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THERMOANALYTICAL BEHAVIOUR OF SOME DICARBOXYLATO-α-DIIMINECOBALT(III) COMPLEXES

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The complexes *cis*-$Co[(AA)_2(OCOR)_2]NO_3$, where AA = 1,10-phenanthroline or 2,2'-bipyridine and R = H, CH_3, C_2H_5, or *n*-C_3H_7 were studied by TG, DTA and spectroscopic methods to obtain information concerning the decomposition mechanism. A comparison of the two series revealed that the first decomposition process involves breaking of Co-N bonds and elimination of the nitrogen ligand in both series; the phenanthroline complexes show a stability sequence, whereas all the bipyridine complexes start to decompose at the same temperature. The results were also compared with previous data on ethylenediamine complexes.

Although the thermal reactions of cobalt(III) complexes with nitrogen ligands have been the subject of many reports [1], few papers have dealt with *o*-phenanthroline or 2,2'-bipyridine complexes of cobalt(III). The present paper reports the thermoanalytical behaviour of two series of mixed cobalt(III) complexes of the type *cis*-$Co[(AA)_2(OCOR)_2]NO_3$, where AA = 1,10-phenanthroline or 2,2'-bipyridine and R = H, CH_3, C_2H_5, or *n*-C_3H_7.

These two series were chosen because they offer an opportunity for study of the effects of the pyridine rings and/or the length of the aliphatic chain in the carboxylato ligands on the thermal stability of the complexes. Furthermore, a comparison of the results with those of the corresponding ethylenediamine series can give information on the effect of the ring [2]. Nitrate was chosen as the counter-ion, in order to minimize anation reactions.

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It is to be noted that this work follows thermoanalytical studies in our laboratory on other cobalt(III) complexes with nitrogen ligands [3-5].

The study was carried out by TGA and DTA techniques in dynamic nitrogen or oxygen gas atmospheres and *in vacuo*.

Experimental

The complexes were prepared as described previously [6].

The thermal measurements were carried out with a Perkin-Elmer TGS-2 thermal analyzer equipped for qualitative magnetic mass change determinations, and with a Perkin-Elmer DTA 1700.

TG runs were made *in vacuo* and in a dynamic nitrogen or oxygen gas atmosphere with a flow rate of about 50 ml min^{-1}; DTA runs were made in dynamic nitrogen or oxygen gas atmospheres. The heating rate was 5 or 10 deg min^{-1}, with samples of 3-5 mg. Infrared spectra were recorded with a Perkin-Elmer 298 spectrophotometer.

Mass spectra were obtained on a Hewlett-Packard 5982 mass spectrometer, coupled with a Hewlett-Packard 5934 A data system, operated in the electron impact mode; source $P = 5.10^{-7}$ torr; electron energy 70 eV; the samples were introduced *via* the direct insertion probe.

Results and discussion

The four complexes of each series exhibit very similar thermoanalytical behaviour, as is clearly seen in Figs 1-4. In particular, the behaviour of one complex from each series is described in detail below.

cis-$[Co(o\text{-}phen)_2(OCOC_3H_7)_2]NO_3$

The TG curve shows that *in vacuo* the anhydrous compound is stable up to 190° and then decomposes in three steps.

The first step is complete at 210-215° and involves a mass loss of about 9.5%.

At 210°, the presence of a sublimate was observed on the inner side of the furnace. It is presumed that this was undecomposed phenanthroline: the sublimate obtained at the above temperature gave the characteristic red colour with Fe(II). Therefore, the first base loss corresponds to the elimination of 0.33 moles of phenanthroline (one mole of the N-ligand *per* three

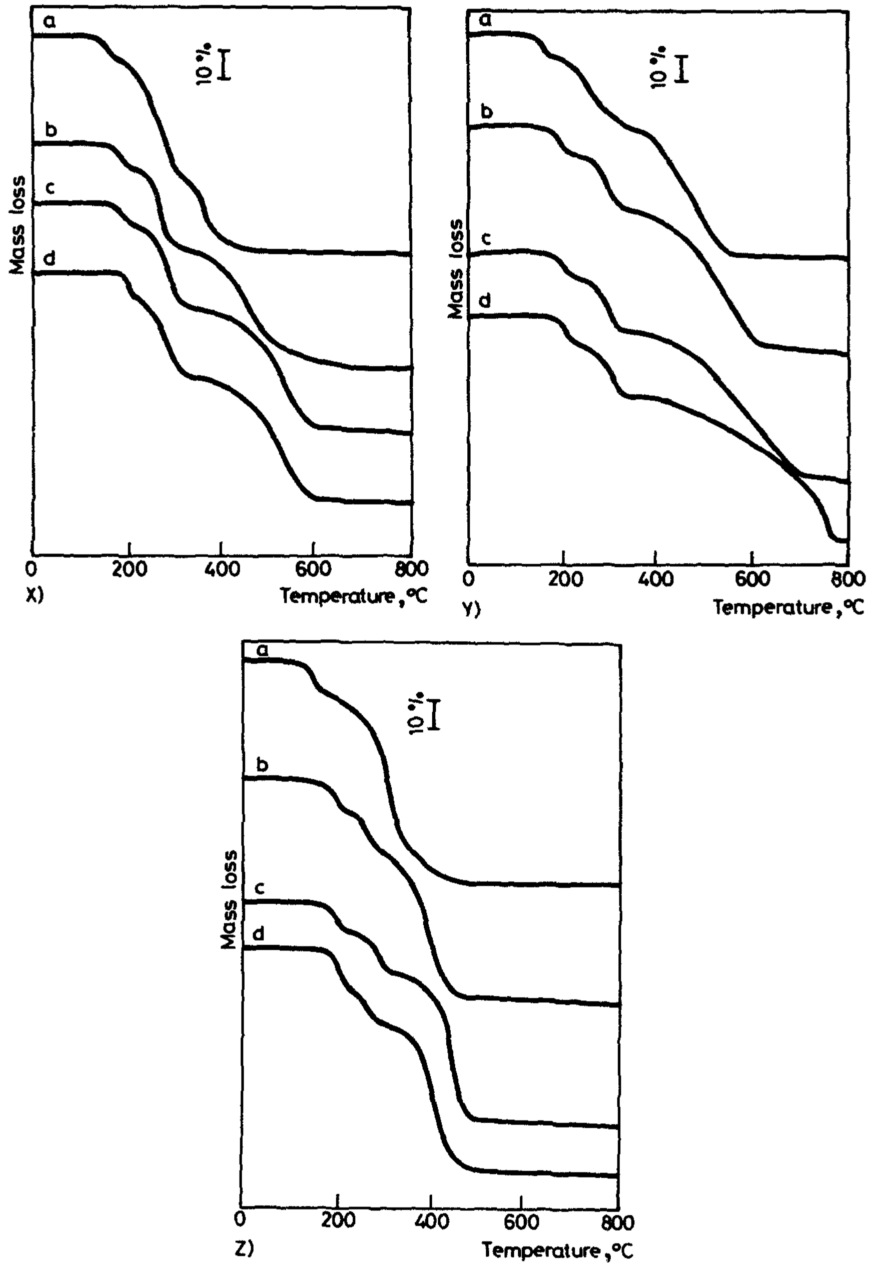

Fig. 1 Thermogravimetric curves for: a) *cis*-[Co(o-phen)$_2$(OCOH)$_2$]NO$_3$; b) *cis*-[Co(o-phen)$_2$(OCOCH$_3$)$_2$]NO$_3$; c) *cis*-[Co(o-phen)$_2$(OCOC$_2$H$_5$)$_2$]NO$_3$; d) *cis*-[Co(o-phen)$_2$(OCOC$_3$H$_7$)$_2$]NO$_3$; in vacuo (1X); in a dynamic nitrogen atmosphere (1Y); in a dynamic oxygen atmosphere (1Z); heating rate 10 deg/min, flow rate 50 ml/min

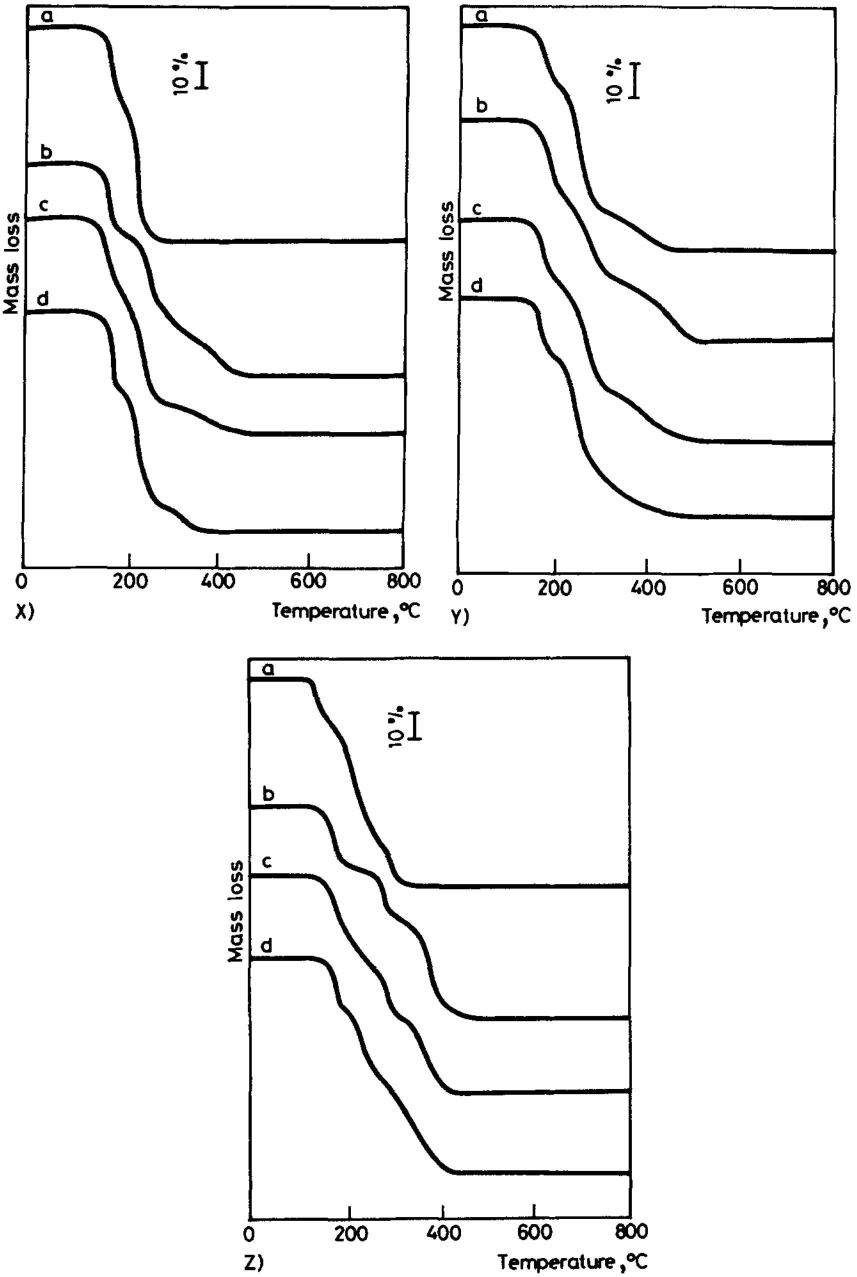

Fig. 2 Thermogravimetric curves for: a) *cis*-$[Co(bipy)_2(OCOH)_2]NO_3$; b) *cis*-$[Co(bipy)_2(OCOCH_3)_2]NO_3$; c) *cis*-$[Co(bipy)_2(OCOC_2H_5)_2]NO_3$; d) *cis*-$[Co(bipy)_2(OCOC_3H_7)_2]NO_3$; *in vacuo* (2X); in a dynamic nitrogen atmosphere (2Y); in a dynamic oxygen atmosphere (2Z); heating rate 10 deg/min, flow rate 50 ml/min

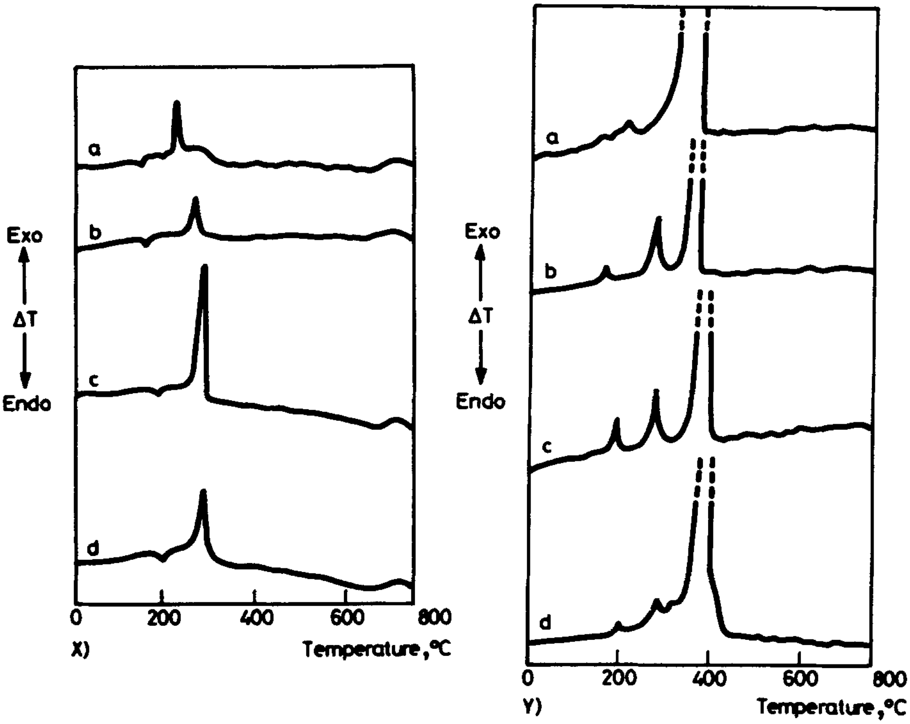

Fig. 3 Differential thermal analysis curves for: a) *cis*-[Co(o-phen)$_2$(OCOH)$_2$]NO$_3$; b) *cis*-[Co(o-phen)$_2$(OCOCH$_3$)$_2$]NO$_3$; c) *cis*-[Co(o-phen)$_2$(OCOC$_2$H$_5$)$_2$]NO$_3$; d) *cis*-[Co(o-phen)$_2$(OCOC$_3$H$_7$)$_2$]NO$_3$; in a dynamic nitrogen atmosphere (3X); in a dynamic oxygen atmosphere (3Y); heating rate 10 deg/min, flow rate 50 ml/min

moles of the complex (calcd. 9.16%)). The second step occurs between 215° and 320°, with a mass loss of 27.5%. The I.R. spectrum of the compound obtained at this temperature gives no evidence of the presence of non-coordinated nitrate ion (characteristic band at 1390 cm^{-1}). Moreover, shown in Fig. 5, the shape of the UV spectrum of a methanolic solution of this residue is different from that of the complex, but accords with the UV spectrum of a methanolic solution of a Co(II)-*o*-phenanthroline complex [7]. It may be presumed that the second decomposition step corresponds to the elimination of 0.67 moles of phenanthroline and 1 mole of nitrate ion (loss found 27.5%; calcd. 27.76%). The process involves reduction to cobalt(II) coupled with the formation of a tetracoordinated compound.

In fact, the TG curve of the intermediate left in air for 24 hrs shows that the complex eliminates two moles of water: it suggests that the remaining positions of the unstable tetracoordinated intermediate complex were oc-

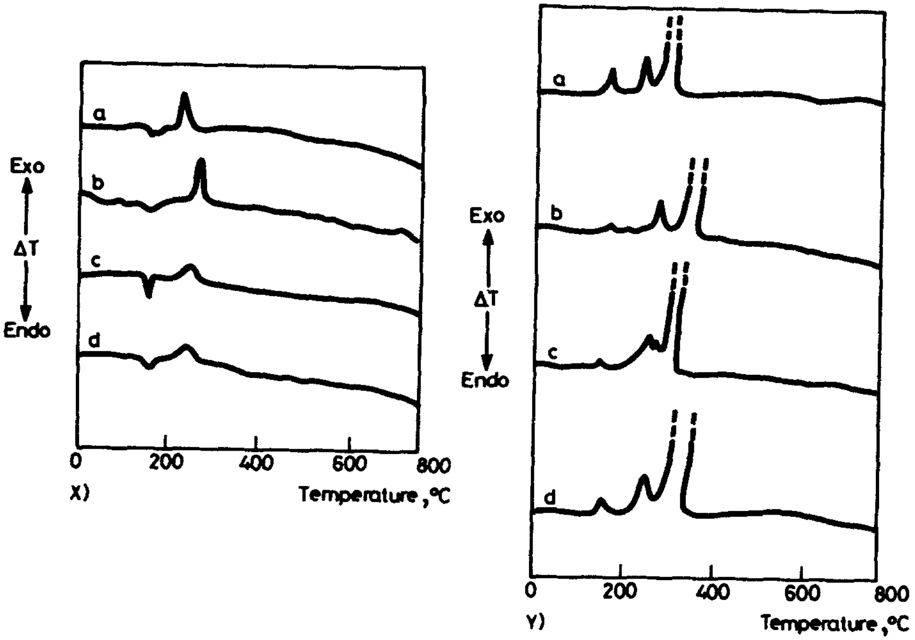

Fig. 4 Differential thermal analysis curves for: a) *cis*-$[Co(bipy)_2(OCOH)_2]NO_3$; b) *cis*-$[Co(bipy)_2(OCOCH_3)_2]NO_3$; c) *cis*-$[Co(bipy)_2(OCOC_2H_5)_2]NO_3$; d) *cis*-$[Co(bipy)_2(OCOC_3H_7)_2]NO_3$; in a dynamic nitrogen atmosphere (4X); in a dynamic oxygen atmosphere (4Y); heating rate 10 deg/min, flow rate 50 ml/min

cupied by 2 moles of water. Finally, the last decomposition process, between 320° and 600°, leads to a residue of metallic cobalt (calcd. 8.99%; found 9.0%).

The TG curves in nitrogen and in oxygen atmospheres show a three-step process, as does the TG curve *in vacuo*: the first decomposition process, as concerns both the temperature interval and the percentage weight loss, is independent of the atmosphere; in nitrogen or oxygen, the second decomposition process at 330-350°, leads to a residue higher than that observed *in vacuo*: this could be due to the experimental conditions not allowing complete elimination of the nitrogen ligand fragments.

The last inflection in the TG curves is strongly dependent on the atmosphere: in nitrogen, the decomposition and the elimination of the organic ligands, leading mainly to metallic cobalt, is delayed (770°); in oxygen, the decomposition occurs with oxidation of the ligand molecules and leads, at 480°, to Co_3O_4 (calcd. 12.25%; found 12.5%). The results obtained by

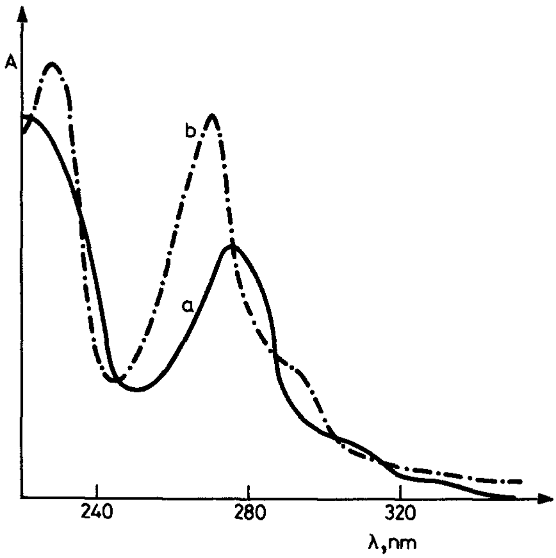

Fig. 5 Absorption UV spectra of: a) *cis*-[Co(o-phen)$_2$(OCOC$_3$H$_7$)$_2$]NO$_3$, and b) the intermediate at about 320°C; in methanolic solution

means of DTA accord with the thermogravimetric behaviour. Indeed, the DTA analysis in a dynamic nitrogen atmosphere shows a first weak endothermic peak, corresponding to the sublimation of the phenanthroline, while in an oxygen atmosphere an exothermic process corresponds to the partial oxidative decomposition of the phenanthroline.

Both in an inert gas atmosphere and in oxygen, the second step is associated with an exothermic peak. The reason for this may be the cobalt reduction and the molecular rearrangement of the complex without the influence of the atmosphere. In the third step, the oxidative decomposition of the intermediate gives a strong exothermic peak in a dynamic oxygen gas atmosphere, while the DTA analysis in a nitrogen atmosphere gives no evidence of this.

cis-[Co(bipy)$_2$(OCOC$_3$H$_7$)$_2$]NO$_3$

The TG curve shows that *in vacuo* the compound is anhydrous and stable up to 145°. The decomposition takes place in three identified processes, the first of them in the temperature range 145-175°. The gas evolution detection curve for the thermal decomposition of the complex, as determined by mass spectroscopy, exhibits a molecular peak (*m*/*e* = 156) that suggests the elimination of 1 mol of bipyridine, which sublimes undecomposed, as shown by the experimental (26.5%) and the calculated (25.70%) weight loss values. In the second step, between 175° and 215°, the second bipyridine molecule is eliminated. In the third step, up to 215°, the molecule of the complex undergoes considerable transformation, with complete elimination of the second bipyridine molecule, elimination of the nitrate ion and decomposition of the butyrate ions. The described trend is supported by the mass spectrum and by the IR spectrum of the intermediate at 215°, which shows the presence of the characteristic absorption band at 1390 cm^{-1} due to the nitrate ion stretching vibration. This last decomposition step leads to a residue of cobalt oxide, i.e. CoO (calcd. 12.35%; found 12.3%), at 370°.

Both in nitrogen and in oxygen gas atmospheres, the initial decomposition temperature is identical to that previously observed *in vacuo*, while it was found that the subsequent curve inflection points occur at higher temperature. The TG curves in nitrogen and oxygen atmospheres display the same decomposition trend up to 230°. Between this temperature and 325°, the rate of decomposition is higher in an inert gas atmosphere than in oxygen. The above temperature range involves elimination of the nitrate ion, the cobalt(III) to cobalt(II) reduction and bipyridine sublimation (in a dynamic nitrogen atmosphere) or its oxidative decomposition (in oxygen). In contrast, in the last stage, the rate of decomposition is higher in oxygen than in nitrogen; in oxygen at 415°, a residue of Co_3O_4 is obtained (calcd. 13.23%; found 13.0%), while in nitrogen at 460°, a stable residue of CoO is found (calcd. 12.35%; found 12.5%).

The DTA results agree with those found previously. In a nitrogen atmosphere, the sublimation of the bipyridine gives an endothermic peak; in an oxygen atmosphere, an exothermic process corresponds to bipyridine oxidation. DTA in nitrogen and oxygen atmospheres leads to an exothermic peak at 250°, due mainly to the reduction of cobalt(III) to cobalt(II).

The last decomposition step takes place only in an oxygen atmosphere and is a strong exothermic process.

The Table 1 reports the individual step temperatures for all the studied complexes.

Table 1 Thermogravimetric data of the studied complexes

		Step 1		
		T, °C		mass loss, %
		T_1	T_2	found
$Co[(o\text{-}phen)_2(OCOC_3H_7)_2]NO_3$	vacuo	190	215	9.5
	O_2	190	215	9.8
	N_2	190	215	9.5
$Co[(o\text{-}phen)_2(OCOC_2H_5)_2]NO_3$	vacuo	175	200	9.0
	O_2	175	215	9.1
	N_2	175	215	8.9
$Co[(o\text{-}phen)_2(OCOCH_3)_2]NO_3$	vacuo	160	200	10.0
	O_2	170	215	12.5
	N_2	155	220	10.6
$Co[(o\text{-}phen)_2(OCOH)_2]NO_3$	vacuo	145	180	11.0
	O_2	145	185	12.5
	N_2	145	170	8.6
$Co[(bipy)_2(OCOC_3H_7)_2]NO_3$	vacuo	145	175	26.5
	O_2	145	185	17.0
	N_2	145	180	21.2
$Co[(bipy)_2(OCOC_2H_5)_2]NO_3$	vacuo	145	175	26.0
	O_2	145	195	17.1
	N_2	145	190	18.1
$Co[(bipy)_2(OCOCH_3)_2]NO_3$	vacuo	145	180	23.1
	O_2	145	200	19.0
	N_2	145	200	22.6
$Co[(bipy)_2(OCOH)_2]NO_3$	vacuo	145	190	25.0
	O_2	130	180	15.2
	N_2	145	190	17.5

T_1, T_2: limit temperatures of the considered step; Res.: the remaining residue; –:the experimental datum could not be interpreted with any certainty

Table 1 Cont.

		Step 2		
		T, °C		mass loss, %
		T_1	T_2	found
$Co[(o\text{-}phen)_2(OCOC_3H_7)_2]NO_3$	vacuo	215	320	27.5
	O_2	215	350	19.0
	N_2	215	330	19.5
$Co[(o\text{-}phen)_2(OCOC_2H_5)_2]NO_3$	vacuo	200	290	29.6
	O_2	215	320	15.0
	N_2	215	320	22.3
$Co[(o\text{-}phen)_2(OCOCH_3)_2]NO_3$	vacuo	200	275	30.5
	O_2	215	325	17.1
	N_2	220	330	21.3
$Co[(o\text{-}phen)_2(OCOH)_2]NO_3$	vacuo	180	295	40.0
	O_2	185	340	21.7
	N_2	170	380	42.3
$Co[(bipy)_2(OCOC_3H_7)_2]NO_3$	vacuo	175	215	24.2
	O_2	185	245	21.4
	N_2	180	230	18.0
$Co[(bipy)_2(OCOC_2H_5)_2]NO_3$	vacuo	175	250	45.2
	O_2	195	300	32.2
	N_2	190	280	38.4
$Co[(bipy)_2(OCOCH_3)_2]NO_3$	vacuo	180	300	32.1
	O_2	200	320	20.4
	N_2	200	310	29.9
$Co[(bipy)_2(OCOH)_2]NO_3$	vacuo	190	–	–
	O_2	180	–	–
	N_2	190	–	–

T_1, T_2: limit temperatures of the considered step; Res.: the remaining residue; –:the experimental datum could not be interpreted with any certainty

Table1 Cont.

		Final heating			
		T, °C	Res.	% (weight)	
				found	calcd.
$Co[(o\text{-}phen)_2(OCOC_3H_7)_2]NO_3$	vacuo	600	Co	9.0	8.99
	O_2	480	Co_3O_4	12.5	12.25
	N_2	770	Co	10.1	8.99
$Co[(o\text{-}phen)_2(OCOC_2H_5)_2]NO_3$	vacuo	570	Co	9.5	9.39
	O_2	480	Co_3O_4	13.0	12.79
	N_2	700	–	–	–
$Co[(o\text{-}phen)_2(OCOCH_3)_2]NO_3$	vacuo	550	Co/CoO	11.0	9.84/12.51
	O_2	460	Co_3O_4	13.5	13.39
	N_2	600	CoO	12.2	12.51
$Co[(o\text{-}phen)_2(OCOH)_2]NO_3$	vacuo	470	CoO	13.0	13.12
	O_2	430	Co_3O_4	13.5	14.05
	N_2	550	–	–	–
$Co[(bipy)_2(OCOC_3H_7)_2]NO_3$	vacuo	370	CoO	12.3	12.35
	O_2	415	Co_3O_4	13.0	13.23
	N_2	460	CoO	12.5	12.35
$Co[(bipy)_2(OCOC_2H_5)_2]NO_3$	vacuo	420	CoO	12.5	12.94
	O_2	420	Co_3O_4	13.4	13.86
	N_2	480	CoO	12.0	12.94
$Co[(bipy)_2(OCOCH_3)_2]NO_3$	vacuo	450	CoO	13.5	13.59
	O_2	430	Co_3O_4	14.5	14.56
	N_2	500	CoO	12.5	13.59
$Co[(bipy)_2(OCOH)_2]NO_3$	vacuo	270	CoO	13.5	14.32
	O_2	330	Co_3O_4	15.7	14.34
	N_2	440	CoO	14.5	14.32

T_1, T_2: limit temperatures of the considered step; Res.: the remaining residue; –:the experimental datum could not be interpreted with any certainty

Conclusions

The thermal stabilities of the Co(III)-*o*-phen complexes are as follows:

di-*n*-butyrate > dipropionate > diacetate > diformate

This sequence results from the temperatures relating to the first decomposition process, in an inert gas atmosphere, which, as previously reported, involves breaking of the bonds between the nitrogen atoms of the 1,10-phenanthroline and the central metal ion.

Examination of this thermal stability sequence reveals that the initial decomposition temperatures are influenced by the alkyl chain length of the carboxylato ligand present in the complexes.

An explanation for this may be that the steric hindrance effects, due to the carboxylato ions in the *cis* position, influence the Co-N bond strength and overcome the effect of the basicity of the carboxylato group. It is well known that the thermal stability may be influenced by inductive effects and/or steric effects. The sequence of stability based on inductive effects would be:

diformate > > diacetate > dipropionate ≈ di-*n*-butyrate

while the observed sequence is just the opposite of this. This indicates clearly that the steric effects are important in determining the relative stability of these complexes. The above considerations agree with those reported by Haim on a study of mixed Co(III) *bis*-ethylenediamine complexes in solution [8].

All the Co(III)-2,2'-bipyridine complexes exhibit the same initial decomposition temperature, and the first decomposition process in nitrogen includes evolution of the undecomposed nitrogen ligand. The reason for this may well be the molecular stress in the complex, due to the *cis* configuration of the bipyridine ligand. Indeed the nitrogen atoms in free 2,2'-bipyridine lie in the *trans* position, and there must be rotation about the C-C bond in order for complex formation to be possible [9]. The heating provides the complex with sufficient energy to break the N-Co bonds and to convert the ligand molecule from the *cis* configuration to the more stable *trans* configuration of the free base. This may explain the elimination of the bipyridine molecule at a temperature independent of the nature of the carboxylato ion bonded to the central metal ion.

The nature of the nitrogen ligand also justifies the hypotheses concerning the different shapes of the TG curves of the two series of complexes. The elimination of the second molecule of nitrogen ligand in an inert gas atmosphere is considerably delayed in the case of the *o*-phenanthroline complexes. This elimination takes place through decomposition which produces a reducing atmosphere and leads to a residue that consists mainly of metallic cobalt, whereas the 2,2'-bipyridine complexes eliminate the second nitrogen ligand molecule as a sublimate at lower temperatures, the reducing environment is not produced and the residue consists of CoO.

The data obtained for the Co(III)-*o*-phen complexes can be compared with those reported in a previous paper following an analogous investigation of the *cis*-[Co(III)-en-OCOR] complexes [2]. This comparison allows us to formulate some considerations on the influence of the nature of the nitrogen ligand on the thermal stability of the examined complexes:

i) in both cases, the first decomposition process involves the breaking of Co–N bonds and elimination of the nitrogen ligand;

ii) the complexes of the two series exhibit the same stability sequence;

iii) the Co(III)-*o*-phenanthroline complexes are thermally more stable than the corresponding Co(III)-ethylenediamine complexes: this is probably due to the favorable interactions of the Co(III)t_{2g} orbitals with the phenanthroline ligand π^* orbitals, as suggested by Martell [10].

Finally, in the Co(III)-bipyridine series it seems that the nature of the carboxylato ligands does not influence the initial decomposition temperature.

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Zusammenfassung — Zur Ermittlung von Informationen über den Zersetzungsmechanismus wurde mittels TG-, DTA- und spektroskopischen Methoden *cis*-$Co[(AA)_2(OCOR)_2]NO_3$ untersucht, wobei AA = 1,10-Phenanthrolin oder 2,2'-Bipyridin sowie R = H, CH_3, C_2H_5 oder *n*-C_3H_7 ist. Ein Vergleich beider Verbindungsreihen ergab, dass der erste Schritt der Zersetzung in der Spaltung der Co-N-Bindung und der Abspaltung des Stickstoffliganden besteht; Phenanthrolinkomplexe zeigen eine gewisse Stabilitätsreihenfolge, während alle Bipyridinkomplexe ihre Zersetzung bei der gleichen Temperature beginnen. Die erhaltenen Ergebnisse wurden weiterhin mit früheren Untersuchungsergebnissen über Ethylendiaminkomplexe verglichen.