

Thermochemical behaviour of α -salicylidene- α -valine and its complexes with cobalt and nickel

M.E.M. Emam, I.M.M. Kenawy *, M.A.H. Hafez

Chemistry Department, Faculty of Science, Mansoura University, Mansoura, Egypt

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Abstract

Salicylidene- α -valine (KHL) and its complexes with Co(II) and Ni(II) of molecular formulae $[\text{CoL}(\text{H}_2\text{O}) \cdot \text{Cl}]$ and $[\text{NiLCl}]$, where H_2L is $\text{C}_6\text{H}_4(\text{OH})\text{CH}=\text{N}-\text{CH}(\text{COOH})-\text{CH}(\text{CH}_3)_2$ and M is Co(II) or Ni(II), were prepared, isolated and characterized by elemental analysis, IR spectroscopy, electronic spectroscopy (UV and visible) and magnetic measurements, and their thermochemical behaviour was studied by thermogravimetry (TG) and differential thermal analysis (DTA). The kinetic and thermodynamic parameters n , ΔE_a , ΔH° , ΔG° and ΔS° , which are the order of the decomposition reaction, the activation energy, and the enthalpy, free energy and entropy change, respectively, were calculated using the TG and DTA curves.

Keywords: Activation energy; Cobalt compound; DTA; Nickel compound; Salicylidene valine; TG

1. Introduction

In spite of the large number of studies reported on the thermal analysis of coordination compounds, there are relatively few reports on the calculation of kinetic and thermodynamic parameters and their relationships with the nature of the bonding in the compounds [1–6].

* Corresponding author.

The aim of the present work was to isolate and characterize a Schiff base derived from α -valine, and some of its metal complexes with Co(II) and Ni(II), and to study their thermal decomposition by analysis of the corresponding TG and DSC curves.

2. Experimental

The ligand (KHL) and metal complexes were prepared as described previously [7]. Their stoichiometry was confirmed by elemental analyses which were performed in the Microanalytical Unit, Mansoura University. The infrared spectra of the complexes using KBr discs and the electronic spectra of the complexes in DMF solution were recorded on a Perkin-Elmer 1430 spectrophotometer and a Perkin-Elmer Lambda 2 UV/VIS spectrophotometer respectively. Magnetic measurements were determined by the Gouy method using a Mettler balance, model HL52.

The thermal decomposition studies were carried out with a standard thermoanalyser, DT40 Shimadzu, Japan. The specimens were placed in a standard platinum crucible. The sample weight taken was 5 mg and the heating rate was 10 K min⁻¹.

3. Results and discussion

3.1. Proof of metal complex structures

The studied metal ions (Co(II) or Ni(II)) from 1:1 metal:ligand complexes with α -salicylidene- α -valine as ligand. The stoichiometries of the isolated complexes, together with some analytical and physical data, are given in Table 1, which includes the percentages of the elements as calculated on the basis of the suggested formulae. Comparison of both calculated and found percentages of the elements determined indicates that the composition of the prepared compounds agree with the suggested formulae.

The bands in the electronic spectra for the cobalt(II) and nickel(II) complexes and the magnetic moments of these complexes at room temperature are recorded in Table 1. The magnetic moment of 5.29 BM (Table 1) for [CoL(H₂O)₂Cl] complex agrees well the reported value [8]. The electronic bands observed at 14 710 cm⁻¹ due to the ${}^4T_{1g} \rightarrow {}^4A_{2g}(v_2)$ spin-allowed transition further support the proposed octahedral arrangement for the cobalt complex. The electronic spectrum of the [NiLCl] complex shows one strong band in the visible region at 15 270 cm⁻¹ due to the $T_1(F) \rightarrow T_1(P)$ transition. The weak band at 7500 cm⁻¹ (near-IR) is due to the $T_1(F) \rightarrow A_2$ transition. The occasional appearance of a green colour in the present tetrahedral nickel(II) complex is attributable to charge transfer absorption tailing into the visible region from the ultra-violet. The magnetic moment of 3.93 BM (Table 1) for the nickel(II) complex and the molar absorptivity of ≈ 198 dm³ mol⁻¹ cm⁻¹ at the peak of the visible band is a further support of the tetrahedral structure for the nickel complex [9,10].

Table 1
Analytical and physical data for α -salicylidene- α -valine and its cobalt(II) and nickel(II) complexes

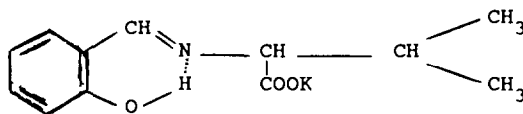
Compounds	Calculated (found)/%				Colour and shape	Magnetic moment, $\mu_{\text{eff}}/\text{BM}$	Ligand field bands ^a /cm ⁻¹
	C	H	N	M			
C ₂₀ H ₁₆ (OH)–CH=N–CH–(COOK)CH(CH ₃) ₂ (KHL)	55.79	5.60	5.40	–	Yellowish brown crystals	–	24390 (1.97 × 10 ⁴)
CoC ₁₁ H ₁₃ NO ₃ Cl(H ₂ O) ₂	(55.76)	(5.72)	(5.43)	–	Pale pink powder	5.29	32051 (2.9 × 10 ⁴) 16400 (325)
[CoL(H ₂ O) ₂ Cl]	39.12	3.85	4.15	17.47			
[NiC ₁₁ H ₁₃ NO ₃ Cl]	(39.10)	(3.84)	(4.16)	(17.44)	Pale green powder	3.93	14710 (320) 15270 (198)
[NiLCl]	43.82	4.31	4.65	19.49			
	(43.80)	(4.28)	(4.62)	(19.45)			

^a Molar extinction coefficient in parentheses, $\epsilon/(\text{mol dm}^{-3} \text{cm}^{-1})$.

Table 2
Important IR bands (cm^{-1}) of α -salicylidene- α -valine (KHL) and its complexes with cobalt and nickel

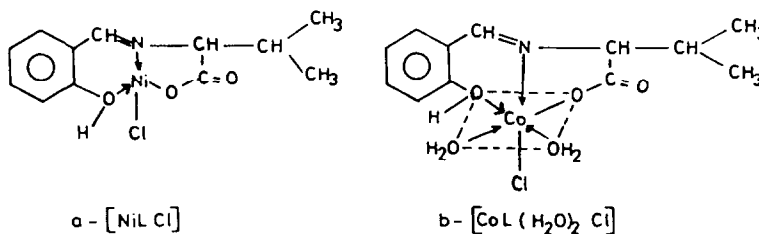
Compound	$\nu(\text{OH})$	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{N})$	$\delta(\text{OH})$	$\nu(\text{phenyl})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
KHL	3420	1635	1615	1325	765	—	—
$[\text{CoL}(\text{H}_2\text{O})_2\text{Cl}]$	3350	1645	1600	1300	760	505	335
$[\text{NiLCl}]$	3355	1650	1650	1315	755	600	400

The IR spectra of α -salicylidene- α -valine and its metal ion complexes were analysed and the most characteristic bands are listed in Table 2. The IR spectrum of the ligand shows a broad band at 3420 cm^{-1} and a series of bands in the range $3200\text{--}3100 \text{ cm}^{-1}$ which can be assigned to $\nu(\text{OH})$ and the combined mode $\nu(\text{NH})$ groups. The presence of $\nu(\text{OH})$ as a broad band at lower wavenumber suggests intramolecular hydrogen bonding, as shown in Structure 1; the spectrum also shows a broad band at 1325 cm^{-1} assigned to $\delta(\text{OH})$ [11].



Structure 1. KHL.

The IR spectra of the studied metal complexes exhibit characteristic bands corresponding to the $\text{C}=\text{N}$, $\text{C}=\text{O}$, OH and $\text{M}-\text{O}$ vibrations. The $(\text{C}=\text{N})$ band in the metal chelates is shifted to lower frequencies by $15\text{--}30 \text{ cm}^{-1}$ when compared to that of the ligand. The band at 3420 cm^{-1} which is attributed to the $\nu(\text{OH})$ group is also shifted to lower frequencies by $30\text{--}25 \text{ cm}^{-1}$. However, the $\nu(\text{C}=\text{O})$ band is shifted to higher frequencies by $15\text{--}10 \text{ cm}^{-1}$ due to the participation of the (COO^-) group in the complexation process. This observation confirms that the complexation occurs through the axomethine nitrogen, the hydroxy oxygen atom and the carbonyl oxygen atoms of the (COOH) group of the ligand. The new bands which appear at $400\text{--}335 \text{ cm}^{-1}$ and $505\text{--}500 \text{ cm}^{-1}$ in the IR spectra of the metal chelates are assigned to $\nu(\text{M}-\text{O})$ [12] and $\nu(\text{M}-\text{N})$ [13] vibrations respectively. The characteristic IR bands and their shift due to chelation are given in Table 2. The structure of the isolated complexes may be represented as in Structure 2.



Structure 2.

3.2. A study of the thermal decomposition of *N*-salicylidene- α -valine and its complexes

During the thermal decomposition of the ligand, *N*-salicylidene- α -valine (KHL), it appears that the obtained TG curve undergoes a series of thermal changes associated with a weight loss. Analysis of the obtained TG curve for the ligand is listed in Table 3. It is clear that the ligand undergoes a series of four decomposition steps starting at 110°C and finishing at 610°C. The first step is in the temperature range 110–235°C, accompanied by 26% weight loss, which may correspond to the evolution of propane gas and a half mole of carbon dioxide. The second, which occurs at 235–345°C, is considered to be due to the degradation of a half mole of salicylaldehyde. The third and the fourth steps, at 345–450°C and 450–610°C, correspond to the decomposition of the second half of the salicylaldehyde molecule and the evolution of a half mole of both carbon monoxide and nitric oxide gases. With a similar treatment, the TG curves of the Co(II) and Ni(II) complexes show four decomposition steps, as given in Table 3. The first step which occurs in the temperature range 105–185°C corresponds to the decomposition of the terminal group, $\text{CH}(\text{CH}_3)_2$, and the decarboxylation process. The second step which occurs at 185–280°C is considered to be due to the degradation of the salicylaldehyde molecule. The third and fourth steps at 280–370°C and 370–550°C correspond to the decomposition of the azomethine group and the metal ion–heteroatom bonds of the ligand, and to the evolution of nitric oxide gas. The final product is the metal oxide in each case (Table 3).

The quantitative treatment of the weight loss in each decomposition step is in good agreement with the proposed products produced in each step as given in Table 3. This means that the mechanism of the decomposition process of both metal complexes is similar.

Fig. 1 represents the obtained DTA curves for salicylidene- α -valine as Schiff base and its cobalt and nickel complexes; the curves show four characteristic peaks (Table 4). The endothermic peaks at 140, 180 and 290°C correspond to decomposition of the terminal group $\text{CH}(\text{CH}_3)_2$, decarboxylation and decomposition of the (N–M–O) group, respectively, while the exothermic peak at 220°C may be due to the liberation of NO gas as described in the third decomposition step.

In order to characterize the obtained TG curves, the kinetic parameters n and E_a of the thermal decomposition processes were obtained using the Coats–Redfern method [14]. A series of relationships $A = -\log\{[1 - (1 - \alpha)^{1-n}]/[T^2(1 - n)]\}$ vs $(1/T) \times 10^3$, where α and T are the rate of the thermal decomposition of the sample and the absolute temperature, respectively, were plotted for a number of assumed values of n . The correct value of n for the thermal decomposition process yields a straight line. The value of E_a is $2.303RS$, where R and S are the gas constant and the slope of the obtained straight line, respectively (see Fig. 2); the values obtained are listed in Table 5. It is clear that the order of the decomposition reactions for all cases is unity. This indicates that the decomposition reactions have the same mechanism. It is also obvious that the activation energies of the compounds fall in the order $\text{KHL} < \text{Co(II)L} < \text{Ni(II)L}$. This means that the stability of the com-

Table 3
Analysis of the obtained TG curves of α -salicylidene- α -valine and its complexes

Compound	Stage	Temperature range/ $^{\circ}$ C	Wt. loss/mg	Percentage wt. loss		Expected component/mole
				Found	Calcd.	
KHL	1st	110–235	1.30	26.0	25.50	Propane + 0.5 CO ₂
	2nd	235–345	1.15	23.0	23.35	0.5 Salicylaldehyde
	3rd	345–450	1.40	28.0	28.75	0.5 Salicylaldehyde + 0.5 NO
	4th	450–610 > 610	0.56 0.59	11.2 11.8	11.20 12.12	0.5 NO + 0.5 CO 0.33 K ₂ O
[CoL(H ₂ O) ₂ Cl]	1st	105–185	0.55	11.0	10.67	2 H ₂ O
	2nd	185–280	0.65	13.0	13.04	0.5 Propane + 0.5 CO ₂
	3rd	280–370	1.45	29.0	29.15	0.5 Salicylaldehydr + 0.5 NO
	4th	370–550 > 550	1.65 0.70	33.0 14.0	32.75 16.38	0.5 Salicylaldehydr + 0.5 Cl ₂ + 0.5 CO 0.33 Co ₂ O ₃
[NiLCI]	1st	105–190	0.65	13.0	14.0	0.33 Propane + 0.5 CO ₂
	2nd	190–280	0.55	11.0	11.3	0.67 Propane
	3rd	280–340	1.40	28.0	29.15	0.5 Salicylaldehyde + 0.5 NO
	4th	340–405 > 405	1.80 0.60	36.0 12.0	36.68 12.40	0.5 Salicylaldehyde + 0.5 Cl ₂ + 0.5 CO 0.5 NiO

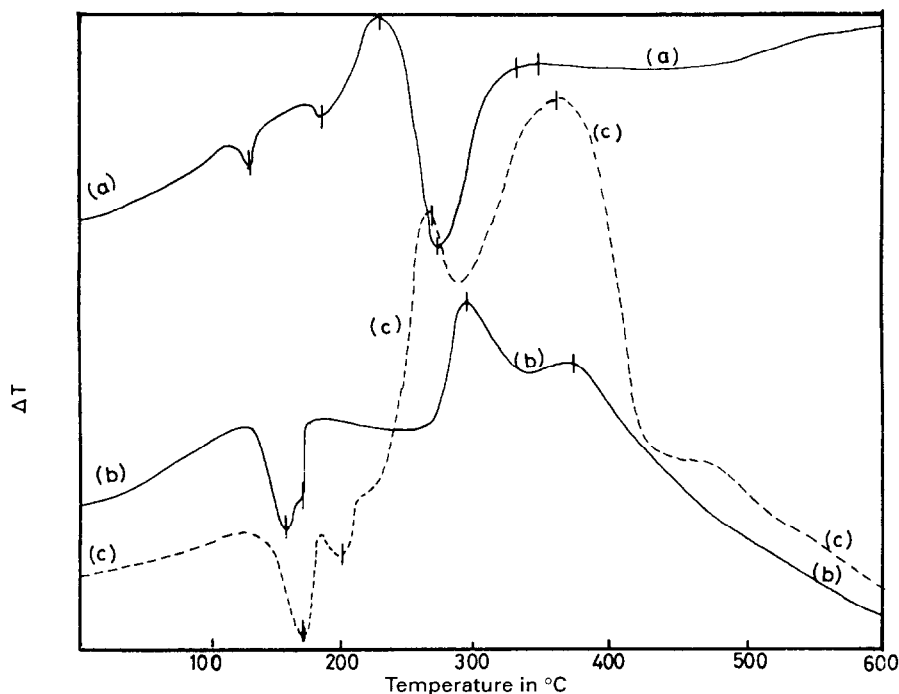


Fig. 1. DTA curves of α -salicylidene- α -valine (KHL) and its metal complexes: (a) KHL; (b) $[\text{Co-LCl}(\text{H}_2\text{O})_2]$; (c) $[\text{Ni-LCl}]$ complexes.

Table 4
Analysis of the obtained DTA curves of α -salicylidene- α -valine and its complexes

Compound	Endothermic		Exothermic	
	Shape	Position/ $^{\circ}\text{C}$	Shape	Position/ $^{\circ}\text{C}$
KHL	Sharp	140		
	Small	180	Broad, sharp	220
	Sharp	290		
$[\text{CoL}(\text{H}_2\text{O})_2\text{Cl}]$	Sharp, moderate	150	Broad, sharp	300
	Small, sharp	160	Small, sharp	380
$[\text{NiLCl}]$	Sharp, moderate	175	Broad, sharp	290
	Small, sharp	200	Small, sharp	380

pounds increases in this direction. Comparing the stability of the cobalt and nickel complexes, it is found that the latter complex is more stable than the former; E_a of the Ni-L complex is greater than E_a of the Co-L complex. This difference in the stability may be due to the difference in the covalent bond character of the Ni-heteroatoms of the ligand and the corresponding cobalt bonds. This is due to the higher electronegativity of the nickel ion which leads to a decrease in the

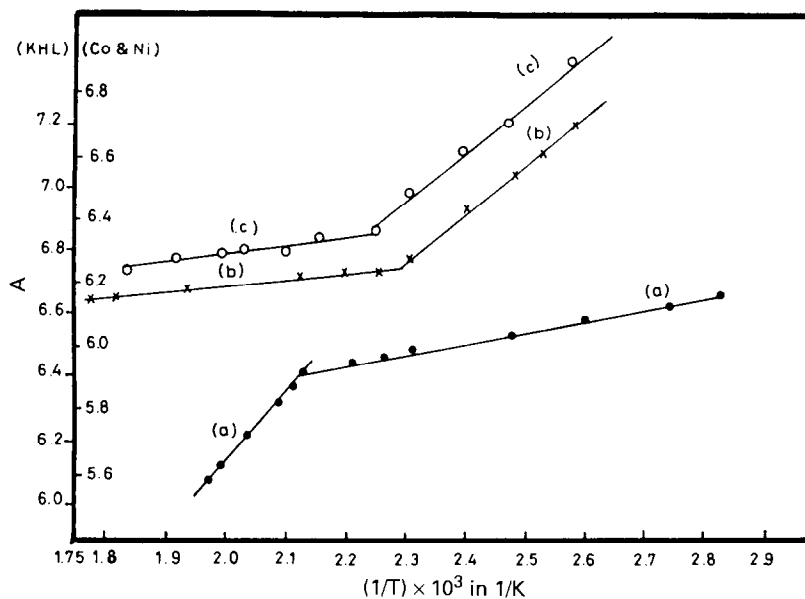


Fig. 2. Graphical determination of the order (n) and the activation energy of the thermal decomposition process (1st and 2nd steps) by the Coats-Redfern method. (a) α -Salicyldine- α -valine (KHL); (b) $[\text{CoLCl}(\text{H}_2\text{O})_2]$ complex; and (c) $[\text{Ni-LCl}]$ complex.

Table 5

Evaluated values of the kinetic and thermodynamic parameters for the thermal decomposition stages of α -salicylidene- α -valine and its complexes

Compound	Stage				
	1st	2nd	3rd	4th	Total
	E_{a1}	E_{a2}	E_{a3}	E_{a4}	$E_{\text{tot}}/(\text{kJ mol}^{-1})$
KHL	5.69	29.83	3.54	8.14	47.20
$[\text{CoL}(\text{H}_2\text{O})_2\text{Cl}]$	10.87	4.17	15.93	18.83	49.80
$[\text{NiLCl}]$	28.94	04.02	20.30	26.73	79.99
	ΔH_1°	ΔH_2°	ΔH_3°	ΔH_4°	$\Delta H_{\text{tot}}^\circ/(\text{kJ mol}^{-1})$
KHL	3.18	27.32	1.03	05.63	37.16
$[\text{CoL}(\text{H}_2\text{O})_2\text{Cl}]$	8.36	1.66	13.42	16.32	39.76
$[\text{NiLCl}]$	26.43	1.51	11.79	24.25	69.98
	$-\Delta G_1^\circ$	$-\Delta G_2^\circ$	$-\Delta G_3^\circ$	$-\Delta G_4^\circ$	$-\Delta G_{\text{tot}}^\circ/(\text{kJ mol}^{-1})$
KHL	52.59	47.67	37.41	42.14	179.8
$[\text{CoL}(\text{H}_2\text{O})_2\text{Cl}]$	48.28	37.35	44.53	41.33	171.49
$[\text{NiLCl}]$	48.75	41.61	45.78	45.49	181.62
	ΔS_1°	ΔS_2°	ΔS_3°	ΔS_4°	$\Delta S_{\text{tot}}^\circ/(\text{J K}^{-1} \text{mol}^{-1})$
KHL	187.16	251.64	128.99	160.03	727.82
$[\text{CoL}(\text{H}_2\text{O})_2\text{Cl}]$	190.00	130.92	194.49	193.47	708.88
$[\text{NiLCl}]$	252.27	144.70	213.31	234.03	844.31

electronegativity difference between the metal ion–heteroatoms bonds of the ligand and, hence, to an increase in the covalent bond character and more stability [15].

The thermodynamic parameters ΔH^\ominus , ΔG^\ominus and ΔS^\ominus for the thermal decomposition process were calculated from rate theory [16] and the obtained values are summarized in Table 5. From this table, it is clear that the values of $\Delta H_{\text{total}}^\ominus$ and $\Delta S_{\text{total}}^\ominus$ for all cases are positive, which means that the decomposition process is endothermic and is accompanied by an increase in the disorder of the system, because the number of decomposed fragments increases. However, the negative values of ΔG^\ominus indicate that the decomposition process is a spontaneous reaction; this may be due to the decrease in the free energy of the final residue. The obtained data in this study are in good agreement with similar findings given in the literature [17–21].

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