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THERMAL DECOMPOSITION OF SOME DIHALOTETRAMMINECOBALT(III) NITRATES

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ABSTRACT

The thermal decomposition of some dihalotetramminecobalt(III) nitrates [tetrammine = $(NH_3)_4$, $(NH_3)_2$(en), (NH_3)(dien), $(en)_2$, $(pn)_2$, (trien), etc.] with different degrees of chelation was studied by various thermoanalytical techniques. A partial oxidation–reduction was observed for these complexes above 200°C which was indicated by a rapid TG mass-loss and a large exothermic DTA peak. A relative order of thermal stability is reported.

INTRODUCTION

The reactions of the geometrical and optical isomers of the dihalotetramminecobalt(III) complexes have been extensively studied in aqueous solution. There has been little work reported, however, on their solid-state dissociation reactions. The thermal dissociation of the halopentamminecobalt(III) nitrates[1], diaquobis(ethylenediamine)cobalt(III) nitrates[2], aquohalobis(ethylenediamine)cobalt(III) nitrates[3], and aquohalotetramminecobalt(III) nitrates[4] have been reported. There have also been reports[5,6] of the thermal dissociation reactions of some related cobalt(III) ammine nitrates. It is not surprising to note that a complex containing vigorous oxidizing (nitrate) and reducing groups (ammonia, ethylenediamine, etc.) should decompose rather violently on heating to elevated temperatures.

The purpose of this investigation is to report the thermal dissociation reactions of compounds of the type, $[CoA_4XY]NO_3$, and its analogs. Of primary interest is the relative thermal stability of the complex, as related to the geometrical isomers, degree of chelation, and the halide ligands present. The techniques of thermogravimetry (TG), differential thermal analysis (DTA), and high temperature reflectance spectroscopy were employed to study the thermal dissociation reactions. Detection of any possible isomerization reactions that occurred before the total disruption of the complex by the oxidation–reduction reaction was made possible by the last technique.

EXPERIMENTAL PART

Preparation of compounds

Most of the dihalonitrate complexes were prepared by adding cold concen-

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trated nitric acid to the cold saturated solutions of corresponding halides. The complex-nitrates precipitated immediately, were filtered off and washed with ethanol and diethyl ether, and dried in air. The initial complex-halides were prepared as described elsewhere: *cis*-α-$[Co(trien)Cl_2]Cl\cdot 1.5H_2O$[7] → *cis*-α-$[Co(trien)Cl_2]NO_3\cdot 0.5H_2O$; *trans*-$[Co(dien)(NH_3)Cl_2]Cl\cdot H_2O$[8] → *trans*-$[Co(dien)(NH_3)Cl_2]NO_3$; *trans*-$[Co(dien)(NH_3)Br_2]Br$[8] → *trans*-$[Co(dien)(NH_3)Br_2]NO_3$; *cis,trans*-$[Co(en)_2Cl_2]Cl$[9] → *cis,trans*-$[Co(en)_2Cl_2]NO_3$; *trans*-$[Co(en)_2Br_2]Br$[10] → *trans*-$[Co(en)_2Br_2]NO_3$; *trans*-$[Co(en)(NH_3)_2Br_2]Br$[11] → *trans*-$[Co(en)(NH_3)_2Br_2]NO_3$; *cis*-[*trans*-$2NH_3$]-$[Co(en)(NH_3)_2Cl_2]Cl$[11] → *cis*-$[Co(en)(NH_3)_2Cl_2]NO_3$; and *trans*-$[Co(NH_3)_4Cl_2]Cl\cdot H_2O$[12] → *trans*-$[Co(NH_3)_4Cl_2]NO_3$. The complex, *trans*-$[Co(pn)_2Cl_2]NO_3\cdot 2H_2O$, was prepared by the same method mentioned above, except that the precipitation was completed in an ice bath (*trans*-$[Co(pn)_2Cl_2]Cl$[13] → *trans*-$[Co(pn)_2Cl_2]NO_3\cdot 2H_2O$). The following complexes, *cis*-$[Co(en)_2ClBr]NO_3$[14,15], *trans*-$[Co(en)_2ClBr]NO_3$[14], *trans*-$[Co(en)_2F_2]NO_3$[16], and *cis*-$[Co(NH_3)_4Br_2]NO_3$[17], were prepared as previously described. The *trans*-$[Co(NH_3)_4Br_2]NO_3$ was prepared by continuously stirring the solid bromide in cold dilute nitric acid (*trans*-$[Co(NH_3)_4Br_2]Br$[18] → *trans*-$[Co(NH_3)_4Br_2]NO_3$. Attempts to prepare the following complex-nitrates from their corresponding halides by precipitating from cold nitric acid were unsuccessful; *cis*-(*cis*-$2NH_3$)-$[Co(en)(NH_3)_2Cl_2]NO_3$, *cis*-$[Co(trien)Cl_2]NO_3$, *cis*-$[Co(pn)_2Cl_2]NO_3$, *cis*-$[Co(tn)_2Cl_2]NO_3$, *trans*-$[Co(tn)_2Cl_2]NO_3$, and *cis*-$[Co(NH_3)_4Cl_2]NO_3$.

TABLE I

ANALYTICAL DATA FOR COMPLEXES

Complex	*Cobalt (%)*		*H_2O (%)*	
	Theor.	*Found*	*Theor.*	*Found*
cis-α-$[Co(trien)Cl_2]Cl\cdot 1.5H_2O$	17.41	17.6	7.98	8.00
cis-α-$[Co(trien)Cl_2]NO_3\cdot 0.5H_2O$	16.98	16.9	2.60	2.86
cis-$[Co(trien)Br_2]NO_3$	14.13	14.0		
trans-$[Co(dien)(NH_3)Cl_2]NO_3$	18.89	18.6		
trans-$[Co(dien)(NH_3)Br_2]NO_3$	14.70	15.1		
trans-$[Co(en)_2F_2]NO_3$	21.11	21.4		
cis-$[Co(en)_2Cl_2]NO_3$	18.89	18.8		
trans-$[Co(en)_2Cl_2]NO_3$	18.89	18.2		
cis-$[Co(en)_2ClBr]NO_3$	16.53	17.1		
trans-$[Co(en)_2ClBr]NO_3$	16.53	16.9		
cis-$[Co(en)_2Br_2]NO_3$	14.70	14.1		
trans-$[Co(en)_2Br_2]NO_3$	14.70	14.6		
$[Co(en)_2Cl(NO_3)]NO_3$	17.40	17.6		
$[Co(en)_2(NO_3)_2]NO_3$	16.13	16.4		
cis-$[Co(en)(NH_3)_2Cl_2]NO_3$	20.61	20.1		
trans-$[Co(en)(NH_3)_2Cl_2]NO_3$	20.61	20.9		
trans-$[Co(en)(NH_3)_2Br_2]NO_3$	15.72	15.5		
trans-$[Co(pn)_2Cl_2]NO_3\cdot 2H_2O$	15.67	16.2	9.58	9.40
trans-$[Co(NH_3)_4Cl_2]NO_3\cdot H_2O$	21.19	21.9	6.48	5.83
trans-$[Co(NH_3)_4Br_2]NO_3$	16.89	15.9		

The complexes, $[Co(en)_2(NO_3)_2]NO_3$ and $[Co(en)_2Cl(NO_3)]NO_3$, were prepared by the thermal deaquation of *cis*-$[Co(en)_2(H_2O)_2](NO_3)_3$[2] and *cis*-$[Co(en)_2H_2OCl](NO_3)_2$[3].

The cobalt metal contents of the complexes were determined by EDTA titration using murexide as end-point indicator[19] while the water contents of the complexes were calculated from TG mass-loss curves. The analytical data for the complexes are given in Table 1.

Thermoanalytical techniques

The thermobalance and DTA techniques have been previously reported[20,21]. A heating rate of 5°C min^{-1} was used in both techniques; the samples were pyrolyzed in a dynamic N_2 atmosphere. The high temperature reflectance technique has previously been described[20].

RESULTS AND DISCUSSION

Mass-loss study

The mass-loss curves of the complexes that were studied are given in Figs. 1–5. The thermal dissociation data, including initial decomposition temperatures, inflection point temperatures, percent mass-loss due to the oxidation–reduction reactions, and other thermal stability calculations are collected in Table 2. The initial dissociation (T_a) and inflection point (T_b) temperatures are indicative of the order of thermal stability of the complex. Strictly speaking, T_a could be the oxidation–reduction reaction initial temperature in the more stable complexes or simply the initial temperature of deamination in the less stable complexes. This means, of course, that the complex is thermally stable if it possess high T_a and T_b values. The stoichiometric mass-loss, (MW) $(\%\Delta W)$, represents the extent of the oxidation–reduction reaction which is directly related to the order of thermal stability of the complex. With few exceptions, complexes with lower stochiometric mass-loss values, (MW) $(\%\Delta W)$, normally showed higher initial dissociation (T_a) and inflection point (T_b) temperatures. Therefore, stochiometric mass-loss values can be conveniently used to define the order of thermal stability of the complexes.

For convenience, this series of complex-nitrates are classified and divided into several groups according to their degrees of chelation and number of nitrate ions per molecule.

$[Co(NH_3)_4X_2]NO_3$ $(X = Cl, Br)$

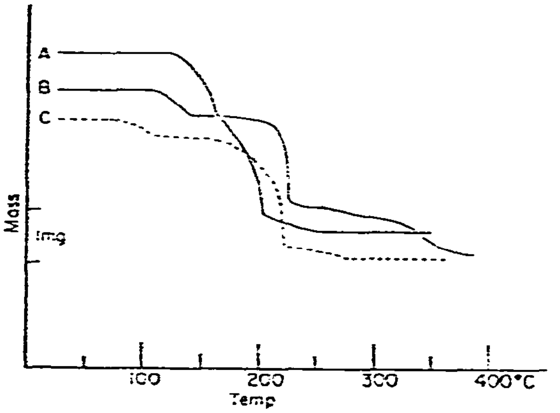
The mass-loss curves of *trans*-$[Co(NH_3)_4Cl_2]NO_3 \cdot H_2O$ and *trans*-$[Co(NH_3)_4Br_2]NO_3$ are shown in Fig. 1 as curves C and A, respectively. The dehydration of the 1-hydrate of *trans*-$[Co(NH_3)_4Cl_2]NO_3 \cdot H_2O$ took place between 75 and 105°C. The high temperature reflectance spectrum did not indicate any geometrical isomerization due to dehydration, although *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ has been found to form *cis*-$[Co(NH_3)_4Cl_2]IO_3$ during the dehydration reaction[22,23]. The *trans*-$[Co(NH_3)_4Cl_2]NO_3$ complex apparently was more stable thermally (excluding dehydration) than *trans*-$[Co(NH_3)_4Br_2]NO_3$, as indicated by their initial dissocia-

TABLE 2

THERMAL STABILITY DATA OF COBALT(III) COMPLEXES

Complexes	T_a(°C)	T_b(°C)	% NO_3	% ΔW	$(MW)(\% \Delta W)$	$\% \Delta W / \% (NO_3)$
cis-α-$[Co(trien)Cl_2]NO_3 \cdot 0.5H_2O$	200	224	18.34	25.0	84.5	1.46
cis-$[Co(trien)Br_2]NO_3$	215	237	14.49	19.1	81.5	1.32
trans-$[Co(dien)(NH_3)Cl_2]NO_3$	175	223	19.87	32.5	101.0	1.63
trans-$[Co(dien)(NH_3)Br_2]NO_3$	160	213	15.46	24.6	115.0	1.59
trans-$[Co(en)_2F_2]NO_3$	238	274	22.15	40.4	112.5	1.82
cis-$[Co(en)_2Cl_2]NO_3$	200	225	19.87	31.6	98.6	1.59
trans-$[Co(en)_2Cl_2]NO_3$	195	227	19.87	32.3	100.5	1.62
cis-$[Co(en)_2ClBr]NO_3$	200	223	17.39	23.9	85.2	1.38
trans-$[Co(en)_2ClBr]NO_3$	200	224	17.39	23.8	84.8	1.37
cis-$[Co(en)_2Br_2]NO_3$	205	223	15.46	23.5	94.2	1.52
trans-$[Co(en)_2Br_2]NO_3$	200	225	15.46	24.1	96.7	1.56
cis-$[Co(en)(NH_3)_2Cl_2]NO_3$	170	216	21.68	36.5	104.4	1.68
trans-$[Co(en)(NH_3)_2Cl_2]NO_3$	165	210	21.68	38.2	109.0	1.76
trans-$[Co(en)(NH_3)_2Br_2]NO_3$	145	200	16.54	30.6	115.0	1.85
trans-$[Co(NH_3)_4Cl_2]NO_3 \cdot H_2O$	150	217	23.85	45.7	118.0	1.91
trans-$[Co(NH_3)_4Br_2]NO_3$	120	195	17.77	54.3	189.0	3.06
trans-$[Co(pn)_2Cl_2]NO_3 \cdot 2H_2O$	205	222	18.25	35.8	121.5	1.96
$[Co(en)_2Cl(NO_3)]NO_3$	192	222	36.63	75.6	256.1	2.06
$[Co(en)_2(NO_3)_2]NO_3$	195	214	50.40	91.1	330.8	1.80

T_a, temperature of initial decomposition due to the oxidation–reduction reaction without considering dehydration. T_b, temperature at inflection point of oxidation–reduction reaction. %(NO_3), calculated from the molecular weight of anhydrous complex. %(ΔW), calculated from mass-loss curveconsidering only anhydrous complex.



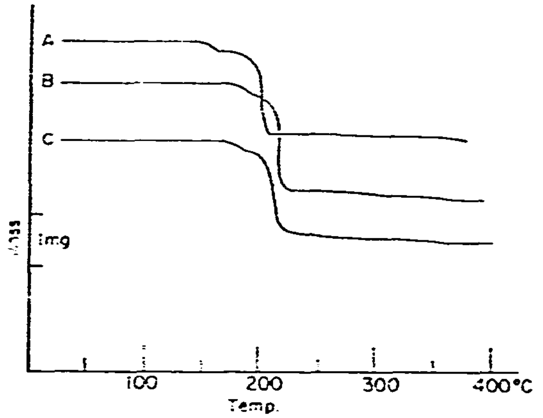


Fig. 1 (left). Mass-loss curves of cobalt(III) complexes. A, *trans*-$[Co(NH_3)_4Br_2]NO_3$; B, *trans*-$[Co(pn)_2Cl_2]NO_3 \cdot 2H_2O$; C, *trans*-$[Co(NH_3)_4Cl_2]NO_3 \cdot H_2O$.

Fig. 2 (right). Mass-loss curves of cobalt(III) complexes. A, *trans*-$[Co(en)(NH_3)_2Br_2]NO_3$; B, *cis*-$[Co(en)(NH_3)_2Cl_2]NO_3$; C, *trans*-$[Co(en)(NH_3)_2Cl_2]NO_3$.

tion, inflection point temperatures, and stoichiometric mass-loss data. The low T_a values for these two complexes indicated that the initial mass-loss was not caused by the oxidation–reduction reaction but was probably due to the deamination reaction.

The thermal stability order found was: *trans*-[Co$(NH_3)_4Cl_2$]NO_3 > *trans*-[Co$(NH_3)_4$-Br_2]NO_3.

[Co(en)$(NH_3)_2X_2$]NO_3 ($X = Cl, Br$)

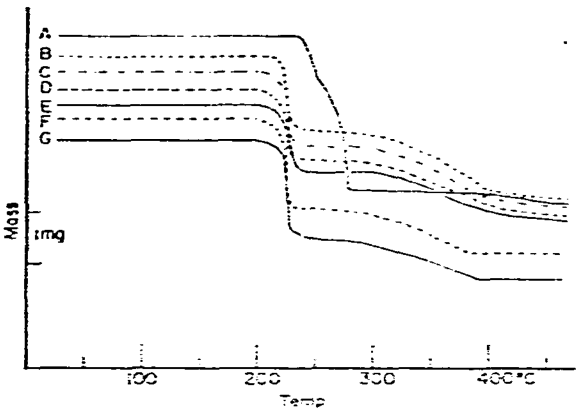
The mass-loss curves of this series of complexes are given in Fig. 2. The dichloro complexes showed a greater variation in thermal stability between geometrical isomers, e.g., *cis*-dichloro-*trans*-diammine(ethylenediamine)cobalt(III) nitrate was more stable than *trans*-dichlorodiammine(ethylenediamine)cobalt(III) nitrate which can be observed from either the mass-loss curves or from the (MW) (%ΔW) values in Table 2. Unfortunately, the other geometrical isomer of the complex, *cis*-dichloro-*cis*-diammine(ethylenediamine)cobalt(III) nitrate, could not be prepared. All three complexes of this series showed a mass loss-plateau immediately before the oxidation–reduction reaction which was probably due to the incompleted deamination of the complex. The *trans*-[Co(en)$(NH_3)_2Br_2$]NO_3 (curve A) complex was the least stable among the three complexes. An order of thermal stability, as obtained from Fig. 2 and Table 2, is as follows: *cis*-[Co(en)$(NH_3)_2Cl_2$]NO_3 > *trans*-[Co(en) $(NH_3)_2$-Cl_2]NO_3 > *trans*-[Co(en)$(NH_3)_2Br_2$]NO_3.

trans-[Co(pn)$_3Cl_2$]$NO_3 \cdot 2H_2O$

The mass-loss curve of this complex is given as curve B in Fig. 1. The two waters of hydration were evolved from 100 to 140 °C and further dissociation due to an oxidation–reduction reaction took place above 205 °C with an inflection point temperature of 222 °C. The complex diaquohydrogen chloride, *trans*-(Co(pn)$_2Cl_2$]-$(H_5O_2)Cl_2$, has been previously reported to undergo a *cis–trans* isomerization during the dehydration and dehydrochlorination reaction[24,25], but it was not possible to detect a similar change during the dehydration of *trans*-[Co(pn)$_2Cl_2$]$NO_3 \cdot 2H_2O$. The thermal stability of this complex is approximately between that for [Co(en)$_2Cl_2$] NO_3 and [Co(en)$(NH_3)_2Cl_2$]NO_3, as determined by the T_a and T_b values given in Table 2. However, this complex showed a relatively higher stoichiometric mass-loss, (MW) (%ΔW), which probably came from the higher equivalent weight (EW) for the chelate ligand (pn = 1, 2-diaminopropane, EW = 37) compared with the other bidentate ligand (en, EW = 30).

[Co(en)$_2X_2$]NO_3 ($X = F, Cl, Br$)

The mass-loss curves of this series of complexes are given in Fig. 3. Except for the complex, *trans*-[Co(en)$_2F_2$]NO_3, all of the *cis*- and *trans*-dihalobis(ethylenediamine)cobalt(III) nitrate complexes were very close in initial dissociation (T_a) and inflection point (T_b) temperatures. Both the *cis*- and *trans*-isomers showed about the same order of thermal stability, as determined by the T_a and T_b values. However, the stoichiometric mass-loss, (MW) (%ΔW), was used to differentiate the order of thermal stability among them. For unknown reasons, *trans*-[Co(en)$_2F_2$]NO_3 (curve A) had exceptionally high initial dissociation (T_a) and inflection point (T_b) temperatures of 238 and 274 °C, respectively. However, *trans*-[Co(en)$_2F_2$]NO_3 also possessed the



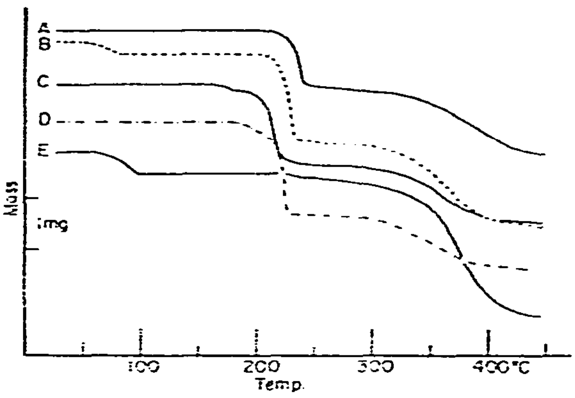


Fig. 3 (left). Mass-loss curves of cobalt(III) complexes. A, *trans*-$[Co(en)_2F_2]NO_3$; B, *cis*-$[Co(en)_2ClBr]NO_3$; C, *trans*-$[Co(en)_2ClBr]NO_3$; D, *cis*-$[Co(en)_2Br_2]NO_3$; E, *trans*-$[Co(en)_2Br_2]NO_3$; F, *cis*-$[Co(en)_2Cl_2]NO_3$; G, *trans*-$[Co(en)_2Cl_2]NO_3$.

Fig. 4 (right). Mass-loss curves of cobalt(III) complexes. A, *cis*-$[Co(trien)Br_2]NO_3$; B, *cis*-α-$[Co(trien)Cl_2]NO_3 \cdot 0.5H_2O$; C, *trans*-$[Co(dien)(NH_3)Br_2]NO_3$; D, *trans*-$[Co(dien)(NH_3)Cl_2]NO_3$; E, *cis*-α-$[Co(trien)Cl_2]Cl \cdot 1.5H_2O$.

highest stoichiometric mass-loss, (MW) (%ΔW), among this series of complexes. This indicates that the *trans*-$[Co(en)_2F_2]NO_3$ complex has the highest thermal stability, as defined by the T_a and T_b values, but the lowest order of thermal stability by (MW) (%ΔW). Thus, the order of thermal stability, according to the (MW) (%ΔW) values for this series complexes is: $[Co(en)_2ClBr]NO_3$ > $[Co(en)_2Br_2]NO_3$ > $[Co(en)_2Cl_2]NO_3$ > $[Co(en)_2F_2]NO_3$.

$[Co(dien)(NH_3)X_2]NO_3$ (X = Cl, Br)

As far as the degree of chelation is concerned, this series of complexes has the same as those of the $[Co(en)_2X_2]NO_3$ complexes. However, their thermal stability was found to be about the same as those for the $[Co(en)(NH_3)_2X_2]NO_3$ complexes. The dibromonitrate (curve C, Fig. 4) began to lose mass at 160°C with an inflection point temperature at 213°C. The dichloronitrate (curve D, Fig. 4) showed a higher thermal stability with initial dissociation and inflection point temperatures of 175 and 223°C, respectively. As was found with the previously discussed $[Co(en)(NH_3)_2X_2]NO_3$ complexes, there was a short mass-loss plateau just before the region in the curve where the oxidation–reduction took place. The thermal stability order found was: *trans*-$[Co(dien)(NH_3)Cl_2]NO_3$ > *trans*-$[Co(dien)(NH_3)Br_2]NO_3$.

$[Co(trien)X_2]NO_3$ (X = Cl, Br)

This series of complexes had the highest degree of chelation and also the highest thermal stability of the complexes investigated. The mass-loss curves for *cis*-α-dichlorotriethylene-tetraminecobalt(III) chloride and nitrate are given as curves E and B in Fig. 4, respectively. The *cis*-α-$[Co(trien)Cl_2]Cl \cdot 1.5H_2O$ complex evolved 1.5 moles of water per mole of complex below 100°C with further dissociation of the complex taking place above 220°C. For the dichloronitrate, *cis*-α-$[Co(trien)Cl_2]NO_3 \cdot 0.5H_2O$, the 0.5 mole of water was evolved from 50 to 80°C with additional mass-loss at 200°C and an inflection point at about 224°C. Comparing the mass-loss curves of these two complexes (curves B and E, Fig. 4), it can be seen that the curve for the nitrate (curve B) after the rapid oxidation–reduction reaction is similar to that of the chloride (curve E). Such results reveal that only a partial oxidation–reduction reaction occurred for the complex-nitrate because one mole of nitrate ion per mole of complex is not sufficient for the total oxidation–reduction reaction. Similar results were also observed for the other complex halides and nitrates curves. The dibromonitrate, *cis*-$[Co(trien)Br_2NO_3$ (curve A, Fig. 4), exhibited even higher initial dissociation and inflection point temperatures than the dichloronitrate; it also had the lowest (MW) $(\%\Delta W)$ and $(\%\Delta W)/(\%NO_3)$ values (81.5 and 1.32) among the complexes studied and thus had the highest thermal stability. The thermal stability order of these complexes was: *cis*-$[Co(trien)Br_2]NO_3$ > *cis*$[Co(trien)Cl_2]NO_3$.

$[Co(en)_2Cl(NO_3)]NO_3$ and $[Co(en)_2(NO_3)]NO_3$

For comparison purposes, the mass-loss curves of *cis*-$[Co(en)_2Cl_2]NO_3$, together with $[Co(en)_2Cl(NO_3)]NO_3$ and $[Co(en)_2(NO_3)_2]NO_3$, are given in Fig. 5. For complexes with two or three moles of nitrate per mole of complex. $[Co(en)_2Cl_2(NO_3)]NO_3$ and $[Co(en)_2(NO_3)_2]NO_3$, the final black residue after the vigorous oxidation–reduction reaction was Co_3O_4. For the complex, $[Co(en)_2Cl(NO_3)]NO_3$, the calculated and experimental weight percent of Co_3O_4 from the mass-loss curve (curve A, Fig. 5) were quite close to each other. However, the experimental percent Co_3O_4 found was far less than the calculated for $[Co(en)_2(NO_3)_2]NO_3$ (8.10% versus 21.98%). This was caused by ejection of the sample during the vigorous oxidation–reduction reaction of the complex. Similar behavior was observed for the decomposition of $[Co(NH_3)_5X](NO_3)_2$[1] and $[Co(NH_3)_6](NO_3)_3$[6]; no appreciable mass-loss was detected after the oxidation–reduction reaction. The calculated and experimental percent of Co_3O_4 values after the oxidation–reduction reaction for this series of complexes are listed in Table 3. The incomplete oxidation–reduction reaction of *cis*-$[Co(en)_2Cl_2]NO_3$ can be easily observed from its 68.4% of mass-loss after the oxidation–reduction reaction compared with a calculated value of 25.75% if the final residue is Co_3O_4. The thermal stability order, from the initial dissociation and inflection point temperature is $[Co(en)_2Cl_2]NO_3$ > $[Co(en)_2Cl(NO_3)]NO_3$ > $[Co(en)_2(NO_3)_2]NO_3$.

TABLE 3

EXPERIMENTAL AND CALCULATED MASS-LOSS DATA

Complex	*Calc. % Co_3O_4*	*Expt. % Co_3O_4*
$[Co(en)_2(NO_3)_2]NO_3$	21.98	8.1
$[Co(en)_2Cl(NO_3)]NO_3$	23.75	24.3
$[Co(en)_2Cl_2]NO_3$	25.72	68.4

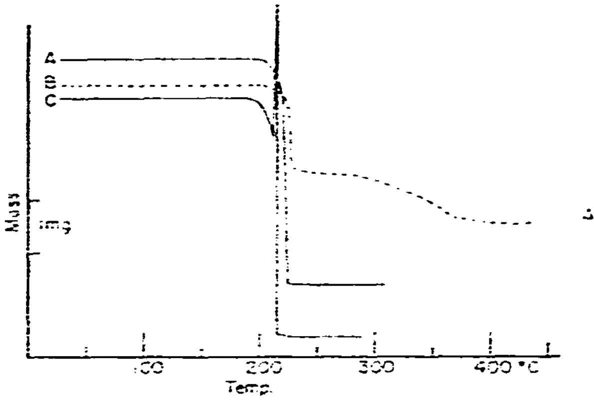
General

As far as the degree of chelation is concerned, the complexes with chelating groups present were of higher thermal stability than those with unidentate groups. Using the dichloronitrate complexes as examples, the order of thermal stability can be obtained by comparing their initial decomposition temperatures (T_a) and stoichiometric mass-loss due to the oxidation–reduction reaction, (MW)(%ΔW),

$$\underset{(200\,^\circ\mathrm{C};\ 84.5)}{\textit{cis}\text{(trien)Cl}_2} > \underset{(195\,^\circ\mathrm{C};\ 98.6)}{\textit{cis}\text{-(en)}_2\text{Cl}_2} \geqslant \underset{(195\,^\circ\mathrm{C};\ 100.0)}{\textit{trans}\text{-(en)}_2\text{Cl}_2} > \underset{(175\,^\circ\mathrm{C};\ 101.0)}{\textit{trans}\text{-(dien)(NH}_3\text{)Cl}_2} >$$

$$\underset{(170\,^\circ\mathrm{C};\ 140.4)}{\textit{cis}\text{-(en)(NH}_3)_2\text{Cl}_2} > \underset{(165\,^\circ\mathrm{C};\ 109.0)}{\textit{trans}\text{-(en)(NH}_3)_2\text{Cl}_2} > \underset{(150\,^\circ\mathrm{C};\ 118.0)}{\textit{trans}\text{-(NH}_3)_4\text{Cl}_2}\ .$$

Considering the coordinated halides present reveals some interesting results; for (trien) complexes: $Br_2 > Cl_2$; for en_2 complexes: $ClBr > Br_2 > Cl_2$; for dien(NH_3), en$(NH_3)_2$, and $(NH_3)_4$ complexes $Cl_2 > Br_2$.



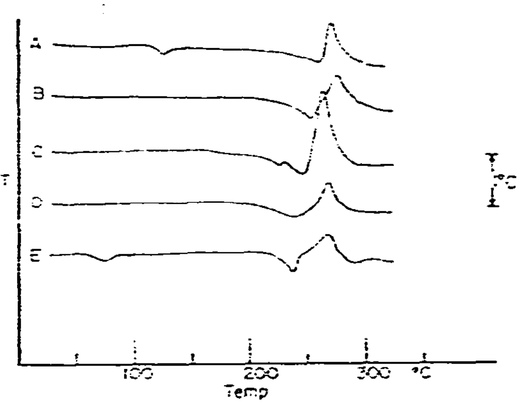


Fig. 5 (left). Mass-loss curves of cobalt(III) complexes. A, $[Co(en)_2Cl(NO_3)]NO_3$; B, *cis*-$[Co(en)_2Cl_2]$ NO_3 ; C, $[Co(en)_2(NO_3)_2]NO_3$.

Fig. 6 (right). Differential thermal analysis curves of some Co(III) complexes. A, *trans*-$[Co(NH_3)_4Cl_2]$ $NO_3 \cdot H_2O$; B, *trans*-$[Co(en)_2Cl_2]NO_3$; C, *trans*-$[Co(en)(NH_3)_2Cl_2]NO_3$; D, *trans*-$[Co(dien)(NH_3)Cl_2]$ NO_3 ; E, *cis*-α-$[Co(trien)Cl_2]NO_3 \cdot 0.5H_2O$.

The dichloro complexes were found to be more stable thermally than the dibromo complexes with lower chelation amine ligands, $(NH_3)_4$, en$(NH_3)_2$, and dien(NH_3), but the order of stability was reversed with higher chelation amine ligands, trien. For the complexes, $[Co(NH_3)_4X_2]NO_3$ (X = Cl, Br), two bromide ions in the complex exhibits a greater steric strain than does two chloride ions. However, such a steric strain effect is decreased as the degree of chelation is increased. The relation between the thermal stability and the geometrical isomer present is not clear enough here to be definitive although the *cis*-isomers were found to be slightly more stable thermally than the *trans*-isomers.

Differential thermal analysis studies

The DTA curves of some selected complexes with different degrees of chelation are shown in Fig. 6. All of the curves were characterized by an exothermic peak in the 265–275°C temperature range. In all cases, however, the exothermic peak was preceded by a broad endothermic peak (two endothermic peaks for *trans*-[Co(en)$(NH_3)_2Cl_2]NO_3$). This behavior was probably due to the fact that the complex first dissociated and was then followed by a vigorous exothermic oxidation–reduction reaction. The peak area of those complex nitrates with two or three moles of nitrate per mole of complex (such as $[Co(en)_2Cl(NO_3)]NO_3$ or $[Co(en)_2(NO_3)_2]NO_3$) was relatively greater than the dihalo-nitrates; quantitative data were not obtained however. The temperatures of the exothermic peak maxima were approximately 40–50°C higher than the inflection point temperatures obtained from the mass-loss study. The causes for such a difference probably come from the different types of gaseous furnace atmospheres that were employed. A static air atmosphere in an enclosed system was used in the DTA study, while a flowing nitrogen atmosphere was used in the TG technique.

CONCLUSIONS

No geometrical isomerization reactions were observed in this study such as *cis*- to *trans*- or *trans*- to *cis*, although such changes for the dihalotetramminecobalt (III) complexes have been previously reported[4,23,24,26,27].

Although the thermal stability of various compounds has been frequently mentioned in thermal analysis studies, its definition is still ambiguous. In some reversible gas–solid systems, the thermal stability is defined as the temperature at which a certain vapor pressure of the system is attained[27] which actually is a definition of thermodynamic stability. However, irreversible systems are found in most thermal analysis studies so that vapor–solid equilibrium can not be attained. The initial decomposition temperature, T_a, is frequently used to define the relative thermal stability of compounds with similar structures. However, the degree of decomposition is neglected when the initial decomposition temperature is used to define the stability parameter. A compound with 5% mass-loss between 50-60°C is considered less stable than another with a 20% mass-loss between 60–70°C. In this study, the initial decomposition temperature of the complex is due to simple deamination or by an oxidation–reduction reaction. The thermal stability temperature ascertained from T_b was due to the oxidation-reaction reaction for the complex. As expected, complexes with a larger inflection point temperature, T_b, have a decreased oxidation–reduction reaction, $(MW)(\%\Delta W)$. Except for very few cases, the relative thermal stability defined by either, T_a, or T_b, or $(MW)(\%\Delta W)$, were in good agreement with each other.

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