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Thermal behaviour of some salicylato(amine)cobalt(III) complexes

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Abstract

The thermal dissociation of a number of salicylato(amine)cobalt(III) complexes has been studied by thermogravimetry, differential temperature analysis, UV–visible spectral analysis of intermediates and XRD of the final products. The final decomposition product was found to be Co_3O_4. Dissociation of $[Co(en)_2(amine)salH](NO_3)_2$ passed through the intermediate $[Co(en)_2sal]$. The intermediate was characterised by UV–visible spectral analysis. The complexes containing chelating salicylate were found to be more stable than those with unidentate ligand and also more stable than unbound salicylic acid.

Keywords: DTA; Salicylato(amine)cobalt(III) complexes; TGA; UVs; XRD

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1. Introduction

The aquation of salicylato(amine)cobalt(III) complexes in solution with varying amine functions have been the subject of a number of investigations [1–5]. These studies indicate that the rate of aquation is dependent on the nature of the amine ligands attached to the cobalt(III) centre. Although there are some reports on thermal decomposition studies of complexes of the type $[CoA_2X_2]NO_3$, where A is en, phen or bipy and is X mono- or dicarboxylate [6–9], the thermal decomposition of salicylato(amine)cobalt(III), where salicylate acts as a unidentate or a bidentate ligand, has not been studied. Further, the loss of one amine ligand from $[Co(NH_3)_6]X_3$, $[Co(NH_3)_5X]Y_2$, $[Co(en)_2(amine)X]Y_2$ or $[Co(en)_3]Y_3$ (X, Y is halide), followed by entry of one outer sphere anion into the inner sphere, has been found in many cases [10–13]. However, there is no report of deamination reactions by coordinated carboxylates, although Horvath and Kristol [14] have reported that the decomposition of $[Co(NH_3)_5CO_3](NO_3)_2$ passes through an intermediate $[Co(NH_3)_4CO_3]NO_3$.

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In view of the above facts, we now report the thermal decomposition of salicylato(amine)cobalt(III) complexes to establish the effects of amine ligands and salicylate coordination (unidentate or bidentate) on their thermal decomposition behaviour.

2. Experimental

The complexes were prepared as their nitrate or chloride salts as described earlier [1-5]. Perchlorate salts were not used in order to avoid unacceptable noise in the recorded signal caused by sputtering phenomena. Sample purities were checked by analysis of the salts and from UV-visible spectral data, which were in good agreement with the theoretical values and those reported earlier [1-5]. All UV-visible spectra were recorded in 0.1 M $HClO_4$ solution except those indicated (Table 1). A JASCO model 7800 recording UV-visible spectrophotometer with matched quartz cells was used for spectral measurements. Thermograms were recorded using a Shimadzu DT-30 automatic thermal analyser with a heating rate of 10°C min^{-1} in static air.

Table 1
Spectral data of salicylato(amine)cobalt(III) complexes[a]

Complex No.	Complex	λ_{max} (ε in $dm^3\,mol^{-1}\,cm^{-1}$)		Ref.
		Found	Reported	
Group I				
1	$[Co(NH_3)_5salH](NO_3)_2 \cdot H_2O$	235(20790) 298(4410) 510(80.4)	235(20800) 298(4417) 510(82.4)	[1]
2	($\alpha\beta s$)-$[Co(tetren)salH](NO_3)_2$	298(4220) 491(172)	298(4318) 491(170)	[17]
Group II				
3	$[Co(en)_2sal]Cl \cdot 2H_2O$	330(2812)[b] 515(220)[b]	330(2800)[b], 352(2940)[c] 516(212)[b], 509(220)[c]	[16]
4	β-*cis*-$[Co(trien)sal]Cl \cdot H_2O$	330(3140)[b] 520(260)[b]	331(3160)[b], 354(3440)[c] 517(269)[b], 510(267)[c]	[16]
Group III				
5	*cis*-$[Co(en)_2(NH_3)salH](NO_3)_2 \cdot H_2O$	235(23600) 300(4465) 500(110)	235(23610) 298(4475) 500(113)	[4]
6	*cis*-$[Co(en)_2(CH_3NH_2)salH](NO_3)_2 \cdot H_2O$	260(1248) 290(1215) 500(118)	261(1243) 291(1209) 498(120)	[5]
7	*cis*-$[Co(en)_2(C_2H_5NH_2)salH](NO_3)_2 \cdot H_2O$	260(1345) 275(1352) 498(128)	260(1347) 277(1345) 498(130)	[5]

[a] Here, salH is $C_6H_4(OH)CO_2^-$, en is ethylenediamine, trien is triethylenetetramine, tetren is tetraethylenepentamine.

[b] In neutral solution. [c] In 0.5 M perchloric acid.

In order to identify the phases present in the final decomposition products, a few samples heated at 500°C for about 30 min were subjected to X-ray diffraction (XRD) studies and the *d*-lines and their relative intensities were compared with those in ASTM cards. X-ray diffractograms were recorded on a Philips semi-automatic X-ray diffractometer using Cu *Kα* radiation and a scan rate of $2° \min^{-1}$. The complexes were numbered from 1 to 7, and were divided into three groups depending on the amine ligands and the salicylate coordination for the sake of convenience (Table 1).

3. Results and discussion

The TG and DTA curves of all the complexes are shown in Fig. 1(A–C). By comparison of the recorded thermograms, the UV–visible spectra of the intermediates (in a few cases) and the XRD patterns of the final products, the following conclusions can be drawn. The decomposition of the complexes was found to proceed through various steps except for complex no. 2. Results of thermogravimetric analysis and DTA peaks are presented in Table 2.

Table 2
Thermal decomposition data by thermogravimetric analysis

Complex No.	Degradation step	Temp. range in °C	DTA peak in °C	Wt. loss in mg		Corresponds to
				Expt.	Calcd.	
1	I	75–100	80(↓)	0.42	0.42	H_2O
	II and III	165–345	170(↓)	0.46	0.426	NH_3
			220(↑)	7.30	7.25	$4NH_3, 2NO_3$, salH
2	I	220–355	230(↑)	8.46	8.42	tetren, salH
3	I	100–195	165(↓)	1.38	1.39	$2H_2O$
	II	230–270	240(↓)	4.62	4.66	2 en
	III	270–630	300(↓)	6.58	6.70	Cl, sal
4	I	80–230	80(↓)	0.65	0.68	H_2O
	II	240–315	245(↓)	3.50	3.35	0.6 (trien)
	III	315–630	330(↓)	8.58	8.77	0.4 (trien), Cl, sal
5	I	100–160	125(↓)	0.36	0.38	H_2O
	II	180–260	200(↑)	3.01	2.99	$2NO_3$, NH_3
	III	250–260	260(↑)	2.57	2.55	2 en
	IV	310–500	–	2.59	2.56	sal
6	I	120–150	125(↓)	0.36	0.37	H_2O
	II	195–245	230(↑)	3.10	3.16	$2NO_3, CH_3NH_2$
	III	250–260	260(↑)	2.42	2.45	2 en
	IV	310–500	–	2.50	2.52	sal
7	I	100–180	130(↓)	0.36	0.36	H_2O
	II	205–260	240(↑)	3.30	3.38	$2NO_3, C_2H_5NH_2$
	III	260–270	265(↑)	2.40	2.40	2 en
	IV	310–515	–	2.45	2.43	sal

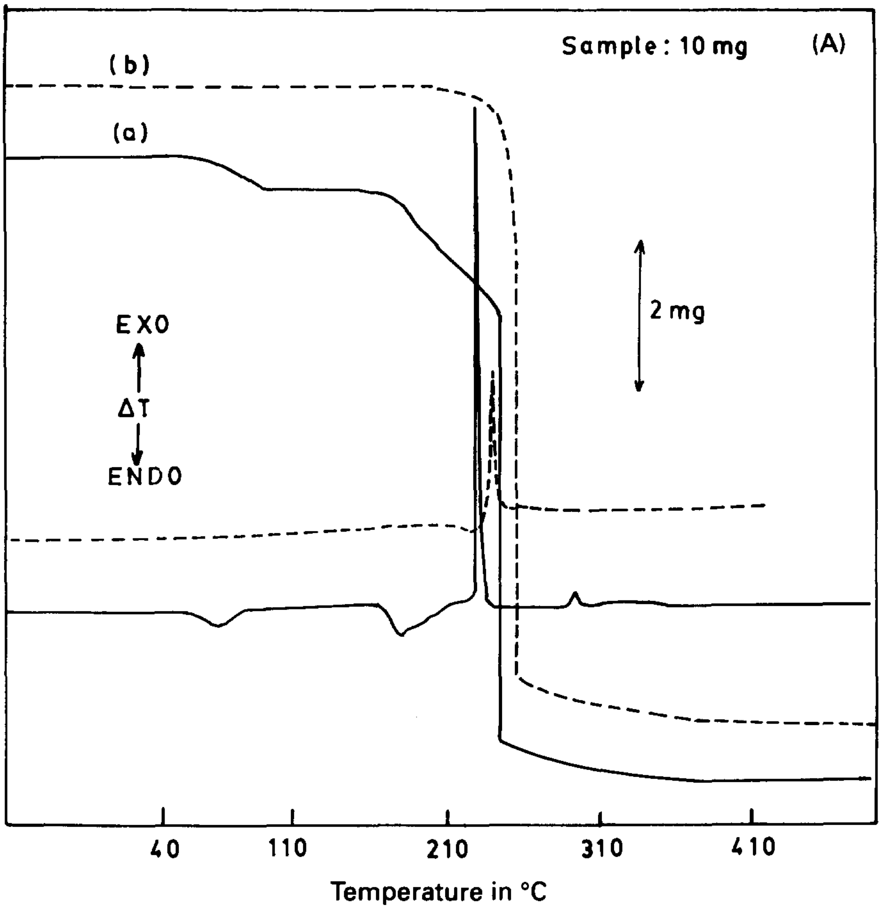

Fig. 1. (A) TG and DTA curves of (a) $[Co(NH_3)_5salH](NO_3)_2H_2O$ and (b) $[Co(tetren)salH](NO_3)_2$. (B) TG and DTA curves of (a) $[Co(en)_2sal]Cl \cdot 2H_2O$ and (b) $[Co(trien)sal]Cl \cdot H_2O$. (C) TG and DTA curves of (a) $[Co(en)_2(CH_3NH_2)salH](NO_3)_2 \cdot H_2O$ and (b) $[Co(en)_2(C_2H_5NH_2)salH](NO_3)_2 \cdot H_2O$.

The first step in the decomposition of complex no. 1, which begins at 80°C with a broad endothermic peak, could be ascribed to the loss of one water molecule from the complex (Fig. 1(A)). The second and third steps overlapped and were rather complicated. At 175°C, an endothermic process could be identified as loss of one NH_3 molecule. Loss of an NH_3 molecule presumably resulted in formation of the chelated product $[Co(NH_3)_4sal]NO_3$. This intermediate, however, could not be isolated. Above 200°C, the decomposition reaction suddenly became an exothermic one, resulting in the maximum loss of weight. A sharp exothermic DTA peak occurred at 220°C. The decomposition was complete at 345°C. A higher temperature of complete decomposition is expected for the chelated salicylate ligand (see later). The above discussion, which indicated that the loss of one NH_3 molecule from the inner coordination sphere

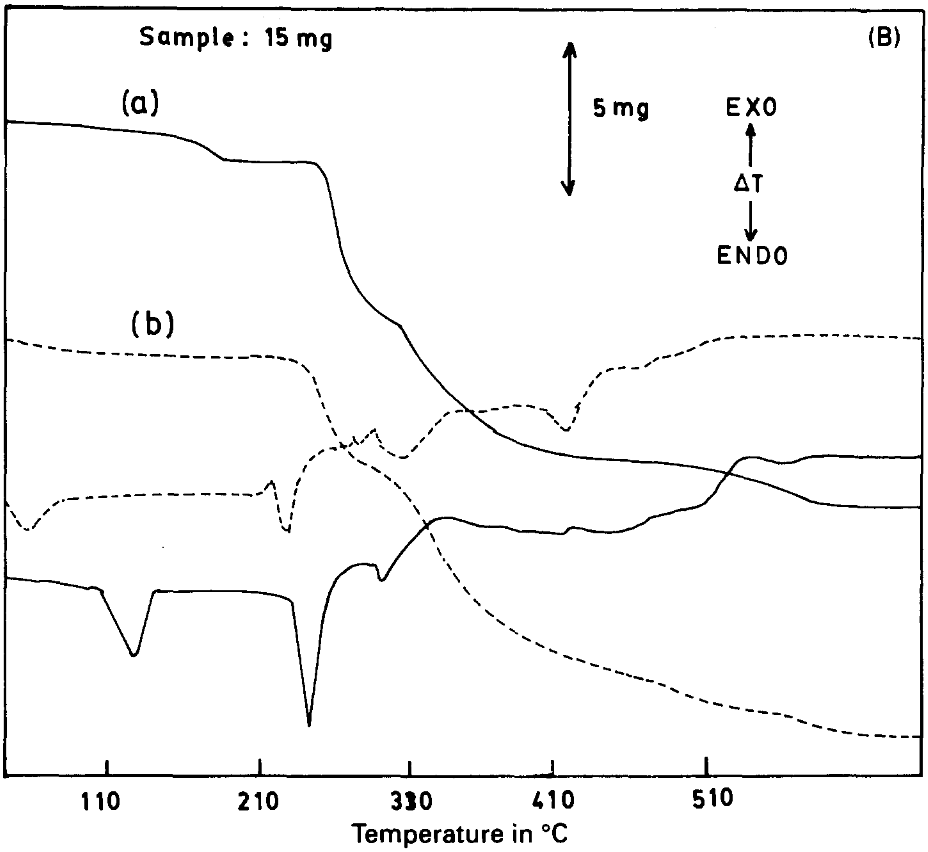

Fig. 1. *(continued)*

was followed by chelation of a pandent salicylate moiety, is rather less conclusive in this case.

In contrast, decomposition of the corresponding tetren analogue (complex no. 2) started at 210°C, proceeding up to 355°C in a single unresolvable step. A single exothermic peak accompained this weight loss. Thus, as expected, the complete decomposition of complexes with a unidentate salicylate ligand occurred at a higher temperature than that of free salicylic acid and at a lower temperature than for the complexes with chelated salicylic. Free salicylic acid melted at 160°C, as indicated by an endothermic peak without loss of mass. The decomposition, which started at 170°C and was complete at 330°C was accompained by an endothermic peak at 260°C. The XRD patterns of the final product indicated the formation of Co_3O_4 (Fig. 2).

The thermograms of group II complexes, in which salicylate acts as a bidentate ligand, showed loss of weight mainly in three stages (Fig. 1(B)). The first step losses were quite well defined and accompanied by endothermic peaks corresponding to loss of one or two water molecule(s), respectively, for complexes no. 4 and no. 3 (Table 2). The

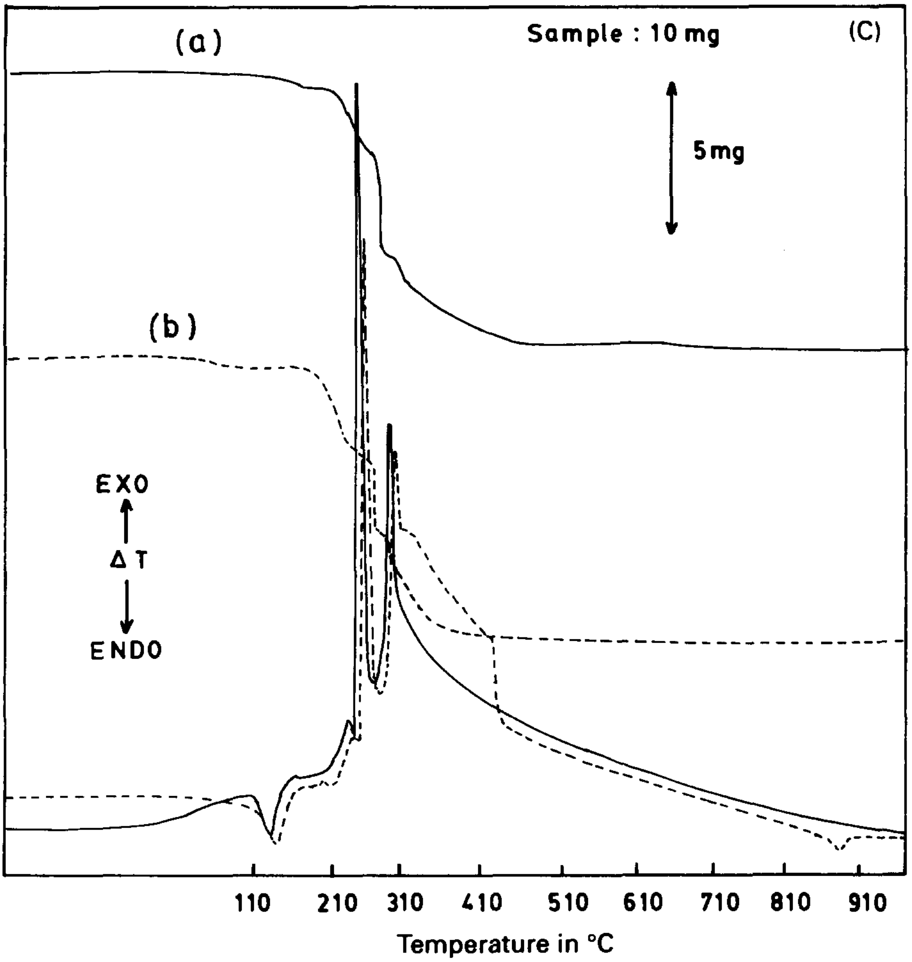

Fig. 1. *(continued)*

figure showed that the anhydrous complexes were stable up to 230°C. The second step losses, which were also accompanied by enthothermic peaks, began at 230 and 240°C, respectively, for complexes no. 3 and no. 4, and most likely correspond to 2 mol of ethylenediamine and 0.6 mol of trien. It may be noted that the loss of trien was not completed in the second step and continued in the third step. The third and final step losses, could be ascribed to the removal of the rest of the ligands, leading to formation of CO_3O_4. Thus, in contrast to the complexes with NO_3 in the outer sphere, which decomposed explosively with exothermic DTA peaks, no such peaks were obtained for these complexes.

The group III complexes having the general formula $[Co(en)_2(amine)salH](NO_3)_2 \cdot H_2O$ also showed multi-stage decompositon (Fig. 1(C)). The first step losses

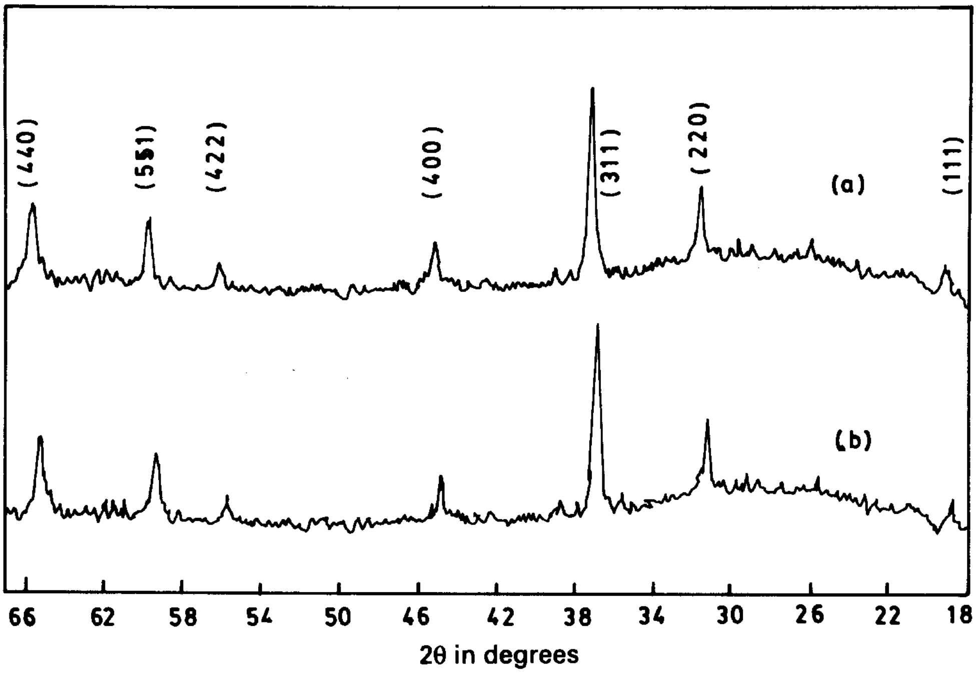

Fig. 2. XRD patterns of the residues of (a) [Co(tetren)salH]$(NO_3)_2$ and (b) $[Co(en)_2(C_2H_5NH_2)salH]$ $(NO_3)_2 \cdot H_2O$.

with endothermic peaks for all three complexes are attributed to the loss of the water molecule. The dehydrated complexes underwent further weight losses, with exothermic peaks at 180, 195 and 205°C, respectively, for complexes, no. 5, 6 and 7. The weight losses could be assigned to the simultaneous loss of NH_3, CH_3NH_2 or $C_2H_5NH_2$ from the cobalt(III) and two outer sphere NO_3^- ions. This resulted in a chelated intermediate $[Co(en)_2sal]$. As such, after the second step, a thermogram similar to that of complex no. 3 is expected. We did in fact obtain a similar type of thermogram. The formation of a chelated salicylato complex was further evident from a comparison of the UV–visible spectra with that of $[Co(en)_2sal]NO_3$. As the second and third step were not well separated, isolation of $[Co(en)_2sal]$ in pure form proved to be difficult. We therefore heated the complexes (nos. 5, 6 and 7) at ≈200°C in an air oven for a few minutes to get a partially chelated product. A representative UV–visible spectrum of the resulting intermediate, along with the spectra of $[Co(en)_2sal]NO_3$ and $[Co(en)_2(C_2H_5NH_2)salH](NO_3)_2$, are presented in Fig. 3(a–c). It is well known [1] that the UV–visible spectra of complexes involving unidentate salicylate remain practically same in the range $[H^+] = 0.05–1.0\,M$, whereas a significant shift of peak position, especially in the UV region, was found in the case of chelated salicylate complexes owing to protonation at the phenolic ($-O$) site [15, 16]. Fig. 3(b) clearly shows the partial formation of a chelated product. The

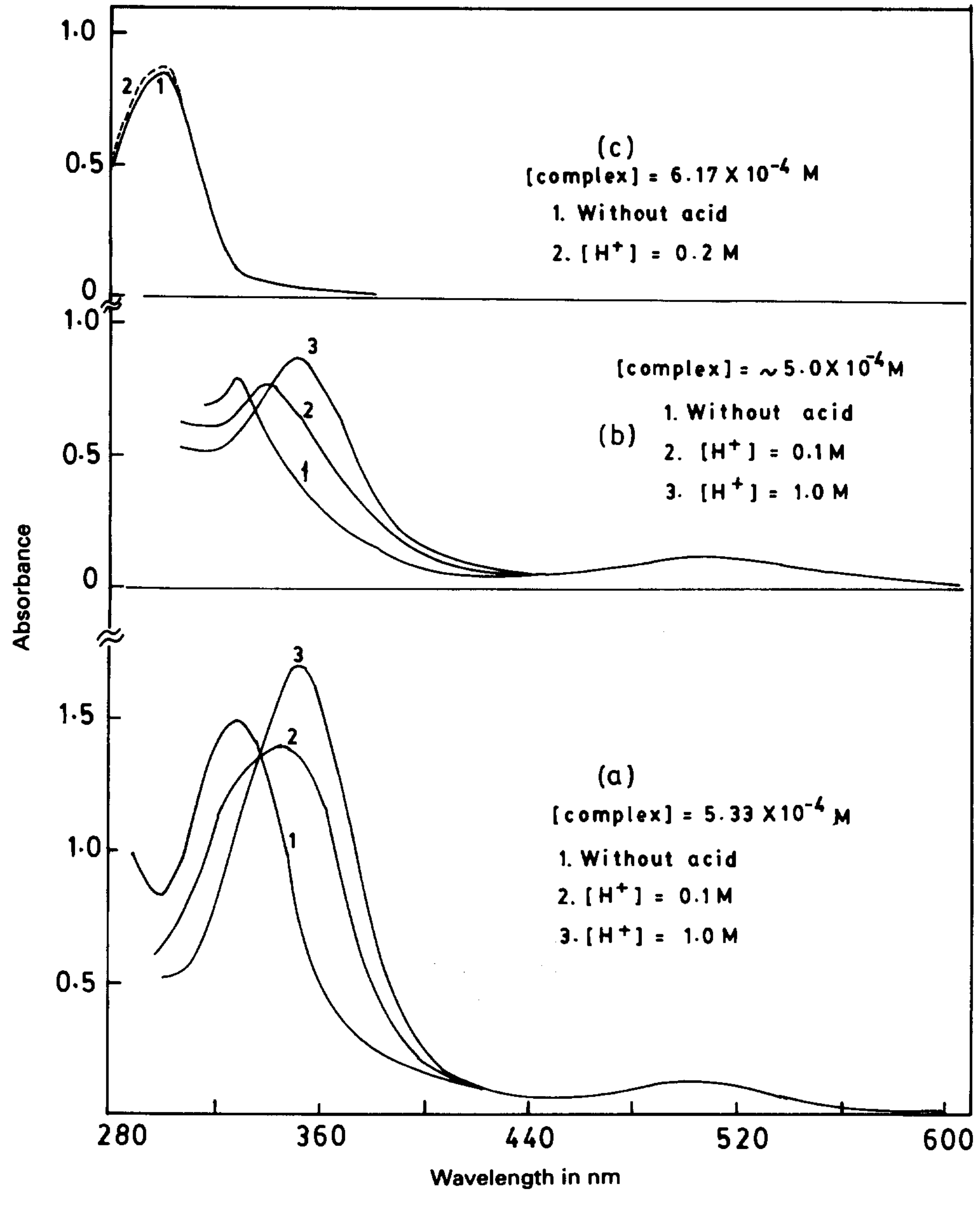

Fig. 3. UV–visible spectra of (a) $[Co(en)_2sal]Cl \cdot 2H_2O$, (b) intermediate formed from $[Co(en)_2(C_2H_5NH_2)salH](NO_3)_2 \cdot H_2O$, and (c) $[Co(en)_2(C_2H_5NH_2)salH](NO_3)_2 \cdot H_2O$.

third step is also accompanied by an exothermic peak attributed to the loss of 2 mol of ethylenediamine. The fourth and final step loss corresponds to the loss of salicylate, leading to the formation of Co_3O_4. Formation of Co_3O_4 was further evident from the XRD patterns presented in Fig. 2.

4. Conclusions

The thermal stability of amine ligands increases with increase in the ring size of the ligands. The thermal stability of the salicylate moiety follows the order: chelated salicylate > unidentate salicylate > unbound salicylic acid. The complexes, $[Co(en)_2(amine)salH](NO_3)_2$ decompose through the intermediate [Co(en)sal]. The final residues remaining (in a few cases) were identified as Co_3O_4.

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