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The thermal behaviour of bis-ethylenediamino complexes of cobalt(III) with benzoic acid and its derivatives

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SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

Chimica. — *The thermal behaviour of* bis-*ethylenediamino complexes of cobalt(III) with benzoic acid and its derivatives* (*). Nota di Giuseppe D'Ascenzo, Vincenzo Carunchio, Andrea Magrì (**) e Aldo Marino, presentata (***) dal Corrisp. G. Sartori.

Riassunto. — È stato studiato il comportamento termochimico dei composti *cis*– e *trans*–$[Coen_2(OCOC_6H_4X)]NO_3$, dove en = etilendiammina e X=H, *p*–CH_3, *p*–Cl. La stabilità termica segue lo stesso ordine per le due serie isomeriche: *p*–clorobenzoato > benzoato > *p*–metilbenzoato. I *cis*–composti mostrano, all'analisi termica differenziale, un picco endotermico, che non è presente nei *trans*–derivati e che è stato attribuito ad un processo di isomerizzazione *cis* → *trans* allo stato solido.

In this work the thermochemical behaviour of some cobalt(III)–*bis*–ethylenediamine–complexes, having in the coordination sphere two molecules of benzoate group or of its derivatives with different substituents (Cl, CH_3) in the *para* position, has been studied with the aim of demonstrating the influence that such groups exert on the decomposition, because of their inductive and conjugative properties.

Nothing about this topic is in the literature, even if some data are reported on reactivity in solution of compounds such as $Coen_2(OCOC_6H_4R)_2^+$ [1]. Nitrate has been chosen as counter ion, in order to minimize anation reactions. Perchlorate has been avoided, due to its explosiveness during heating process.

EXPERIMENTAL

Apparatus.

Du Pont 951 thermobalance; Air or nitrogen dynamic atmosphere; Heating speed 10° C; Samples of 5–10 mg.

Du Pont 950 apparatus for differential thermal analysis; Air or nitrogen dynamic atmosphere; Heating speed 10° C; Samples of 5–10 mg.

Beckman DK–2 A and DB–GT spectrophotometers.

Preparation of the compounds.

The preparation of the perchlorates corresponding to the examined compounds is known [2]. By using analogous methods to prepare nitrates, satisfactory results have been seldom obtained probably due to the larger tendency of nitrate ion to enter the coordination sphere.

(*) Lavoro eseguito con il contributo del CNR.

(**) Borsa di studio della « Fondazione Guido Donegani » (Accademia Nazionale dei Lincei).

(***) Nella seduta del 9 marzo 1974.

Therefore, a new way has been followed to synthesize the complexes, starting from *cis*– or *trans*–[$Coen_2Cl_2$]NO_3 obtained from the corresponding [$Coen_2Cl_2$]Cl complexes [3]. Then, nitrates reacted with the silver salts of the acids to be studied (benzoic; *p*–chlorobenzoic or *p*–methylbenzoic acid), obtained according to the literature [4, 5].

Cis–compounds. *Cis*–isomers have been prepared by the following scheme: $1.74 \cdot 10^{-2}$ equivalents of the silver salt and the same amount of *cis*–[$Coen_2 Cl_2$]NO_3 equivalents are suspended into 250 ml 99,9 % methanol in an Erlenmeyer flask. The mixture is stirred and then kept to stay 24 hrs in the dark. The AgCl precipitate is removed by filtration on a sintered glass and the filtrate put into an ice bath. After another filtration, the clear solution is evaporated under vacuum at 30° C. The solid formed is eliminated by filtration until a pitchy residue is obtained.

The latter is then washed with methanol and diethyl ether and kept at reduced pressure for 48 hrs until red crystals are obtained.

Trans–compounds. $1.74 \cdot 10^{-2}$ equivalents of the examined acid silver salts and an equal amount of *trans*–[$Coen_2Cl_2$]NO_3 are suspended in 250 ml 99.9 % methanol in an Erlenmeyer flask, stirred and then kept to stay two hours in the dark. The precipitate AgCl is removed by suction on sintered glass; then the clear solution, which is found to be a mixture of the *cis*– and *trans*– derivatives, poured into a flash equipped with a reflux condenser, is kept in a thermostated bath at 70° C.

As to benzoate– and *p*–methylbenzoate–complexes, 48 hrs have to elapse for them to complete their isomerization, hence are filtered again and evaporated under vacuum at 30° C. Then the procedure was that described for the *cis*–derivatives. As to the *p*–chloroderivative, needle crystals have already precipitated after ten hours, without going through the pitchy residue.

After elimination of the crystallization head, it was kept 24 hours in a thermostated bath. The precipitate was washed with methanol, then with diethyl ether, and finally dried 48 hrs under vacuum at 30° C.

Product analysis.

The cobalt content of the compounds has been determined by EDTA titrations, after melting of a known amount of the complex with potassium bisulfate. The results, confirmed by TG–Analysis, are collected in Table I. The isomeric purity grade of the compounds has been checked by chromatographic analysis on cationic exchange paper (Mache Ray, Nagel, and Co.M.N.) in Na^+ form, using 1 M $NaNO_3$ as eluent: the *trans*– compounds have a higher Rf value that than of the corresponding *cis*–isomers.

The isomeric characterization of each compound has been performed by reflectance spectra carried on the solids and by absorption spectra carried out on the solutions of the compounds, and by comparing the results, with the behaviour of analogous compounds [2].

TABLE I

Cobalt content in the complexes $[Coen_2(OCOC_6H_4X)_2]NO_3$

X	Calculated (%)	Found %	
		Complexonometric method	Thermogravimetric method
cis–isomers			
H	12.20	12.1	12.1
p–CH_3	11.53	11.5	11.6
p–Cl	10.67	10.7	10.7
trans–isomers			
H	12.20	12.1	12.1
p–CH_3	11.53	11.6	11.7
p–Cl	10.67	10.7	10.6

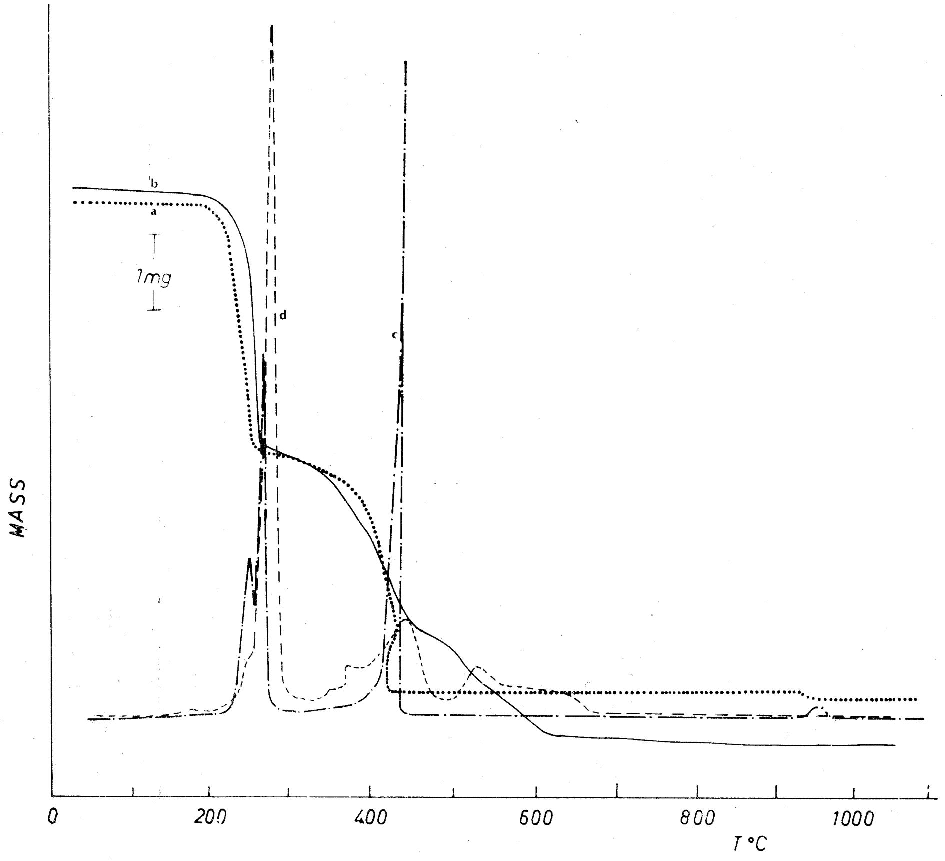

Fig. 1. – TG and DTG curves of *trans*–$[Coen_2(C_6H_5COO)_2]NO_3$ Heating rate 10° C min^{-1}. *a*) and *c*) TG and DTG air atmosphere; *b*) and *d*) TG and DTG nitrogen atmosphere.

RESULTS

For each complex, briefly discussed, the mentioned temperatures are the ptd ones. The obtained data are reported in Tables II.

Trans–dibenzoato*bis*(ethylenediamine)cobalt(III) nitrate.

The compound remains stable up to 200°C (fig. 1). The first decomposition is a two steps reaction corresponding to the elimination of both the ethylenediamine molecules and the nitrate group. According to Lobanov [6, 7] it may be admitted that ethylenediamine reacts with nitrate, cobalt(III), and the atmospheric oxygen. Thus, a modification of the cobalt oxidation state results, yielding cobalt(II) benzoate as the last product. (Calcd. 37.75 %; Found. 37.9 %). The reaction trend has been confirmed by the analysis of the gases developed during these stages. The residue obtained after this process contains neither nitrate nor ethylenediamine. Elemental analysis of the residue is in agreement with the hydrogen and carbon values calculated for cobalt(II) benzoate and confirms the absence of nitrogen. Cobalt(II) benzoate degrades in the air to yield Co_3O_4, which is first converted into Co_2O_3 and then into CoO (Calcd. 15.50 %; Found. 15.6 %). Under a nitrogen atmosphere the reaction behaviour changes and cobalt(II) benzoate yields first the carbonate and then the oxide.

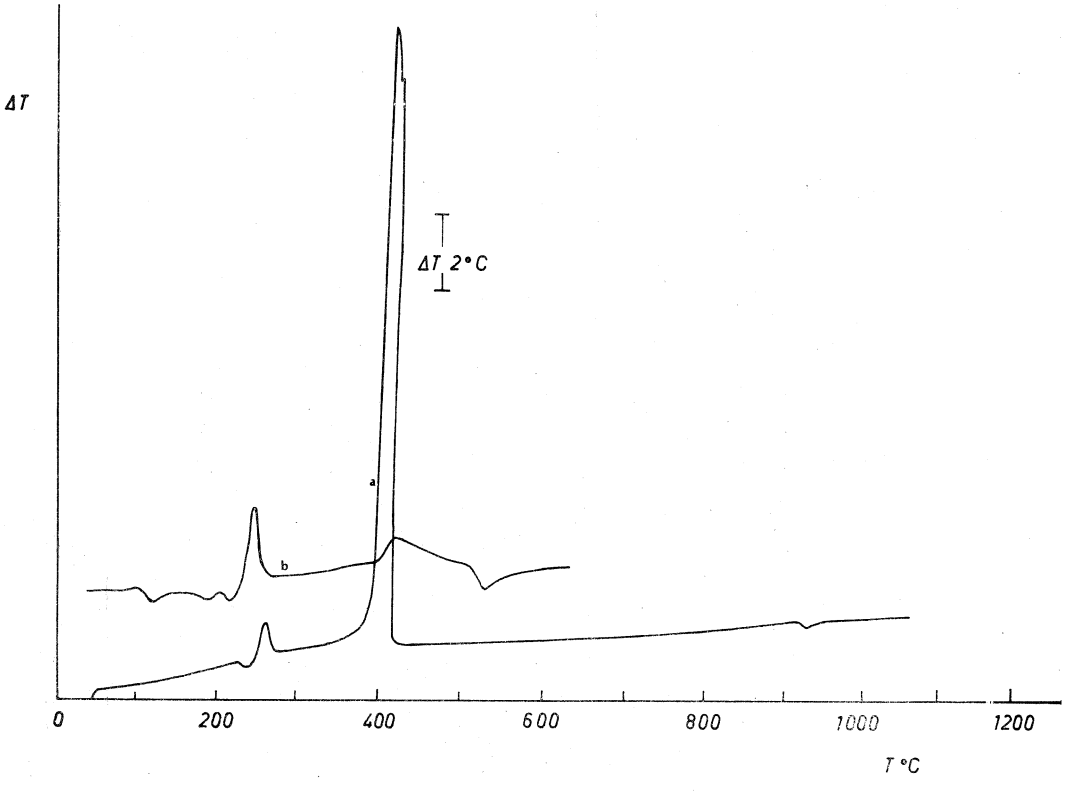

Fig. 2. – DTA curves of *trans*–$[Coen_2(C_6H_5COO)_2]NO_3$ Heating rate 10° C min^{-1}: *a*) air atmosphere; *b*) nitrogen atmosphere.

TABLE II

Decomposition temperatures from TG *and* DTA *curves in air atmosphere of complexes* [Coen$_2$(OCOC$_6$H$_4$X)$_2$]NO$_3$

X	TG				DTA					
cis–isomers										
H	245 (a) 190–260 (c)	420 260–430	935 910–950		185 (b) ↑ 160–200	220 215–240 ↓	255 ↑ 240–280	400 ↑ 280–430	915 905–940 ↓	
p–CH$_3$	225,245 180–260	400 260–420	930 910–950		160 ↑ 150–170	215 205–225 ↓	250 ↑ 225–270	400 ↑ 270–430	920 905–940 ↓	
p–Cl	245 210–260	380 260–470	550 470–620	930 910–955	190 ↑ 170–210	240 215–245 ↓	255 ↑ 245–270	445 ↑ 270–480	545 ↑ 480–650	915 905–940 ↓
Trans–isomers										
H	230,250 190–260	415 260–430	930 910–955		220 215–230 ↓	248 ↑ 230–270	390 ↑ 270–410	918 910–945 ↓		
p–CH$_3$	225 150–245	430 245–575	930 910–950		210 200–220 ↓	240 ↑ 220–270	450 ↑ 270–600	920 905–945 ↓		
p–Cl	250 210–265	410 265–475	550 475–640	930 910–950	240 220–245 ↓	255 ↑ 245–280	460 ↑ 280–480	550 ↑ 480–630	915 905–940 ↓	

(*a*) Maximum rate.
(*b*) Peak minimum or maximum.
(*c*) Temperatures at beginning and end of reaction.

DTA in air (fig. 2) shows a first endothermic process, immediately followed by an exothermic one. Such a behaviour may be attributed to the initial bond-breaking between ethylenediamine and the coordinating metal and to the successive redox reaction among nitrate ion, ethylenediamine and cobalt(III) with the partecipation of the atmospheric oxygen. DTA in nitrogen shows that, also under an inert atmosphere, in correspondence to the first breaking process an exothermic peak appears, which is less strong, due to the lack of the oxidative contribution from the atmosphere. Moreover, the exothermic peak localized at about 400° C, which in air is attributed to the oxidative demolition of cobalt(II) benzoate, disappears. These data confirm the hypothesis proposed for the reaction procedure.

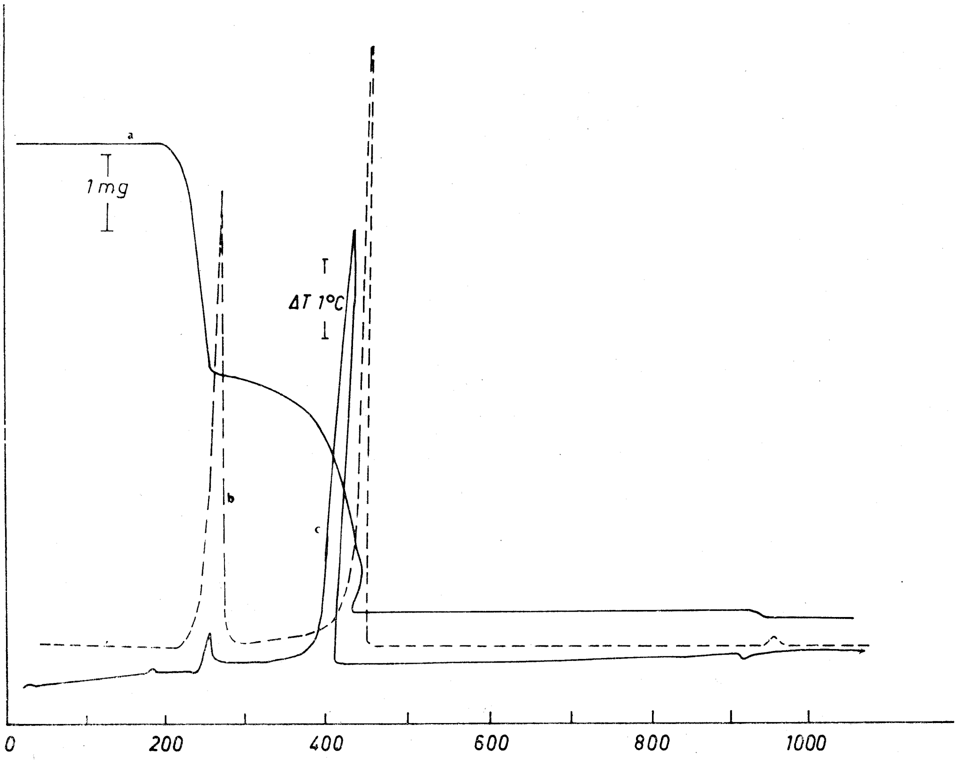

Fig. 3. – TG, DTG and DTA curves of *cis*–[Coen$_2$(C$_6$H$_5$COO)$_2$]NO$_3$ Heating rate 10°C min^{-1}. Air atmosphere: *a*) TG; *b*) DTG; *c*) DTA.

Cis–dibenzoato*bis*(ethylenediamine)cobalt(III) nitrate.

The decomposition behaviour of this compound is quite similar to that of the corresponding *trans*– isomer, as TG, DTG and DTA analysis (fig. 3) show. DTA curves both in air and nitrogen, show a low exothermic peak, with a maximum localized at 180° C to which no weight loss corresponds. This phenomenon does not happen in the case of the *trans*– compound, thus suggesting that such a peak is due to the *cis* → *trans* isomerization of the examined compound.

Spectrophotometric analysis, carried out on the sample solution at the end of this step shows the presence of a mixture of *cis–* and *trans–* compounds. The final reaction stage yields Co_3O_4, which changes into Co_2O_3 and then into CoO (Calcd. 15.50 %; Found. 15.5 %).

Trans–di(*p*–chlorobenzoato)*bis*(ethylenediamine)cobalt(III) nitrate

TG, DTG and DTA curves relative to this compound are reported in fig. 4. The first decomposition step is similar to that of the *trans* dibenzoate, with the elimination of both ethylenediamine groups and the nitrate ion and the subsequent decomposition of cobalt(II) *p*–chlorobenzoate to give a compound, which seems to be $CoCl_2$ on the basis of the thermal behaviour and the analysis of the residue obtained. Then, $CoCl_2$ is transformed into Co_3O_4, which is then changed into Co_2O_3 and finally into CoO (Calcd. 13.56%; Found. 13.5%).

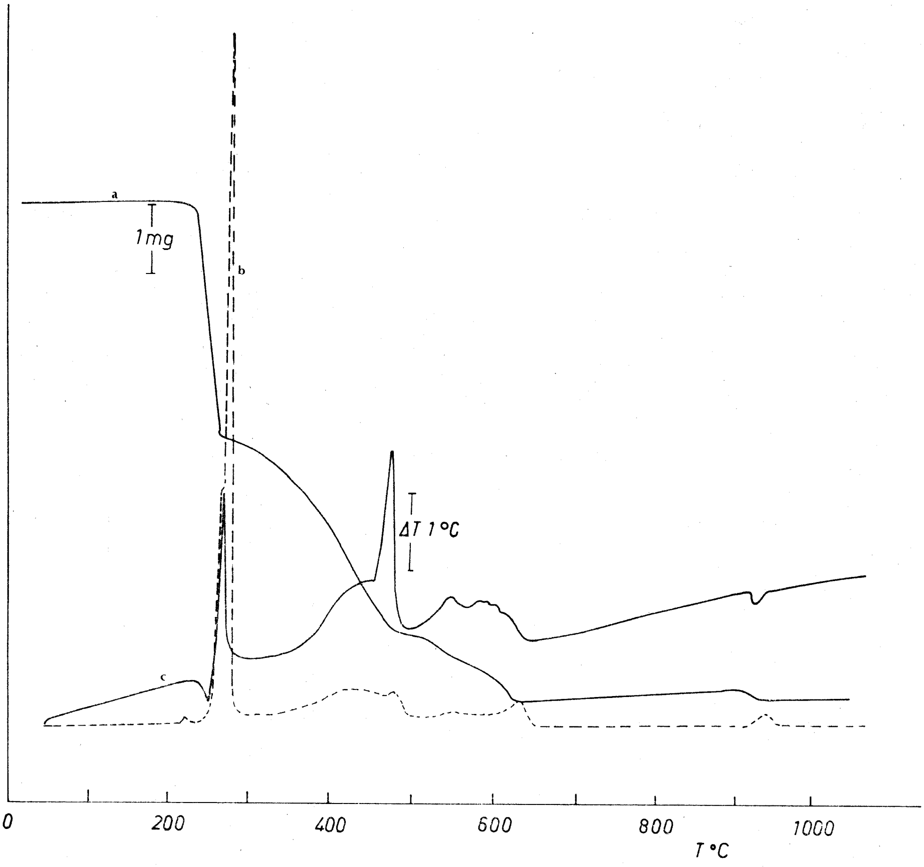

Fig. 4. – TG, DTG and DTA curves of *trans*–[$Coen_2(p\text{-}ClC_6H_4COO)_2]NO_3$. Heating rate 10° C min^{-1}. Air atmosphere: *a*) TG; *b*) DTG; *c*) DTA.

The analysis of the gases developed from the first decomposition reaction and of the residues obtained after stopping the temperature increase in correspondence to the characteristic values, confirms such a behaviour. It may be supposed that the first DTA peak is due to the bond breaking ethylenediamine-metal (endothermic), and the second to the exothermic redox reaction among the operative atmosphere, ethylenediamine, nitrate ion and cobalt(III), with formation of cobalt(II) *p*–chlorobenzoato, which, through two exothermic steps, yields $CoCl_2$, and successively Co_3O_4. This compound becomes Co_2O_3 and, then, CoO.

Cis–di(*p*–chlorobenzoato)*bis*(ethylenediamine)cobalt(III) nitrate

The first weight loss may be attributed to the elimination of the two ethylenediamine molecules and nitrate group.

The decomposition behaviour is similar to that of the corresponding *trans*– isomer: the DTA curve shows a first exothermic process, not associated with a weight loss, which is not present in the *trans*– compound DTA curves. This process may be supposed an isomerization reaction, as previously suggested. The last reaction stage is the oxide Co_3O_4 formation, which by further heating gives Co_2O_3 and then CoO (Calcd. 13.56 %; Found. 13.7 %).

Trans–di(*p*–methylbenzoato)*bis*(ethylenediamine)cobalt(III) nitrate.

TG, DTG and DTA curves relative to this compound are reported in fig. 5. First step may be attributed to the process characteristic of this series of compounds, i.e. to the loss of the two ethylenediamine molecules and the nitrato group. Such a reaction was confirmed by analysis of the developed gases and of the residue obtained after this step, which put into evidence the nitrogen absence. The last reaction stage through the oxidative demoli-

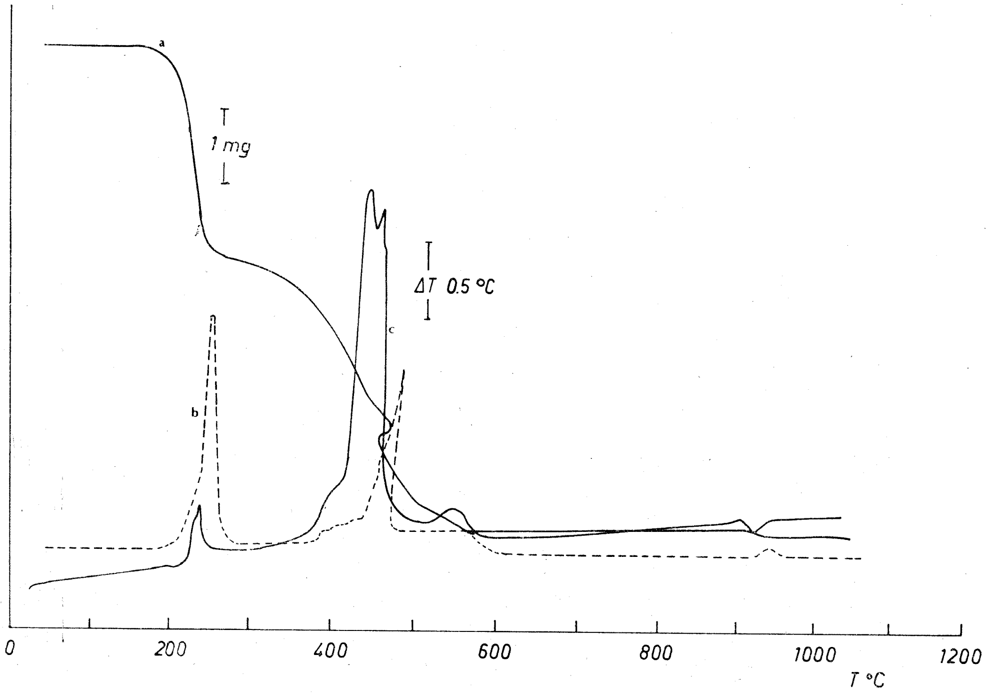

Fig. 5. – TG, DTG and DTA curves of *trans*–[$Coen_2(p\text{–}CH_3C_6H_4COO)_2]NO_3$. Heating rate 10° C min^{-1}. Air atmosphere: *a*) TG; *b*) DTG; *c*) DTA.

tion of cobalt(II) *p*–methylbenzoate yields Co_3O_4, which undergoes the already described transformation into CoO (Calcd. 14.65 %; Found. 14.7%). The DTA curves are in agreement with a described process.

Cis–di(*p*–methylbenzoato)*bis*(ethylenediamine)cobalt(III) nitrate.

Also for this compound, the first process related to a weight loss, can be connected with the elimination of the two ethylenediamine molecules and the nitrato group. Then the last product decomposes to give Co_3O_4, that subsequently becomes Co_2O_3 and finally CoO (Calcd. 14.65 %; Found. 14.6 %).

The DTA curves shows as first process an exothermic low peak, characteristic of the *cis*– compounds.

The thermal phenomenon is therefore strongly analogous to the one observed for the previous compounds, with respect to the stage connected with the elimination of the ethylenediamine molecules and the nitrate ion. Afterwards, the residue decomposes by oxidation as indicated by the exothermic peaks relative to this stage.

DISCUSSION

By examining the decomposition temperatures (Table II) relative to the first endothermic process, i.e., the one regarding the bond-breaking between ethylenediamine and the central ion, it can be seen that the temperatures are influenced by the other ligand present in the molecule.

In particular, a stability scale

p–chlorobenzoate > benzoate > *p*–methylbenzoate

is obtained.

This behaviour may be explained by taking into account that chlorine in the *para* position exerts both — I and + R effects. Nevertheless, the inductive effect prevails on the conjugative one.

Thus an electron withdrawing effect occurs through the benzene ring toward chlorine with consequent electronic delocalization from the central cobalt to the aromatic ring and hence with an increase in the bond strength between Co(III) and ethylenediamine

As to *p*–methylbenzoate, the methyl group induces + I and + R effects. Thus, an electronic release through the ring occurs with electronic delocalization of Co(III) and consequent decrease on the bond strength between Co(III) and ethylenediamine.

On considering the DTA curves for the *cis* and *trans* isomers, the former compounds show a first exothermic peak which is not present in the *trans*–derivatives, to which no weight loss corresponds. Thus, a structural change must be involved. Such a change occurs with energy release from the system to the environment and therefore it cannot be attributed to the melting of the compound itself. The process is likely to be an isomerization one at the solid state, induced by temperature increase.

In order to confirm this hypothesis, *cis*–[Coen$_2$(C$_6$H$_5$COO)$_2$]NO$_3$ was heated at 100° C, 130° C and 140° C, i.e., at temperature lower that pdt relative to the examined phenomenon, but high enough to induce isomerization, by using sufficiently long heating times and avoiding that decomposition become the prevailing process. No changes occur at 100° C; after 24 hrs at 130° C some appreciable changes begin to appear in the reflectance and absorption spectra performed on hydroalcoholic solutions of the samples, giving rise to the maxima of the *trans*– compounds. Changes at 140° C are much faster, in agreement with the data reported for Coen$_2$X$_2^+$ type compounds, where a 10° C temperature increase usually makes the isomerization reaction twice as high.

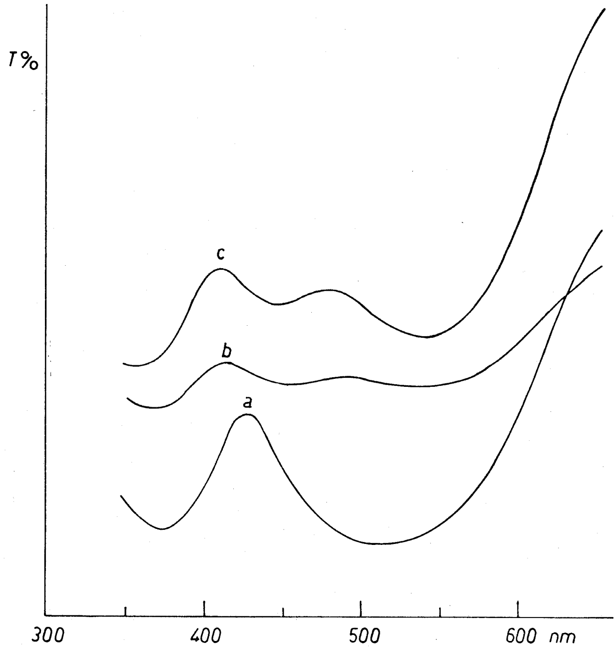

Fig. 6. – Reflectance spectra of *a*) *cis*–[Coen$_2$(C$_6$H$_5$COO)$_2$]NO$_3$; *b*) *cis*–[Coen$_2$(C$_6$H$_5$COO)$_2$]NO$_3$ after 165 min at 140° C; *c*) *trans*–[Coen$_2$(C$_6$H$_5$COO)$_2$]NO$_3$.

After 24 hrs at 140° C the spectra assume the *trans*– compound characteristic trend. The reflectance spectra, which allow the characterization of this transformation, are reported in fig. 6. However, from tests performed in solution, the molar absorptivity at 540 nm of the compound obtained after heating 24 hrs the *cis*– derivative at 140° C is lower than that of the *trans*– compound obtained by synthesis.

Such a result, in agreement with thermal analysis, may be attributed to the start of the first step of the decomposition, which, as shown by DTA, overlaps the last step of the first exothermic process, the latter being due to the isomerization process in the solid state, as already proved.

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