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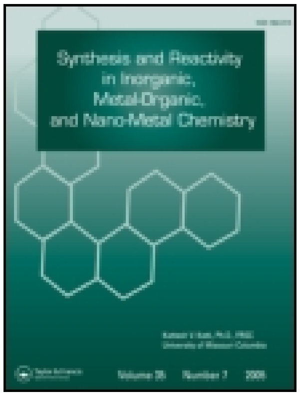

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PREPARATION AND THERMAL STUDY OF NEW COMPLEXES OF SALICYLIDENE-2-AMINOTHIOPHENOL SCHIFF BASES

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PREPARATION AND THERMAL STUDY OF NEW COMPLEXES OF SALICYLIDENE-2-AMINOTHIOPHENOL SCHIFF BASES

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ABSTRACT

New complexes of the Schiff base salicylidene-2-aminothiophenol with VO(IV), Co(II), Ni(II), Cu(II) and Zn(II) have been synthesized and studied by thermogravimetric analysis and a general scheme of thermal decomposition of these complexes is proposed. The thermal dehydration and decomposition of these complexes were studied kinetically using the integral method applying the Coats-Redfern equation. It was found that the thermal decompositions of the complexes follow first order kinetics. The thermodynamic parameters of the decomposition are also reported.

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INTRODUCTION

A large number of Schiff bases and their complexes have been studied for their interesting and important properties, *e.g.*, their ability to reversibly bind oxygen,[1] catalytic activity in the hydrogenation of olefins[2] and transfer of an amino group,[3] photochromic properties,[4] complexing ability towards some toxic metals[5] and so on. Metal complexes of Schiff bases derived from substituted salicylaldehydes and various amines have been widely investigated.[6–13] However, little attention has been given to Schiff bases which include the ONS donor system.

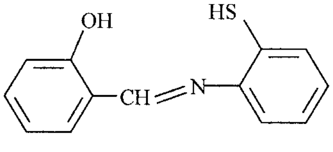
The aim of the present work is to synthesize and study the chelate formed between salicylidene-2-aminothiophenol, the Schiff base H_2L (Fig. 1), and vanadyl(IV), cobalt(II), nickel(II), copper(II) and zinc(II) ions using thermogravimetric analysis.

EXPERIMENTAL

All chemicals used in this work were of analytical grade from BDH. Vanadyl sulfate·$3/2H_2O$, cobalt acetate hexahydrate, copper acetate, nickel chloride hexahydrate or zinc acetate were used as the metal salts. The organic solvents used were obtained as pure-grade materials from BDH or purified by the recommended methods.[14]

Preparation of the Schiff Base H_2L

The title Schiff base (H_2L) was prepared by a condensation reaction between 0.05 mole of salicylaldehyde (6.10 g, 5.24 mL, d = 1.164) with 0.05 mole of *o*-aminothiophenol (6.23 g) 5.31 mL d = 1.179) in 100 mL



H_2L

Figure 1. Salicylidene-2-aminothiophenol Schiff base H_2L.

ethanol. The ethanolic solution was refluxed for two hours, left to cool and the solid Schiff base obtained was filtered, washed several times with alcohol then ether and dried. The Schiff base was recrystallized from 50% acetic acid to a sharp melting point; m.p. 128 °C (lit.[9] m.p: 128 °C).

Preparation of Complexes

The solid complexes of the Schiff base H_2L with the divalent VO(IV), Co(II), Ni(II), Cu(II) and Zn(II) metal salts were prepared by mixing 5.0 mmole of the metal salt with the requisite amount of Schiff base (1.145 g, 5 mmole or 2.29 g, 10 mmole) to form 1:1 (M:L) or 1:2 (M:HL) complexes, respectively. The reagents were dissolved in 250 mL of 80% v/v ethanol water whose pH had been adjusted to 5.0–6.0 with alcoholic ammonium hydroxide. The solution was refluxed for 2 h and then evaporated under vacuum to 100 mL and cooled overnight to precipitate the solid complexes which were filtered and washed several times with ethanol until the filtrate became colorless.

Measurements

The isolated complexes were characterized by elemental micro-analyses. The C, H, N and S analyses were repeated twice. The metal contents in the complexes were determined by the method of MacDonald.[15] The conductimetric measurements were carried out in DMF using a model CM-1K TOA conductivity bridge. The thermal analyses of the complexes were carried out using a Shimadzu thermogravimetric analyzer with a TGA-50H detector in nitrogen atmosphere (flow rate = 30.0 mL/min). The % weight loss was measured from ambient temperature up to 800 °C at a heating rate of 10 °C/min.

RESULTS AND DISCUSSION

The Schiff base (H_2L) complexes with VO(IV), Co(II), Ni(II), Cu(II) and Zn(II) ions were prepared by refluxing the appropriate amount of vanadyl sulphate·3/2 H_2O, cobalt acetate hexahydrate, copper acetate, nickel chloride hexahydrate or zinc acetate and the Schiff base synthesized by the condensation of salicylaldehyde and 2-aminothiophenol (Fig. 2).

The results of elemental analyses of the Schiff base H_2L complexes are listed in Tables I and II. These results are in good agreement with those

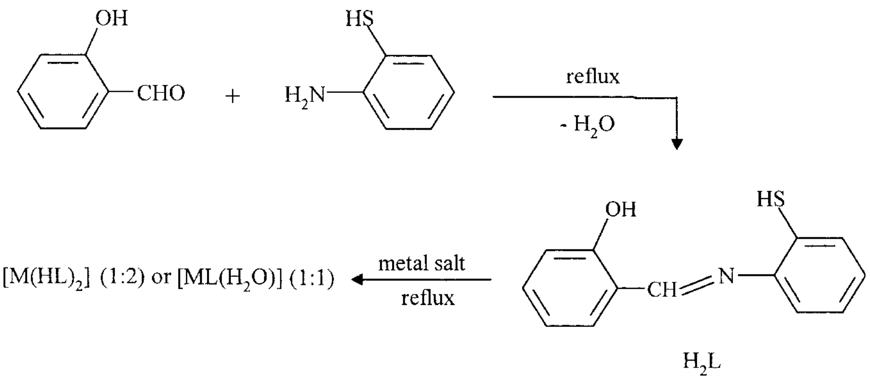


Figure 2. Scheme of the formation of the Schiff base H_2L and its metal complexes.

required by the proposed formulae. The metal percentage found is an average value of the metal content determination[15] and thermal analysis (% metal oxide residue).

Electrical conductivities of the complexes in DMF (0.001 M) lie in the 1.23–3.75 $\mathrm{S\,cm^{-2}\,mol^{-1}}$ range, indicating their non-electrolytic nature. For the 1:1 complexes, the chelation is brought about by proton displacement from the phenolic OH and thiophenolic SH groups to satisfy the divalency of the metal ions. On the other hand, the 1:2 complexes may be formed through proton displacement of the two phenolic OH groups only and the two SH groups may form two coordinate bonds to the metal without proton displacement[16] (Fig. 3).

Thermogravimetric Analysis

In the present investigation, heating rates were suitably controlled at 10 $\mathrm{°C\,min^{-1}}$ under a nitrogen atmosphere and the weight loss was measured from ambient temperature up to 800 °C. The TG (and DTG) curves are represented in Fig. 4. The weight losses for each chelate were calculated for the corresponding temperature ranges and are shown in Tables III and IV. The metal percentages calculated from the metal oxide residues were compared with those determined by the analytical metal content determination.[15]

The hydration water molecules are associated with complex formation and found outside the coordination sphere formed around the central metal ion. The dehydration of this type of water takes place in the temperature

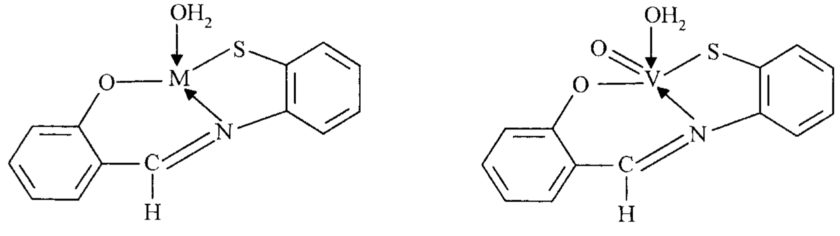
Table I. Elemental Analyses of the Schiff Base H_2L and Its 1:1 Metal Chelates

					Analyses Found (Calcd.), %				
Complex	Empiricial Formula	Formula Weight	Yield (%)	Melting Point (°C)	C	H	N	S	M
H_2L	$C_{13}H_{11}NOS$	229.296	98	128	67.80 (68.10)	4.82 (4.84)	6.30 (6.11)	13.94 (13.98)	–
$[VOL(H_2O)]$	$C_{13}H_{11}NO_3SV$	311.94	90	331	50.20 (50.00)	3.30 (3.53)	4.37 (4.49)	10.12 (10.26)	16.30 (16.35)
$[CoL(H_2O)]$	$C_{13}H_{11}CoNO_2S$	303.93	92	366	51.50 (51.33)	3.67 (3.62)	4.56 (4.61)	10.61 (10.53)	19.19 (19.39)
$[NiL(H_2O)]$	$C_{13}H_{11}NNiO_2S$	303.70	89	291	51.00 (51.37)	3.70 (3.62)	4.30 (4.61)	10.20 (10.54)	19.86 (19.33)
$[CuL(H_2O)]$	$C_{13}H_{11}CuNO_2S$	308.55	95	270	51.00 (50.56)	3.45 (3.57)	4.89 (4.54)	10.18 (10.37)	20.41 (20.60)
$[ZnL(H_2O)]$	$C_{13}H_{11}NO_2SZn$	310.38	93	304	50.30 (50.26)	3.51 (3.54)	4.48 (4.51)	10.29 (10.31)	20.86 (21.06)

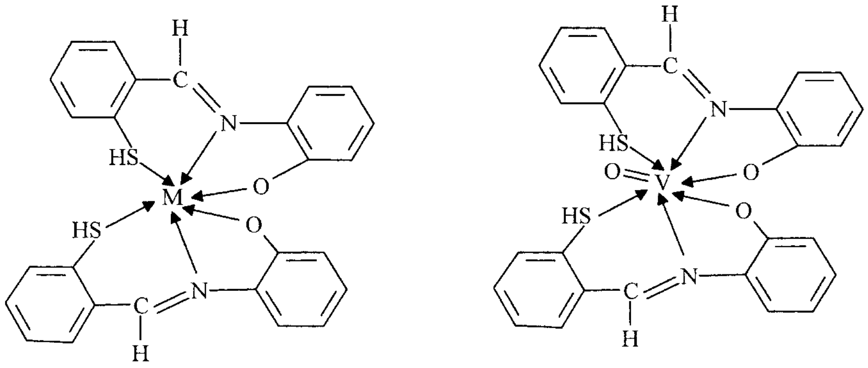
Table II. Elemental Analyses of the Schiff Base H_2L and Its 1:2 Metal Chelates

Complex	Empiricial Formula	Formula Weight	Yield (%)	Melting Point (°C)	Analyses Found (Calcd.), %				
					C	H	N	S	M
$[VO(HL)_2]$	$C_{26}H_{20}N_2O_3S_2V$	522.94	87	213	59.20	4.00	5.40	12.16	9.83
					(59.66)	(3.82)	(5.35)	(12.24)	(9.74)
$[Co(HL)_2]\cdot H_2O$	$C_{26}H_{22}CoN_2O_3S_2$	532.93	85	288	57.95	4.06	5.05	12.12	11.00
					(58.54)	(4.13)	(5.25)	(12.01)	(11.05)
$[Ni(HL)_2]$	$C_{26}H_{20}N_2NiO_2S_2$	514.70	82	271	59.85	3.82	5.38	12.35	11.32
					(60.06)	(3.86)	(5.44)	(12.43)	(11.40)
$[Cu(HL)_2]$	$C_{26}H_{20}CuN_2O_2S_2$	519.55	90	223	60.00	3.75	5.42	12.41	12.19
					(60.05)	(3.85)	(5.39)	(12.32)	(12.23)
$[Zn(HL)_2]$	$C_{26}H_{20}N_2O_2S_2Zn$	521.38	90	210	59.30	3.81	5.29	12.21	12.48
					(59.84)	(3.84)	(5.37)	(12.28)	(12.54)

Calculated values are given between parentheses.



M = Co(II), Ni(II), Cu(II) and Zn(II)



M = Co(II), Ni(II), Cu(II) and Zn(II)

Figure 3. The suggested structures of the Schiff base complexes (water of hydration is excluded).

range 50–160 °C. The dehydration step for the Co(II) complex (1:2) was found in the temperature range 54–130 °C. The weight loss corresponds to one water molecule. On the other hand, the coordinated water molecules are eliminated at higher temperatures than the water molecules of hydration. The water of coordination is usually eliminated in the temperature range[8,17] 150–250 °C. This is found in the case of VO(IV) (1:1), Ni(II) (1:1), Co(II) (1:1), Cu(II) (1:1) and Zn(II) (1:1) complexes in which the dehydration took place in the temperature range 128–327 °C.

The organic part of the complexes may decompose in one or more steps with the possibility of the formation of one or two intermediates. These intermediates may include the metal ion with a part of the Schiff base in case of the 1:1 or 1:2 complexes.[16] These intermediates may finally decompose to stable metal oxides.

The [VOL(H_2O)], [CoL(H_2O)], [NiL(H_2O)], and [ZnL(H_2O)] complexes were found to decompose in three steps. The first decomposition step

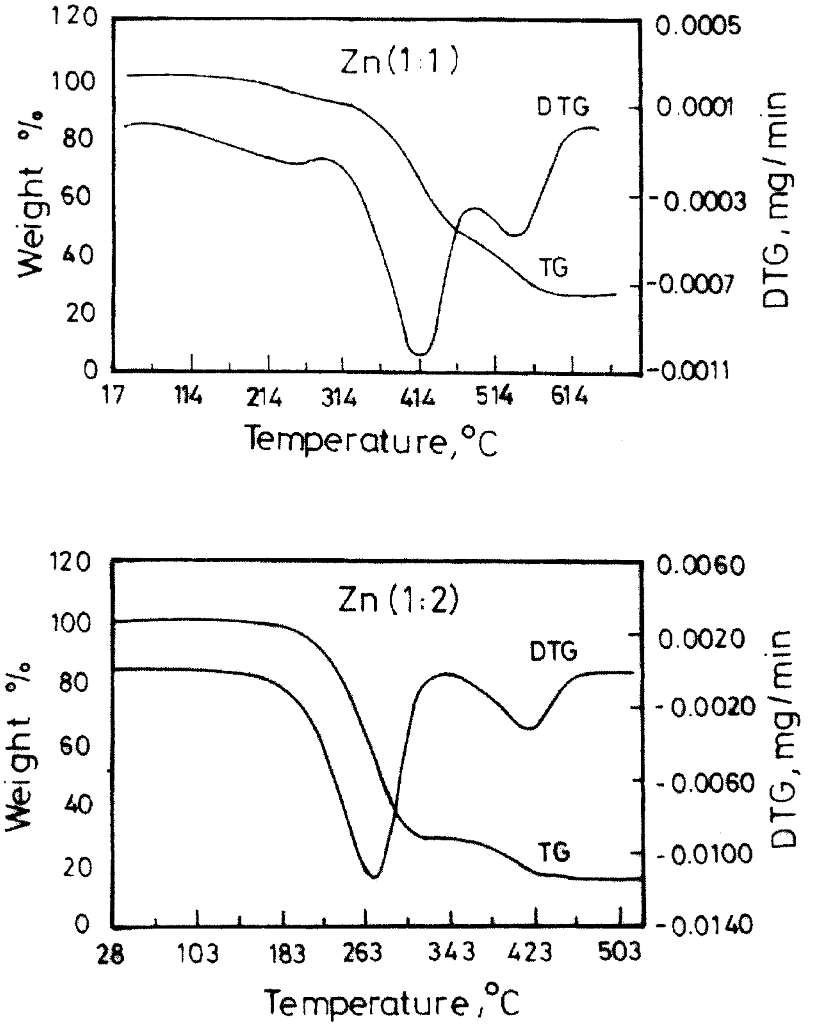


Figure 4. TG and DTG curves of Zn(II) complexes.

was in the temperature range 291–477 °C and the second decomposition step in the temperature range 445–804 °C. The decomposition of the [CuL(H_2O)] complex was completed after three decomposition steps in the temperature ranges 270–380, 414–487 and 514–590 °C.

The [VO(HL)$_2$], [Co(HL)$_2$]·H_2O, [Ni(HL)$_2$] and [Zn(HL)$_2$] complexes were found to decompose in two steps in the temperature ranges 210–465 °C

Table III. Thermal Analysis Data of the Schiff Base 1:1 Chelates

	Dehydration Stage					Oxide Formation				
		%H_2O Loss							% Metal	
Formula	Temp. Range; °C	Calc.	Found	No. of H_2O mol.	Decomp. Stage °C	Temp. °C	% Residue	Oxide Form	Calc.	Found
[VOL(H_2O)]	219–316	5.8	5.7	1	331–412 450–570	570	26.85	VO_2	16.38	16.50
[CoL(H_2O)]	100–170	5.9	5.6	1	366–477 545–804	804	24.31	CoO	19.39	19.12
[NiL(H_2O)]	128–240	5.9	5.7	1	291–346 445–501	575	25.45	NiO	19.33	20.00
[CuL(H_2O)]	207–267	5.8	5.7	1	270–380 414–487 514–590	590	45.55	Cu_2O	20.60	20.23
[ZnL(H_2O)]	150–290	4.85	4.80	1	304–427 488–590	590	26.03	ZnO	21.06	20.91

Table IV. Thermal Analysis Data of the Schiff Base 1:2 Chelates

	Dehydration Stage					Oxide Formation				
		% H_2O Loss							% Metal	
Formula	Temp. Range; °C	calc.	found	No. of H_2O mol.	Decomp. Stage°C	Temp. °C	% Residue	Oxide form	Calc.	Found
$[VO(HL)_2]$	–	–	–	–	213–462 496–600	600	16.30	VO_2	9.74	10.01
$[Co(HL)_2]{\cdot}H_2O$	54–130	3.3	3.0	1	288–465 525–650	650	14.46	CoO	11.06	11.37
$[Ni(HL)_2]$	–	–	–	–	271–450 496–660	660	14.38	NiO	11.28	11.30
$[Cu(HL)_2]$	–	–	–	–	223–367 407–445 461–530	530	27.25	Cu_2O	12.23	12.10
$[Zn(HL)_2]$	–	–	–	–	210–311 366–460	460	15.41	ZnO	12.54	12.38

and 366–660 °C. The $[Cu(C_{13}H_{10}NOS)_2]$ complex decomposed in three steps in the temperature ranges 223–367, 407–445 and 461–530 °C. The weight losses with their suggested formulae are given in Table V.

The decomposition of all complexes ended with oxide formation. The oxides were found to be stoichiometric oxides (Tables III and IV). The metal content percentages of the complexes were calculated from the corresponding stoichiometric metal oxides formed in the final step and compared with those obtained from the metal content as determined by microanalysis.[17] The average metal percentages were found to be in good agreement with those calculated from the tentative formulae based on the elemental analyses.

The initial decomposition and inflection temperatures have been used as an indication of the thermal stability of the complexes.[18] On the basis of the data of Tables III and IV, the relative thermal stability of the complexes may be given as $[Zn(HL)_2] < [VO(HL)_2] < [Cu(HL)_2] < [Ni(HL)_2] < [Co(HL)_2]{\cdot}H_2O < [CuL(H_2O)] < [NiL(H_2O)] < [ZnL(H_2O)] < [VOL(H_2O)] < [CoL(H_2O)]$. The relative lower temperature assigned to the first step decomposition for the 1:2 complexes may be attributed to the presence of two organic ligands around the metal ion.

On the basis of the above observations, general schemes of thermal decomposition may be proposed for the Schiff base, $[VOL(H_2O)]$, $[VO(HL)_2]$, $[CoL(H_2O)]$, $[Co(HL)_2]{\cdot}H_2O$, $[NiL(H_2O)]$, $[Ni(HL)_2]$,and $[ZnL(H_2O)]$ complexes (Fig. 5). For $[CuL(H_2O)]$ and $[Cu(HL)_2]$ there are three decomposition steps (233–380, 407–487 and 461–590 °C) with the formation of two intermediates (367–414 and 445–514 °C).

Kinetics of Thermal Decomposition of Complexes

Determination of Reaction Order of Decomposition

The Horowitz and Metzger[19] equation, $C_s = (n)^{1/1-n}$, where C_s is the weight fraction of the substance present at the DTG peak temperature, T_s, and given by

$$C_s = (W_s - W_\infty)/(W_0 - W_\infty) \qquad (1)$$

was used for the determination of the values of the reaction order. Here W_s stands for the weight remaining at a given temperature T.

For the DTG peak temperatures, W_0 and W_∞, are the initial and final weights of the substance, respectively. It was reported that the first order

Table V. The Temperature Ranges and the Suggested Formulae of the Intermediates

Complex	Mol. Wt	Intermediate Formation			
		Intermediate Range	%Weight Loss	Molecular Weight	Suggested Formula
[VOL(H_2O)]	311.94	412–450	44.86	140.00	C_6H_6NOS
[CoL(H_2O)]	303.93	477–545	50.02	152.00	C_7H_6NOS
[NiL(H_2O)]	303.7	346–445	39.52	119.00	C_7H_5NO
[CuL(H_2O)]	308.55	380–414	22.04	49.00	HOS
		487–514	59.26	152.00	C_7H_6NOS
[ZnL(H_2O)]	310.38	427–488	55.05	170.00	$C_{12}H_{10}O$
[VO(HL)$_2$]	522.94	462–496	60.19	315.00	$C_{20}H_{13}NOS$
[Co(HL)$_2$]·H_2O	532.93	465–525	62.34	333.00	$C_{20}H_{15}NO_2S$
[Ni(HL)$_2$]	514.70	450–496	41.10	211.00	$C_{13}H_9NS$
[Cu(HL)$_2$]	519.55	367–407	20.93	109.00	C_6H_5S
		445–461	41.35	211.00	$C_{13}H_9NS$
[Zn(HL)$_2$]	521.38	311–366	69.61	363.00	$C_{20}H_{15}N_2OS_2$

For 1:1 Complexes

$$[ML{\cdot}H_2O] \xrightarrow[100\text{-}316\ °C]{-H_2O} [ML] \xrightarrow[270\text{-}510\ °C]{\text{partial decomposition}} \text{intermediate}$$

$$\xrightarrow[400\text{-}804\ °C]{\text{final decomposition}} \text{metal oxides}$$

For 1:2 complexes

$$[M(HL)_2]{\cdot}H_2O \xrightarrow[54\text{-}130\ °C]{-H_2O} [M(HL)_2]^{a} \xrightarrow[210\text{-}495\ °C]{\text{partial decomposition}} \text{intermediate}$$

$$\xrightarrow[322\text{-}660\ °C]{\text{final decomposition}} \text{metal oxide}$$

[a] the dehydration step is proposed for the Co (1:2) complex only.

Figure 5. The proposed schemes of the thermal decomposition of the Schiff base complexes.

reaction has a C_s value of 0.368 and the second order one has a C_s value of 0.5.[19] The values of C_s for the thermal decomposition of the Schiff base complexes are in the range 0.30—0.39 which indicates that the decomposition follows first order kinetics.

Integral Method Using the Coats-Redfern Equation[20]

For a first order process the Coats-Redfern equation may be written in the following form:

$$\log\left[\frac{\log(W_f/(W_f - W))}{T^2}\right] = \log\left[\frac{AR}{\theta E*}\left(1 - \frac{2RT}{E*}\right)\right] - \frac{E*}{2.303\,RT} \qquad (2)$$

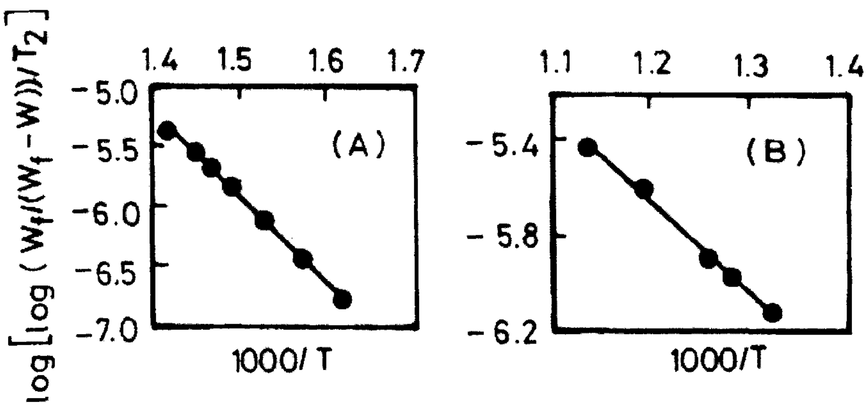


Figure 6. Coats-Redfern plots of the first (A) and second (B) decomposition steps of [ZnL(H_2O)].

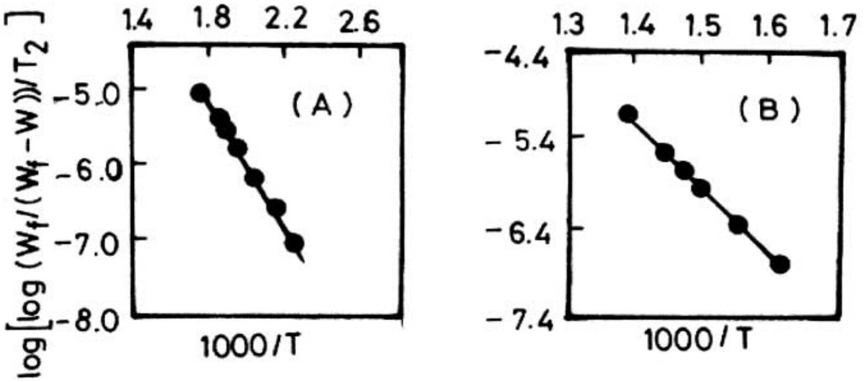


Figure 7. Coats-Redfern plots of the first (A) and second (B) decomposition steps of [Zn(HL)$_2$].

where W_f is the mass loss at the completion of the reaction, W is the mass loss up to temperature T, W_r is the mass remaining at temperature T; ($W_r = W_f - W$), R is the gas constant, E* is the activation energy in $Jmol^{-1}$, θ is the heating rate. Since $1-(2RT)/E^* \cong 1$, a plot of the left-hand side of Eq. (2) against 1/T was drawn (Figs. 6, 7) and E* was calculated from the slope and A (Arrhenius constant) was found from the intercept.

The activation entropy S*, the activation enthalpy H* and the free energy of activation G* were calculated using the following equations:

Table VI. Kinetic Data of the Thermal Decomposition of the Schiff Base 1:1 Complexes

Complex	Decomp. Steps °C	E* kJ mol^{-1}	R^2	A S^{-1}	S* J K^{-1} mol^{-1}	H* kJ mol^{-1}	G* kJ mol^{-1}	Cs
[VOL(H_2O)]	291–439	169.27	0.991	8.2×10^{12}	−0.51	163.80	164.14	0.33
	439–570	150.68	0.998	2.4×10^{9}	−8.83	144.13	151.08	0.34
[CoL(H_2O)]	366–387	98.81	0.988	4.0×10^{6}	−15.11	92.97	103.57	0.36
	529–804	96.71	0.993	2.4×10^{4}	−20.51	88.90	108.14	0.37
[NiL(H_2O)]	350–470	256.81	0.984	2.37×10^{16}	7.248	250.12	244.28	0.33
	470–575	255.21	0.980	9.16×10^{22}	22.76	250.44	237.40	0.35
[CuL(H_2O)]	270–390	108.48	0.998	2.81×10^{8}	−88.89	103.54	156.26	0.33
	400–510	142.45	0.998	3.07×10^{9}	−8.52	136.36	142.59	0.32
	510–590	156.67	0.991	1.9×10^{9}	−9.10	149.89	157.31	0.36
[ZnL(H_2O)]	304–467	90.90	0.999	2.37×10^{6}	−15.60	85.30	95.80	0.36
	467–590	169.34	0.994	2.04×10^{10}	−6.70	162.80	168.06	0.37

Table VII. Kinetic Data of the Thermal Decomposition of the Schiff Base 1:2 Complexes

Complex	Decomp. Steps °C	E* KJ mol^{-1}	R^2	A S^{-1}	S* J K^{-1} mol^{-1}	H* kJ mol^{-1}	G* kJ mol^{-1}	C_s
$[VO(HL)_2]$	213–478	131.1	0.997	2.55×10^{9}	−8.63	125.45	131.31	0.32
	478–600	181.94	0.989	1.17×10^{11}	−4.98	175.19	179.23	0.36
$[Co(HL)_2]\cdot H_2O$	288–495	126.34	0.998	8.98×10^{8}	−9.69	120.61	127.28	0.35
	497–650	139.79	0.992	4.66×10^{7}	−12.87	132.62	143.72	0.39
$[Ni(HL)_2]$	271–479	138.75	0.984	3.13×10^{10}	−6.12	133.08	137.26	0.36
	479–660	110.67	0.992	2.08×10^{6}	−15.96	103.63	117.13	0.34
$[Cu(HL)_2]$	223–398	189.58	0.992	2.51×10^{15}	5.26	184.10	181.10	0.35
	398–460	518.38	0.971	1.52×10^{38}	57.61	512.53	472.03	0.37
	460–530	134.02	0.969	3.01×10^{8}	−10.88	127.68	135.97	0.38
$[Z(HL)_2]$	210–322	78.46	0.999	1.39×10^{7}	−13.61	74.49	81.80	0.36
	322–460	144.24	0.999	3.66×10^{10}	−6.06	138.55	142.70	0.38

$R^2 =$ Correlation coefficient of the fitted straight line.

$$S{*} = 2.303\left(\log\frac{Ah}{KT}\right)R \tag{3}$$

$$H{*} = E{*} - RT \tag{4}$$

$$G{*} = H{*} - T_sS{*} \tag{5}$$

where K and h are the Boltzman's and Plank's constants, respectively. The calculated values of E*, A, S*, H* and G* for the dehydration and the decomposition steps are given in Tables VI and VII.

The activation energies of decomposition were found to be in the range 78–518 $kJmol^{-1}$. The high values of the activation energies reflect the thermal stability of the complexes. The entropy of activation was found to have negative values for almost all of the complexes, which indicates that the decomposition reactions proceed at a lower rate. The positive values of the entropy of activation for $[NiL(H_2O)]$ and $[Cu(HL)_2]$ indicate that the decomposition of these two complexes occurs at a higher rate than that of the other complexes.

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