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Energetics of lead(II), cadmium(II) and zinc(II) complexes with amino acids

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Abstract The molar heat capacity and the standard ($p^0 = 0.1$ MPa) molar enthalpies of formation of the crystalline of *bis*(glycinate)lead(II), Pb(gly)$_2$; *bis*(DL-alaninate)lead(II), Pb(DL-ala)$_2$; *bis*(DL-valinate)lead(II), Pb(DL-val)$_2$; *bis*(DL-valinate)cadmium(II), Cd(DL-val)$_2$ and *bis*(DL-valinate)zinc(II), Zn(DL-val)$_2$, were determined, at $T = 298.15$ K, by differential scanning calorimetry, and high precision solution-reaction calorimetry, respectively. The standard molar enthalpies of formation of the complexes in the gaseous state, the mean molar metal–ligand dissociation enthalpies, M(II)–amino acid, $\langle D_m \rangle$(M–L), were derived and compared with analogous copper(II)–ligand and nickel(II)–ligand.

M(II)–amino acid	$\Delta_f H_m^o$(cr)/kJ mol^{-1}
Bis(glycinate)lead(II), Pb(gly)$_2$	−998.9 ± 1.9
Bis(DL-alaninate)lead(II), Pb(ala)$_2$	−1048.7 ± 1.8
Bis(DL-valinate)lead(II), Pb(val)$_2$	−1166.3 ± 2.5
Bis(DL-valinate)cadmium(II), Cd(val)$_2$	−1243.7 ± 2.7
Bis(DL-valinate)zinc(II), Zn(val)$_2$	−1306.1 ± 2.3

Keywords Molar heat capacity · Standard molar enthalpy of formation · Amino acid complexes · Solution calorimetry · Mean metal–ligand molar dissociation enthalpies · Energetics · Differential scanning calorimetry

Introduction

In the past decades, significant progress has been achieved in understanding the chemistry of transition metal complexes with ligands coordinating through the oxygen and nitrogen atoms. Most of the model studies have been based in the studies of complexes with amino acids and Schiff base ligands [1, 2]. The coordination chemistry of typical systems with a filled "d electronic shell" could be described by metal complexes formed by Zn(II), Cd(II) or Pb(II) with the most common model ligands, and have been extensively explored as a model for the understanding of the metal binding and bioinorganic chemistry, in systems with a full occupied "d" orbital's configuration [3, 4]. Metal complexes with amino acids are the most obviously and simple type of metal complexes to be used as model compounds in the study of the interaction, or function, of metals with biological materials like proteins, enzymes or membranes, where metal–oxygen and metal–nitrogen bonds are formed [3, 5]. Metal amino acid complexes, including zinc(II), cadmium(II), lead(II), copper(II) and nickel(II) complexes, are a promising class of compounds under test as metal-based antibacterial and antifungal [6] as well as antiviral, do to their capability of interaction and binding with proteins [4, 7, 8].

Divalent metal complexes of amino acids are usually obtained as diaquocomplexes in which the water molecules are easy to remove by warming under reduced pressure. Amino acid complexes are formed typically as distorted tetrahedron coordination sphere [9] and their very low volatility is mainly the result of the cooperative hydrogen bonding [10]. The complexes explored in this study are schematically represented in Fig. 1.

This study on the thermochemistry of crystalline *bis*(glycinate)lead(II), Pb(gly)$_2$, *bis*(DL-alaninate)lead(II),

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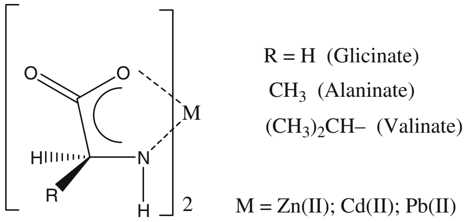

Fig. 1 Schematic formula for the metal–amino acid complexes. $Pb(gly)_2$ = *bis*(glycinate)lead(II); Pb(DL-ala)$_2$ = *bis*(DL-alaninate)lead (II); Pb(DL-val)$_2$ = *bis*(DL-valinate)lead(II); Cd(DL-val)$_2$ = *bis*(DL-valinate)cadmium(II); Zn(DL-val)$_2$ = *bis*(DL-valinate)zinc(II)

Pb(DL-ala)$_2$, *bis*(DL-valinate)lead(II), Pb(DL-val)$_2$, *bis*(DL-valinate)cadmium(II), Cd(DL-val)$_2$ and *bis*(DL-valinate) zinc(II), Zn(DL-val)$_2$ reports the determination of their standard molar enthalpies of formation, in the crystalline forms, at $T = 298.15$, determined by high precision solution-reaction calorimetry and the molar heat capacities, at constant pressure, studied between $T = 298$ K and $T = 500$ K, obtained by differential scanning calorimetry.

Based on the estimation of the enthalpies of sublimation of each metal complex, the standard molar enthalpies of formation of the complexes in the gaseous state were calculated and the mean molar dissociation enthalpies, M(II)–amino acid, $[\langle D_m \rangle(M{-}O) + \langle D_m \rangle(M{-}N)]$, were derived for lead(II), cadmium(II) and zinc(II).

The obtained results are compared with the previous results obtained for the Cu(II) [11] and Ni(II) [12] complexes with the same ligands.

Experimental

Syntheses

The amino acid complexes were prepared adapting the procedure previously described for the syntheses of divalent copper and nickel analogues [11, 12]. The formation and precipitation in the diaquo form complexes was done in water, using the amino acids in the full deprotonated forms. The water was removed by heating under reduced pressure, at $T = 380$ K, during 5 h.

Bis(glycinate)lead(II), $Pb(gly)_2$; *bis*(DL-alaninate)lead (II), $Pb(ala)_2$; *bis*(valinate)lead(II), $Pb(val)_2$: 9 mmol of the amino acid was dissolved in methanol (30 cm^3) and heated until reflux; 4 mmol of $PbNO_3$ in water (45 cm^3) was added dropwise, followed by the addition under stirring of 9 mmol of NaOH previously dissolved in water (15 cm^3). The mixture was kept in reflux during 30 min. After cooling down overnight, the crystals formed were filtered off and dried under reduced pressure, at $T = 380$ K, for 5 h. White crystals were obtained.

Bis(valinate)cadmium(II), $Cd(val)_2$ was prepared following the procedure used to the syntheses of the lead(II) complexes. 9 mmol of valine was dissolved in water (30 cm^3) and heated until reflux; 9 mmol of NaOH previously dissolved in water (15 cm^3) was added, under stirring, followed by dropwise addition of 4 mmol of $Cd(NO_3)_2{\cdot}4H_2O$ dissolved in water (45 cm^3). The mixture was kept in reflux during 30 min. After cooling down overnight, the crystals formed were filtered off and dried under reduced pressure, at $T = 380$ K, for 5 h. White crystals were obtained.

Bis(valinate)zinc(II), $Zn(val)_2$: 9 mmol of valine was dissolved in water (30 cm^3) and heated until reflux; 9 mmol of NaOH previously dissolved in water (15 cm^3) and 4 mmol of $ZnSO_4{\cdot}7H_2O$ previously dissolved in water (15 cm^3) were added, dropwise, under stirring. The mixture was cooled to the room temperature, and the white crystals formed were filtered off and washed with water. The crystalline powder was then dried under reduced pressure, at $T = 330$ K, for 6 h.

Elementary analysis and infrared spectra, confirmed that, all the studied complexes, were obtained in the anhydrous form. The powdered samples were kept in schlenk flasks.

The purities of the samples were checked by elemental analysis for the determination of the fraction of carbon, nitrogen and hydrogen, whereas the metal fraction was determined by EDTA titration analysis [13]; the mass fraction w of C, H, N and metal (M) were as follows: for Pb(GLY)$_2$, $C_4H_6O_4N_2Pb$, found $10^2w(C) = 13.3$, $10^2w(H) = 2.1$, $10^2w(N) = 7.6$, $10^2w(Pb) = 58.2$, calculated $10^2w(C) = 13.52$, $10^2w(H) = 2.27$, $10^2w(N) = 7.88$, $10^2w(Pb) = 58.31$; for Pb(DL-ala)$_2$, $C_6H_{10}O_4N_2Pb$, found $10^2w(C) = 18.9$, $10^2w(H) = 3.2$, $10^2w(N) = 7.1$, $10^2w(Pb) = 54.3$, calculated $10^2w(C) = 18.80$, $10^2w(H) = 3.16$, $10^2w(N) = 7.31$, $10^2w(Pb) = 54.05$; for Pb(DL-val)$_2$, $C_{10}H_{18}O_4N_2Pb$, found $10^2w(C) = 27.6$, $10^2w(H) = 4.5$, $10^2w(N) = 6.3$, $10^2w(Pb) = 47.1$, calculated $10^2w(C) = 27.33$, $10^2w(H) = 4.59$, $10^2w(N) = 6.37$, $10^2w(Pb) = 47.15$; for Cd(DL-val)$_2$, $C_{10}H_{18}O_4N_2Cd$, found $10^2w(C) = 33.9$, $10^2w(H) = 5.9$, $10^2w(N) = 8.4$, calculated $10^2w(C) = 34.85$, $10^2w(H) = 5.85$, $10^2w(N) = 8.13$; for Zn(DL-val)$_2$, $C_{10}H_{18}O_4N_2Zn$, found $10^2w(C) = 39.9$, $10^2w(H) = 6.9$, $10^2w(N) = 9.0$, $10^2w(Zn) = 21.5$, calculated $10^2w(C) = 40.35$, $10^2w(H) = 6.77$, $10^2w(N) = 9.41$, $10^2w(Zn) = 21.27$.

Solvents, solutions and metal(II) salts

The solution of acetic acid, 2.000 mol dm^{-3}, which corresponds to $CH_3COOH{\cdot}24.82H_2O$, was prepared by dilution with distiled water of a Merck Titrisol solution. The solution of nitric acid, 2.000 mol dm^{-3}, was prepared by dilution with distiled water of a Merck Titrisol solution.

Zinc(II) acetate dihydrate, (Merck p.a.), cadmium(II) acetate dihydrate, (Merck p.a.) and lead(II) acetate trihydrate, (Merck p.a.), were powdered from freshly open samples, and their compositions were confirmed by means of EDTA titration analysis [13] and found to be, respectively, $Zn(CH_3COO)_2{\cdot}2.00H_2O$, $Cd(CH_3COO)_2{\cdot}2.00H_2O$, $Pb(CH_3COO)_2{\cdot}3.00H_2O$. The powdered samples were kept in schlenk flasks until use.

Solution calorimetry

The determination of the standard molar enthalpies of formation of the amino acid complexes was done in an isoperibol high precision solution-reaction calorimeter with an all-glass Dewar type vessel, containing 120.0 cm^3 of solvent. The calorimeter is submersed in a 0.050 m^3 water bath, controlled at $T = (298.150 \pm 0.001)$ K by a Tronac PTC41 temperature controller. The samples were sealed in thin glass ampoules that were broken into the appropriate solvent by compression between two glass rings. The calorimetric temperatures were measured to $\pm(1 \times 10^{-4})$ K, at time intervals at 10 s, using a quartz thermometer (Hewlett-Packard HP2804A). The adiabatic temperature change, ΔT_{ad}, was calculated using the equal area method [14]. Data acquisition and the calculation of ΔT_{ad} were performed using the program Labtermo [15]. The calorimeter was calibrated electrically for each experiment. The accuracy and performance of the calorimeter were tested by measuring the molar enthalpy of solution of tris(hydroxymethyl)aminomethane (THAM, Merck p.a.) in HCl (aq, $c = 0.1000$ mol dm^{-3}), at $T = 298.15$ K: $\Delta_r H_m^o = -(29.710 \pm 0.055)$ kJ mol^{-1}, mean of seven experiments, which is in good agreement with the value reported by Irving and Wadsö: $\Delta_r H_m^o = -(29.723 \pm 0.021)$ kJ mol^{-1} [16, 17].

The molar masses were those recommended by the IUPAC Commission [18]. Each uncertainty interval quoted is twice the standard deviation of the mean of at least five independent determinations [19].

The reaccional schemes used for the determination of the standard molar enthalpies of formation of the crystalline of *bis*(glycinate)lead(II), *bis*(DL-alaninate)lead(II), *bis*(DL-valinate)lead(II), *bis*(DL-valinate)cadmium(II), and *bis*(DL-valinate)zinc(II), were based on the thermochemical reactions described by the following equation:

$$\begin{aligned}&(49.64 - n)H_2O(l) + 2\ HL(cr)\\&\quad + M(CH_3COO)_2{\cdot}nH_2O(cr)\\&\quad \rightarrow 2\ CH_3COOH \cdot 24.82H_2O(l) + ML_2(cr),\end{aligned} \qquad (1)$$

where HL(cr) = glycine, DL-alanine, DL-valine; $n = 2$ for Zn(II) and Cd(II) complexes and $n = 3$ for Pb(II). M = Zn(II); Cd(II); Pb(II).

A volume of 120.0 cm^3 of nitric acid solution (2.000 mol dm^{-3}) was used as calorimetric solvent for the reaction represented by Eq. 1. Ampoules containing the reactants, according to the previous equation, were added consecutively to the solvent as indicated in the reaction scheme, and the corresponding molar $\Delta_i H_m$ values were measured. To a second portion of the same solvent, ampoules containing the products were added, also in a successive way, and the corresponding $\Delta_i H_m$ values were measured. Rigorous control of the stoichiometry was maintained through each series of experiments, to ensure that the final solutions resulting from the dissolution and reaction of the reactants were of the same compositions as those from the dissolution and reaction of the products. This was verified using UV–Vis analysis of the resulting solutions and also by no detection of enthalpy change when breaking, in the calorimeter, ampoules of solutions resulting from the dissolution of all the reactants into solutions resulting from the dissolution of all the products.

Differential scanning calorimetry

The differential scanning calorimetric (d.s.c.) measurements were carried out in a heat power compensation d.s.c. type calorimeter, model DSC 141 from Setaram. The heat flow and temperature scales calibration were performed measuring the melting reference samples of In, Sn, Pb and Zn at different heating rates. The measurements of the temperature and enthalpies of fusion of benzoic acid (NIST SRC39i) and 4-methoxybenzoic acid (sample purified by repeated sublimation, under reduced pressure, until mass fraction was better than 99.9%) were used to check the accuracy of the heat flow and temperature scales [17, 20].

The heat capacity measurements at different temperatures were done using the step method procedure [21, 22] with temperature steps of 10 K, at a speed rating of 0.0166 K s^{-1}, followed by isothermal periods of 900 s. The system was calibrated using the same experimental procedure based in the heat capacity measurement of synthetic sapphire (α-Al_2O_3, NIST SRM 78). Baseline blank runs were also done in the same conditions and taken in account in the measurements of the samples and in the calibration experiments. The heat capacity of thianthrene (NIST SRM 1556) and benzoic acid (NIST SRM 39i) were used to evaluate the uncertainty of the heat capacity measurements. For the benzoic acid, an average of 0.5%, and maximum of 1% of the heat capacity deviation was observed, in the temperature interval between $T = 310$ and $T = 360$ K. For the thianthrene an average of 1.0%, and maximum of 5% of the heat capacity deviation was observed, in the temperature interval between $T = 310$ and $T = 410$ K. The deviations of the experimental results are accounted from the recommended C_p data in the considered temperature interval [17, 23].

Results

High precision solution-reaction calorimetry

Tables 1 lists the average values of at least five independent determinations of the molar enthalpies of solution and reaction for the metal(II) amino acid complexes.

The enthalpy of solution and reaction, $\Delta_r H_m^o$ involving the metal(II) amino acid complexes were derived as follows:

$$\Delta_r H_m^o\left[\mathrm{Pb(gly)_2}\right] = +46.44\Delta_1 H_m + 2\Delta_{2a} H_m + \Delta_{3a} H_m - 2\Delta_4 H_m - \Delta_{5a} H_m, \tag{2}$$

$$\Delta_r H_m^o\left[\mathrm{Pb(DL\text{-}ala)_2}\right] = +46.44\Delta_1 H_m + 2\Delta_{2b} H_m + \Delta_{3b} H_m - 2\Delta_4 H_m - \Delta_{5b} H_m, \tag{3}$$

$$\Delta_r H_m^o\left[\mathrm{Pb(DL\text{-}val)_2}\right] = +46.44\Delta_1 H_m + 2\Delta_{2c} H_m + \Delta_{3c'} H_m + 2\Delta_4 H_m + \Delta_{5c'} H_m, \tag{4}$$

$$\Delta_r H_m^o\left[\mathrm{Cd(DL\text{-}val)_2}\right] = +47.44\Delta_1 H_m + 2\Delta_{2c} H_m + \Delta_{3c''} H_m - 2\Delta_4 H_m - \Delta_{5c''} H_m, \tag{5}$$

$$\Delta_r H_m^o\left[\mathrm{Zn(DL\text{-}val)_2}\right] = +47.44\Delta_1 H_m + 2\Delta_{2c} H_m + \Delta_{3c'''} H_m - 2\Delta_4 H_m - \Delta_{5c'''} H_m. \tag{6}$$

The derived standard molar enthalpies of reaction, $\Delta_r H_m^o$, and the standard molar enthalpies of formation in the crystalline phase, $\Delta_f H_m^o(\mathrm{cr})$, are listed in Table 2. In order to derive the standard molar enthalpies of formation of the crystalline metal(II) complexes with the amino acids, the necessary auxiliary quantities, at $T = 298.15$ K, are resumed in Table 3.

Heat capacity measurements

The experimental results determined for the molar heat capacity of each metal(II) amino acid complex studied, which are derived from the average of five independent measuring runs, are plotted in Fig. 2. Based in the uncertainty of the results obtained for the test compounds and, in the standard deviation of the measurements with these compounds, the uncertainty associated with the measured heat capacities was derived to be ≈3% of the heat capacity values. Table 4 lists the numerical values calculated for the molar heat capacities of the metal(II) amino acid complexes, which were obtained from the interpolation of the experimental data, using a linear fitting with the temperature.

At the temperature of 330 K the complex, Pb(DL-ala)$_2$, shows a second-order phase transition with decrease of molar heat capacity of ≈20 J K^{-1} mol^{-1}. Identical phase transition, with similar magnitude of molar heat capacity drop, was found in the Pb(DL-val)$_2$ but at significantly higher temperature (420 K). The molar heat capacities in the crystalline phase of the zinc(II), cadmium(II) and lead(II) complexes with valine are very similar with each other, indicating a very small dependence of the molar heat capacity towards the metal identity. It is observed that the

Table 1 Molar enthalpies of solution and reaction, $\Delta_i H_m$, at $T = 298.15$ K, for the study of the *bis*(glycinate)lead(II), Pb(gly)$_2$, *bis*(DL-alaninate)lead(II), Pb(DL-ala)$_2$, *bis*(DL-valinate)lead(II), Pb(DL-val)$_2$, *bis*(DL-valinate)cadmium(II), Cd(DL-val)$_2$ and *bis*(DL-valinate)zinc(II), Zn(DL-val)$_2$, using HNO$_3$ 2.000 mol dm^{-3} (solvent A)

i	Reagent	Solvent	Solution formed	Number of exp.	$\Delta_i H_m$	$\Delta_i H_m$/kJ mol^{-1}
1	H_2O(l)	HNO_3·2.000 mol dm^{-3}	S_1	9	$\Delta_1 H_m$	−0.01382 ± 0.00070
2a	Glycine(cr)	S_1	S_{2a}	9	$\Delta_{2a} H_m$	5.76 ± 0.45
2b	Alanine(cr)	S_1	S_{2b}	6	$\Delta_{2b} H_m$	4.42 ± 0.16
2c	Valine(cr)	S_1	S_{2c}	6	$\Delta_{2c} H_m$	4.09 ± 0.31
3a	$Pb(CH_3COO)_2$·3.00H_2O(cr)	S_{2a}	S_{3a}	8	$\Delta_{3a} H_m$	−2.99 ± 0.52
3b	$Pb(CH_3COO)_2$·3.00H_2O(cr)	S_{2b}	S_{3b}	7	$\Delta_{3b} H_m$	−0.73 ± 0.21
3c′	$Pb(CH_3COO)_2$·3.00H_2O(cr)	S_{2c}	$S_{3c'}$	6	$\Delta_{3c'} H_m$	−0.486 ± 0.068
3c″	$Cd(CH_3COO)_2$·2.00H_2O(cr)	S_{2c}	$S_{3c''}$	5	$\Delta_{3c''} H_m$	−11.03 ± 0.31
3c‴	$Zn((CH_3COO)_2$·2.00H_2O(cr)	S_{2c}	$S_{3c'''}$	5	$\Delta_{3c'''} H_m$	−23.52 ± 0.38
4	CH_3COOH·24.82H_2O(l)	HNO_3·2.000 mol dm^{-3}	S_4	7	$\Delta_4 H_m$	−0.911 ± 0.054
5a	Pb(gly)$_2$(cr)	S_4	S_{5a}	6	$\Delta_{5a} H_m$	−72.05 ± 0.74
5b	Pb(DL-ala)$_2$(cr)	S_4	S_{5b}	6	$\Delta_{5b} H_m$	−90.41 ± 0.54
5c′	Pb(DL-val)$_2$(cr)	S_4	$S_{5c'}$	5	$\Delta_{5c'} H_m$	−82.56 ± 0.89
5c″	Cd(DL-val)$_2$(cr)	S_4	$S_{5c''}$	5	$\Delta_{5c''} H_m$	−72.0 ± 1.2
5c‴	Zn(DL-val)$_2$(cr)	S_4	$S_{5c'''}$	5	$\Delta_{5c'''} H_m$	−72.45 ± 0.95

Table 2 Derived standard ($p^0 = 0.1$ MPa) molar enthalpies of reaction, $\Delta_r H_m^o$, and standard molar enthalpies of formation, $\Delta_f H_m^o$(cr), for the crystalline complexes, at $T = 298.15$ K

Complex	Reaction	Calorimetric solvent	$\Delta_r H_m^o$/kJmol^{-1}	$\Delta_f H_m^o$(cr)/kJmol^{-1}
Pb(gly)$_2$(cr)	Equation 2	HNO_3·2.000 mol dm^{-3}	81.8 ± 1.3	−998.9 ± 1.9
Pb(DL-ala)$_2$(cr)	Equation 3	HNO_3·2.000 mol dm^{-3}	99.70 ± 0.67	−1048.7 ± 1.8
Pb(DL-val)$_2$(cr)	Equation 4	HNO_3·2.000 mol dm^{-3}	91.4 ± 1.1	−1166.3 ± 2.5
Cd(DL-val)$_2$(cr)	Equation 5	HNO_3·2.000 mol dm^{-3}	70.3 ± 1.4	−1243.7 ± 2.7
Zn(DL-val)$_2$(cr)	Equation 6	HNO_3·2.000 mol dm^{-3}	58.3 ± 1.2	−1306.0 ± 2.3

Table 3 Auxiliary data at $T = 298.15$ K

Compound	$\Delta_f H_m^o$/kJ mol^{-1}	Ref.
$Pb(CH_3COO)_2 \cdot 3.00H_2O$(cr)	−1851.5 ± 1.0	[24]
$Cd(CH_3COO)_2 \cdot 2.00H_2O$(cr)	−1622.0 ± 1.2	[25]
$Zn(CH_3COO)_2 \cdot 2.00H_2O$(cr)	−1672.3 ± 0.2	[24]
CH_3COOH in $24.82H_2O$(aq)	−485.156 ± 0.010	[24]
Glycine(cr)	−528.5 ± 0.5	[26]
Glycine(g)	−384.7 ± 2.1	[26, 27]
DL-Alanine(cr)	−562.35 ± 0.65	[28]
DL-Alanine(g)	−422.6 ± 1.2	[27]
DL-Valine(cr)	−617.0 ± 1.0	[29]
DL-Valine(g)	−445.3 ± 1.4	[27, 29]
H_2O(l)	−285.830 ± 0.042	[30]
H(g)	+217.965 ± 0.001	[24]
Pb(g)	+195.0 ± 0.2	[24]
Cd(g)	+112.01 ± 0.02	[24]
Zn(g)	+130.729 ± 0.002	[24]

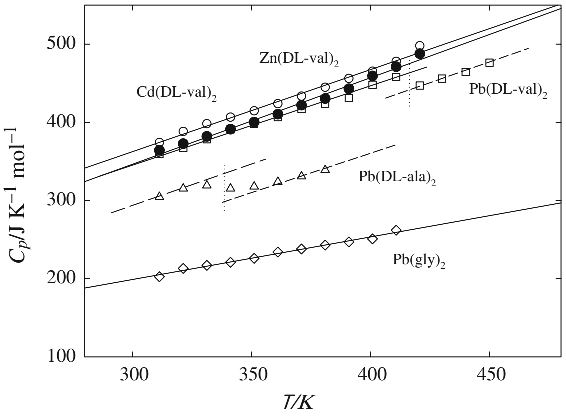

Fig. 2 Experimental molar heat capacity of the metal amino acid complexes in the crystalline state, C_p: Pb(DL-val)$_2$ *open square*, Pb(DL-ala)$_2$ *open triangle*, Pb(gly)$_2$ *open diamond*, Cd(DL-val)$_2$ *filled circle*, Zn(DL-val)$_2$ *open circle*

molar heat capacity of the amino acid complexes, at $T = 298.15$ K, is reasonably correlated as twice the molar heat capacity of the amino acids at the same temperature [31].

Table 4 Molar heat capacities, C_p, for the crystalline compounds calculated based on the fitting of the experimental results

T/K	C_p(cr)/J K^{-1} mol^{-1}				
	Pb(gly)$_2$	Pb(DL-ala)$_2$	Pb(DL-val)$_2$	Cd(DL-val)$_2$	Zn(DL-val)$_2$
298.15	198	296	337	344	360
300	199	297	339	346	362
310	205	305	350	357	373
320	210	312	360	368	383
330	215	$T_{trans.}$	371	380	394
340	221	309	381	391	404
350	226	316	392	402	415
360	232	324	402	413	425
370	237	331	413	424	436
380	243	338	423	435	446
390	248	345	434	446	457
400	254	352	444	457	467
410	259	359	455	468	478
420	265	366	$T_{trans.}$	479	488
430	270	373	456	490	499
440	276	380	466	501	509
450	281	387	475	512	520
460	287	394	485	523	530
470	292	401	495	535	541
480	297	408	504	546	551
490	303	415	514	557	562
500	308	422	524	568	572

$T_{trans.}$, 2nd order phase transition temperature

Discussion

The enthalpies of sublimation of the metal(II) amino acids could not be measured due to its very low volatility. The standard molar enthalpies of sublimation of Pb(gly)$_2$, Pb(DL-ala)$_2$, Pb(DL-val)$_2$, Cd(DL-val)$_2$ and Zn(DL-val)$_2$ were estimated, assuming the same enthalpies of sublimations as the analogues of copper(II) [11] and nickel(II) [12] complexes: $\Delta_{cr}^{g} H_m[\mathrm{Pb(gly)_2}] = (120 \pm 20)$ kJ mol^{-1}, $\Delta_{cr}^{g} H_m[\mathrm{Pb(DL\text{-}ala)_2}] = (110 \pm 20)$ kJ mol^{-1}, $\Delta_{cr}^{g} H_m[\mathrm{Pb(DL\text{-}val)_2}] = (170 \pm 20)$ kJ mol^{-1}, $\Delta_{cr}^{g} H_m[\mathrm{Cd(DL\text{-}val)_2}] = (170 \pm 20)$ kJ mol^{-1} and $\Delta_{cr}^{g} H_m[\mathrm{Zn(DL\text{-}val)_2}] = (170 \pm 20)$ kJ mol^{-1}.

With these estimations, the standard molar enthalpies of formation of the studied metal(II) amino acid complexes in the gaseous phase were derived and are registered in Table 5, together with the corresponding values in the crystalline phase.

A least square treatment (correlation coefficient 0.996) of the data for the enthalpies of formation of the crystalline complexes of lead(II) amino acids, $PbL_2(cr)$, with the crystalline amino acid ligands, HL(cr), gives

$$\Delta_f H_m^o(PbL_2, cr) = 19.60 + 1.92 \Delta_f H_m^o(HL, cr), \quad (7)$$

so, with a slope (1.92 ± 0.18), hence ≈2, within the experimental error, as expected for metal complexes [32]. Figure 3 shows the plot of $\Delta_f H_m^o(ML_2, cr)$ versus $\Delta_f H_m^o(HL, cr)$ for several metal(II) amino acid complexes, where the straight line represents Eq. 7 for the lead(II) amino acid complexes. As it has been previously observed for Cu(II) and Ni(II) amino acid complexes [11, 12], as well as for metal complexes of other ligands [32–34], this system shows a nice linear trend between the standard molar enthalpies of formation in the crystalline state, of the amino acids versus the complexes of the same metal.

Table 5 Derived standard ($p^0 = 0.1$ MP) standard molar enthalpies of formation for the crystalline $\Delta_f H_m^o(cr)$ and the gaseous $\Delta_f H_m^o(g)$ complexes, at $T = 298.15$ K

Complex	$\Delta_f H_m^o(cr)/kJ\ mol^{-1}$	$\Delta_f H_m^o(g)/kJ\ mol^{-1}$
$Pb(gly)_2(cr)$	−998.9 ± 1.9	−879 ± 20
Pb(DL-ala)$_2$(cr)	−1048.7 ± 1.8	−939 ± 20
Pb(DL-val)$_2$(cr)	−1166.3 ± 2.5	−996 ± 20
Cd(DL-val)$_2$(cr)	−1243.7 ± 2.7	−1074 ± 20
Zn(DL-val)$_2$(cr)	−1306.0 ± 2.3	−1136 ± 20

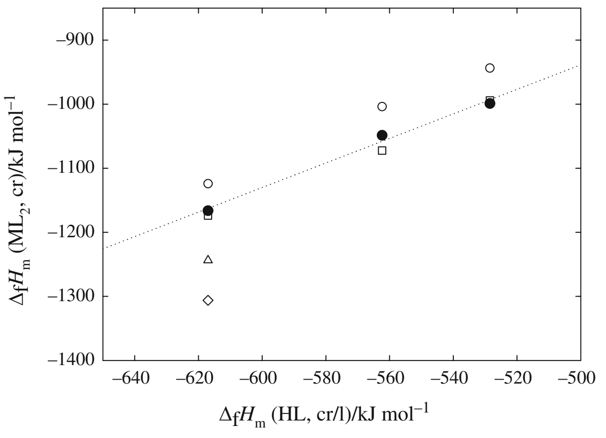

Fig. 3 Plot of the standard ($p^0 = 0.1$ MPa) molar enthalpies of formation of the metal–amino acid complexes in the crystalline state, $\Delta_f H_m^o(ML_2, cr)$, with the standard molar enthalpies of formation of the amino acid in the crystalline state, $\Delta_f H_m^o$(HL, cr/l), at $T = 298.15$ K. Ni(II) *open square*, Zn(II) *open diamond*, Cu(II) *open circle*, Pb(II) *filled circle*, Cd(II) *open triangle*

The mean molar metal to ligand bond dissociation enthalpy, $\langle D_m \rangle(M-L)$, may be defined as one-half of the enthalpy of the disruption reaction.

$$ML_2(g) \rightarrow M(g) + 2L^\bullet(g), \quad (8)$$

$$\begin{aligned}\langle D_m \rangle(M-L) = 1/2\{&\Delta_f H_m^o(M, g) + 2\Delta_f H_m^o(HL, g)\\ &- 2\Delta_f H_m^o(H, g) - \Delta_f H_m^o(ML_2, g)\\ &+ 2D_m(H-L,\ HL,\ g)\},\end{aligned} \quad (9)$$

where D_m(H–L, HL, g) is the molar bond dissociation enthalpy of the hydrogen of the amino acid, D_m(O–H, HL, g).

To the best of our knowledge, no experimental value of the dissociation enthalpy of the hydrogen of the amino acid hydroxyl group, D_m(O–H, g) is known. In order to overcome this problem, it may be more appropriate to calculate the values of $\{\langle D_m \rangle(M-L) - D_m(H-L, HL,\ g)\}$ which represent the differences between the mean molar M–L dissociation enthalpies in each metal(II) amino acid and the molar O–H bond dissociation enthalpy of the amino acid ligand.

This quantity is a measure of the enthalpy of transfer of the ligand from the hydrogen to the metal and, in the event that the ligand structure is unchanged, it provides a direct measure of the difference in binding enthalpies. Hence, from Eq. 9,

$$\begin{aligned}\{\langle D_m \rangle(M-L) - D_m(H-L, HL, g)\} = 1/2\{&\Delta_f H_m^o(M, g)\\ - \Delta_f H_m^o(ML_2, g)\} - 2\Delta_f H_m^o(H, g) + 2(HL, g).&\end{aligned} \quad (10)$$

As in the previous articles [11, 12], we also assume for all the amino acids the same value for the D_m(O–H, HL, g) (433 ± 20) kJ mol^{-1} in order to derive the mean molar metal to amino acid bond dissociation enthalpies $\langle D_m \rangle$ (M–L). With the literature values of the standard molar enthalpies of formation of the gaseous metals, registered in Table 3, the differences $\{\langle D_m \rangle(M-L) - D_m\ (H-L, HL,\ g)\}$ between the mean molar M–L dissociation enthalpies in each metal(II) amino acid, $\langle D_m \rangle(M-L)$, and the molar dissociation enthalpies of the amino acid hydrogen, D_m (H–L, HL, g) were calculated and are listed in Table 6, together with the values of the mean metal–ligand bond dissociation enthalpies, $\langle D_m \rangle(M-L) = \{\langle D_m \rangle(M-O) + \langle D_m \rangle(M-N)\}$.

From the obtained results it can be seen that for the M = Pb(II) the $\{\langle D_m \rangle(M-L) - D_m(H-L)\}$ is almost constant, within the experimental uncertainties associated with them, for all the amino acid ligands. The $\{\langle D_m \rangle(M-L) - D_m(H-L)\}$ obtained for the cadmium(II) with valine is identical to the same value observed for lead(II) but significantly lower that the $\{\langle D_m \rangle(M-L) - D_m(H-L)\}$ value for the zinc(II) complex.

Table 6 Derived differences of the standard ($p^0 = 0.1$ MPa) mean molar bond dissociation enthalpies of the metal complexes and of the ligands, $\{\langle D_m\rangle(\mathrm{M{-}L}) - \langle \mathrm{D}\rangle(\mathrm{H{-}L})\}$, and mean metal–ligand bond dissociation enthalpy, $\langle D_\mathrm{m}\rangle(\mathrm{M{-}L})$, at $T = 298.15$ K (values in kJ mol^{-1})

Complex	$\{\langle D_\mathrm{m}\rangle(\mathrm{M{-}L}) - \langle \mathrm{D}\rangle(\mathrm{H{-}L})\}$	$\{\langle D_\mathrm{m}\rangle(\mathrm{M{-}O}) + \langle D_\mathrm{m}\rangle(\mathrm{M{-}N})\}$[a]
Pb(gly)$_2$	−66 ± 10	367 ± 22
Pb(DL-ala)$_2$	−74 ± 10	359 ± 22
Pb(DL-val)$_2$	−68 ± 10	365 ± 22
Cd(DL-val)$_2$	−70 ± 10	362 ± 22
Zn(DL-val)$_2$	−29 ± 10	403 ± 22
Cu(DL-val)$_2$	−20 ± 10[b]	413 ± 22[b]
Ni(DL-val)$_2$	65.8 ± 10[c]	499 ± 22[c]

[a] Considering $\langle D\rangle(\mathrm{H{-}L}) = (433 \pm 20)$ kJ mol^{-1} [11]

[b] Reference [11]

[c] Reference [13]

The following qualitative order of the metal(II) to amino acid bond dissociation enthalpies $\langle D_\mathrm{m}\rangle$ (M–L) is seen from this work:

$$\langle D_\mathrm{m}\rangle(\mathrm{Ni{-}L}) > \langle D_\mathrm{m}\rangle(\mathrm{Cu{-}L}) > \langle D_\mathrm{m}\rangle(\mathrm{Zn{-}L}) > \langle D_\mathrm{m}\rangle(\mathrm{Cd{-}L}) \approx \langle D_\mathrm{m}\rangle(\mathrm{Pb{-}L})$$

The observed order in the dissociation enthalpies, follows the valence configuration of the series of Ni(II)—d^8, Cu(II)—d^9 and Zn(II), Cd(II), Pb(II)—d^{10} and shows that the binding enthalpy of zinc(II) to the amino acids is higher than for cadmium(II) and lead(II).

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