

## COBALT(III) AMINOACIDATE BIS-PHENANTHROLINE CHLORIDES: PREPARATION AND CHARACTERISATION BY THERMAL ANALYSIS AND OTHER ANALYTICAL METHODS

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### ABSTRACT

The thermal properties of some mixed complexes of Co(III) with *o*-phenanthroline and several amino acids were determined by thermogravimetry (TG) and differential thermal analysis (DTA). The thermal stability derived from decomposition temperatures is discussed in terms of the molecular properties of the amino acids which affect the distribution of the intermolecular bonds in the solid lattice.

With reference to the weight losses and IR spectra of the heated compounds, the thermal decomposition pathways of these complexes were also determined. Modifications to the methods of preparation cited in the literature were also proposed to increase the yields and to simplify operating procedures.

### INTRODUCTION

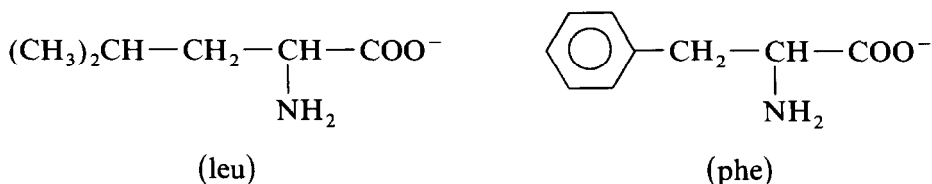
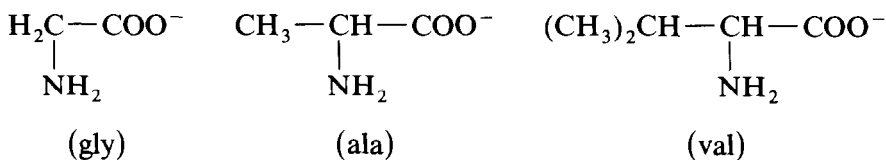
In connection with the studies carried out in our laboratory on the thermoanalytical behaviour of different complexes [1–8] we undertook the preparation of the following series of complexes:  $[\text{Cophen}_2\text{aa}]\text{Cl}_2$ , where aa = glycinate (gly), L-alaninate (ala), L-valinate (val), L-leucinate (leu), L-serinate (ser), L-threoninate (treo), L-phenylalaninate (phe) and phen = *o*-phenanthroline.

The behaviour of these solid compounds when heated, as shown by the TG and DTA results, and the IR spectra of the heated compounds, can suggest hypotheses concerning the reaction mechanism. Some molecular properties of the complexes can also be derived [1–3,8].

The interest in these compounds derives from the possible use of cobalt(III) complexes as N-protecting and C-activating groups, for example, during peptide synthesis [9]. It is known that the coordination of  $\alpha$  amino acids to metal ions produces an increase in the nucleophilic reactivity at the

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$\alpha$  position through bond polarisation promoted by the metal ion. This chelation effect could be also considered as a simple model for the action of metal ions in some biological transformations of amino acids themselves. So the Co(III) complexes of amino acids and azo dye ligand could be considered as structural analogues of certain biological systems.

We report here the synthesis, characterisation and thermoanalytical behaviour of these complexes. Although different preparation techniques have already been reported for these complexes [10–14], low yield and tedious desalting procedures often make these methods unsatisfactory. In this paper a modification to the published methods of synthesis is proposed in order to overcome those problems. The purity of the complexes obtained was checked by TLC and visible–UV spectroscopy.

## EXPERIMENTAL

### *Apparatus and materials*

The thermal stabilities of the aminoacidate bis(phenanthroline) cobalt(III) chloride complexes were studied by TG and DTA in dynamic  $\text{N}_2$  and  $\text{O}_2$  atmospheres with a flow rate of  $50 \text{ ml min}^{-1}$ .

TG and DTA measurements were made with Perkin–Elmer models TGS-2 and 1700 respectively, at a heating rate of  $10^\circ \text{C min}^{-1}$ . The weight of each sample was approximately 1 mg in all runs.

The IR spectra of the prepared compounds were recorded using a Perkin-Elmer 125 grating infrared spectrophotometer (KBr discs). The visible-UV spectra were measured on aqueous solutions of the solid compounds, using 1 cm quartz cells in a Perkin-Elmer 320 spectrophotometer.

Precoated silica gel plates (Kieselgel 60, art. 5635 from Merck) were used for TLC. Aqueous solutions of the dissolved complexes, as well as those of  $[\text{Cophen}_2\text{Cl}_2]\text{Cl}$  and of the amino acids as references, were applied 1 cm from the lower edge of the plates ( $5 \times 5$  cm) and were developed in 10–20 min using ethanol:6M  $\text{LiNO}_2$  (7:3 v/v) as mobile phase.

The complexes were prepared by the procedure described below, using analytical grade chemicals from Merck.

#### *Preparation of the aminoacidate bis(phenanthroline) cobalt(III) chloride complexes*

A mixture of amino acid ( $3.8 \times 10^{-4}$  mol) and *N,N*-dimethylbenzylamine (DMB) ( $2 \times 10^{-3}$  mol) was dissolved in water:ethanol (1:2 v/v). An equimolar amount of solid *cis*- $[\text{Cophen}_2\text{Cl}_2]\text{Cl}$ , obtained as described in ref. 15, was added to the solution and the temperature was increased to  $50^\circ\text{C}$  while stirring for 15 min. The solution thus obtained was set aside at room temperature for one day. Addition of acetone caused the precipitation of the  $[\text{Cophen}_2\text{aa}]\text{Cl}_2$  hydrate complexes. They were recrystallised by dissolving them in the minimum amount of hot water and by cooling the solution in an ice bath. The complexes, obtained as orange crystals by filtration, were washed with pure ethanol and ethyl ether, and vacuum dried. The yields of  $[\text{Cophen}_2\text{aa}]\text{Cl}_2$  were in the 40–60% range.

The purity of the synthesised complexes was controlled by TLC. The spots of the complexes were highlighted with  $(\text{NH}_4)_2\text{S}_x$ , those of the amino acids were highlighted with an alcoholic solution of ninhydrin.

## RESULTS

The  $R_f$  values obtained by TLC are shown in Table 1, both for amino acids and the corresponding complexes. A single spot indicates a highly pure compound. Complexes formed with gly, ala, val and ser display the highest mobility, followed by that formed with treo, and finally by those with phe and leu.

The IR spectra of the seven complexes were very similar, displaying the same bands with only minor differences. Some of these, for the glycinate, free glycine and phenanthroline, are reported with their assignments in Table 2. The IR spectra account for the coordination of the ligands: the shifting of the  $\nu_{\text{a}(\text{COO})}$  and  $\nu_{\text{s}(\text{COO})}$  bands to higher and lower wavenumbers respectively, and of the  $\nu_{(\text{N}-\text{H})}$  band to lower wavenumbers with respect to

TABLE 1

TLC  $R_f$  values of  $[\text{Cophen}_2\text{aa}]^{2+}$  complexes and of free amino acids

aa	$R_f$	Amino acids	$R_f$
gly	0.71	Glycine	0.83
ala	0.71	Alanine	0.88
val	0.71	Valine	0.90
leu	0.65	Leucine	1.0
phe	0.63	Phenylalanine	1.0
ser	0.71	Serine	0.87
treo	0.66	Threonine	0.83
$[\text{Cophen}_2\text{Cl}_2]\text{Cl}$	0.00		

those of free amino acids, suggest that both the carboxylate and amino groups are involved in metal ion complexation [16]. Due to the coordination on the N atoms, the  $\nu_{(\text{C}=\text{N})}$  bands of the coordinated phenanthroline, and consequently the  $\nu_{(\text{C}=\text{C})}$  bands, are also slightly shifted towards higher wavenumbers with respect to those of free phenanthroline.

The complexes were also characterised by their visible spectra: the molar absorptivity and wavelengths corresponding to the two observed maxima are listed in Table 3. The spectra suggest a *cis* conformation and an octahedral

TABLE 2

IR bands displayed by  $[\text{Cophen}_2\text{gly}]\text{Cl}_2$ , referred to as cplx, pure phen and pure gly

Wavenumbers ( $\text{cm}^{-1}$ )	Assignment	Moiety
3170	$\nu_{(\text{N}-\text{H})}$	cplx
3190	$\nu_{(\text{N}-\text{H})}$	gly
3050	$\nu_{(\text{C}-\text{H})}$	cplx
3060	$\nu_{(\text{C}-\text{H})}$	phen
1660	$\nu_{\text{a}}(\text{COO})$	cplx
1590	$\nu_{\text{a}}(\text{COO})$	gly
1520	$\nu_{(\text{C}=\text{C})}$	cplx
1490	$\nu_{(\text{C}=\text{C})}$	phen
1430	$\nu_{(\text{C}=\text{N})}$	cplx
1400	$\nu_{(\text{C}=\text{N})}$	phen
1380	$\nu_{\text{s}}(\text{COO})$	cplx
1420	$\nu_{\text{s}}(\text{COO})$	gly
1330	$\rho_{\text{w}}(\text{CH}_2)$	cplx
1330	$\rho_{\text{w}}(\text{CH}_2)$	gly
1040	$\nu_{\text{a}}(\text{CCN})$	cplx
1030	$\nu_{\text{a}}(\text{CCN})$	gly
850	$\delta_{(\text{C}-\text{H})}$	cplx
840	$\delta_{(\text{C}-\text{H})}$	phen
725	$\delta_{(\text{C}-\text{H})}$	cplx
720	$\delta_{(\text{C}-\text{H})}$	phen

TABLE 3

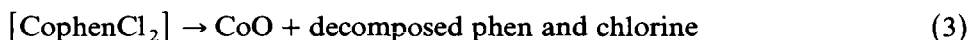
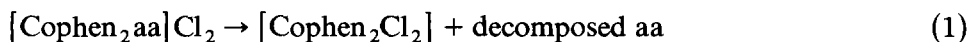
Molar absorptivities,  $\epsilon$  ( $\text{mol}^{-1} \text{l cm}^{-1}$ ) at two wavelengths,  $\lambda$ , (nm) corresponding to the two maxima of the spectrum of  $[\text{Cophen}_2\text{aa}]\text{Cl}_2$  complexes

aa	$\lambda$	$\epsilon$	aa	$\lambda$	$\epsilon$
Gly	270	42000	Phe	270	54000
	470	120		455	92
Ala	270	38500	Ser	270	41100
	480	94		470	122
Val	270	38000	Treo	270	35700
	460	90		480	117
Leu	270	43300			
	460	85			

configuration for the cobalt(III), as expected when considering the already observed arrangement of the two phenanthroline chelating molecules and the formation of the five-membered aminoacidate ring [17].

The TG results in oxygen flow are summarised in Table 4. As an example, the TG curve for  $[\text{Cophen}_2\text{gly}]\text{Cl}_2$  complex, together with that in flowing  $\text{N}_2$ , is reported in Fig. 1. The presence of water of crystallisation, generally lost in the 50–120 °C temperature range, can be observed in all compounds. Dehydration occurs in one step and weight losses are in agreement with those calculated from the proposed formulae as reported in Table 4. The expected endothermic behaviour for such processes has been observed in the DTA curves over the same temperature range; Fig. 1 also shows the DTA curves of  $[\text{Cophen}_2\text{gly}]\text{Cl}_2$  complex as an example, both in oxygen and nitrogen flow.

The anhydrous complexes are stable below 130–150 °C. Above this temperature thermal decomposition occurs in three partially overlapping steps. From the observed weight losses, the following reaction scheme can be proposed: elimination of the amino acid molecule with consequent reduction of Co(III) to Co(II); elimination of the first molecule of phenanthroline; and formation of cobalt oxide due to the elimination of the last molecule of phenanthroline and of chlorine. The thermal decompositions in oxygen of the ser and treo complexes do not follow this scheme, cobalt(III) also being present in the final residues, as suggested by the found weight. The thermal decomposition can be summarised by the following reactions.



In the IR spectra of those compounds previously heated under oxygen flow at 10 °C  $\text{min}^{-1}$  up to 260 °C, the  $\nu_{\text{s(COO)}}$ ,  $\nu_{\text{a(COO)}}$  and  $\nu_{\text{(N-H)}}$  bands of

TABLE 4

TG summary of the [Cophen<sub>2</sub>aa]Cl<sub>2</sub>·xH<sub>2</sub>O series at 10 °C min<sup>-1</sup> in O<sub>2</sub> flowing at 50 ml min<sup>-1</sup>; sample weight around 1 mg. Water loss, always occurring in the 50–120 °C range, is reported as percent of the sample. For reactions (1)–(3) described in the text, the starting and ending temperatures, T<sub>i</sub> and T<sub>f</sub>, are in °C, whilst the residue at the end of each step are percent weights referred to anhydrous compounds

aa	x	Water loss		React. (1)		Residue		React. (2)		Residue		React. (3)		Residue	
		Calc.	Found	T <sub>i</sub>	T <sub>f</sub>	Calc.	Found	T <sub>i</sub>	T <sub>f</sub>	Calc.	Found	T <sub>i</sub>	T <sub>f</sub>	Calc.	Found
gly	1	3.08	3.3	140	260	86.72	87.2	270	470	54.84	56.3	470	640	13.25	12.9
ala	1	3.01	3.3	140	270	84.63	85.1	290	430	53.51	54.5	430	640	12.93	12.8
val	2	5.59	5.8	130	260	80.72	81.1	290	430	51.04	51.9	430	640	12.33	12.0
leu	1	2.81	3.5	170	260	78.90	79.7	290	440	49.89	51.1	440	650	12.05	11.9
phe	2	5.20	4.9	145	260	74.81	75.8	270	420	47.31	48.7	410	650	11.43	11.2
ser	2	5.70	5.2	130	230	82.35	82.0	290	—	—	—	—	630	12.58	12.9
treo	1	2.87	3.1	170	280	80.46	81.7	290	—	—	—	—	630	12.29	12.6

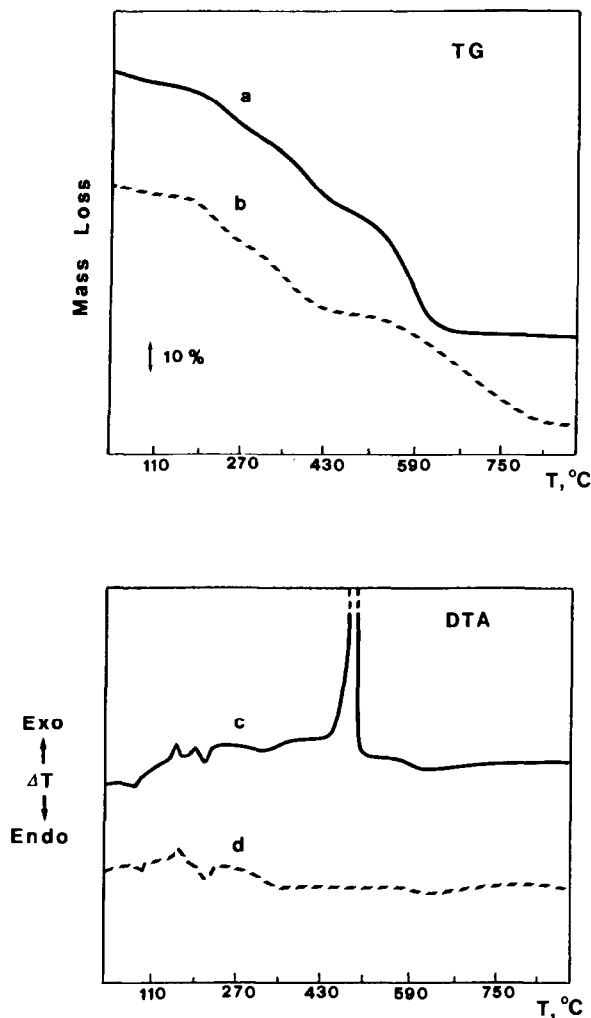


Fig. 1. TG and DTA curves of  $[\text{Cophen}_2\text{gly}]\text{Cl}_2$  in dynamic oxygen (a,c) and nitrogen (b,d) atmospheres at a flow rate of  $50 \text{ ml min}^{-1}$  and a heating rate of  $10^\circ \text{C min}^{-1}$ .

the aa have disappeared, as shown in Fig. 2 for the  $[\text{Cophen}_2\text{gly}]\text{Cl}_2$  complex. The phenanthroline  $\nu_{(\text{C}=\text{C})}$  and  $\nu_{(\text{C}=\text{N})}$  bands can still be observed in the IR spectrum of compounds heated up to  $470^\circ \text{C}$  under the same conditions.

The temperature at which the anhydrous complexes begin to decompose varies with the amino acid ligand. Decomposition reaction (1) takes place in different steps, as indicated by the first exothermic and subsequent endothermic (under nitrogen flow) reactions observed in the DTA curves in the temperature range where the TG curves show the loss of one aa molecule. The second endothermic effect at around  $300^\circ \text{C}$  observed in both  $\text{O}_2$  and  $\text{N}_2$ , corresponds to the loss of the first molecules of phen (reaction (2)),

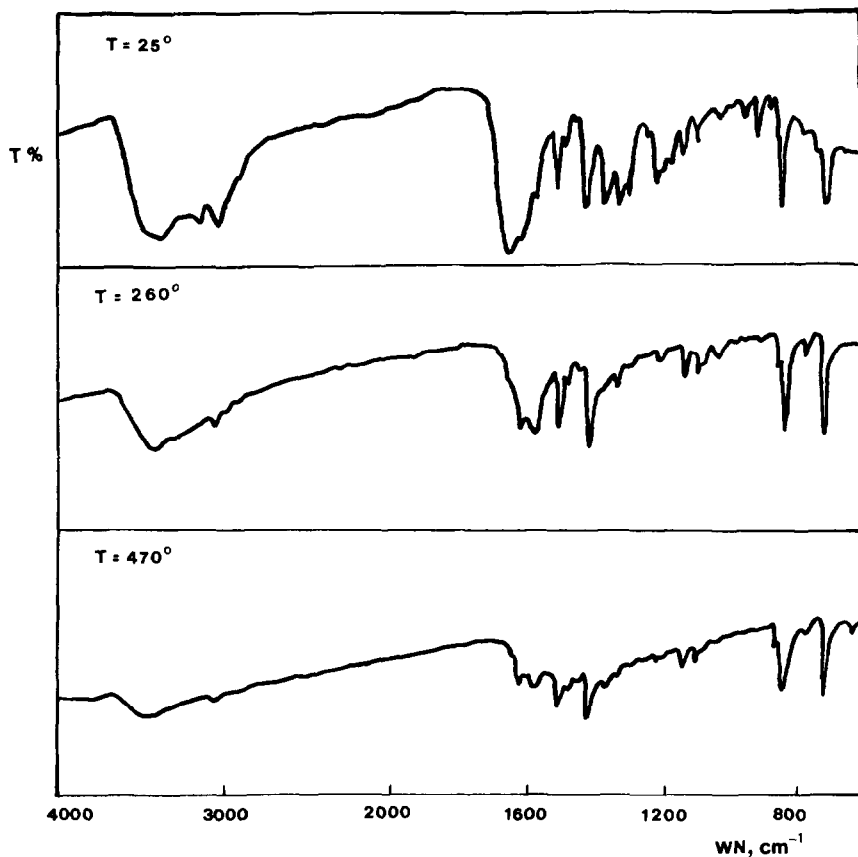


Fig. 2. IR spectra of  $[\text{Cophen}_2\text{gly}]\text{Cl}_2$  after heating to temperature,  $T^\circ\text{C}$ , in an  $\text{O}_2$  flow. Other conditions are similar to those employed for the corresponding TG.

confirmed by a chemical test (pH indicator) which indicated that the evolved gas was basic. Indeed, the sublimate obtained at the above temperature gives the characteristic red colour with  $\text{Fe}(\text{II})$ , due to formation of the  $\text{Fe}(\text{phen})_3^{2+}$  complex ion [18].

The final thermal decomposition at around  $500^\circ\text{C}$  (reaction (3)) is accompanied by the strong exothermic oxidation of the phenanthroline in  $\text{O}_2$ , whilst no effect is displayed in  $\text{N}_2$ .

## DISCUSSION

In the preparation of  $[\text{Cophen}_2\text{aa}]\text{Cl}_2$  hydrated compounds, the use of  $N,N$ -dimethylbenzylamine (DMB) instead of  $\text{NaOH}$  [11,14] or  $\text{LiOH}$  [12,13], is the most relevant modification to the previously reported procedures.



Deprotonation of aa is conveniently achieved in situ by the addition of DMB, thus allowing the aa to enter the coordination sphere of cobalt(III) as chelating agent. The chloride salt of the complex formed was precipitated from the solution by lowering its solubility by addition of acetone, whilst DMB still maintains a high solubility. In such a way the tedious desalting procedures necessary to eliminate sodium or lithium ions, are not required. Moreover, a better yield is obtained, 40–60% against 30% when alkaline hydroxides were used [12].

The  $R_f$  values from TLC cannot be used to give information on the structure of the complexes, as previously reported [8]. The eluent needed to enhance the mobility (or to reduce the retention) of the (2 +)-complex ions studied in this work, is in fact much more polar than that used in the above-cited paper where (1 +)-ions were treated. Consequently, the  $R_f$  values mainly reflect the behaviour of a solute–eluent interaction-controlled process rather than a solute–support ionic interaction [19], where differences in charge density induce differences in retention. In fact, the charge densities can be expected to be about the same for all the complexes because of the presence of the large phenanthroline molecules in a *cis* configuration which mainly affects the mean ionic radius. Free acids do not have this “saturation” effect of phenanthroline on the ionic radius and consequently they display the highest mobility for phenylalanine and leucine, where charge density could be assumed to be lowest (Table 1). On the contrary the observed  $R_f$  sequence of the complexes (Table 1) suggests a higher mobility when short hydrophobic chains are present, as when gly, ala, val and ser are the complexing agents. The mobility decreases when the carbon chain increases in length, as when treo or leu is the ligand, down to the lowest value for the phe complex, where an aromatic ring is present.

The presence of phenanthroline in the coordination sphere of cobalt(III) leads to a high, broad absorption band in the UV region at around 270 nm, that masks the charge-transfer band of cobalt(III) complexes generally displayed near 350–370 nm. Therefore, the spectrophotometric characterisation includes the UV band of the phenanthroline. Of course this band depends on the cobalt(III) environment in a very limited way, as shown by the molar absorptivity values which are very close in the examined series, except for the phe complex, see Table 3. In the phe complex, an interaction between aromatic rings could be responsible for the high absorptivity.

The coordination of cobalt(III) ion through the formation of chelate rings, both with aminoacidate and phenanthroline molecules, increases the rigidity of those bonds involved in vibrations. Thus, the IR bands of coordinated aminoacidates,  $\nu_{\text{a(COO)}}$  and  $\nu_{\text{(CCN)}}$ , and of phenanthroline,  $\nu_{\text{(C=N)}}$  and  $\nu_{\text{(C=C)}}$ , are shifted towards higher wavenumbers with respect to those of the corresponding uncomplexed species, as shown in Table 2. On the other hand the coordinated positive metal ion induces bond polarisation, thus lowering the oscillator strength constant of the nearest bonds: Table 2 shows

TABLE 5

“True” kinetic parameters calculated from TG curves of [Cophen<sub>2</sub>aa]Cl<sub>2</sub> complexes limited to the step described in reaction (1). Rounded values of  $Z$  and  $E$  are in sec<sup>-1</sup> and kJ mol<sup>-1</sup> respectively. Calculated half-lives,  $t_{1/2}$ , are in sec at a chosen reference temperature of 180 °C, temperatures,  $T_i$ , in °C are calculated at 10% of reaction at a heating rate of 10 °C min<sup>-1</sup>

aa	$Z$	$E$	$n$	$t_{1/2}$	$T_i$
gly	$8.6 \times 10^3$	60.6	0.54	667	172
ala	$3.3 \times 10^4$	64.2	0.95	532	166
val	$3.2 \times 10^6$	81.2	0.60	441	161
leu	$6.4 \times 10^7$	98.6	0.20	1938	201
phe	$7.5 \times 10^9$	112.2	1.00	797	180
ser	$5.4 \times 10^5$	72.8	0.67	282	157
treo	$8.7 \times 10^7$	96.3	1.31	1129	186

that the  $\nu_{(N-H)}$  and  $\nu_{s(COO)}$  of gly, as well as the  $\nu_{(C-H)}$  of phen, are shifted towards lower wavenumbers.

All the complexes examined show similar behaviours when heated, and the first hypothesised reaction alone (reaction (1) in the results section) could be used in principle to highlight differences in thermal stability. However, the onset temperature of reaction (1) is difficult to measure with sufficient accuracy. A better evaluation can be achieved by using TG curve analysis [20,21]. In such a way, “true” kinetics parameters, appearing in an Arrhenius-like kinetic law of reaction, i.e. the  $Z$ ,  $E$  and  $n$  of the expression  $-(dw/dt) = Z \exp[-E/(RT)]w^n$  (where  $1 - w$  is the degree of reaction, depending on time  $t$  and temperature  $T$ ) can be evaluated and used to provide a valid description of the TG behaviour with no other physical meaning.

The low mass values used, i.e. one milligram, due to the availability of the synthesised products, were sufficient for a simple TG analysis [20] with no simultaneous regression with respect to calorimetric parameters [21].

With the kinetics parameters thus obtained, the starting temperatures of reaction (1) can be expressed very accurately as temperatures, for example, at 10% of reaction. In Table 5, these temperatures are reported together with the kinetics parameters and the half-life times calculated for a chosen temperature. Half-life times are also a satisfactory way of comparing the stabilities of a series of compounds [21]. The following thermal stability order can be recognized for the examined complexes, depending on the coordinated aminoacidates: leu > treo > phe > gly > ala > val > ser.

The total basicity of the aminoacidates, measured from  $(pk_1 + pk_2)$  at 25 °C and 0.1 mol l<sup>-1</sup> ionic strength [22], does not agree with the expected sequence [2]. This discrepancy comes from two causes: the  $(pk_1 + pk_2)$  values all lie in the 11.2–12.0 range with values too close for an accurate

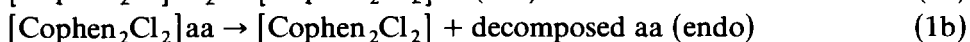
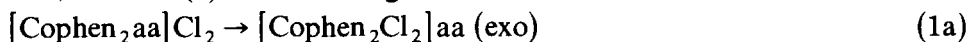
evaluation of relative differences; and the coordinated molecules mainly differ from each other in the side chain of the  $-\text{CH}(\text{NH}_2)-\text{COO}^-$  group, whose effect, therefore, prevails in determining solid lattice stability [3].

Molecules with long side chains, such as leu, treo and phe, have the highest thermal stability. This suggests that  $-\text{CH}_2\text{CH}(\text{CH}_3)_2$ ,  $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$  and  $-\text{CH}_2\text{Ar}$ , in the reported order, can act as intermolecular bridges by mutual interactions, thus giving a high thermal stability to the solid lattice [1].

This is not the case for val and ser, where the  $-\text{CH}(\text{CH}_3)_2$  and  $-\text{CH}_2\text{OH}$  side chains can be assumed to be too short to interact with other molecules in the solid state. Therefore, short side chains with no intermolecular bridges may be assumed to be responsible for a decrease in thermal stability, due to their thermal vibrations or steric hindrance. This explains the stability sequence from gly with no side chain, to ala, with just  $-\text{CH}_3$ , up to val and ser.

The presence of an  $-\text{OH}$  group in the molecule does not seem to affect the thermal stability, except to the extent expected on the basis of its dimensions. Even though this seems to be true, the presence of  $-\text{OH}$  causes the thermal decomposition to become different after its start, as shown in Table 4. When oxygen flows in the TG apparatus, ser and treo complexes show overlapping reaction steps and the final residues are higher in mass than those calculated for cobalt(II) oxide. The presence of Co(III), throughout the entire examined temperature range, can explain this behaviour. Therefore the product of reaction (1) would be a mixture of  $[\text{Cophen}_2\text{Cl}_2]$  and  $[\text{Cophen}_2\text{Cl}_2]\text{OH}$ . The cobalt(III) remains unchanged yielding  $\text{Co}_2\text{O}_3$  in the final residue and modifying the subsequent reaction steps (reactions (2) and (3)). Due to the low relative weight of an  $-\text{OH}$  group, the calculated residues in Table 4 for reaction (1), still agree with those found. In contrast, the final found residues agree with this hypothesis, being heavier than the amounts calculated as  $\text{CoO}$ .

For considering the DTA results, of the two peaks assigned to reaction (1), the first peak at around  $160^\circ\text{C}$  requires some explanation. Its exothermicity is due to two chloride ions entering the coordination sphere of the metal, with substitution of a mono-negative aminoacidate molecule. The resulting approach of one more negative ion to the positive metal ion causes the system to lose energy, displayed by the exothermic DTA peak. Therefore, reaction (1) should be regarded as a sum of two reactions



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