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KINETIC ANALYIS OF TG DATA
XXXV. Spectroscopic and thermal studies of some cobalt(III) chelates with ethylenediamine

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Abstract

A number of 30 $[Co(en)_3]Y_3$, $[Co(en)_2X_2]Y$ and $[Co(en)_2X(amine)]Y_2$ type complexes (X=Cl, Br; Y=Cl, Br, I, NCO, NCS, NO_3, ClO_4, etc.; *amine*=aromatic and alkylamines) were obtained from *trans*-$[Co(en)_2Cl_2]Cl$ by double decomposition and by substitution reactions, respectively. The structure of the complexes was proved by means of far and middle FTIR spectra. The thermal decomposition was studied by TG, DTA and DSC measurements. Mass spectra were also recorded. In the case of $[Co(en)_3]Y_3$ complexes the nitrate, perchlorate and dimesoperiodates decompose suddenly, frequently explosion like. The halides and thiocyanates seem to substitute an ethylenediamine ligand, yielding a rather unstable intermediate. The pyrolysis of $[Co(en)_2X_2]Y$ type derivatives yields no relatively stable intermediates, but the decomposition temperatures may be correlated with the nature of Y and with the *cis* or *trans* configuration of the compound. With the $[Co(en)_2X(amine)]Y_2$ type complexes one observes the formation of $[Co(en)_2XY]Y$ as intermediate product. From the TG curves kinetic parameters were derived for some dehydration and deamination processes, by using the nomogram method. The validity of a nonlinear kinetic compensation law was observed.

Keywords: cobalt(III) complexes, DSC, DTA, kinetics, FTIR and IR spectra of Co(III) complexes, TG

Introduction

The aromatic, alicyclic, N-heterocyclic and especially the various aliphatic diamines form homogeneous ($[Co(diamine)_n]^{2+,3+}$) and mixed chelates ($[Co(diamine)_2AB]$) with Co(II) and Co(III). From coordination chemical point of view the most important complexes are the ethylenediamine Co(III) derivatives, with very stable five member Co-heterocyclic ring systems. The homologues of this aliphatic diamine: 1,2-, 1,3-, 1,4-, 1,5-diamines form also complex compounds with the above mentioned metal ion. The stability of these chelate ring systems decreases in the order:

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en>1,2-propane>1,3-propane>1,4-butane>1,5-diamines.

The formation of 7...10 atomic chelate rings is very difficult due to steric hindrances.

Some attempts were also made aiming the synthesis of N-substituted mono- and di-ethylenediamine derivatives as ligands for coordination chemical purposes (mono- and dialkyl, mono- and diphenyl ethylenediamines were also mentioned in the literature) [1–6].

The most significant cobalt(III) complex with ethylene diamine, the *trans*-$[Co(en)_2Cl_2]Cl$, is the starting material in various substitution reactions, as seen in Fig. 1.

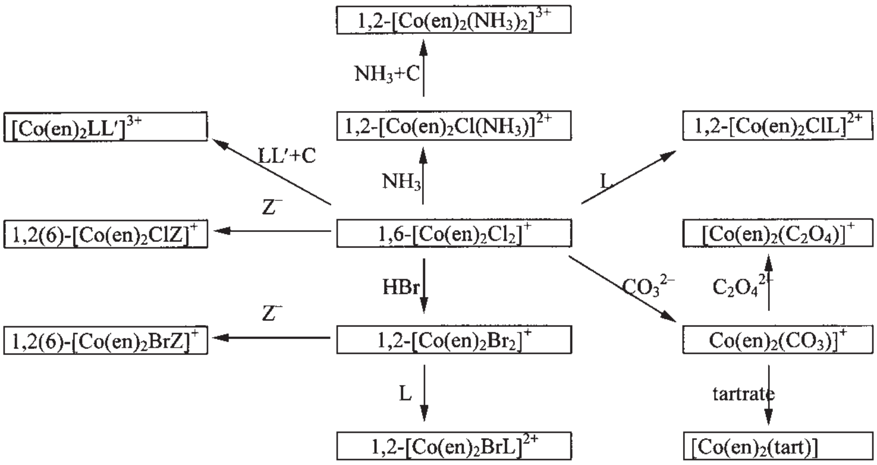

Fig. 1 Substitution reactions of 1,6-$[Co(en)_2Cl_2]^+$.
L – various amines (4<p*K*<11); *LL′* – 1,2-diamines; Z^- – CN^-, NCO^-, NCS^-, $NCSe^-$, NO_2^-, NH_3^-; C – catalyst

It is worth mentioning, that unlike the $[Co(Diox.H)_2I_2]^-$ and the $[Co(Diox.H)_2I(amine)]$ derivatives (diox.H_2 stands for an aliphatic or alicyclic α-dioxime), the $[Co(en)_2I_2]^+$ and $[Co(en)_2I(amine)]^{2+}$ derivatives cannot be obtained.

The substitution reactions of $[Co(en)_2Cl_2]^+$ and $[Co(en)_2Br_2]$ with aliphatic, alicyclic and heterocyclic monoamines (basicity constant: 4<pK_b<11) lead to the formation of monoacido-pentamin-derivatives (excepting α-picoline, 2,6-lutidine, 2,4,6-symm.collidine, which exhibit steric hindrances). In the presence of the latter pyridine derivatives and with very weak bases (12p<K_b<14) *trans-cis* geometric isomerisation can be observed. Nevertheless, the pK_b value of the amine is not the only factor determining the above mentioned substitution processes [7–11].

The substitution of the halogens (Cl^-, Br^-) may be performed also in the presence of catalysts (e.g. charcoal, silicagel, etc.) and various mono- and di-amines (*L* –NH_3, *LL′* -en, pn, dyp, o-phen, etc.) e.g.:

$$[Co(en)_2X_2]^+ + LL' \rightarrow [Co(en)_2(LL')]^{3+} + 2X^- \qquad (1)$$

Results and discussions

In this paper a number of 30 $[Co(en)_3]Y_3$, $[Co(en)_2X_2]Y$ and $[Co(en)_2X(amine)]Y_2$ type complexes (*X* – Cl, Br; *Y* – halides and pseudohalides, oxoanions, etc.) were studied by spectral and thermal methods. The Co(III)-complexes studied are characterized in Tables 1–3.

Table 1 $[Co(en)_3]Y_3$ type complexes

No.	Formula	Mol. mass calc.	Appearance (microscopic)	Analysis		
					calc.	found
1	$[Co(en)_3]Cl_3{\cdot}3H_2O$	399.3	brown great prisms	Co	14.7	14.6
				Cl	26.6	26.7
				H_2O	13.5	13.3
2	$Co(en)_3]Br_3{\cdot}3H_2O$	532.7	orange prisms	Co	11.1	11.2
				Br	45.0	44.7
				H_2O	10.1	10.8
3	$[Co(en)_3]I_3{\cdot}H_2O$	637.7	brown crops	Co	9.2	9.5
				I	59.7	60.1
				H_2O	2.8	3.1
4	$[Co(en)_3](NCS)_3$	413.2	orange plates	Co	14.2	13.8
				NCS	42.1	43.0
5	$[Co(en)_3](ClO_4)_3$	537.3	orange needles	Co	10.9	11.1
6	$[Co(en)_3](NO_3)_3$	425.0	orange irreg.cryst.	Co	13.9	13.5
7	$[Co(en)_3]HI_2O_9{\cdot}3H_2O$	691.8	sparkling yellow needles	Co	8.5	8.4
				I	36.7	37.0
8	$[Co(en)_3]_4(I_2O_9)_3$	2149.2	voluminous microcryst.	Co	11.0	10.8
				I	35.4	35.0
9	$[Co(en)_3][Cr(NCS)_6]$	639.5	brown microcryst.	Co+Cr	17.3	17.7
				NCS	54.5	55.0
10	$[Co(en)_3][Cr(NCS)_4(NH_3)_2]_3$	1194.0	reddish brown microcryst.	Co+Cr	18.0	18.3
				HN_3	8.5	8.2

Synthesis

The starting compounds, $[Co(en)_3]Cl_3$, and *trans*-$[Co(en)_2Cl_2]Cl$ were obtained by air oxidation of a mixture of $CoCl_2$ and ethylene diamine in aqueous solution in the presence of catalyst (in the case of $[Co(en)_3]Cl_3$), and in its absence (with the $[Co(en)_2Cl_2]Cl$ derivative). For double decomposition reactions an excess of NaX solutions was used (*X* – Br^-, I^-, NCS^-, NCO^-, NO_3^-, ClO_4^-, IO_4^-, $1/3[Cr(NCS)_6]^{3-}$, $[Cr(NCS)_4(NH_3)_2]^-$).

Table 2 $[Co(en)_2X(amine)]Y_2$ type complexes

No.	Formula	Mol. mass calc.	Appearance	Analysis		
					calc.	found
11	*cis*-$[Co(en)_2Cl$-(trimethylamine)$]Cl_2\cdot H_2O$	362.4	thick red prisms	Co Cl H_2O	16.2 29.3 5.0	16.4 28.9 5.3
12	*cis*-$[Co(en)_2Cl$-(aniline)$]Cl_2\cdot H_2O$	396.3	great red irreg. prisms	Co Cl H_2O	14.9 26.8 4.5	14.8 27.0 4.2
13	*cis*-$[Co(en)_2Cl$-(*o*-ethylaniline)$]Cl_2\cdot H_2O$	424.3	red needles	Co Cl H_2O	13.9 25.0 4.2	14.1 25.2 4.5
14	*cis*-$[Co(en)_2Cl$-(*o*-anisidine)$]Cl_2\cdot 2H_2O$	444.3	sparkling red stars	Co Cl H_2O	13.2 23.9 8.1	13.5 23.6 8.0
15	*cis*-$[Co(en)_2Cl$-(benzylamine)$]I_2$	575.4	brown plates in star form	Co I	10.2 44.1	10.1 43.9
16	*cis*-$[Co(en)_2Br$-(benzylamine)$]I_2$	619.8	square brown plates	Co I	9.5 40.9	9.4 41.2

Table 3 $[Co(en)_2X_2]Y$ type complexes

No.	Formula	Mol. mass calc.	Appearance	Analysis		
					calc.	found
17	*cis*-$[Co(en)_2Cl_2]Cl\cdot H_2O$	303.8	violet prisms	Co	19.4	19.4
18	*trans*-$[Co(en)_2Cl_2]Cl$	285.3	green prisms	Co	20.6	20.6
19	*cis*-$[Co(en)_2Cl_2]Br\cdot H_2O$	347.8	violet tables	Co	16.9	16.7
20	*trans*-$[Co(en)_2Cl_2]Br$	329.8	green plates	Co	17.9	17.9
21	*cis*-$[Co(en)_2Cl_2]I$	376.8	brown needles	Co	15.6	15.5
22	*trans*-$[Co(en)_2Cl_2]I$	376.8	yellow-brown prisms	Co	15.6	15.7
23	*cis*-$[Co(en)_2Cl_2]NCS$	307.9	violet plates	Co	19.1	19.0
24	*trans*-$[Co(en)_2Cl_2]NCS$	307.9	green plates	Co	19.1	19.3
25	*cis*-$[Co(en)_2Cl_2]NCO$	291.9	violet prisms	Co	20.2	20.3
26	*trans*-$[Co(en)_2Cl_2]NCO$	291.9	green prisms	Co	20.2	20.1
27	*trans*-$[Co(en)_2Br_2]Br\cdot H_2O$	436.7	green-yellow prisms	Co H_2O	13.5 4.1	13.4 4.3
28	*trans*-$[Co(en)_2Br_2]I$	465.7	green-brown needles	Co	12.6	12.5
29	*trans*-$[Co(en)_2Br_2]NCO$	380.8	green prisms	Co	15.5	15.6
30	*trans*-$[Co(en)_2Br_2]NCS$	396.8	green needles	Co	14.9	14.7

Spectral studies

Some FTIR spectral data in the middle IR region for several complexes studied are presented in Table 4. These data show the green $[Co(en)_2Cl_2]Cl$ and the $[Co(en)_2Br_2]Br$ to have a trans geometric configuration (a single δ_{rCH_2} band in the 870–910 cm^{-1} region). The $[Co(en)_2Cl(amine)]Y_2$ and the $[Co(en)_2Br(amine)]Y_2$ derivatives present a *cis* sterical arrangement (two deformation bands in the mentioned spectral range) [12].

Table 4 Middle FTIR spectral data on some cobalt(III)-ethylene-diamine complexes

Assignment	1	2	3	4	5
$\nu_{N–H}$	3245 s	3230 m		3240 s	3250 s
	3200 m		3180 s		
	3160 m	3155 s	3100 s	3150 m	3160 m
$\nu_{C–H}$	2955 vs	2965 s	2980 m	2975 m	2980 s
	2860 m	2860 m	2885 m	2885 m	2870 s
δ_{sNH_2}	1610 vs	1610 vs	1630 m	1625 m	1620 s
$\nu_{C–C(arom)}$	–	1590 vs	1575 m	1585 vs	–
δ_{CH_2}	1460 vs	1475 m	1460 vs	1470 m	1470 vs
δ_{NH_2}	1395 vs	1395 vs	1395 s	1380 s	1380 vs
δ_{CH_2}	1355 s	1365 m	1365 vs	1320 m	1350 s
		1340 s	1320 vs		
δ_{rCH_2}	890 m	890 m	900 m	905 m	900 m
		870 s	880 m	875 m	
γ_{NH_2}	845 m	830 s	840 w	810 s	840 s
$\gamma_{C–H}$	730 m	705 s	765 vs	710 vs	730 s
			710 vs		

1 – *trans*-$[Co(en)_2Cl_2]I$; 2 – *cis*-$[Co(en)_2Cl(aniline)]Cl_2$; 3 – *cis*-$[Co(en)_2Cl(benzylamine)]I_2$; 4 – *cis*-$[Co(en)_2Br(benzylamine)]I_2$; 5 – $[Co(en)_3]Cl_3$

The $\nu_{N–H}$ (3250–3150 cm^{-1}), δ_{sNH_2}, (1610–1630 cm^{-1}) and δ_{as} (1380–1390 cm^{-1}) frequencies show strong covalent Co–N bonds. The $\nu_{C–H}$ and δ_{CH_2} bands are not affected by coordination effects.

In the far IR region the $\nu_{Co–N(en)}$, $\nu_{Co–N(L)}$, $\nu_{Co–Cl}$, $\nu_{Co–Br}$ stretching vibrations and the N_{en}–Co–N_{en}, N_{en}–Co–N_L, N_{en}–Co–Cl, N_{en}–Co–Br, N_L–Co–Cl, etc., and various skeletal vibrations of the aromatic and heterocyclic *L* ligands and those of the five-membered chelate rings (250–50 cm^{-1}) appear. Generally, these bands are in some extent overlapped by each other.

Certain discrepancies appear at the assignement of the metal-nitrogen vibrations in metal-ethylenediamine complexes. Large frequency ranges are assigned to the M–N vibration (550–350 cm^{-1}). The difficulty in making the assignment may arise from the coupling of the vibration with the NH_2 rocking mode and with a low frequency skeletal mode. The Co–N bond in ethylenediamine complexes is stengthened

Table 5 Far infrared spectral data of some Co(III)-ethylenediamine complexes

Formula	$\nu_{Co–N}$	δ_{NH_2}	$\delta_{N–Co–N}$	$\nu_{Co–X}$	Skeletal bending	Skelet. co-octahedral (lattice)
$[Co(en)_3]I_3$	580 s 545 m	497 m 439 s	305 m 271 vs	–	153 w 144 m 136 w 119 s	40 m 30 m
cis-$[Co(en)_2Cl(aniline)]Cl_2$	583.5 s 572 m 553 s	515 w 503 s 425 s	354 s 332 w 271 vs	286 w 179 m	149 vs 135 s 119 m	31 m
cis-$[Co(en)_2Cl($*o*-anisidine$)]Cl_2$	589 s 569 vs 528 m	496 s 465 s	341 w 323 w 277 vs	289 s 205 s 183 s	151 s 126 vs	30 s
cis-$[Co(en)_2Cl$- (o-ethylaniline$)]Cl_2$	578.5 vs 510 vs	460 s 442 w	321 s 269 vs	285 s 185 vs	145 w 130 s	30 m
cis-$[Co(en)_2Cl(benzylamine)]I_2$	575 vs 565 s 515 m	459 ws	323 w 304 m 263 vs	207 s 190 m	52 m 143 m	35 m 31 m
cis-$[Co(en)_2Cl$- (trimethylamine)$]Cl_2$	577.8 vs 510 s	484 m	347 m 321 m 267.8 vs	285 s 210 m	167 m 130 m 110 m	31 m

primarily by the chelation effect, as any π interaction would be slight. When ethylenediamine coordinates to a metal as a chelating ligand, it may adopt eight different conformations, especially with the $[Me(en)_3]^{n+}$ ions. Thus, it is rather difficult to obtain sure conformational information from the vibrational spectra [13–14].

In Table 5 an attempt is made to assign several far IR bands to different molecular vibrations.

Thermal investigations

Thermal decomposition of ethylenediamine and substituted ethylenediamine containing transition metal (Ni, Cu, Pd) complexes has been studied in air atmosphere by means of thermogravimetry in order to determine the decomposition temperatures and to obtain information concerning the stoechiometry of the pyrolysis [15–20]. The derivatographic study of $[Co(en)_3]Y_3$ type complexes in air atmosphere suggested the idea that if Y=Cl, a partial deamination reaction may occur corresponding to [21–22]

$$[Co(en)_3]Y_3 \rightarrow [Co(en)_2Y_2]Y+en \quad (2)$$

A similar reaction was observed to occur in almost stoechiometric extent in the case of the analogous $[Cr(en)_3]Y_3$ complexes [23–24] and this reaction is valorified in the thermal matrix method, allowing the preparation of $[Cr(en)_2Y_2]Y$ type complexes which cannot be synthesized in aqueous solutions [25–26].

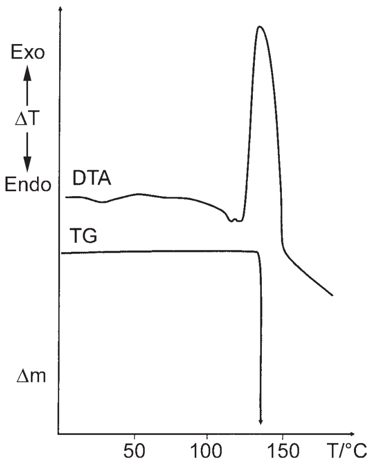

Fig. 2 TG and DTA curves of $[Co(en)_3](ClO_4)_3$

The present thermal study of the $[Co(en)_3]Y_3$ type complexes showed that if Y is the anion of some oxyacids as nitric, perchloric, dimesoperiodic acids, the decomposition is explosion like. The TG curves show only a decomposition temperature and nothing else, the DTA one exhibits a sharp exothermic peak, as seen from Fig. 2. If the anion is a complex one, the decomposition of the cation and of the anion occurs in

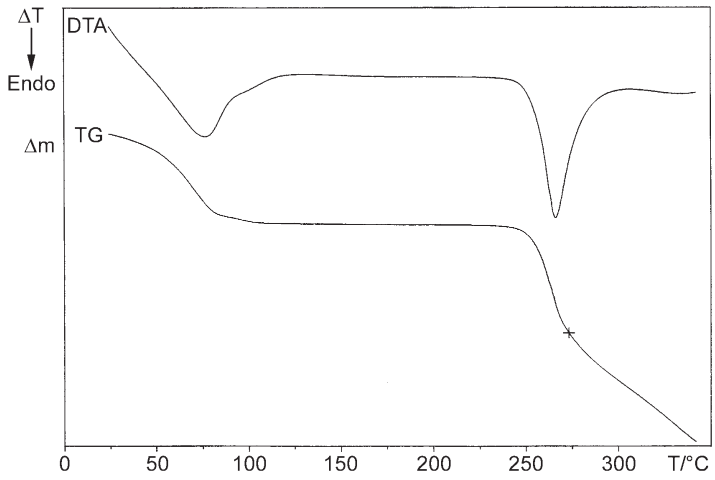

Fig. 3 TG and DTA curves of $[Co(en)_3]Cl_3 \cdot 3H_2O$

the same time and a continuous mass loss is observed without mass loss stops or inflexions at stoechiometric ratios until the sample is transformed into a mixture of oxides of the corresponding transition metals.

If the anion is a halogen, or NCS, the shape of the TG curve is consistent with the presumption that after the loss of the crystallization water, reaction (3) occurs. No mass loss stop is observed, only an inflexion point. Thus in this decomposition $[Co(en)_2Y_2]Y$ is not a sufficiently stable intermediate and the reaction is more complicated than with the analogous $[Cr(en)_3]Y_3$ complexes. Presumably, the relative instability of the intermediate is correlated with the possibility of Co(III) → Co(II) redox reactions. Mass spectral data are in agreement with this hypothesis. As an example we give in Fig. 3 the TG and DTA curve of $[Co(en)_3]Cl_3 \cdot H_2O$. As seen, the first step of the pyrolysis is an endothermic dehydration and at about 240°C begins reaction (2). The elimination of an en ligand corresponds to 15% mass loss (marked in Fig. 3) and the decomposition rate slows down at about this point but the decomposition continues, i.e. reaction (2) is partially overlapped by other processes.

It is interesting to compare the endothermic DTA peak temperatures of different complexes, both in the case of dehydration and deamination reactions. As seen from Table 6, the dehydration peak temperature of $[Co(en)_3]Y_3$ complexes increases in the order Cl<Br<I. This means that the thermal stability of the hydrated anions increases in the same order. With respect to the deamination peak temperatures, one observes that it is much lower in the case of the NCS^- as compared to the halogen ions. This must be correlated with the high stability of the Co–NCS bond, due to the possibility of π-bond formation.

Table 6 Endothermic DTA peak temperatures (°C) of $[Co(en)_3]Y_3$ and $[Co(en)_2X(amine)]Y_2$ type complexes

Formula	Dehydration	Deamination
$[Co(en)_3]Cl_3 \cdot 3H_2O$	76	267
$[Co(en)_3]Br_3 \cdot 3H_2O$	109	279
$[Co(en)_3]I_3 \cdot H_2O$	121	275
$[Co(en)_3](NCS)_3$	–	216
cis-$[Co(en)_2Cl$-(trimethylamine)$]Cl_2 \cdot H_2O$	130	240
cis-$[Co(en)_2Cl$(aniline)$]Cl_2 \cdot H_2O$	81	239
cis-$[Co(en)_2Cl$-(*o*-ethylaniline)$]Cl_2 \cdot H_2O$	131	241
cis-$[Co(en)_2Cl$-(*o*-anisidine)$]Cl_2 \cdot 2H_2O$	89	170
cis-$[Co(en)_2Cl$(benzylamine)$]I_2$	–	177
cis-$[Co(en)_2Br$(benzylamine)$]I_2$	–	178

The thermal decomposition of $[Co(en)_2X(amine)]Y_2$ type complexes may also imply a deamination reaction, namely the substitution of the amine ligand for the external sphere anion, i.e.

$$[Co(en)_2X(amine)]Y_2 \rightarrow [Co(en)_2XY]Y + amine \qquad (3)$$

If *Y* is a halide or a pseudohalide, the TG curves show an inflexion at a mass loss corresponding to an amine molecule, suggesting that reaction (3) occurs indeed, but it is partially overlapped by other decomposition processes. The DTA endothermic peak temperatures given also in Table 6, show that the nature of the external sphere anion is the most important. This temperature is much lower for *Y*=I, than for *Y*=Cl. Obviously, it is influenced also by the nature of the amine ligand, which is substituted. Thus, in the case of the *o*-anisidine derivative, the decomposition temperature is lower due to the steric hindrance diminishing the strength of the Co–N bond.

Table 7 Endothermic DTA peak temperatures (°C) at the deamination of $[Co(en)_2X_2]Y$ type complexes

Y	*X*=Cl		*X*=Br
	cis	*trans*	*trans*
Cl	182	192	–
Br	178	181	185
I	174	176	184
NCS	168	162	182
NCO	152	168	160

At the thermal decomposition of $[Co(en)_2X_2]Y$ type complexes, up to about 150°C, neither the TG, nor the DTA curves show any changes. This means, that under our working conditions, no ionization metameric transformation occurs. The begin-

Table 8 Kinetic parameters derived from the TG curves of some $[Co(en)_3]Y_3$ and $[Co(en)_2X(amine)]Y_2$ type complexes

Formula	Reaction	$T_{0.1}$/K	n	E/ kJ mol^{-1}	log$A$	logA'
$Co(en)_3]Cl_3 \cdot 3H_2O$	dehydr.	313.8	1.40	60.8	7.2	7.29
$Co(en)_3]Cl_3 \cdot 3H_2O$	deamin.	524.1	0.91	402.8	37.5	37.70
$Co(en)_3]Br_3 \cdot 3H_2O$	dehydr.	355.6	1.07	110.9	13.6	13.62
$Co(en)_3]Br_3 \cdot 3H_2O$	deamin.	539.2	1.42	802.1	75.4	75.55
$Co(en)_3]I_3 \cdot H_2O$	dehydr.	370.9	1.32	144.6	17.7	17.76
cis-$[Co(en)_2Cl$(trimethylamine)$]Cl_2 \cdot H_2O$	dehydr.	386.8	1.58	260.6	32.8	32.82
cis-$[Co(en)_2Cl$(aniline)$]Cl_2 \cdot H_2O$	dehydr.	330.3	2.17	117.3	15.8	15.96
cis-$[Co(en)_2Cl$(aniline)$]Cl_2 \cdot H_2O$	deamin.	449.7	1.60	708.2	80.0	80.20
cis-$[Co(en)_2Cl$(*o*-ethylaniline)$]Cl_2 \cdot H_2O$	dehydr.	381.7	1.31	157.7	19.1	19.00
cis-$[Co(en)_2Cl$(*o*-anisidine)$]Cl_2 \cdot 2H_2O$	dehydr.	336.7	1.33	109.3	14.3	14.32

ning of the decomposition is marked on the DTA curve by an endothermic peak. The corresponding peak temperatures are presented in Table 7.

As seen from this table, the peak temperatures are shifted towards lower values as function of the external sphere anion in the following order:

$$\mathrm{Cl} > \mathrm{Br} > \mathrm{I} > \mathrm{NCS} > \mathrm{NCO}$$

This order might be correlated with the Co–Y bond strength, which increases in the same order. One may observe further that the thermal stability of the *trans* isomers is higher than that of the *cis* ones. The decomposition temperature is influenced also by the nature of the *X* ligand, víz. the DTA peak temperatures are a little higher in the case of the bromo derivatives, as compared to the chloro ones. On the TG curves the formation of no relatively stable intermediate is observed, i.e. the pyrolysis is a complex process consisting of several simultaneous reactions.

The shape of several TG curves allowed us to derive kinetic parameters for a few decomposition steps, víz. for dehydration of crystallohydrates and deamination of some $[\mathrm{Co(en)_2X(amine)}]\mathrm{Y_2}$ type complexes. For this purpose the nomogram method [28, 29] was used. Results are presented in Table 8.

In this table $T_{0.1}$ stands for the temperature at which the conversion in the considered decomposition stage attains $\alpha=0.1$. The magnitudes *n*, *E* and *A* stand for the apparent reaction order, activation energy and the pre-exponential factor in the Arrhenius equation, respectively. As seen from this table, the apparent activation energies are higher in the case of the deamination reactions, as compared to the dehydration ones, but it is obvious, that the *E* values cannot be correlated with the molecular structure. This is in agreement with our view, that the apparent activation parameters derived from TG curves do not characterize the chemical process. They are parameters characterizing the TG curve of the given sample and they depend on a considerable number of procedural variables.

One observes further that log*A* values increase with increasing *E* values. This is the so-called kinetic compensation effect. As shown in our earlier paper [30], this effect obeys the following non-linear law:

$$\log A' = \frac{E}{RT_{0.1}\ln 10} + \log\left(\frac{qE}{T_{0.1}^2}\right) - 1.85 \tag{4}$$

In this equation *R* and *q* stand for the gas constant and for the heating rate, respectively, the latter one being expressed in K $\mathrm{s^{-1}}$. The log*A′* values calculated by means of Eq. (4) are presented in the last column of Table 8. These calculated values are in good agreement with log*A* values derived directly from the TG curves.

Mass spectral data

The *m/z* values for six complexes are pesented in Table 9. The fragmentation of the complex ion occurs in a complicated manner and between the products always appear the peaks of the single and double ionized en (at 60 and 30, respectively), of the coordinated *X* ligand (at 36 and 79, respectively), of the coordinated amine as aniline (93), *o*-anisidine (123), benzylamine (106). Other fragmentation products correspond to Co(en)Cl, double ionized $Co(en)_2$ and to $Co(en)_2Cl$, the latter one being in agreement with the above presumed reaction (3). One observes further the signal of the external sphere anion at 36 and 127 respectively. In the case of the iodides there is a signal at 254, corresponding to I_2, which means that also redox reactions may occur.

Table 9 Mass spectral data of some Co(III)-ethylenediamine complexes

Formula	*m*/*z*		
cis-$[Co(en)_2Cl(aniline)]Cl_2$	28(30%)	60(5%)	182(15%)
	30(50%)	65(30%)	224(18%)
	36(20%)	66(6%)	246(15%)
	39(25%)	93(100%)	373(4%)
	54(8%)	128(10%)	571.5(6%)
cis-$[Co(en)_2Cl$(*o*-ethylaniline)$]Cl_2$	28(58%)	106(4%)	313(3%)
	30(100%)	128(23%)	373(4%)
	35(27%)	186(3%)	445(12%)
	43(13%)	215(3%)	572(18%)
	60(5%)	246(25%)	
cis-$[Co(en)_2Cl$(*o*-anisidine)$]Cl_2$	28(43%)	80(70%)	186(8%)
	30(100%)	92(15%)	246(30%)
	36(37%)	108(78%)	373(5%)
	53(30%)	123(77%)	445(6%)
	60(7%)	127(10%)	572(10%)
	65(24%)	154(20%)	
cis-$[Co(en)_2Cl(benzylamine)]I_2$	28(34%)	79(20%)	154(5%)
	30(100%)	91(15%)	186(5%)
	36(10%)	106(55%)	254(20%)
	51(10%)	118(10%)	313(5%)
	77(15%)	127(15%)	373(5%)
cis-$[Co(en)_2Br(benzylamine)]I_2$	28(70%)	70(40%)	254(15%)
	32(15%)	91(20%)	313(5%)
	63(10%)	106(100%)	
	77(25%)	127(15%)	
$[Co(en)_3]I_3$	28(33%)	88(10%)	254(35%)
	30(100%)	127(30%)	313(10%)
	43(12%)	186(20%)	373(18%)
	59(15%)	198(8%)	445(10%)
	60(10%)	215(10%)	572(30%)
	75(6%)	246(80%)	614(5%)

In all spectra appears a quite strong signal at *m*/*z*=28. It could be assigned to N_2 and/or to $CH_2–CH_2$. Besides the fragmentation processes also condensation ones must occur since one observes a considerable number of peaks at *m*/*z* values depassing the molar mass of the complex ion. Presumably, the coordinated amine molecules are at first eliminated, further the break up of the Co(en) chelate ring occurs, allowing the free NH_2 group of en to be linked to an other Co atom. Thus polynuclear formations appear, such as $(en)_2Co(en)Co(en)NH$ (313), $(en)_2Co(en)Co(en)_2NH$ (373), $(en)_2Co(en)Co(Cl)(en)Co(en)_2$ (572).

Experimental

$[Co(en)_3]Y_3$

0.1 mol $CoCl_2$ and 0.3 mol en in 500 mL aqueous solution, in the presence of 0.5 g charcoal were oxidized by air bubbling during 5–6 h. After filtration the brown solution was used for double decomposition reactions with 2–10% solutions of NaY salts. The mesoperiodates were prepared with a mixture of KIO_4+dil. H_2SO_4 and dil. KOH, respectively.

$[Co(en)_2X(amine)]Y_2$

0.05 mol *trans*-$[Co(en)_2Cl_2]Cl$ or *trans*-$[Co(en)_2Br_2]Br$ were treated with 0.06 mol amine and 5–10 mL water in a mortar. After 2–5 h stirring the red-violet mass is diluted with water, filtered and crystallized by standing 24–48 h. Some salts were obtained by double decomposition.

Analysis

Co was determined complexometrically, Cl, Br, I potentiometrically by titration with 0.01 N $AgNO_3$, NCS as $BaSO_4$ (gravimetrically), the sum Co+Cr by calcination at 800°C (Co_3O_4+Cr_2O_3).

Thermal measurements

Thermal measurements were performed with 951-TG and 910-DSC calorimeter (DuPont Instruments) in argon atmosphere at a heating rate of 10 K min^{-1}. The derivatographic ones with a MOM Derivatograph (Budapest) in air atmosphere.

Spectral measurements

Far IR spectra were recorded with Bio-Rad-Ninn spectrophotometer in polyethylene pellets, while the middle FTIR ones with Perkin Elmer 2000 apparatus in KBr pellets.

* * *

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