

COBALT(III) DICARBOXYLATO BIS-ETHYLENEDIAMINE NITRATES: PREPARATION AND CHARACTERIZATION BY THERMAL ANALYSIS AND OTHER ANALYTICAL METHODS

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Compounds with the general formula *cis* or *trans*-[Coen₂(RCOO)₂]NO₃ were prepared by modifications of known procedures; R was H, CH₃, C₂H₅ or C₃H₇, and *en* was ethylenediamine. The compounds were characterized by TLC and UV-Vis spectrophotometry, and their thermal behaviour was examined via TG and DTA, and via IR spectra on heated samples.

The thermal stabilities are discussed in terms of the strengths of the bonds in the solids [1] and steric hindrance; the thermal decompositions are described with the aid of hypothesized intermediates and IR spectra.

Reaction steps are identified and the thermal stability sequence is discussed: the *cis* compounds are less stable than the corresponding *trans* compounds, due to the lower reticulation effect; the sequence of the *cis* compounds is the reverse of the sequence of carboxylate ion basicity, while the sequence displayed by the *trans* compounds can be interpreted in terms of solid lattice stabilization.

In systematic investigations of the thermal behaviour of solid metal complexes containing carboxylato groups in the coordination shell [2–6], compounds of general formula *cis*- or *trans*-[Coen₂(RCOO)₂]NO₃ were prepared, characterized and examined by TG and DTA. These compounds contain cobalt(III); R = H, CH₃, C₂H₅ or C₃H₇ corresponds to formate, acetate, *n*-propionate or *n*-butyrate, and *en* represents ethylenediamine.

The presence of *en* allows the possibility of examining the behaviour of the *cis* and *trans* isomers, while the increasing length of R affects steric hindrance and/or solid reticulation.

Whereas dicarboxylato bis-ethylenediamine cobalt(III) complexes are generally prepared as perchlorates, in the present work they were made as nitrates. The reason for this is the general behaviour of perchlorate during heating: sputtering phenomena are frequent, introducing unacceptable noise in the recorded signals

(TG and DTA). Anions such as chloride were not employed in order to avoid anation reactions (chloride in the outer sphere of cobalt(III) replacing carboxylato in the inner sphere); such anation reactions reduce the yield of the preparation and complicate the thermal degradation by introducing additional reaction steps.

Experimental

Apparatus and materials

Thermal analyses were carried out with a Perkin-Elmer TGS-2 for TG and model 1700 for DTA. Dynamic oxygen or nitrogen atmospheres were used, with a flow rate of 50 ml/min. TG starting decomposition temperatures were detected when the mass losses were more than 1% of the initial mass; in a similar way the end-temperatures were measured by using 1% of the final residue as tolerance; when two reaction steps overlapped, the inflection point was chosen as the end-temperature of the first step and as the starting temperature of the subsequent one. The IR spectra were recorded on a Perkin-Elmer 125 grating infrared spectrophotometer, using KBr discs, on samples heated up to the temperature corresponding to the estimated end of the reaction step (as detected by TG). The UV-visible spectra were recorded with a Perkin-Elmer 320 spectrophotometer, in 1 cm quartz cells.

The TLC measurements were made on precoated silica gel (Kieselgel 60, art. 5635, Merck). All the employed reagents were analytical grade commercial products (Merck).

Preparation of cis compounds

$[\text{Coen}_2\text{CO}_3]\text{NO}_3$ was obtained by the Linhard and Stirn method [7], starting from *trans*- $[\text{Coen}_2\text{Cl}_2]\text{NO}_3$ prepared according to Kamada and Tsuschida [8]. To 10 ml of an aqueous solution containing 1.8 g of *cis*- $[\text{Coen}_2\text{CO}_3]\text{NO}_3$, RCOOH solution was added until the molar ratio carboxylate/cobalt was equal to 3/1. The resulting solution was stirred for one hour and then evaporated to half of the initial volume. This solution was left to stand for 12 hours at 0°. After checking for the presence of $[\text{Coen}_2\text{CO}_3]^+$ by TLC, and removal of this latter (when present) by fractional precipitation, the solution was evaporated. The solid microcrystals obtained were washed with acetone and then with diethyl ether.

The yields of *cis*- $[\text{Coen}_2(\text{RCOO})_2]\text{NO}_3$ were in the range 25–40%; the shorter the chain-length in R, the higher the yield was.

Preparation of *trans* compounds

The compounds *trans*-[Coen₂(RCOO)₂]NO₃ were obtained by introducing some changes into the Jackman method [9].

0.30 g of *trans*-[Coen₂(H₂O)₂]NO₃, prepared by the Bjerrum procedure [10], was dissolved in 10 ml of dimethylformamide. Acetic, propionic or butyric anhydride was added to the solution, to give a carboxylate/cobalt ratio of 3/1, followed by N,N-dimethylbenzylamine (0.37 ml). The solution was shaken vigorously for 5 min. The *trans* acetato complex was easily precipitated from solution by the slow addition of diethyl ether during stirring. In contrast, a thick, sticky material was obtained for the propionate or butyrate complex. Accordingly, acetone was added to the oily product to precipitate the complexes, which were removed by filtration. After filtration, the complexes were washed with ethanol and ether. On re-precipitation, pure *trans*-dicarboxylato-bis(ethylenediamine)cobalt(III) nitrate was obtained, with a yield of 35–40%. *Trans*-[Coen₂(OCOH)₂]NO₃ was prepared directly by suspending 2.5 g of [Coen₂CO₃]NO₃ in 12.5 ml of water, and treating the suspension with 1.25 ml of HCOOH for 5 hours at 80°. The solution was then evaporated under reduced pressure and the residue (1.5 g) was treated with 120 ml of methanol. The clear solution, which was found to be a mixture of the *cis* and *trans* derivatives, was placed in a flask equipped with a reflux condenser, and was kept in a bath at 80° for 30 hours. The solution was then evaporated to give a wet solid. The addition of ethanol, in the presence of nitric acid and ether, caused precipitation of *trans*-[Coen₂(OCOH)₂]NO₃. It was purified until the UV-vis spectrum was unchanged on further re-precipitation. The precipitate was removed by filtration, washed with ethanol and ether, and vacuum-dried. The overall yield was 20%.

Characterization of the compounds

The *cis* and *trans* isomers were identified through their UV-visible spectra. The agreement with the known spectra [11, 12] is quite good. In Fig. 1, the spectra of the *trans* propionate and *trans* butyrate are shown to supplement the available literature data; in Table 1, the molar absorptivities are listed for all the prepared compounds at several characteristic points of their spectra.

The well-known splitting of the maximum at 500 nm into two bands at 450 and 550 nm can be recognized on passing from the *cis* to the *trans* isomers.

The TLC results obtained on polar silica gel are summarized in Table 2. An increasing *R_f* can be observed on going from formate to butyrate, corresponding to the decreasing charge density of the ionic compound [13]. The *trans* compounds have larger *R_f* values than those of the corresponding *cis* compounds, due to the lower electric dipole of the *trans* compounds.

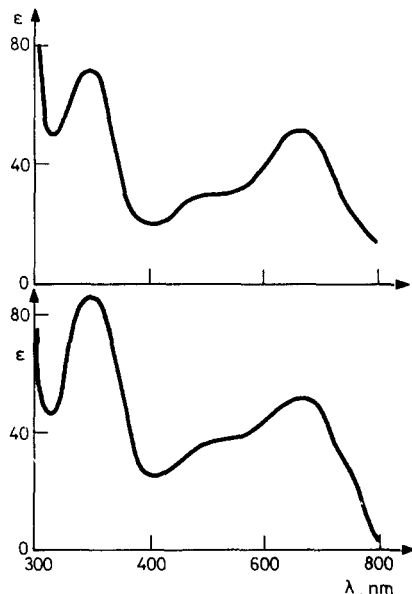


Fig. 1 Absorption spectra of $\text{trans-[Coen}_2(\text{RCOO})_2]^+$ expressed as molar absorptivities ϵ , in $\text{mol}^{-1} \text{L cm}^{-1}$, vs λ , in nm. R = C_2H_5 , upper spectrum; R = C_3H_7 , lower spectrum. Nitrate salt dissolved in water at 25 °C

Table 1 Molar absorptivities ϵ , in $\text{mol}^{-1} \text{L cm}^{-1}$, at characteristic points λ , in nm, of the absorption spectra (maxima or zero derivative) for the compounds of general formula *cis*- or *trans*- $[\text{Coen}_2(\text{RCOO})_2]^+$. The solid nitrates were dissolved in water at 25 °C

| Configura-tion | R | λ | ϵ | Configura-tion | R | λ | ϵ |
|----------------|--------------------------------|-----------|------------|----------------|--|-----------|------------|
| <i>cis</i> | H | 500 | 128 | <i>trans</i> | H | 540 | 51 |
| | | 360 | 85 | | | 463 | 31 |
| <i>cis</i> | CH_3 | 504 | 153 | <i>trans</i> | CH_3 | 357 | 66 |
| | | 361 | 98 | | | 540 | 61 |
| | | | | | | 450 | 29 |
| <i>cis</i> | C_2H_5 | 503 | 139 | <i>trans</i> | C_2H_5 | 355 | 72 |
| | | 360 | 91 | | | 540 | 52 |
| | | | | | | 455 | 30 |
| <i>cis</i> | C_3H_7 | 508 | 146 | <i>trans</i> | C_3H_7 | 355 | 72 |
| | | 360 | 109 | | | 540 | 61 |
| | | | | | | 455 | 36 |
| <i>cis</i> | $[\text{Coen}_2\text{CO}_3]^+$ | 500 | 132 | <i>trans</i> | $[\text{Coen}_2(\text{H}_2\text{O})_2]^{3+}$ | 350 | 86 |
| | | 360 | 120 | | | 540 | 31 |
| | | | | | | 440 | 36 |
| | | | | | | 340 | 55 |

Table 2a TLC on silica gel $Si_{60}F_{254}$: starting compounds for preparation of the examined compounds. Eluent: aqueous solution of $LiNO_3$, 5 mol/L: ethanol = 3:7 (v:v)

| Compound | R_f |
|--|-------|
| <i>trans</i> - $[Coen_2(H_2O)_2]^{3+}$ | 0.00 |
| $[Coen_2CO_3]^+$ | 0.59 |
| <i>trans</i> - $[Coen_2Cl_2]^+$ | 0.75 |

Table 2b TLC on silica gel $Si_{60}F_{254}$: obtained compounds of general formula *cis*- or *trans*- $[Coen_2(RCOO)_2]^+$. Eluent: dimethylsulfoxide:methanol:methanolic solution of $LiNO_3$, 0.13 mol/L = 3:2:1 (v:v:v). Nitrate salt used

| Configuration | R | R_f | Configuration | R | R_f |
|---------------|-------------------------------|--|---------------|-------------------------------|--------------|
| <i>cis</i> | H | 0.40 | <i>trans</i> | H | 0.61 |
| <i>cis</i> | CH ₃ | 0.47 | <i>trans</i> | CH ₃ | 0.68 |
| <i>cis</i> | C ₂ H ₅ | 0.56 | <i>trans</i> | C ₂ H ₅ | 0.72 |
| <i>cis</i> | C ₃ H ₇ | 0.63 | <i>trans</i> | C ₃ H ₇ | 0.74 |
| | | $[Coen_2CO_3]^+$ | | | $R_f = 0.15$ |
| | | <i>trans</i> = $[Coen_2(H_2O)_2]^{3+}$ | | | $R_f = 0.00$ |

Thermoanalytical results

The TG results are shown in Fig. 2, while Fig. 3 reports the DTA of selected compounds to illustrate the behaviour, which is similar for $R = H$ or CH_3 , and for $R = C_2H_5$ or C_3H_7 .

TG reveals at least three reaction steps before the last one at about 850°. To assist assignment of these steps, a list of possible residues has been calculated and is reported in Table 3.

Such data have been used to make tentative assignments in Table 4, where the DTA behaviour is also reported. To support the assignment, made exclusively on a stoichiometric basis, several IR spectra were recorded on compounds heated up to a chosen temperature (corresponding to the presumed end of a given reaction step). The IR spectra are shown in Fig. 4.

Discussion

The preparation of *cis*- $[Coen_2(H_2O)_2]NO_3$, suggested by other authors [9] as starting material for the preparation of the *cis* series, gave poor yields. The preparation described above led to higher yields. The results of TLC and the UV-vis

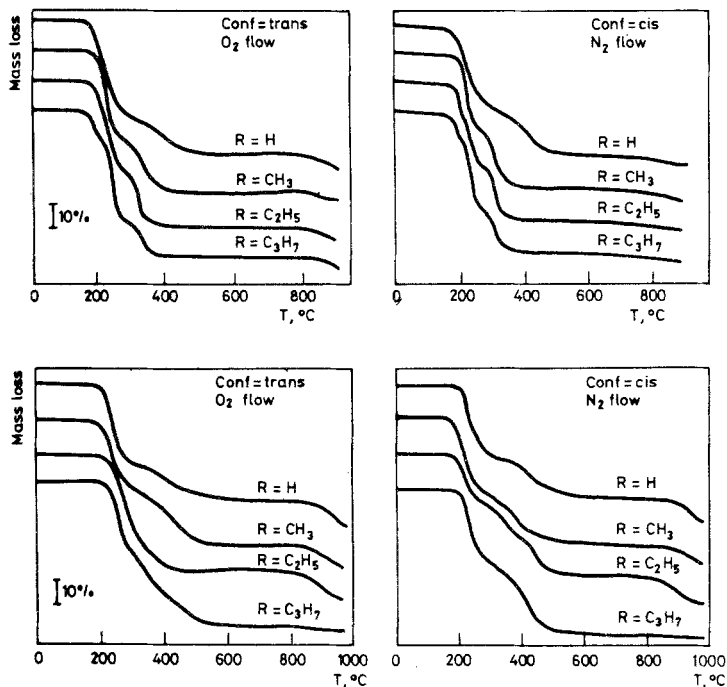


Fig. 2 TG (percentage of initial mass) of compounds of general formula *cis*- or *trans*- $[\text{Coen}_2(\text{RCOO})_2]\text{NO}_3$ at heating rate of 10 deg/min with a N_2 or O_2 flow rate of 50 ml/min. Initial masses used are:

| | | | | | |
|-------------------|--------------------------|--------|-------------------|--------------------------|--------|
| <i>trans</i> | R = H | 1.6 mg | <i>trans</i> | R = H | 1.8 mg |
| O_2 flow | = CH_3 | 1.5 mg | N_2 flow | = CH_3 | 1.6 mg |
| | = C_2H_5 | 1.5 mg | | = C_2H_5 | 1.5 mg |
| | = C_3H_7 | 1.7 mg | | = C_3H_7 | 2.0 mg |
| <i>cis</i> | R = H | 1.4 mg | <i>cis</i> | R = H | 1.8 mg |
| O_2 flow | = CH_3 | 1.7 mg | N_2 flow | = CH_3 | 1.6 mg |
| | = C_2H_5 | 2.0 mg | | = C_2H_5 | 1.9 mg |
| | = C_3H_7 | 1.9 mg | | = C_3H_7 | 1.7 mg |

spectra accord with the proposed formulas and with the final residue found at 850° (Table 4).

The UV-vis spectra allowed the identification of the *cis* and *trans* configurations [11, 12].

The TLC techniques gave a check on the purity of the compounds obtained.

TLC also gave information on the *cis* and *trans* configurations, $R_f(\textit{trans}) > R_f(\textit{cis})$, and carbon chain length. $R_f(\text{C}_3\text{H}_7) > R_f(\text{C}_2\text{H}_5) > R_f(\text{CH}_3) > R_f(\text{H})$. This sequence is known from chromatography [13]; it is explained by the strengths of the electric interactions

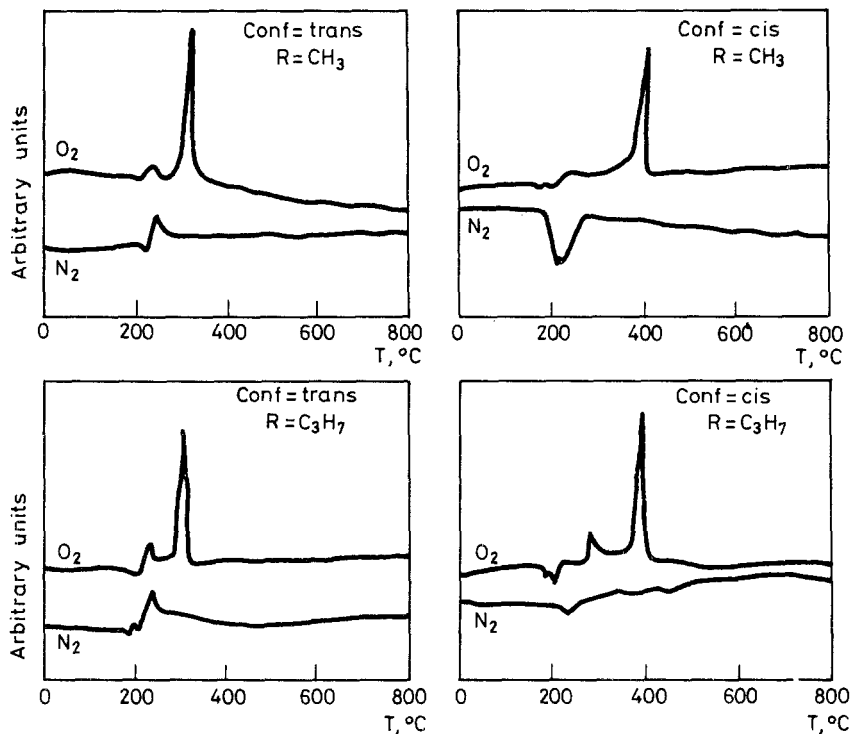


Fig. 3 DTA of some compounds of general formula *cis*- or *trans*-[Coen₂(RCOO)₂]NO₃ at a heating rate of 10 deg/min with a N₂ or O₂ flow rate of 50 mL/min. Initial masses are about the same as used for the corresponding TG

with the polar stationary phase. This latter retains ions the more strongly, the higher the molecular dipole moment (*trans/cis* sequence) and the lower the mean ionic radius (C_nH_{2n+1} sequence). Both properties affect the charge density displayed by the ion. It is interesting to observe the trend of R_f in Table 2b: the values for the *cis* compounds increase linearly with the carbon chain length, while those for the *trans* compounds tend to a limiting value. This behaviour suggests that one site of the *trans* compound interacts with silica gel, while both sites interact when the *cis* configuration is present. The molecular geometry is described below (without the *en* representation) [14]:



On the assumption that the interaction between the complexes and silica gel sites

Table 3 Calculation of residues (expressed as percentages of initial mass) relative to the compound hypothesized from thermal decomposition of general formula $[\text{Coen}_2(\text{RCOO})_2]\text{NO}_3$. Mass losses are expressed stoichiometrically with no hypothesis about the evolved gases. MW are the rounded molecular weights; en = ethylenediamine; R = alkyl radical

| Symbol | Compound | Loss | R | H | CH ₃ | C ₂ H ₅ | C ₃ H ₇ |
|--------|---|--|-----|------|-----------------|-------------------------------|-------------------------------|
| c0 | Coen ₂ (RCOO) ₂ NO ₃ | — | MW | 331 | 359 | 387 | 415 |
| | | | Res | 100 | 100 | 100 | 100 |
| c1 | Coen ₂ (RCOO) ₂ NO ₃ | en | MW | 271 | 299 | 327 | 415 |
| | | | Res | 81.9 | 83.3 | 84.5 | 85.5 |
| c1.1 | Coen ₂ (RCOO) ₂ | NO ₂ + ½O ₂ | MW | 269 | 297 | 325 | 353 |
| | | | Res | 81.3 | 82.7 | 84.0 | 85.1 |
| c2 | Coen(RCOO) ₂ | en + NO ₂ + ½O ₂ | MW | 209 | 237 | 265 | 293 |
| | | | Res | 63.1 | 66.0 | 68.5 | 70.6 |
| c3 | Co(RCOO) ₂ | 2 en + NO ₂ + ½O ₂ | MW | 149 | 177 | 205 | 233 |
| | | | Res | 45.0 | 49.3 | 53.0 | 56.1 |
| c4 | CoCO ₃ | 2 en + NO ₂ + ½O ₂ + CO + R ₂ | MW | 119 | 119 | 119 | 119 |
| | | | Res | 36.0 | 33.1 | 30.7 | 28.7 |
| c5 | CoO | 2 en + NO ₂ + ½O ₂ + CO + R ₂ + CO ₂ | MW | 75 | 75 | 75 | 75 |
| | | | Res | 22.7 | 20.9 | 19.4 | 18.1 |
| c5.1 | ½Co ₂ O ₃ | 2 en + NO ₂ + ½O ₂ + CO + R ₂ + CO ₂ -¼O ₂ | MW | 83 | 83 | 83 | 83 |
| | | | Res | 25.1 | 23.1 | 21.5 | 20.0 |

is mainly electrostatic, the distribution coefficient D , i.e. the ratio of the "activity in the stationary phase" to the "activity in the mobile phase", could be represented by

$$2.3 RT \log D = nq/r - \Delta G_{\text{sol}}$$

were ΔG_{sol} is the free energy of the solvated ion, and n is the number of interacting sites ($n=1$ and 2 for *trans* and *cis* compounds, respectively, if the assumptions are correct). In both cases, r represents the mean distance of approach between silica gel sites and carboxylato groups, and q is the ion charge.

Rearrangement of the dependence of R_f on D [15] leads to the expression

$$\log D = \log(1/R_f - 1) - \log(A_s/A_m)$$

where A_s/A_m is the ratio of planar sections for the stationary and the mobile phase, respectively. Combination of the above expressions gives the relation

$$\log(1/R_f - 1) = An 1/r - B + C$$

where $A = q/2.3RT$, $B = \Delta G_{\text{sol}}/2.3RT$, and $C = \log(A_s/A_m)$.

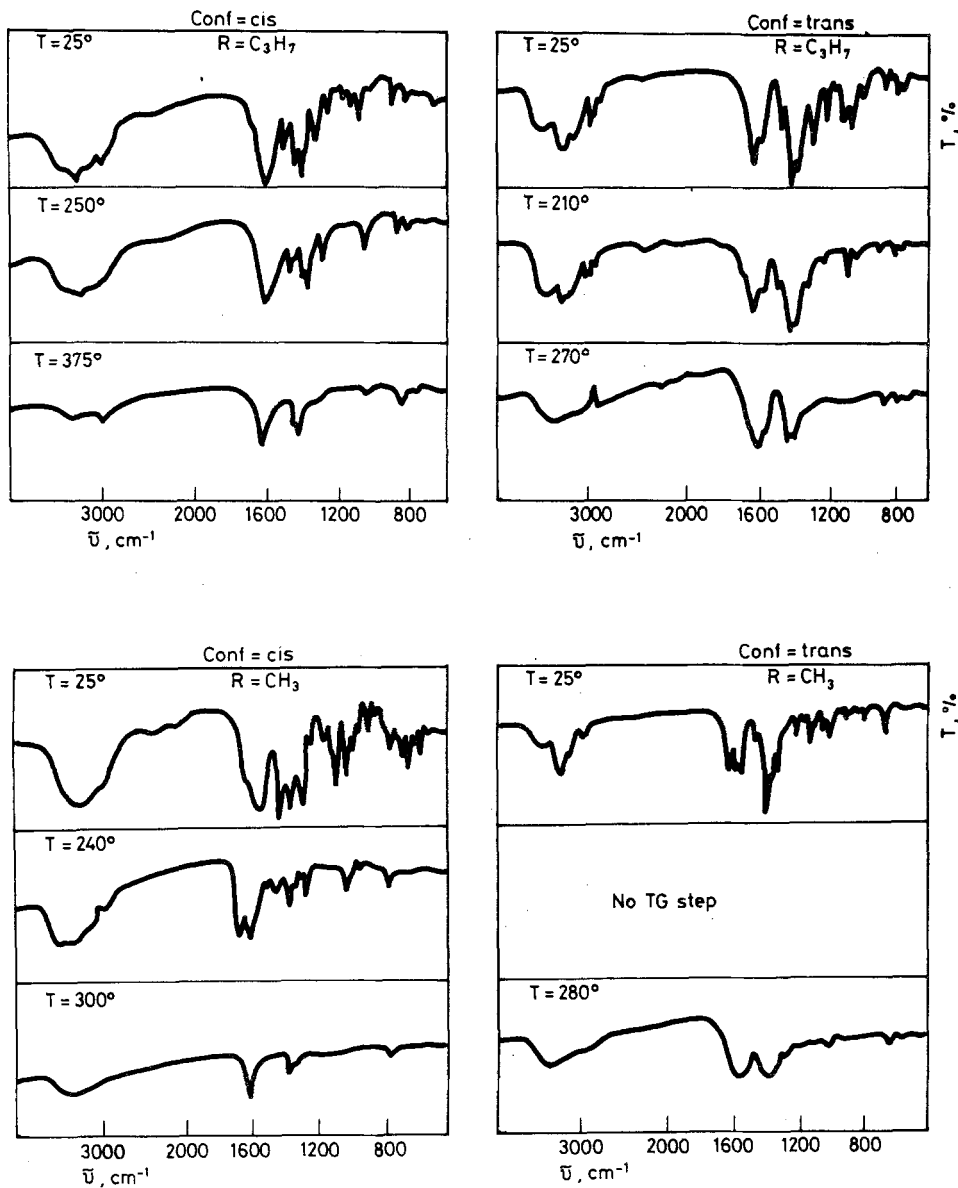


Fig. 4 IR spectra of some compounds of general formula *cis*- or *trans*-[Coen₂(RCOO)₂]NO₃ after heating at 10 deg/min up to temperature *T*, in °C, in an O₂ flow. Other conditions are similar to those employed for the corresponding TG

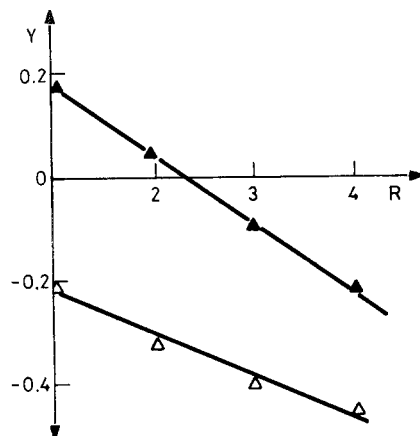


Fig. 5 $y = \log(1/R_f - 1)$ vs. carbon chain-length $R = \text{H}$ for abscissa 1, $R = \text{CH}_3$ for 2, $R = \text{C}_2\text{H}_5$ for 3, $R = \text{C}_3\text{H}_7$ for 4; *cis*-[Coen₂(RCOO)₂]⁺: ▲, *trans*-[Coen₂(RCOO)₂]⁺: △

When r is large enough, small increments in the carbon chain-length will produce a linear change in $\log(1/R_f - 1)$, with the angular coefficients depending on n :

$$\Delta \log(1/R_f - 1) = -A/r^2 n \Delta r$$

From Fig. 5, it can be seen that the slope for the *cis* series is about twice that for the *trans* series, in accordance with the hypothesis that two sites are involved when the *cis* molecules bond to silica gel, while only one site is involved for the *trans* molecules.

As concerns the thermoanalytical results, the assignment of the residues in Table 4 (made simply on the basis of the possible mass losses listed in Table 3) is confirmed through the IR spectra reported in Fig. 4 for $R = \text{CH}_3$ and C_3H_7 , and from the DTA data shown in Fig. 3 for the same compounds and listed in Table 4 for all compounds.

All the IR spectra exhibit the following bands:

| $\nu \text{ cm}^{-1}$ | Assignment | Moiety |
|-----------------------|----------------------|------------------------------|
| -3200 | $\nu(\text{N-H})$ | en |
| -2950 | $\nu(\text{C-H})$ | en, RCOO ⁻ |
| -1620 | $\delta(\text{N-H})$ | en |
| -1600 | $\nu_a(\text{C-O})$ | RCOO ⁻ |
| -1580 | $\nu_a(\text{N-O})$ | NO ₃ ⁻ |
| -1400 | $\nu_s(\text{C-O})$ | RCOO ⁻ |
| -1320 | $\nu_s(\text{N-O})$ | NO ₃ ⁻ |
| -1300 | $\nu(\text{C-C})$ | en, RCOO ⁻ |
| -1050 | $\nu(\text{C-N})$ | en |
| ~ 800 | $\delta(\text{C-H})$ | en, RCOO ⁻ |

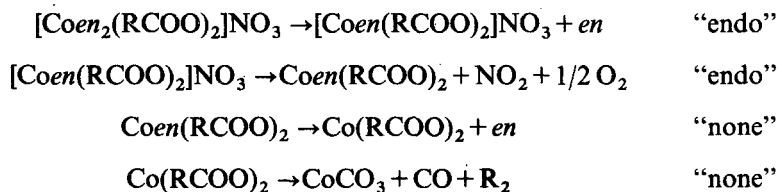
Cis compound: $R = \text{CH}_3$. At 240° the NO_3^- bands disappeared, while the *en* bands were still present, confirming the residue as a mixture of $\text{Coen}(\text{RCOO})_2$ and $\text{Co}(\text{RCOO})_2$. DTA step 1, endo in N_2 , becomes exo in O_2 , as result of *en* oxidation. At 309° , the *en* bands disappeared, indicating residual $\text{Co}(\text{RCOO})_2$; DTA step 2, exo in O_2 , is due to *en* oxidation.

Trans compound: $R = \text{CH}_3$. The residue at the end of step 1 cannot be isolated. At 280° , both *en* molecules were lost, together with nitrate, through an exo DTA process corresponding to step 2, giving $\text{Co}(\text{RCOO})_2$ as residue. The bands of NO_3^- and *en* disappeared.

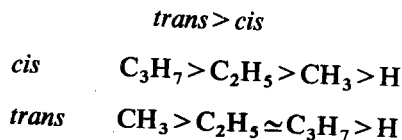
Cis compound: $R = \text{C}_3\text{H}_7$. At 250° , the NO_3^- bands disappeared while the *en* bands were still present, indicating residual $\text{Coen}(\text{RCOO})_2$. DTA step 1, endo in N_2 , was masked in O_2 by *en* oxidation.

At 375° , the *en* bands disappeared, while the C–H and C–C bonds of the carbon chain still displayed bands. This was in agreement with $\text{Co}(\text{RCOO})_2$ as residue, obtained through the loss of *en*, oxidized in O_2 , as shown by the exo process corresponding to DTA step 2.

Trans compound: $R = \text{C}_3\text{H}_7$. At 210° , bands of NO_3^- could still be recognized, in accordance with the residual mixture $[\text{Coen}(\text{RCOO})_2]\text{NO}_3/\text{Coen}(\text{RCOO})_2$. DTA step 1 was endo both in N_2 and in O_2 , suggesting that a little *en* was lost: $\text{Coen}(\text{RCOO})_2$ has about the same molecular weight as the hypothesized $[\text{Coen}(\text{RCOO})_2]\text{NO}_3$, so the choice between them is difficult. At 270° both NO_3^- and *en* bands disappeared, suggesting residual $\text{Co}(\text{RCOO})_2$, while C–H and C–C bands of the carbon chain still remained. DTA step 2 exo was observed both in O_2 and in N_2 . The hypothesized reaction steps are summarized below, with the corresponding thermal effect displayed in N_2 :



The first two reactions generally overlapped in a single TG step. It is not possible to correlate the reaction steps for all the examined compounds, owing to the different degrees of overlapping displayed by the reactions. For the first step this can be done: the following thermal stability scale, relative to carbon chain R of the carboxylates, was found:



All the *trans* compounds displayed a higher thermal stability than that of the corresponding *cis* compound (except for the formates, which are roughly equal in thermal stability).

This behaviour can be explained by considering that the solid lattice reticulation of the *trans* compound is higher than that of the corresponding *cis* compound: the spatial geometry increases the intermolecular bonds available through carboxylato groups (each being opposite the other).

The thermal stability sequence, expected to be the reverse of that for RCOO^- basicity, can be recognized for the *cis* compounds. The basic principle is that, the higher the metal to ligand bond strength, the weaker the intermolecular bonds (solid lattice) [6]. The reactivity of the complexes in the aquation reaction follows the same model [11]: a more basic carboxylate is less reactive to substitution, owing to the fact that the metal acceptor power, responsible for water coordination in the activated state, is reduced.

In the *trans* compounds, the thermal stability is not basicity-driven. Thus, it may be assumed that solid reticulation through the first term of the carbon chain prevails, with a higher thermal stability when $\text{R} = \text{CH}_3$ than when $\text{R} = \text{H}$. Subsequent CH_2 addition to the chain reduces the lattice rigidity and consequently the thermal stability. In a similar way, the observed thermal stabilities can also be explained for the *trans* compounds.

In conclusion, the reticulation effect seems to be important only for the *trans* compounds, where the spatial geometry enhances the bonds between the molecules (each bond through a carboxylato donor group is opposite the other). The *cis* compounds, with a less favourable geometry, follow the general rule of thermal stability, reversed with respect to carboxylato ion basicity. The result is that they are less stable towards thermal decomposition than the corresponding *trans* compounds.

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Zusammenfassung — Unter Durchführung einiger Abänderungen des bekannten Verfahrens wurden Verbindungen der allgemeinen Formel $\text{conf-Co(en}_2\text{(RCOO)}_2\text{)NO}_3$ hergestellt. Der Alkylrest R war H, CH_3 , C_2H_5 , C_3H_7 und en war Ethylendiamin. Die Verbindungen mit $\text{conf} = \text{cis}$ oder trans wurden mittels TLC und UV-Spektrophotometrie charakterisiert. Ihr thermisches Verhalten wurde anhand von TG, DTA und IR-Spektren von erhitzten Proben untersucht. Die thermische Stabilität wurde untersucht und in Abhängigkeit von Bindungsstärke und sterischer Behinderung diskutiert; weiterhin wurden die thermischen Zersetzungen mit Hilfe angenommener Intermediäre und deren IR-Spektren beschrieben. Die Reaktionsschritte wurden identifiziert und eine Stabilitätsreihe aufgestellt und diskutiert: cis -Verbindungen erwiesen sich als instabiler als die entsprechenden trans -Verbindungen, was einem geringeren Vernetzungseffekt zuzuschreiben ist; Die Reihenfolge folgt im Falle von cis dem Reziproken der Carboxylationenbasizität, während die Reihenfolge im Falle von trans mittels der Gitterstabilisierung erklärt werden kann.

Резюме — Путем модифицирования некоторых известных методов, получены соединения общей формулы $\text{конф-[Coen}_2\text{(RCOO)}_2\text{)NO}_3$, где $R = \text{H, CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7$, а $en = \text{этилендиамин}$. Соединения с cis - или trans -конформацией были охарактеризованы тонкослойной хроматографией и абсорбционной спектроскопией в УФ- и видимой области. Термическое поведение их изучено методами ТГ и ДТА, а также высокотемпературной ИК спектроскопией. Найденная термоустойчивость данных соединений обсуждена на основе силы твердых связей и стерических препятствий. Термическое разложение их описано, исходя из предполагаемых промежуточных продуктов и их ИК спектров. Идентифицированы реакционные стадии и обсуждена последовательность их термоустойчивости: cis -соединения менее устойчивы, чем соответствующие trans -соединения, вследствие их сетчатого строения. Порядок устойчивости cis -соединений обратный основности карбоксилат-иона, тогда как для trans -соединений этот порядок может быть объяснен на основе устойчивости твердотельной решетки.