CRITICAL COMPARISON OF THERMAL PROPERTIES OF SOME DIVALENT METAL ION COMPLEXES WITH ALANINE, LEUCINE AND VALINE

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ABSTRACT

The thermal properties of the complexes of alanine, leucine and valine with several divalent metal ions [Co(II), Ni(II), Cu(II)] were determined using TG and DSC analyses and compared with those of analogous glycinate complexes. The thermal stability order of the series of complexes examined does not correlate with the Irving and Williams series for the stability of complexes in solution; however, a reverse correlation results with the order of basicity of the ligands.

INTRODUCTION

The thermal properties of three series of complexes, obtained by reaction of the divalent metal ions Co(II), Ni(II) and Cu(II) with alanine, leucine and valine, have been studied by thermogravimetry and differential scanning calorimetry. The thermal stabilities of these compounds have been compared and discussed, within each series and between the series, in terms of the strength of the inter- and intramolecular bonds [1–3]. A comparison has also been carried out concerning the thermodynamic values (ΔH, ΔS and ΔG) corresponding to the formation of complexes of Co(II), Ni(II) and Cu(II) with alanine, and those with glycine, whose thermal properties have been given in a previous paper [4].

EXPERIMENTAL

Instrumentation

TG, DTG and DSC curves of the solid complexes were obtained using a Du Pont model 990 DSC cell and console and a model 951 thermobalance. The heating rate used was 10°C min^{-1} on samples of mass ranging from 5

to 10 mg. The furnace atmosphere was dry air at a flow rate of 100 ml min^{-1}. All temperatures were corrected for thermocouple non-linearity and are, of course, procedural temperatures.

Materials

The α-alanine, leucine, valine and glycine were obtained from Sigma Chemical Co. The other chemicals employed, all of analytical grade, were obtained from Merck.

Preparation of compounds

The bis-glycine complexes of Co(II), Ni(II) and Cu(II) were obtained as previously reported [4].

The bis-alaninate, -valinate and -leucinate complexes of Co(II), Ni(II) and Cu(II) were prepared by adding stoichiometric amounts of aqueous solutions of each amino acid to solutions of metal hydroxide, or to suspensions of dibasic metal carbonate [5–7]. The mixtures obtained were heated for a few minutes in a water bath and then filtered and left to crystallize. Small amounts of ethanol were sometimes added to achieve precipitation. The crystals obtained were collected by filtration, washed with ethanol and dried. When necessary, the precipitates were recrystallized from water–ethanol solutions. Water content and residual metal oxide were determined by thermogravimetry. The metal content was also obtained by complexometric titration.

RESULTS

Figures 1–9 show the TG curves, in flowing air (100 ml min^{-1}), of the complexes of Co(II), Ni(II) and Cu(II) with alanine, valine and leucine. The operational temperature range is 20–900°C.

Figures 10–12 show the DSC curves of the same complexes, obtained under the same experimental conditions in the temperature range 20–500°C.

The loss of the crystallization solvent is complete in the temperature range 140–180°C for all compounds except copper–leucine and cobalt–valine complexes.

The decomposition of the anhydrous compounds is very fast and often occurs in a single exothermic step, giving the respective oxides at 250–350°C. The thermal data, percentages of solvent and of the residual oxides found are given in Tables 1–3.

The same data, for the glycine complexes of the divalent cations studied, whose thermogravimetric curves were published in a previous paper [4], are collected in Table 4.
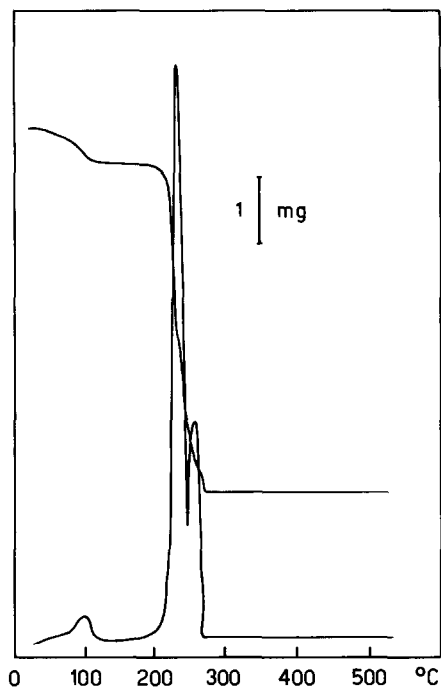
Fig. 1. TG and DTG curves of cobalt(II)–alanine complex in air flowing at 100 ml min⁻¹. Heating rate 10°C min⁻¹.

Fig. 2. TG and DTG curves of nickel(II)–alanine complex in air flowing at 100 ml min⁻¹. Heating rate 10°C min⁻¹.

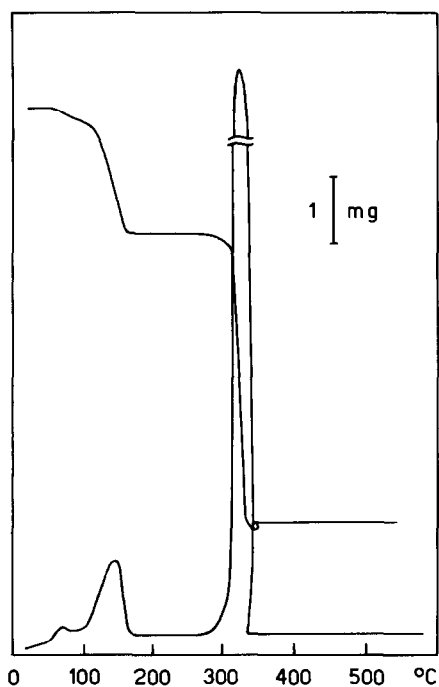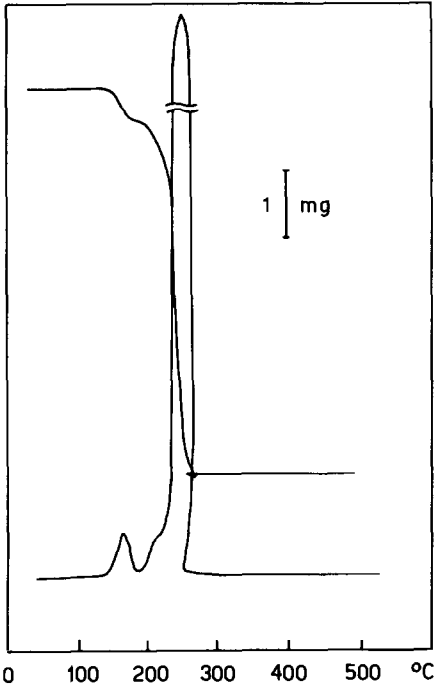Fig. 3. TG and DTG curves of copper(II)–alanine complex in air flowing at 100 ml min^{-1}. Heating rate 10°C min^{-1}.
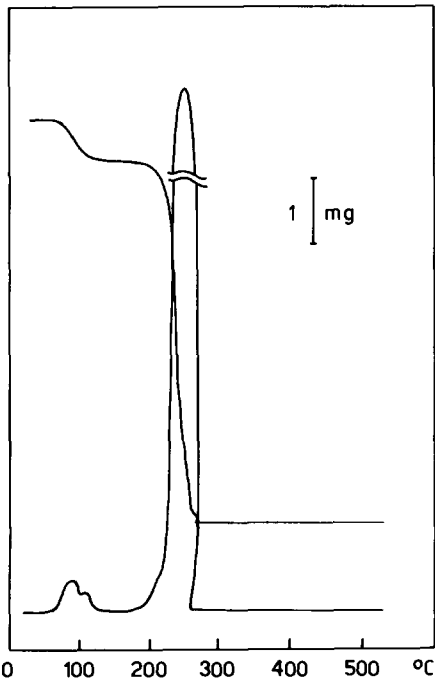

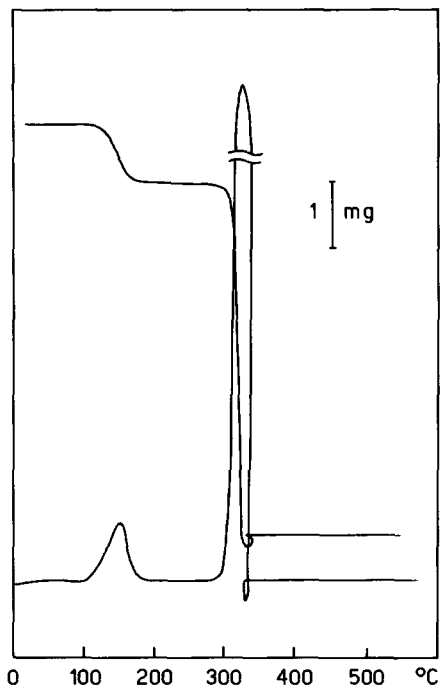Fig. 4. TG and DTG curves of cobalt(II)–leucine complex in air flowing at 100 ml min^{-1}. Heating rate 10°C min^{-1}.

Fig. 5. TG and DTG curves of nickel(II)–leucine complex in air flowing at 100 ml min^{-1}. Heating rate 10°C min^{-1}.
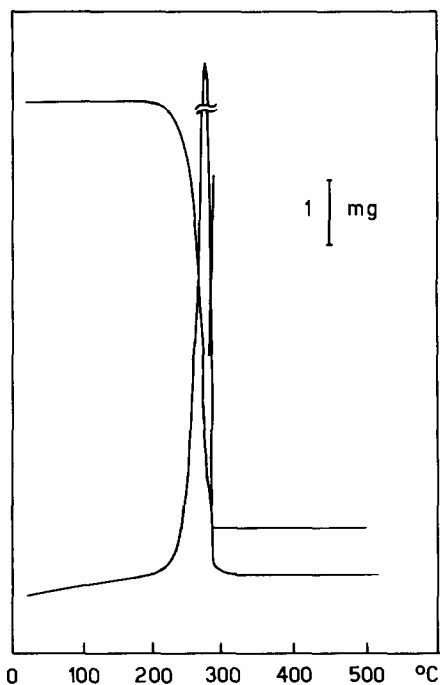

Fig. 6. TG and DTG curves of copper(II)–leucine complex in air flowing at 100 ml min^{-1}. Heating rate 10°C min^{-1}.
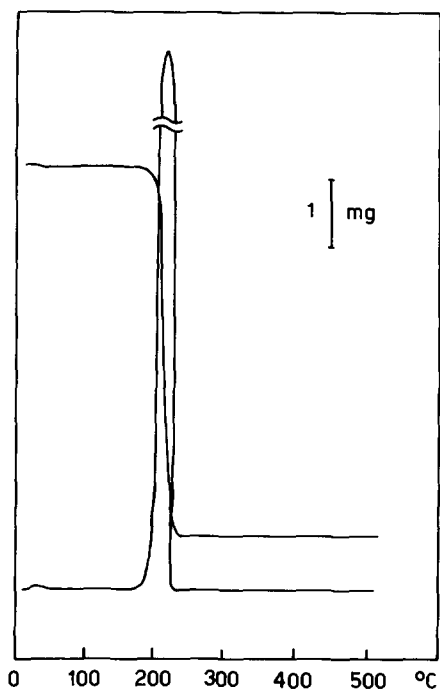
Fig. 7. TG and DTG curves of cobalt(II)–valine complex in air flowing at 100 ml min^{-1}. Heating rate 10°C min^{-1}.

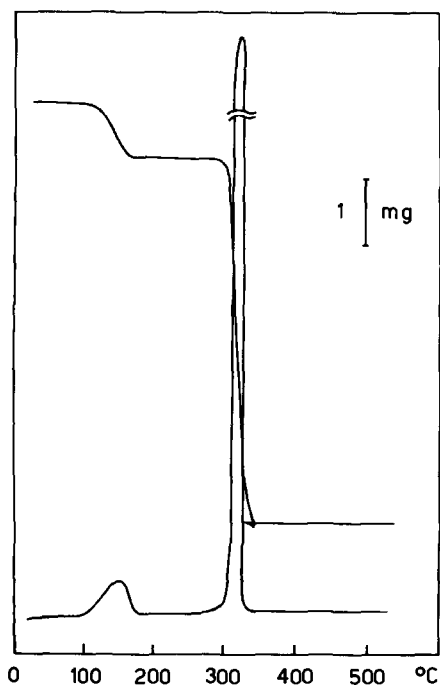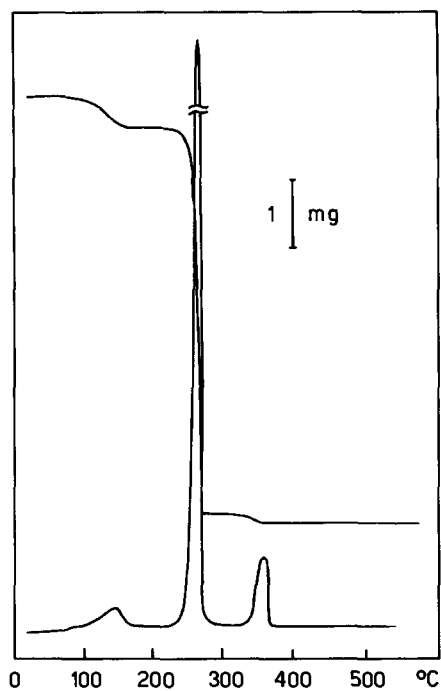Fig. 8. TG and DTG curves of nickel(II)–valine complex in air flowing at 100 ml min^{-1}. Heating rate 10°C min^{-1}.

Fig. 9. TG and DTG curves of copper(II)–valine complex in air flowing at 100 ml min^{-1}. Heating rate 10°C min^{-1}.

Fig. 10. DSC curves of alanine complexes with (a) copper(II), (b) nickel(II) and (c) cobalt(II), in air flowing at 100 ml min^{-1}. Heating rate 10°C min^{-1}.

Fig. 11. DSC curves of leucine complexes with (a) copper(II), (b) nickel(II)and (c) cobalt(II), in air flowing at 100 ml min^{-1}. Heating rate 10°C min^{-1}.
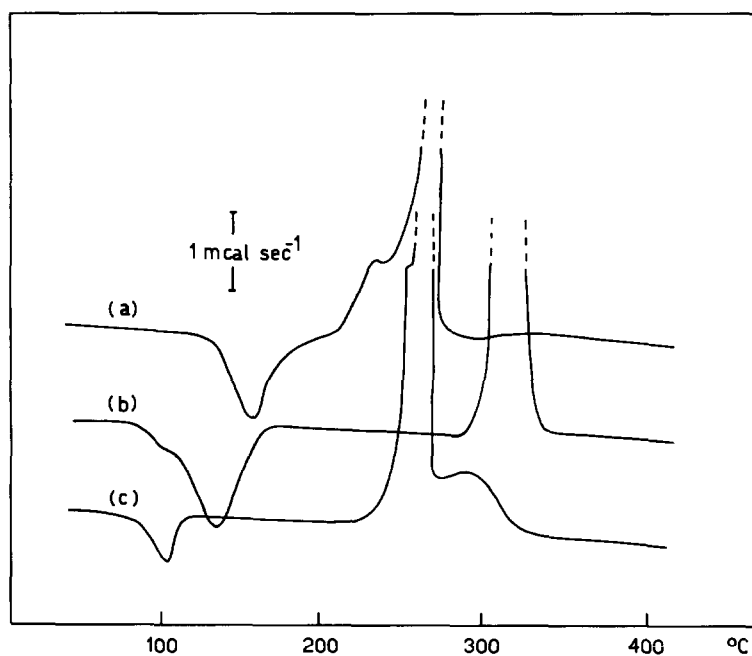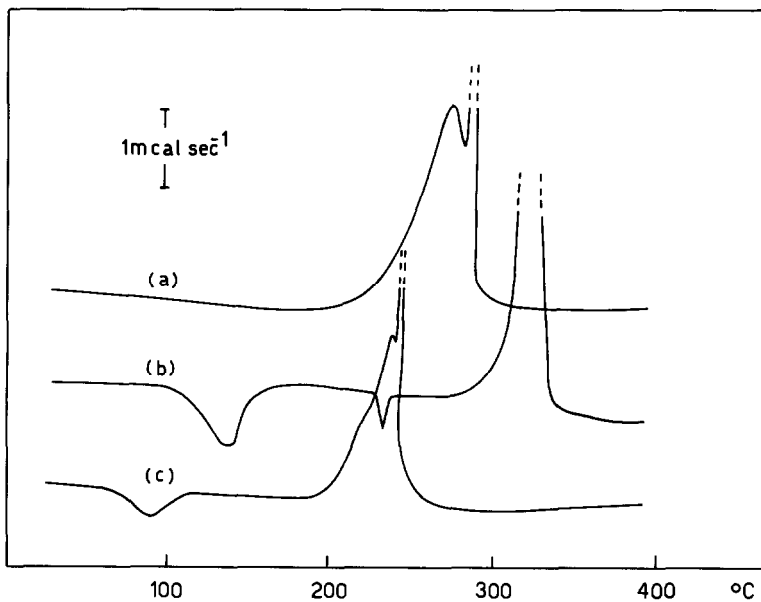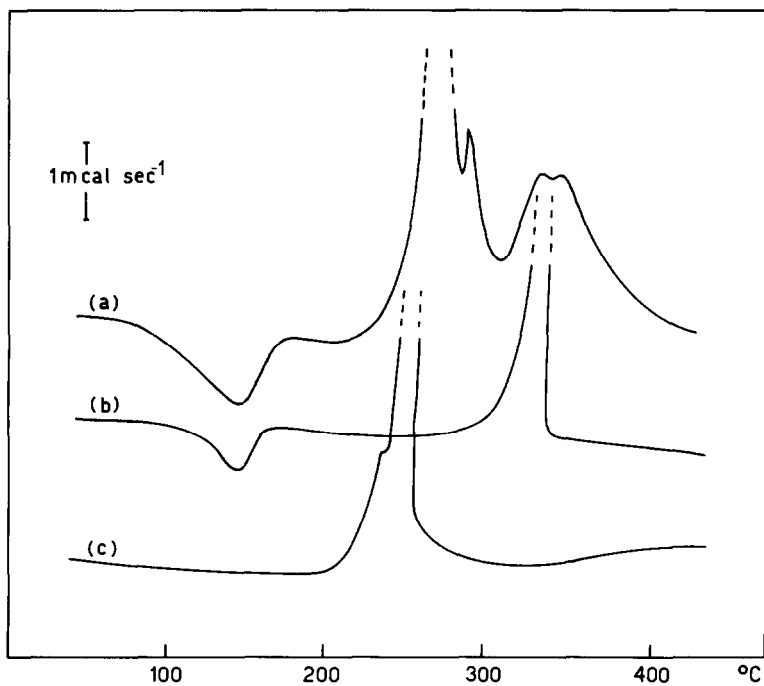

Fig. 12. DSC curves of valine complexes with (a) copper(II), (b) nickel(II) and (c) cobalt(II), in air flowing at 100 ml min^{-1}. Heating rate 10°C min^{-1}.

TABLE 1

TG of complexes with general formula Me(II)Ala$_2 \cdot$S$_x$ [a]

Metal ion	Solvent loss		Decomposition process		
	Found (%)	PDT	Calc. (%)	Found (%)	PDT
			(as Co$_3$O$_4$)		
Co(II)	− 7.1	40	33.9	33.5	180
		95			240
		140			281
Ni(II)	− 29.5	50	(as NiO)		280
		140	31.5	31.7	330
		180			360
Cu(II)	− 6.4	120	(as CuO)		195
		165	32.9	33.3	240
		180			270

[a] Me(II) = divalent transition metal ion; Ala = Alanine; S = crystallization solvent. Results were obtained in flowing air (flow rate 100 ml min^{-1}) at a heating rate of 10°C min^{-1}. Percentage values are reported with respect to the anhydrous compounds. Values reported for solvent loss are preceded by a minus sign, indicating a "mass loss" during the step, while the remainder are expressed as "residual" at the completion of the step. Procedural decomposition temperatures (PDT) are also reported.

TABLE 2

TG of complexes with general formula Me(II)Leu$_2 \cdot$S$_x$ [a]

Metal ion	Solvent loss		Decomposition process		
	Found (%)	PDT	Calc. (%)	Found (%)	PDT
Co(II)	− 8.2	60	(as Co$_3$O$_4$)		190
		90	25.0	25.3	240
		130			280
Ni(II)	− 11.9	90	(as NiO)		285
		150	23.3	23.6	320
		200			345
Cu(II)	−	−	(as CuO)		200
			24.4	24.5	275
					300

[a] See Table 1. Leu = leucine.

DISCUSSION

The order of thermal stability for the complexes, from the experimental data (Tables 1–3 and Fig. 13), is, for each of the series studied: Ni(II) > Co(II) ⩽ Cu(II). This is similar enough to that found for the corresponding glycine complexes [4]: Ni(II) > Co(II) > Cu(II). This stability order does not

TABLE 3

TG of complexes with general formula $Me(II)Val_2 \cdot S_x$ [a]

Metal ion	Solvent loss		Decomposition process		
	Found (%)	PDT	Calc. (%)	Found (%)	PDT
Co(II)	−0.8	25	(as Co_3O_4)		190
		30	27.4	26.0	215
		60			245
Ni(II)	−11.4	80	(as NiO)		288
		150	25.5	25.0	320
		180			350
Cu(II)	−6.2	40	(as CuO)		210
		140	26.7	26.2	260
		175			365

[a] See Table 1. Val = valine.

agree with that found for many other series of complexes [1,2], that is practically the reverse of that found by Irving and Williams for the stability constants of the same complexes in solution [8].

This behaviour can be discussed taking into account the observations pointed out for the corresponding glycine complexes:

(i) The oxygen–metal bond must be essentially electrostatic in these complexes and the contribution of the electrostatic bond is, within each series, Ni(II) ⩾ Co(II) > Cu(II), which is in sufficiently good agreement with the thermal behaviour within the series.

(ii) Tetragonal distortion of the octahedral symmetry, particularly evident for Cu(II) which is subject to the Jahn–Teller effect [9], increases the covalent character of the Cu–N bond in the x–y plane. This reduces the

TABLE 4

TG of complexes with general formula $Me(II)Gly_2 \cdot S_x$ [a]

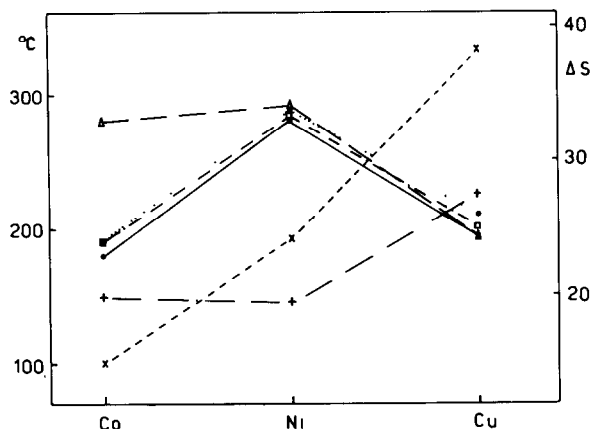| Metal ion	Solvent loss		Decomposition process		
	Found (%)	PDT	Calc. (%)	Found (%)	PDT
Co(II)	−14.8	140	(as Co_3O_4)		282
		160	33.0	33.2	325
		200			375
Ni(II)	−14.7	80	(as NiO)		290
		100	30.8	31.1	345
		200			400
Cu(II)	−8.0	125	(as CuO)		195
		170	34.6	34.4	280
		180			320

[a] See Table 1. Gly = glycine.

Fig. 13. PDTs (procedural decomposition temperatures) for Me(II)Gly$_2$($\triangle$), Me(II)Val$_2$ (O), Me(II)Leu$_2$ ($\square$), Me(II)Ala$_2$ ($\bullet$) and entropy change data for the formation of Me(II)Gly$_2$ (+) and Me(II)Ala$_2$ (×) complexes in aqueous solutions.

distance between Cu and N, thus producing increased intramolecular bonding and decreased intermolecular bonding, with a consequent decrease in thermal stability, especially for the Cu(II) complexes.

(iii) The order of thermal stability for the anhydrous compounds, taking the constant to be the central ion and the variable the ligand, according to Tables 1–3, is (Fig. 13):

$$Co(Ala)_2 < Co(leu)_2 = Co(val)_2$$

$$Ni(Ala)_2 < Ni(leu)_2 < Ni(val)_2$$

$$Cu(Ala)_2 < Cu(leu)_2 < Cu(val)_2$$
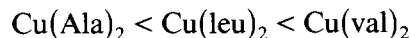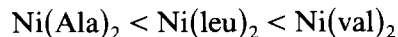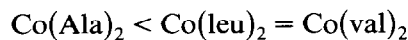
This order is, in agreement with previous ones [10,11], the reverse of the basicity of the ligands, consistent with the pK values reported in Table 5. The pK_1 values, considering the small experimental differences for the current data, are of the same order, while both the pK_2 and the pK_1 + pK_2 values decrease in the order:

Ala > leu > val
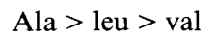
TABLE 5

Stability constants at 20–25°C and 0.1–0.15 mol l^{-1} KCl or NaClO$_4$ (from ref. 12)

Amino acid	(pK_2)	(pK_1)	(pK_1 + pK_2)
Glycine	9.62	–	–
Alanine	9.93	2.30	12.23
Leucine	9.76	2.33	12.09
Valine	9.65	2.24	11.89

TABLE 6

Thermodynamic data [13] for the formation of glycinate (Gly) and alaninate (Ala) (ligand/metal ratio 2:1) complexes in aqueous solutions

Metal ion	ΔH_{Gly}	ΔH_{Ala}	ΔS_{Gly}	ΔS_{Ala}	ΔG_{Gly}	ΔG_{Ala}
Co(II)	−6.37	−5.7	20.0	15	−11.71	−10.3
Ni(II)	−9.6	−7.2	19.5	24.2	−15.35	−14.4
Cu(II)	−13.18	−9.8	27.5	38.2	−21.37	−21.1

Comparing the values of the main thermodynamic parameters, collected in Table 6 and obtained in aqueous solutions [12] for the complexes of the glycine and alanine series, it can be seen that the enthalpic change associated with the formation of the complexes of the glycine series is always higher than those associated with the formation of the corresponding complexes of the alanine series (Fig. 14). Moreover, the free energy changes associated with the formation of the glycine complexes show the same behaviour when compared with the ΔG formation of the alanine complexes (Fig. 14), that according to the general trend of ΔH values of these complexes, becomes less negative with increasing complexity of the amino acid [13]. The methylic group present on the alanine accounts for the higher basicity of the aminic group of this amino acid, compared with the same group of the glycine (see the respective pK_2 values in Table 5). These results are in good agreement with both the results discussed in a previous paper [4] that show that the contribution to the total ΔH value of the carboxylic group is small but greater than one of the amino groups, and with the behaviour of the thermal stabilities of the two series concerning the Co(II) and Ni(II) complexes; on the contrary for the copper complexes the Jahn–Teller effect seems to play the main role (Fig. 13).
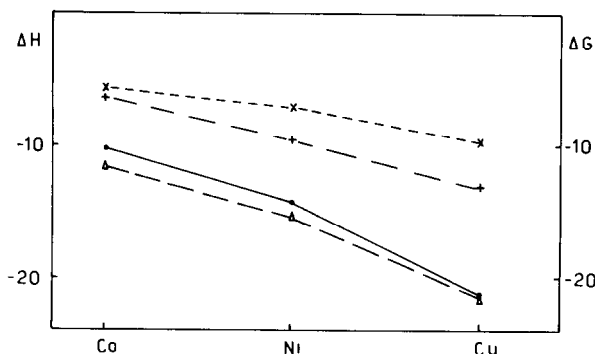

Fig. 14. Thermodynamic data (ΔH and ΔG) for the formation of Me(II)Gly$_2$ and Me(II)Ala$_2$ complexes in aqueous solutions. Me(II)Gly$_2$: ΔH (+), ΔG (●); Me(II)Ala$_2$: ΔH (×), ΔG (△).

Within the two series of glycinate and alaninate complexes, the behaviour of the thermodynamic parameters ΔH, ΔS and ΔG is quite analogous; particularly. As shown in Figs. 13 and 14, the orders obtained are:

$$\Delta H_{Cu(AA)_2} > \Delta H_{Ni(AA)_2} > \Delta H_{Co(AA)_2}$$

$$\Delta G_{Cu(AA)_2} > \Delta G_{Ni(AA)_2} > \Delta G_{Co(AA)_2}$$

$$\Delta S_{Cu(AA)_2} > \Delta S_{Ni(AA)_2} \geqslant \Delta S_{Co(AA)_2}$$

where AA = amino acid (glycine or alanine). These series were obtained using the absolute values of the thermodynamic data given in Table 6.

Considerations about these series [4] are confirmed; for instance, the Jahn–Teller effect is particularly evident for the Cu(II) complex, with a subsequent high change of ΔH and ΔS values.

Finally, it can be seen that, on the basis of previous considerations [4], i.e., considering a variation of about 2–3 entropic units for each amino group, a variation of 3–7.5 entropic units for each carboxylic group is obtained for the alanine complexes examined.

ACKNOWLEDGEMENT

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