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Thermochemistry of some metallic amino acid complexes. Part 1. Copper(II) complexes

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Abstract

The standard ($p^{\ominus} = 0.1$ MPa) molar enthalpies of formation of the following crystalline copper(II) amino acid complexes were determined at 298.15 K by solution–reaction calorimetry: $\Delta_f H_m^{\ominus}[\mathrm{Cu(gly)_2, cr}] = -943.7 \pm 1.3$ kJ mol^{-1}; $\Delta_f H_m^{\ominus}[\mathrm{Cu(ala)_2, cr}] = -1003.7 \pm 1.5$ kJ mol^{-1}; $\Delta_f H_m^{\ominus}[\mathrm{Cu(val)_2, cr}] = -1124.1 \pm 2.2$ kJ mol^{-1}; $\Delta_f H_m^{\ominus}[\mathrm{Cu(leu)_2, cr}] = -1177.8 \pm 2.1$ kJ mol^{-1}; $\Delta_f H_m^{\ominus}[\mathrm{Cu(isol)_2, cr}] = -1156.3 \pm 1.8$ kJ mol^{-1}; $\Delta_f H_m^{\ominus}[\mathrm{Cu(Phgly)_2, cr}] = -772.3 \pm 1.9$ kJ mol^{-1}; $\Delta_f H_m^{\ominus}[\mathrm{Cu(Phala)_2, cr}] = -831.8 \pm 2.6$ kJ mol^{-1}.

The results suggest a linear correlation between the standard molar enthalpies of formation of the crystalline copper(II) amino acid complexes and those of the corresponding crystalline amino acids. Estimations of the standard molar enthalpies of sublimation of the copper(II) amino acid complexes are presented. The total binding energy between the copper(II) and the amino acid ligand is derived and compared with the corresponding parameter for copper(II) acetylacetonate.

INTRODUCTION

Amino acids are bidentate ligands which chelate to the majority of transition metals through the amino nitrogen atom and the carboxyl group, yielding very stable complexes. The biological importance of these complexes is well known, and can be illustrated by some of the applications of the compounds: some complexes have been tested for antitumour activity [1], and others show antiviral activity against certain viruses [2]. It has been shown during the last twenty years that amino acids generally increase the diffusibility of metal complexes, and thus their biological activity inside the cell [3], and also that some of the complexes are readily absorbed through the skin [4]. Although there is a considerable amount of thermodynamic data available for the formation, mainly in aqueous solution, of transition

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metal complexes with several different amino acids [5], as well as for some peptide complexes, very little information is available on the thermochemistry of their crystalline compounds. Numerous spectroscopic investigations [6] and X-ray crystal structures [7] for the copper(II) amino acid complexes have been reported recently.

In this paper we present the determination of the standard molar enthalpies of formation, at 298.15 K, of the crystalline copper(II) complexes with seven amino acid ligands.

EXPERIMENTAL

Materials

Glycine (Hgly), DL-alanine (Hala) and DL-valine (Hval), chromatographic grade (BDH Chemicals, Ltd.) were used without further purification. L-(α)-Leucine (Hleu), L-(α)-isoleucine (Hisoleu), L-(α)-phenylglycine (HPhgly) and L-(α)-phenylalanine (HPhala) (Janssen Chimica), better than 99% pure, were used without further purification. Purity was assessed by elemental analyses (Table 1).

The copper(II) complexes with glycine, alanine and valine were prepared by a method similar to that described by Greenstein and Winitz [8], recrystallized from a mixture of ethanol–water, dried in an oven at about 100°C and characterized by microanalyses and IR spectroscopy. The decomposition temperatures of the three copper(II) amino acid complexes

TABLE 1

Mass percentage analyses

	Found (%)				Expected (%)			
	C	H	N	Cu	C	H	N	Cu
Hgly(cr)	32.4	6.7	18.3		32.00	6.71	18.66	
Hala(cr)	40.7	8.0	15.7		40.44	7.92	15.72	
Hval(cr)	51.2	9.5	12.0		51.26	9.46	11.96	
Hleu(cr)	54.4	10.1	10.6		54.94	9.99	10.68	
Hisoleu(cr)	54.7	10.1	10.7		54.94	9.99	10.68	
HPhgly(cr)	62.7	6.0	9.2		63.57	6.00	9.27	
HPhala(cr)	65.2	6.8	8.5		65.44	6.71	8.50	
$Cu(gly)_2(cr)$	22.6	3.7	13.1	30.3	22.69	3.81	13.24	30.02
$Cu(ala)_2(cr)$	29.9	5.0	11.7	26.2	30.06	5.04	11.69	26.51
$Cu(val)_2(cr)$	40.4	7.0	9.6	21.2	40.60	6.83	9.47	21.48
$Cu(leu)_2(cr)$	45.0	7.6	8.6	19.0	44.49	7.48	8.65	19.54
$Cu(isoleu)_2(cr)$	45.0	7.5	8.6	19.2	44.49	7.48	8.65	19.54
$Cu(Phgly)_2(cr)$	52.9	4.5	7.5	17.9	52.81	4.43	7.70	17.46
$Cu(Phala)_2(cr)$	54.2	5.0	7.0	16.1	55.17	5.14	7.15	16.22

were 239, 240–242 and 260°C, for the glycinate, alaninate and valinate respectively. The complexes $Cu(leu)_2$ and $Cu(isoleu)_2$ were prepared by mixing aqueous solutions of the amino acids with an aqueous solution of copper(II) chloride and adding dropwise a 0.5 mol dm^{-3} solution of sodium hydroxide until precipitation started. The precipitate was filtered off under vacuum and washed with water. The complexes were dried under vacuum at 120–140°C for at least 5 h, stored in Schlenk tubes under dry nitrogen (because they are hygroscopic) and characterized by IR spectra and microanalyses. $Cu(Phgly)_2$ and $Cu(Phala)_2$ were each prepared by dissolving the amino acid in an aqueous solution of sodium hydroxide, followed by the dropwise addition of 4 mol dm^{-3} hydrochloric acid until pH 9 was reached. The resulting solution was heated to 60°C, and slowly mixed with an aqueous solution of copper(II) chloride. The blue precipitate was filtered off, dried under vacuum at 120–140°C for at least 8 h, stored in Schlenk tubes under dry nitrogen and characterized by IR spectra and microanalyses. The mass percentage analyses of the complexes are given in Table 1.

Copper(II) sulphate pentahydrate (BDH, AnalaR) was dried over silica gel, and its composition was confirmed by analysis of the metal as being $CuSO_4 \cdot 5.00H_2O$.

A 1 mol dm^{-3} sulphuric acid solution was made from Merck concentrated volumetric solution; the concentration was checked by titration against $Na_2B_4O_7 \cdot 10H_2O$ and found to be (from a series of six titrations) 1.000 ± 0.004 mol dm^{-3}, which corresponds [9] to the composition $H_2SO_4 \cdot 53.54H_2O$.

Concentrated HCl (Merck, p.a.) was diluted with distilled water; the concentration was determined by titration against $Na_2B_4O_7 \cdot 10H_2O$ and found to be (from a series of six titrations) 1.967 ± 0.001 mol dm^{-3}, which corresponds [9] to the composition $HCl \cdot 27.11H_2O$.

Carbon, hydrogen and nitrogen microanalyses were carried out at the Microanalytical Services of either the University of Surrey or the University of Manchester, UK.

Copper(II) analyses, both for the amino acid complexes and for the copper(II) sulphate, were performed by a volumetric method [10].

Solution–reaction calorimeter

The isoperibol LKB 8700 solution and reaction precision calorimeter was used for the study of the copper(II) complexes of glycine, alanine and valine. Tests on the accuracy of its performance have been reported recently [11].

The remaining copper(II) amino acid complexes were studied in a reaction–solution calorimeter with an all-glass reaction vessel [12,13] containing 120.0 cm^3 of solvent. The samples were sealed in thin glass ampoules, which were broken under the solvent at the appropriate time by compression between two glass rings; the energy associated with the breaking of an ampoule was less than 0.05 J. The calorimeter was equipped with a twin-bladed glass stirrer rotated at 4.5 Hz. Calorimeter temperatures were measured to 10^{-4} K, at intervals of 20 s, with a quartz thermometer (Hewlett–Packard HP 2804A) and recorded by a thermal printer (HP 5150A). The temperature profile for each experiment was divided into a fore-period, about 15 min, a main period, about 10 min, and an after-period of about 15 min. The adiabatic temperature change was calculated using the equal area method [14]. The calorimeter was calibrated electrically for each experiment. An electrical heater (49.95 Ω) was placed in an oil-filled glass tube and the current for the heater was provided from a stabilized power supply. The potential difference across the heater was measured using a potentiometer (Cropico P107) and the current was determined from the change in potential across a standard 10 Ω resistor. The period for the calibration current was controlled to a resolution of 10^{-2} s by a quartz timer (CFUP). The calorimeter top plate was sealed to the Dewar vessel with an O-ring. The calorimeter was submerged in a water thermostat maintained at 298.150 ± 0.001 K using a Tronac PTC-41 controller. The calibration and experimental procedure were tested by measuring the molar enthalpy of a solution of tris(hydroxymethyl)aminomethane (THAM, Aristar, BDH) in 0.100 mol dm^{-3} HCl(aq) at 298.15 K. The value obtained, $\Delta_{\text{sol}}H_{\text{m}}^{\ominus}(\text{cr}) = -29.753 \pm 0.034$ kJ mol^{-1} (mean of five experiments), was in agreement with the literature value of Kilday and Prosen: -29.770 ± 0.032 kJ mol^{-1} [15].

The relative atomic masses used are as recommended by IUPAC Commission [16]. All uncertainty intervals given are twice the standard deviation of the mean.

RESULTS

Preliminary tests of solubility showed that rapid hydrolysis occurred with aqueous solutions of strong acids; 1 mol dm^{-3} H_2SO_4 was used for the copper(II) complexes of glycine, alanine and valine and a 1.967 mol dm^{-3} solution of HCl was used for the other four complexes.

The thermochemical reactions for determining the enthalpies of formation of the copper(II) amino acid complexes were

$$48.54H_2O(l) + CuSO_4 \cdot 5.00H_2O(cr) + 2HL(cr)$$
$$= H_2SO_4 \cdot 53.54H_2O(l) + CuL_2(cr) \qquad (1)$$

The standard enthalpies of these reactions were determined by measuring, or calculating from reference data, the enthalpy of solution of each reactant and product successively in the calorimetric solvent. In all cases,

TABLE 2

Molar enthalpies of solution and reaction at 298.15 K for the $Cu(gly)_2$ and $Cu(ala)_2$ complexes

i	Reactant	Solvent	Solution	Number of expts.	$\Delta_i H_m$ (kJ mol^{-1})
1	$H_2O(l)$	Initial [a]	A_1	Calc.	-0.03 ± 0.01
2	$CuSO_4 \cdot 5.00H_2O(cr)$	A_1	A_2	6	$+22.38 \pm 0.33$
3a	Hgly(cr)	A_2	A_{3a}	6	$+6.90 \pm 0.08$
3b	Hala(cr)	A_2	A_{3b}	5	$+5.44 \pm 0.08$
4	$H_2SO_4 \cdot 53.54H_2O(l)$	Initial [a]	B_1	Calc.	0.00
5a	$Cu(gly)_2(cr)$	B_1	A_{3a}	6	-42.26 ± 0.42
5b	$Cu(ala)_2(cr)$	B_1	A_{3b}	5	-52.84 ± 0.08

[a] Initial, 100.0 cm^3 $H_2SO_4 \cdot 53.54H_2O(l)$.

ampoules containing the reactants were added consecutively, in the order given in the equation, to the solvent, and the corresponding $\Delta_i H_m$ values were measured (or calculated). To a second portion of the same solvent were also added consecutively ampoules containing the products, in the order given in the equation, and the corresponding $\Delta_i H_m$ values were measured (or calculated). Special attention was paid to the control of stoichiometry ratios of reactants and products, in each series of experiments, to ensure that the final solutions resulting from the dissolution and reaction of the reactants were of the same composition as those from the dissolution and reaction of the products. As a check on the validity of this, ampoules of the final solution of all the reactants were broken into the final solution of all the products in the calorimeter; no enthalpy change was detected.

Table 2 lists the molar enthalpies of solution and reaction for the study of copper(II) complexes of glycine and alanine; both systems were studied in the LKB 8700 calorimeter, using as solvent 100.0 cm^3 of a 1 mol dm^{-3} solution of H_2SO_4. Table 3 lists the results obtained in the study of the copper(II) complex of valine, which was also done in the LKB 8700

TABLE 3

Molar enthalpies of solution and reaction at 298.15 K for the $Cu(val)_2$ complex

i	Reactant	Solvent	Solution	Number of expts.	$\Delta_i H_m$ (kJ mol^{-1})
1′	$H_2O(l)$	Initial [a]	A'_1	Calc.	-0.03 ± 0.01
2′	$CuSO_4 \cdot 5.00H_2O(cr)$	A'_1	A'_2	5	$+20.84 \pm 0.25$
3′c	Hval(cr)	A'_2	A'_{3c}	6	$+4.90 \pm 0.13$
4′	$H_2SO_4 \cdot 53.54H_2O(l)$	Initial [a]	B'_1	Calc.	0.00
5′c	$Cu(val)_2(cr)$	B'_1	A'_{3c}	6	-44.35 ± 0.42

[a] Initial, 80.0 cm^3 $H_2SO_4 \cdot 53.54H_2O(l)$.

TABLE 4

Molar enthalpies of solution and reaction at 298.15 K for the $Cu(leu)_2$, $Cu(isoleu)_2$, $Cu(Phgly)_2$ and $Cu(Phala)_2$ complexes

i	Reactant	Solvent	Solution	Number of expts.	$\Delta_i H_m$ (kJ mol^{-1})
1″	$H_2O(l)$	Initial [a]	A''_1	5	-0.086 ± 0.003
2″	$CuSO_4 \cdot 5.00H_2O(cr)$	A''_1	A''_2	5	$+37.50 \pm 0.41$
3″d	Hleu(cr)	A''_2	A''_{3d}	5	$+0.383 \pm 0.045$
3″e	Hisoleu(cr)	A''_2	A''_{3e}	5	$+1.238 \pm 0.064$
3″f	HPhgly(cr)	A''_2	A''_{3f}	5	$+8.46 \pm 0.21$
3″g	HPhala(cr)	A''_2	A''_{3g}	5	$+4.70 \pm 0.15$
4″	$H_2SO_4 \cdot 53.54H_2O(l)$	Initial [a]	B''_1	7	0.000 ± 0.002
5″d	$Cu(leu)_2(cr)$	B''_1	A''_{3d}	5	-26.60 ± 0.38
5″e	$Cu(isoleu)_2(cr)$	B''_1	A''_{3e}	5	-47.69 ± 0.18
5″f	$Cu(Phgly)_2(cr)$	B''_1	A''_{3f}	6	-32.2 ± 1.1
5″g	$Cu(Phala)_2(cr)$	B''_1	A''_{3g}	5	-22.92 ± 0.82

[a] Initial, 120.0 cm^3 $HCl \cdot 27.11H_2O(l)$.

calorimeter but using only 80.0 cm^3 of a solution of 1 mol dm^{-3} H_2SO_4 as solvent. Finally, Table 4 lists the molar enthalpies of solution and reaction for the study of the copper(II) complexes of leucine, isoleucine, phenylglycine and phenylalanine, which was performed in the glass Dewar calorimeter using as initial solvent 120.0 cm^3 of a 1.967 mol dm^{-3} solution of HCl.

The standard molar enthalpies of the thermochemical reactions were calculated by means of eqn. (2) and are listed in Table 5.

$$\Delta_r H_m^{\ominus}[CuL_2] = 48.54\Delta_1 H_m + \Delta_2 H_m + 2\Delta_3 H_m - \Delta_4 H_m - \Delta_5 H_m \qquad (2)$$

To derive the standard molar enthalpies of formation of the copper(II) complexes in the crystalline state, it is necessary to know the standard

TABLE 5

Standard ($p^{\ominus} = 0.1$ MPa) molar enthalpies of reaction and formation at 298.15 K for the copper(II) amino acid complexes

CuL_2	$\Delta_r H_m^{\ominus}$ (kJ mol^{-1})	$\Delta_f H_m^{\ominus}(CuL_2, cr)$ (kJ mol^{-1})
$Cu(gly)_2$	76.98 ± 0.74	-943.7 ± 1.3
$Cu(ala)_2$	84.64 ± 0.61	-1003.7 ± 1.5
$Cu(val)_2$	73.53 ± 0.73	-1124.1 ± 2.2
$Cu(leu)_2$	60.69 ± 0.58	-1177.8 ± 2.1
$Cu(isoleu)_2$	83.49 ± 0.49	-1156.3 ± 1.8
$Cu(Phgly)_2$	82.4 ± 1.3	-772.3 ± 1.8
$Cu(Phala)_2$	65.65 ± 0.97	-831.8 ± 2.6

TABLE 6

Standard ($p^{\ominus} = 0.1$ MPa) molar enthalpies of formation of crystalline amino acids at 298.15 K

Compound	$\Delta_f H_m^{\ominus}$ (kJ mol^{-1})	Ref.	Remark
H_2O(l)	−285.830 ± 0.042	17	
H_2SO_4 in $53.54H_2O$(l)	−886.85 ± 0.30	18	
$CuSO_4 \cdot 5.00H_2O$(cr)	−2279.65 ± 0.21	18	
Glycine(cr)	−528.53	19	
	−537.23	20	
	−528.61 ± 0.34	22	
	−528.5 ± 0.5	23	Selected value
L-Alanine(cr)	−561.23	24	
	−562.75	20	
	−561.08 ± 0.71	25	
	−556.18 ± 11.08	26	
	−559.48 ± 0.64	22	
D-Alanine(cr)	−561.12	19, 24	
	−560.06 ± 0.76	25	
DL-Alanine(cr)	−563.57	19, 24	
	−562.35 ± 0.65	25	Selected value
L-Valine(cr)	−617.89 ± 0.63	27	
DL-Valine(cr)	−617.0 ± 1.0	28	Selected value
L-(α)-Leucine(cr)	−637.4 ± 1.0	19	Selected value
L-(α)-Isoleucine(cr)	−638.06 ± 0.84	21	Selected value
L-(Phenylglycine(cr)	−445.53 ± 0.63	29	Selected value
L-Phenylalanine(cr)	−466.9 ± 1.2	21	Selected value

molar enthalpies of formation of the crystalline amino acids. There are several values for these in the literature, which are listed in Table 6. In view of this, it was necessary to select one of the values for each amino acid, and this is also indicated in Table 6. Table 6 also contains other auxiliary data which, together with the enthalpies of the thermochemical reactions, were necessary to derive the standard molar enthalpies of formation of the crystalline copper(II) complexes with the amino acids; the results are summarized in Table 5.

DISCUSSION

The standard molar enthalpies of formation of some crystalline copper(II) complexes with some amino acids have been previously reported. Jones and co-workers [30] reported $\Delta_f H_m^{\ominus}[\mathrm{Cu(gly)_2, cr}] = -777.3$ kJ mol^{-1}, $\Delta_f H_m^{\ominus}[\mathrm{Cu(ala)_2, cr}] = -1066.7$ kJ mol^{-1} and $\Delta_f H_m^{\ominus}[\mathrm{Cu(val)_2, cr}] = -1162.7$ kJ mol^{-1}, derived from combustion calorimetry of these compounds. The experimental work involved in the combustion study by Jones et al. [30] has been shown to be of very low accuracy [31], probably because insufficient attention was paid to controlling the combustion with auxiliary aids and (mainly) to defining the completeness of the combustion and the nature of the combustion products. These deficiencies can account for the differences between the present results and those of Jones et al. [30]. A value of $\Delta_f H_m^\ominus[\mathrm{Cu(gly)_2, cr}] = -940.8 \pm 1.7$ kJ mol^{-1} has been reported recently [32], agreeing with the value reported here, but again in disagreement with the NBS tables [18], which give for the α form -938.5 kJ mol^{-1} and for the β form -932.6 kJ mol^{-1}. The sources of the NBS values are not given and no conclusion can be drawn about these discrepancies. Bernard et al. [33] measured the enthalpies of solution of some copper(II) amino acid complexes at 298.15 K; experimental details are not given in their paper, nor are the values of the enthalpies of formation used in the calculations, except that their source of these ancillary data is the NBS Circular 500 [34]. Their derived standard molar enthalpies of formation, $\Delta_f H_m^\ominus(\mathrm{cr})$ kJ mol^{-1}, are as follows: $\mathrm{Cu(ala)_2} = -1016.6 \pm 3.4$; $\mathrm{Cu(val)_2} = -1098.1 \pm 3.3$;$\mathrm{Cu(isoleu)_2} = -1162.9 \pm 3.5$. These cannot be compared directly with the values calculated in the present paper in view of the lack of information, as stated above.

For a complex of general form ML_n, the mean metal–ligand bond dissociation enthalpy is derived from the enthalpy of disruption $\Delta_r H^\ominus$ for

$$\mathrm{ML}_n(\mathrm{g}) = \mathrm{M(g)} + n\mathrm{L(g)} \tag{3}$$

$$\langle D\rangle(\mathrm{M{-}L}) = (1/n)[\Delta_f H_m^\ominus(\mathrm{M, g}) + n\Delta_f H_m^\ominus(\mathrm{L, g}) - \Delta_f H_m^\ominus(\mathrm{ML}_n, \mathrm{g})] \tag{4}$$

The ligand–hydrogen dissociation enthalpy is the enthalpy of the reaction

$$\mathrm{HL(g)} = \mathrm{H(g)} + \mathrm{L(g)} \tag{5}$$

so

$$D(\mathrm{H{-}L}) = \Delta_f H_m^\ominus(\mathrm{H, g}) + \Delta_f H_m^\ominus(\mathrm{L, g}) - \Delta_f H_m^\ominus(\mathrm{HL, g}) \tag{6}$$

Hence, from eqns. (4) and (6)

$$\begin{aligned}\langle D\rangle(\mathrm{M{-}L}) - D(\mathrm{H{-}L}) &= (1/n)[\Delta_f H_m^\ominus(\mathrm{M, g}) - \Delta_f H_m^\ominus(\mathrm{ML}_n, \mathrm{g})] \\ &\quad - \Delta_f H_m^\ominus(\mathrm{H, g}) + \Delta_f H_m^\ominus(\mathrm{HL, g})\end{aligned} \tag{7}$$

It has been discovered experimentally that for a series of complexes of a given metal with the same type of ligand, $\langle D\rangle(\mathrm{M{-}L}) - D(\mathrm{H{-}L})$ is constant. This has been demonstrated for Cu(II) β-diketonates [35,36] and for the β-diketonate complexes of Fe(III) [37], Mn(III) [38], Co(III) [11,39], Cr(III) [40], Al(III) [41–44], Be(II) [42,45], Mn(II) [46–48], Co(II) [46,48,49] and Ni(II) [48,50,51]. The constancy of $\langle D\rangle(\mathrm{M{-}L}) - D(\mathrm{H{-}L})$ implies that

$\Delta_f H_m^\ominus(\mathrm{ML}_n, \mathrm{g})$ should be linear with respect to $\Delta_f H_m^\ominus(\mathrm{HL}, \mathrm{g})$, with slope n, i.e.

$$\Delta_f H_m^\ominus(\mathrm{ML}_n, \mathrm{g}) = n\Delta_f H_m^\ominus(\mathrm{HL}, \mathrm{g}) + \{\Delta_f H_m^\ominus(\mathrm{M}, \mathrm{g}) - n\Delta_f H_m^\ominus(\mathrm{H}, \mathrm{g}) - n[\langle D\rangle(\mathrm{M{-}L}) - D(\mathrm{H{-}L})]\} \tag{8}$$

As

$$\Delta_f H_m^\ominus(\mathrm{g}) = \Delta_f H_m^\ominus(\mathrm{cr}) + \Delta_{\mathrm{cr}}^{\mathrm{g}} H_m^\ominus \tag{9}$$

then

$$\begin{aligned}\Delta_f H_m^\ominus(\mathrm{ML}_n, \mathrm{cr}) = {} & n\Delta_f H_m^\ominus(\mathrm{HL}, \mathrm{cr}) + [\Delta_f H_m^\ominus(\mathrm{M}, \mathrm{g}) - n\Delta_f H_m^\ominus(\mathrm{H}, \mathrm{g})] \\ & - n[\langle D\rangle(\mathrm{M{-}L}) - D(\mathrm{H{-}L})] \\ & - [\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m^\ominus(\mathrm{ML}_n) - n\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m^\ominus(\mathrm{HL})]\end{aligned} \tag{10}$$

The term $[\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m^\ominus(\mathrm{ML}_n) - n\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m^\ominus(\mathrm{HL})]$, the difference between the enthalpies of sublimation of the complex and the total number of its ligands, is expected to be small and if it is regarded as constant then $\Delta_f H_m^\ominus(\mathrm{ML}_n, \mathrm{cr})$ should be linear with respect to $\Delta_f H_m^\ominus(\mathrm{HL}, \mathrm{cr})$, with slope n.

In view of the assumptions made and the experimental errors in the measurements, it is expected that the slope of $\Delta_f H_m^\ominus(\mathrm{ML}_n, \mathrm{cr})$ versus $\Delta_f H_m^\ominus(\mathrm{HL}, \mathrm{cr})$ will not be exactly n, although it should be close to n. For those terms related to the structure of the molecule, n is exactly defined, but for those depending on experimental measurements, n must be determined as n', hence eqn.(10) should be written as

$$\begin{aligned}\Delta_f H_m^\ominus(\mathrm{ML}_n, \mathrm{cr}) = {} & n'\Delta_f H_m^\ominus(\mathrm{HL}, \mathrm{cr}) + [\Delta_f H_m^\ominus(\mathrm{M}, \mathrm{g}) - n\Delta_f H_m^\ominus(\mathrm{H}, \mathrm{g})] \\ & - n[\langle D\rangle(\mathrm{M{-}L}) - D(\mathrm{H{-}L})] \\ & - [\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m^\ominus(\mathrm{ML}_n) - n'\Delta_{\mathrm{cr}}^{\mathrm{g}} H_m^\ominus(\mathrm{HL})]\end{aligned} \tag{11}$$

A least-squares treatment (correlation coefficient 0.997) of the data for the crystalline complexes of copper(II) amino acids $\mathrm{ML_2(cr)}$ and for the crystalline amino acid ligands HL(cr) gives

$$\Delta_f H_m^\ominus(\mathrm{CuL}_2, \mathrm{cr}) = 119.60 + 2.014\Delta_f H_m^\ominus(\mathrm{HL}, \mathrm{cr}) \tag{12}$$

hence $n' = 2$ to within the experimental error; comparison of the experimental and calculated values is given in Table 7. The average deviation between the experimental and the calculated values is 7.2 kJ mol^{-1}, which shows remarkably good concordance for such a simple relationship applied to the crystalline state.

Figure 1 shows the plot of $\Delta_f H_m^\ominus(\mathrm{CuL}_2, \mathrm{cr})$ versus $\Delta_f H_m^\ominus(\mathrm{HL}, \mathrm{cr})$, where the straight line represents eqn. (12): the agreement with the standard molar enthalpies of formation determined in this paper is good. Figure 1 shows also the values determined by Bernard et al. [33] for the same complexes studied in this paper, as well as their values for the standard molar enthalpies of formation of the crystalline copper(II) com-

TABLE 7

Experimental and calculated thermochemical parameters for crystalline copper(II) amino acid complexes at 298.15 K

HL	$\Delta_f H_m^{\ominus}$[HL, cr] (kJ mol^{-1})	CuL$_2$	$\Delta_f H_m^{\ominus}$[CuL$_2$, cr] (kJ mol^{-1})		Δ(expt. – calc.) (kJ mol^{-1})
			Expt.	Calc.	
Glycine	–528.5 ±0.5	Cu(gly)$_2$	–943.7±1.3	–944.8	+1.1
Alanine	–562.35±0.65	Cu(ala)$_2$	–1003.7±1.5	–1013.0	+9.3
Valine	–617.0 ±1.0	Cu(val)$_2$	–1124.1±2.2	–1123.0	–1.1
Leucine	–637.4 ±1.0	Cu(leu)$_2$	–1177.8±2.1	–1164.1	–13.7
Isoleucine	–638.06±0.84	Cu(isoleu)$_2$	–1156.3±1.8	–1165.5	+9.2
Phenylglycine	–445.53±0.63	Cu(Phgly)$_2$	–772.3±1.9	–777.7	+5.4
Phenylalanine	–466.9 ±1.2	Cu(Phala)$_2$	–831.8±2.6	–820.7	–11.1

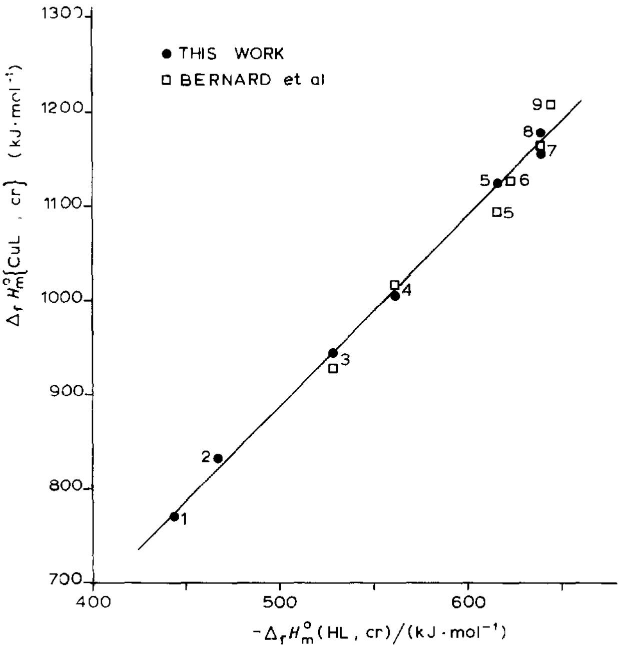

Fig. 1. Variation of the standard molar enthalpies of formation of the crystalline copper(II)–amino acid complexes with the standard molar enthalpies of formation of the amino acid ligands, in the crystalline state: 1, phenylglycine; 2, phenylalanine; 3, glycine; 4, alanine; 5, valine; 6, norvaline; 7, isoleucine; 8, leucine; 9, norleucine.

plexes with norvaline and with norleucine, respectively: $\Delta_f H_m^{\ominus}[\text{Cu(norval)}_2, \text{cr}] = -1127.8 \pm 3.4$ kJ mol^{-1} and $\Delta_f H_m^{\ominus}[\text{Cu(norleu)}_2, \text{cr}] = -1203.8 \pm 3.6$ kJ mol^{-1}. The values of Bernard et al. do not fit this line, and the slope of a line through their values is certainly larger than two. This example shows how these kinds of correlation are useful in critically examining thermochemical data.

The only enthalpy of sublimation reported for a copper(II) amino acid complex is that for the copper(II) glycinate, $\Delta_{cr}^{g} H_m^{\ominus}[\text{Cu(gly)}_2] = 111 \pm 15$ kJ mol^{-1} [52]. Table 8 lists the available literature values for the standard molar enthalpies of sublimation of the ligand amino acids. In the case of more than one literature value existing for the same amino acid, a selection has been made. This table also includes the selected values for the standard molar enthalpies of formation of the crystalline amino acids (see also Table 6) and the calculated values of the standard molar enthalpies of formation of the gaseous amino acids, which will be used below in the discussion.

From the intercept

$$119.60 = [\Delta_f H_m^{\ominus}(\text{Cu, g}) - 2\Delta_f H_m^{\ominus}(\text{H, g})] - 2[\langle D\rangle(\text{Cu–L}) - D(\text{H–L})] \\ - [\Delta_{cr}^{g} H_m^{\ominus}(\text{CuL}_2) - 2.014\Delta_{cr}^{g} H_m^{\ominus}(\text{HL})] \quad (13)$$

TABLE 8

Standard ($p^{\ominus} = 0.1$ MPa) molar enthalpies of sublimation and of formation of amino acids at 298.15 K

Amino acid	$\Delta_{cr}^{g}H_m^{\ominus}$ (kJ mol^{-1})	$\Delta_f H_m^{\ominus}$(cr) (kJ mol^{-1})	$\Delta_f H_m^{\ominus}$(g) (kJ mol^{-1})
Glycine	143.8 ± 2.0 [53] [a] 146.2 ± 0.3 [54] [b] 139.4 ± 0.5 [22] [b]	−528.5 ± 0.5 [23]	−384.7 ± 2.1
Alanine	139.7 ± 1.0 [53] [a] 147.8 ± 1.0 [54] [b] 140 ± 2 [22] [b]	−562.35 ± 0.65 [25]	−422.6 ± 1.2
Valine	171.7 ± 1.0 [54] [a,b]	−617.0 ± 1.0 [28]	−445.3 ± 1.4
Leucine	160.0 ± 1.0 [54] [a,b]	−637.4 ± 1.0 [19]	−477.4 ± 1.4
Isoleucine	129.3 ± 1.0 [54] [b] [160.0 ± 1.0] [a,c]	−638.06 ± 0.84 [21]	−478.1 ± 1.3
Phenylglycine	165.0 ± 6.0 [29] [a,d]	−445.53 ± 0.63 [29]	−280.5 ± 6.0
Phenylalanine	163.7 ± 1.0 [54] [a,b]	−466.9 ± 1.2 [21]	−303.2 ± 1.6

[a] Selected value.

[b] Value corrected to 298.15 K, using $\Delta C_p = -60$ J K^{-1} mol^{-1}, as recommended in ref. 53.

[c] Estimated value, as for leucine.

[d] This value includes a large correction from the experimental temperature to 298.15 K, allowing for the transition in the solid state at 337 K.

with $\Delta_f H_m^{\ominus}(\text{Cu, g}) = 337.6 \pm 1.2$ kJ mol^{-1} [17], $\Delta_f H_m^{\ominus}(\text{H, g}) = 218.00 \pm 0.01$ kJ mol^{-1} [17], $\Delta_{cr}^{g}H_m^{\ominus}[\text{Cu(gly)}_2] = 111 \pm 10$ kJ mol^{-1} [52] and $\Delta_{cr}^{g}H_m^{\ominus}(\text{Hgly}) = 143.8 \pm 2.0$ kJ mol^{-1} [53], and assuming that $[\Delta_{cr}^{g}H_m^{\ominus}(\text{CuL}_2) - 2.014\Delta_{cr}^{g}H_m^{\ominus}(\text{HL, cr})]$ is the same for all these complexes and equal to the experimental values for glycine, then

$$\langle D \rangle(\text{Cu–amino acid}) - D(\text{H–amino acid}) = -19.7 \text{ kJ mol}^{-1} \qquad (14)$$

The derivation of this value involves the measurements on all the complexes studied in this work and does not apply solely to the glycine complex for which $\Delta_{cr}^{g}H_m^{\ominus}$ is available.

The enthalpies of sublimation of the complexes can now be estimated from

$$\left[\Delta_{cr}^{g}H_m^{\ominus}(\text{CuL}_2) - 2.014\Delta_{cr}^{g}H_m^{\ominus}(\text{HL})\right] = -178.6 \text{ kJ mol}^{-1} \qquad (15)$$

and the reported enthalpies of sublimation of the amino acids to derive the $\Delta_f H_m^{\ominus}(\text{CuL}_2, \text{g})$ values listed in Table 9. An uncertainty of ±10 kJ mol^{-1} is estimated for $\Delta_{cr}^{g}H_m^{\ominus}$ and ±12 kJ mol^{-1} for the $\Delta_f H_m^{\ominus}$(g).

The derived standard molar enthalpies of formation of the copper(II) amino acid complexes in the gaseous state correlate (correlation coefficient 0.997) with the standard molar enthalpies of formation of the amino acid ligands in the gaseous state by

$$\Delta_f H_m^{\ominus}(\text{CuL}_2, \text{g}) = -62.4 + 2.006\Delta_f H_m^{\ominus}(\text{HL, g}) \qquad (16)$$

the slope again being two within the experimental error.

TABLE 9

Derived values of standard molar enthalpies of sublimation and standard molar enthalpies of formation in the gaseous state at 298.15 K for copper(II) amino acid complexes

Complex	$\Delta_f H_m^{\ominus}$(cr) (kJ mol^{-1})	$\Delta_{cr}^{g} H_m^{\ominus}$ (kJ mol^{-1})	$\Delta_f H_m^{\ominus}$(g) (kJ mol^{-1})
Cu(gly)$_2$	-943.7 ± 1.3	111 ± 10	-833 ± 12
Cu(ala)$_2$	-1003.7 ± 1.5	103 ± 10	-901 ± 12
Cu(val)$_2$	-1124.1 ± 2.2	167 ± 10	-957 ± 12
Cu(leu)$_2$	-1177.8 ± 2.1	144 ± 10	-1034 ± 12
Cu(isoleu)$_2$	-1156.3 ± 1.8	144 ± 10	-1013 ± 12
Cu(Phgly)$_2$	-772.3 ± 1.9	154 ± 10	-619 ± 12
Cu(Phala)$_2$	-831.8 ± 2.6	151 ± 10	-681 ± 12

The constancy of [$\langle D \rangle$(M–L) – D(H–L)] implies that those factors which affect D(H–L) have a similar effect on $\langle D \rangle$(M–L). For Cu(gly)$_2$ we calculate (eqn. (14))

$$\langle D \rangle(\text{Cu–gly}) - D(\text{H–gly}) = -19.7 \text{ kJ mol}^{-1} \qquad (17)$$

Assuming D(H–gly) = D(CH$_3$COO–H) = 433 kJ mol^{-1} [55], then $\langle D \rangle$(Cu–gly) = $\langle D \rangle$(Cu–O) + $\langle D \rangle$(Cu–N) ≈ 413 kJ mol^{-1}. It is not sensible to apportion the sum between the two bonds. However we note that this sum is greater than 2$\langle D \rangle$(Cu–O) = 334 kJ mol^{-1} in Cu(acac)$_2$ [35], so that the bonding of an aminoacid radical to Cu(II) is certainly stronger than the bonding of an acetylacetonate radical by ca. 80 kJ mol^{-1}.

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