_2O$	90–210 ± 3	433	6 50	2 25	0 346	0 100
(VI) $VO(5SSA)_2$ $2H_2O$	110–260 ± 4	493	6 25	2 00	0 320	0 100

[a] W is the total weight loss in dehydration step

In almost all cases, the second decomposition period occurs in a longer temperature range and the partial reactions (2a), (2b) and (2c) usually occur in parallel resulting in a combined step It was difficult to separate the partial decomposition steps involved in the second decomposition period and to establish the existence of intermediates However, in some cases the DTG curves of the complexes resolve the close lying steps and indicate the multistep nature of the second decomposition period

In some cases the expansion of the second decomposition period may cause error through the overlapping of two decomposition steps following one another closely This may even give rise to the formation of a single decomposition step in the TG curve

Shapes of DTA curves

The recorded DTA curves (Figs 1–3) are observed to have unusual shapes, however, we have compared them with those reported by us [39–43] as well as some other earlier workers [45–48] for other salicylates, and observed that they too have obtained exothermic DTA peaks with unusual shapes It is worthy of note to mention that such abnormal shapes are also found for malato-aquo [49] and EDTA [50] complexes

The abnormal shape of the exothermic peaks in the DTA curves is probably due to the various combustion products escaping as a consequence of the decomposition of the organic skeleton, i e the 5-sulphosalicylate moiety of the complex Large, broad exothermic peaks in a wide temperature range in the DTA curve of decomposition of the dehydrated complexes indicate oxidation and combustion processes besides decomposition

It is worthy to note that the decomposition of metal carbonate into metal oxide with the evaluation of CO_2 is always endothermic, however, the oxidation of products of cracking from the preceding decomposition process, or that of carbon probably produced an exothermic effect shown on the DTA curve

Kinetic parameters

Taking into account the complexity of the thermal decomposition of the metal complexes an attempt was made to select the appropriate method for determining various kinetic parameters of the thermal decomposition of the complexes The methods of Horowitz and Metzger [31] and Fuoss et al [32] are found to be suitable for this purpose

Various kinetic parameters for the thermal dehydration reactions (the rate determining step) have been evaluated However, the kinetic parameters of pyrolysis of the dehydrated complexes could not be computed due to the absence of an exact inflection point, as the steps of pyrolysis were overlapped due to rapid thermal decomposition

Determination of order of reaction

The order of reaction, n, was determined by applying the Horowitz and Metzger [31] equations

$$C_s = (n)^{1/1-n}\frac{W_s - W_f}{W_0 - W_f}$$

where W_s = weight fraction at T_s, i e the DTG peak temperature, W_0 and W_f are the initial and final weights of the substance The order of thermal dehydration in each case is obtained by comparing the C_s value yielded by the above method with values given in the Horowitz–Metzger [31] table

Results presented in Table 5 indicate that in all cases the order of the dehydration reaction corresponding to the escape of water molecules is unity, showing that the dehydration follows first-order kinetics

Evaluation of other kinetic parameters

For first-order kinetics the Fuoss method [32] is employed to evaluate the activation energy $E^\star$ and frequency factor Z using expressions (3) and (4)

$$E^\star = \frac{R/T_i^2}{W_i}\left(\frac{\mathrm{d}w}{\mathrm{d}T}\right)_i \tag{3}$$

$$Z = \frac{a}{W_i}\left(\frac{\mathrm{d}w}{\mathrm{d}T}\right)\exp\frac{E^\star}{RT_i} \tag{4}$$

In these equations T_i = inflection temperature (K), W_i = weight at the point on the TG curve where it goes from concave down to concave up, $(\mathrm{d}w/\mathrm{d}T)_i$ = rate of change in weight at the point of inflection, and a = heating rate

Activation entropy $S^\star$, free energy of activation $G^\star$ and specific reaction rate constant K_r have been calculated using their interrelationship [33] given in eqns (5), (6) and (7), respectively

$$S^\star = (\log Zh/kT)R \tag{5}$$

$$G^\star = E^\star - T_t S^\star \tag{6}$$

$$K_r = Z \exp \frac{-E^\star}{RT_t} \tag{7}$$

In eqn (5) k and h are the Boltzmann and Planck constants, respectively The kinetic parameters so obtained are presented in Table 6

Perusal of Table 6 shows that the activation energies ($E^\star$) for the splitting of H_2O–M bonds lie between 15–25 kcal mol^{-1} with an estimated uncertainty of $\pm 0\ 5$ kcal mol^{-1} The values are comparable with the usual values of the activation energy for a dehydration reaction [10,33]

Activation energy of the thermal dehydration reaction of the complexes has been found to decrease roughly in the order Mn(II)–Fe(II) < Ni(II) < Co(II) < Cu(II) < VO(II) This is in the order of binding strength of the water molecules to the metal ion These effects suggest that the coordinated water molecules tend to be liberated in the aforementioned sequence

The enthalpy of activation $H^\star$ has been evaluated from the relationship

$$H^\star = E^\star - RT_t \tag{8}$$

and it differs by an average of 1 00 kcal mol^{-1} This small difference could not be differentiated experimentally and we can safely say that $E^\star$ and $H^\star$ are equivalent The error limit in values of $H^\star$ is ± 0.5 kcal mol^{-1}

Dependence of S★ *on* G★

It may be useful to compare the thermodynamic functions for the thermal dehydration of 5SSA complexes which fulfil a mutual linear relation [34] This can be expressed for our purposes as

$$S^\star = \alpha + \beta G^\star \tag{9}$$

The coefficients of eqn (9) were computed by the least-squares method The value of correlation coefficient (0 997) indicates that the method of least squares is applicable and that the correlation of $S^\star$ and $G^\star$ is genuine (Fig 4)

Estimation of isokinetic temperature, β

An attempt has also been made to calculate isokinetic temperature β from the relationship

$$H^\star = H_0^\star + \beta S^\star \tag{10}$$

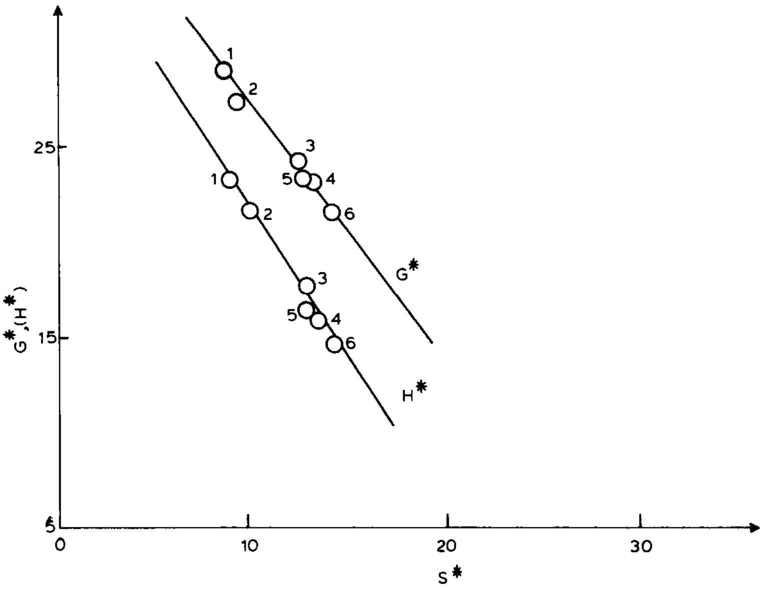

Fig 4 Correlation of S with G (S with H) for bis-(5-sulphosalicylato)-diaquo complexes of (1), Cu(II), (2) Ni(II), (3), Co(II), (4), Mn(II), (5), Fe(II) and (6), VO(II)

A straight line graph obtained plotting $H^\star$ and $S^\star$ indicates that the correlation of $H^\star$ and $S^\star$ is genuine (Fig 4)

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

The values of all other kinetic parameters (Table 6) obtained are within the range usually observed for first-order reactions [10,35] Thus it can be concluded that the thermal dehydration of these complexes is 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 [36] 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

$$\log Z = aE^\star + b$$

One can observe the log Z values to be related linearly with the $E^\star$ values, indicating the "kinetic compensation effect" [36]

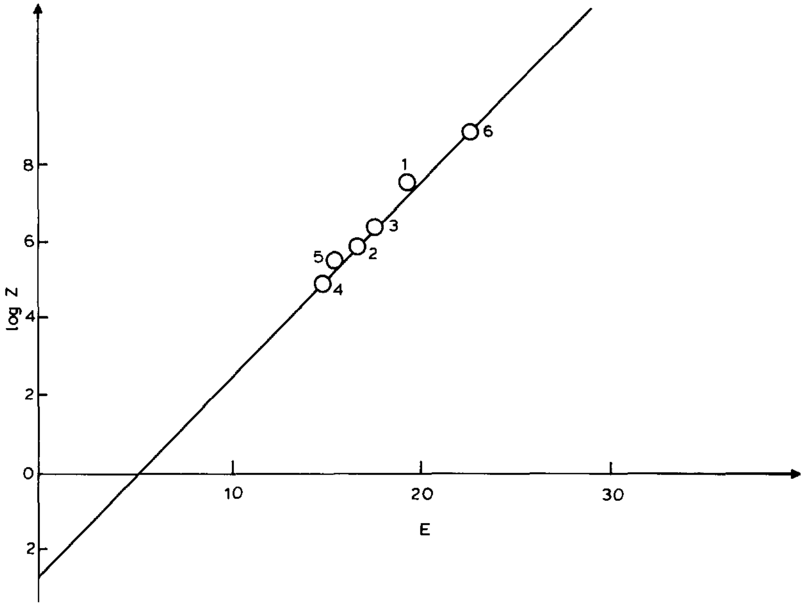

Fig 5 Correlation of log Z with E for bis-(5-sulphosalicylato)-diaquo complexes of (1), Cu(II), (2), Ni(II), (3), Co(II), (4), Mn(II), (5), Fe(II), and (6) VO(II)

A graphical plot of log Z against $E^{\star}$ for all the complexes in the present study is shown in Fig 5 A close look at this figure indicates that the same linear compensation law operates for the loss of coordinated water molecules in the whole class of complexes studied

The regression analysis of the data, using the method of least squares, gave the value of a and b as 0 810 and b as -2 887, respectively The value of Jaffe's [37] correlation coefficient (0 998) 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 the one obtained for the loss of crystallization water [38]

Comparison of results

It is interesting to compare the results obtained in the present study with the data reported earlier by us [39–43] for the thermal dehydration of the corresponding complexes with salicylic (SA) and 4-amino-salicylic (4ASA) acids The earlier [42,43] kinetic and thermodynamic parameters for SA and 4ASA complexes are given in Table 7 The data obtained for 5SSA complexes in the present study are also included in this table for comparison

A close look at Table 7 indicates that the thermal decomposition of 4ASA and 5SSA complexes is more complicated than that of the corresponding SA complexes This may be attributed to the structural complexities of 4ASA

TABLE 6

Kinetic and thermodynamic parameters of the thermal dehydration of bis-(5-sulphosalicylato)-diaquo complexes

Complex	$E^\star$	$H^\star$	$S^\star$	$G^\star$	K_r	Z
(I) $Cu(5SSA)_2\ 2H_2O$	22 227	21 313	−10 33	27 11	$3\ 33\times10^{-3}$	$6\ 22\times10^{7}$
(II) $Ni(5SSA)_2\ 2H_2O$	16 933	16 097	−13 76	22 89	$3\ 03\times10^{-3}$	$1\ 06\times10^{6}$
(III) $Co(5SSA)_2\ 2H_2O$	18 122	17 247	−13 43	24 06	$2\ 96\times10^{-3}$	$1\ 64\times10^{6}$
(IV) $Mn(5SSA)_2\ 2H_2O$	15 063	14 265	−14 88	21 21	$2\ 96\times10^{-3}$	$2\ 77\times10^{5}$
(V) $Fe(5SSA)_2\ 2H_2O$	16 557	15 721	−14 15	22 97	$2\ 96\times10^{-3}$	$6\ 75\times10^{5}$
(VI) $VO(5SSA)_2\ 2H_2O$	24 346	23 194	−09 50	28 83	$3\ 33\times10^{-3}$	$1\ 69\times10^{8}$

Key $E^\star$ = energy of activation (kcal mol^{-1}), $H^\star$ = enthalpy of activation (kcal mol^{-1}), $S^\star$ = activation entropy (e u), $G^\star$ = free energy of activation (kcal mol^{-1}), K_r = specific reaction rate (s^{-1}), Z = frequency factor (s^{-1})

and 5SSA moieties Further, the difference in decomposition temperature of 4ASA and 5ASA complexes in comparison to SA complexes could be due to the difference in the ionic character of the metal–ligand bond brought about by complex formation The quantitative estimate of this can be obtained by the comparison of various kinetic and thermodynamic parameters listed in Table 6

A perusal of Table 7 shows that, in general, the thermal stability of the complexes follows the following sequence

M–5SSA > M–4ASA > M–SA

which is in accordance with the protonation constants and the corresponding formation constants of the metal complexes of SA, 4ASA and 5SSA moieties [44]

Analysis of intermediate products and residues, and their identification

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

TABLE 7

Comparison of the kinetic parameters ($E^\star$ and Z) in metal complexes of salicylic (SA), 4-amino-salicylic (4ASA) and 5-sulphosalicylic acids (5SSA)

Metal complexes	$E^\star$ (kcal mol^{-1})			Z (s^{-1})		
	SA	4ASA	5SSA	SA	4ASA	5SSA
Cu(II)	18 52	20 21	22 23	$1\ 00\times10^{6}$	$6\ 33\times10^{6}$	$6\ 22\times10^{7}$
Ni(II)	16 44	16 99	16 93	$2\ 30\times10^{5}$	$4\ 35\times10^{5}$	$1\ 06\times10^{6}$
Co(II)	16 68	17 48	18 12	$7\ 84\times10^{5}$	$7\ 71\times10^{5}$	$1\ 64\times10^{6}$
Mn(II)	14 56	14 53	15 06	$2\ 52\times10^{4}$	$1\ 38\times10^{5}$	$2\ 77\times10^{5}$
Fe(II)	14 90	14 33	16 56	$8\ 87\times10^{4}$	$4\ 38\times10^{4}$	$6\ 75\times10^{5}$
VO(II)	22 16	24 25	24 35	$5\ 76\times10^{7}$	$5\ 82\times10^{8}$	$1\ 69\times10^{5}$

temperatures and the residues were analysed Mean results of three determinations are listed in Table 1 A close look at the table indicates that both the water molecules are lost, giving dehydrated products Disappearance of characteristic bands due to coordinated water in the IR spectra of the samples further confirms the dehydration It is noteworthy that all the intermediate products of the thermal decomposition steps could not be isolated and identified owing to the lack of a clearcut horizontal on the TG curves

The final residue, in each case, appears to be the corresponding metal oxide The FT-IR spectra of the residues exhibit bands at 610(m), 500(s), 410(m), 570(sb), 385(mb), 600(s), 475(sb), 393(m), 650(w), 465(svb), 595(svb), 395(w), 288(w) and 650(s), 635(sh), 460(b) and 300(w) cm^{-1} indicating the formation of CuO, Fe_3O_4, Mn_3O_4, NiO, V_2O_5 and Co_3O_4 as in the corresponding bis-(4-aminosalicylato)-diaquo complexes of transition metal ions [51-53]

The X-ray *K*-absorption spectra obtained for the residues left in the thermal decomposition of Cu and Co complexes were identical with those for CuO and Co_3O_4, further confirming the formation of oxide as the end product

X-ray K*-absorption as a probe to investigate the changes in stereochemistry as a consequence of thermal decomposition*

In our earlier communications [6-8] we have used optical spectra as a probe for investigating the changes in stereochemistry which are likely to occur during thermal decomposition However, we observed that the optical method is not a suitable probe, particularly in investigating the stereochemistry of Cu(II), Co(II) and Fe(II) complexes As an alternative, it was found that the X-ray *K*-absorption is the most suitable probe in deciding the changes in stereochemistry

In the present study only Cu(II) and Co(II) complexes and their dehydrated products were considered and their X-ray K-absorption studied before and after thermal degradation The details of this study will be communicated elsewhere However, it is worth noting that X-ray *K*-absorption spectra of chelates of Cu(II) and Co(II) with 5SSA, before thermal dehydration, resemble type Ia curves of Van Nordstrand [54] indicating octahedral stereochemistry in each case The spectra obtained for dehydrated products, however, resemble closely type IVb curves, normally obtained for compounds with tetrahedral stereochemistry The splitting of the principal absorption edge, in each case, into two components, K and K_1, further confirms tetrahedral stereochemistry [55-59] The X-ray *K*-absorption discontinuities, therefore, suggest that both Cu(II) and Co(II) ions are octahedrally surrounded in the hydrous complexes, while in the dehydrated products the surrounding of the ions is tetrahedral Thus, X-ray *K*-absorption provides a better method of distinguishing between octahedral and tetrahedral surroundings of metal ions in chelates

It is interesting to note that the edge-widths of the dehydrated products are greater than that of the chelates containing coordinated water molecules These results reveal the lowering of stereochemistry from octahedral to tetrahedral [58] as a consequence of the thermal dehydration The same conclusion can be drawn by comparing the corresponding chemical shifts According to Glen and Dodd [60] chemical shifts 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 in present case are in fair agreement with these findings

CONCLUSIONS

Results of this study on thermal decomposition of 5-sulphosalicylic acid (5SSA) complexes showed that thermal analyses can be useful for the determination of the number of molecules of water bound to a metal ion, for detecting contamination of starting reagents, for estimating stereochemistry and for investigation into the composition of a compound It also provides a means for correlation of the changes in stereochemistry with thermal degradation

The knowledge of heating curves is useful for gravimetric analysis of a compound For quantitative analysis of the compound studied, a horizontal formed at the first and the last stage of decomposition, i e dehydration and oxide level, is only suitable Particularly, the latter is of great quantitative importance

The study also indicates that the thermal dehydration follows first-order kinetics and that it is governed by a linear kinetic compensation law

During thermal dehydration, the octahedral stereochemistry changes to tetrahedral, and the final residues are the corresponding metal oxides It is now confirmed that X-ray *K*-absorption is a better probe than optical spectra for elucidating the changes in stereochemistry as a consequence of thermal dehydration

Finally, it can be concluded that the activation energy of the thermal dehydration decreases in the order VO(II) > Cu(II) > Co(II) > Ni(II) > Fe(II) > Mn(II)

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