# Thermochemistry of some metallic amino acid complexes. Part 2. Nickel(II) complexes

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## Abstract

The standard ($p^{\ominus} = 0.1$ MPa) molar enthalpies of formation of the following crystalline nickel(II) amino acid complexes were determined, at 298.15 K, by solution–reaction calorimetry: $\Delta_f H_m^{\ominus}$[Ni(gly)$_2$, cr] = $-994.2 \pm 1.8$ kJ mol$^{-1}$; $\Delta_f H_m^{\ominus}$[Ni(ala)$_2$, cr] = $-1072.4 \pm 2.3$ kJ mol$^{-1}$; $\Delta_f H_m^{\ominus}$[Ni(val)$_2$, cr] = $-1173.7 \pm 2.5$ kJ mol$^{-1}$; $\Delta_f H_m^{\ominus}$[Ni(leu)$_2$, cr] = $-1243.4 \pm 2.7$ kJ mol$^{-1}$; $\Delta_f H_m^{\ominus}$[Ni(isol)$_2$, cr] = $-1224.1 \pm 2.1$ kJ mol$^{-1}$; $\Delta_f H_m^{\ominus}$[Ni(Phgly)$_2$, cr] = $-857.0 \pm 2.8$ kJ mol$^{-1}$; $\Delta_f H_m^{\ominus}$[Ni(Phala)$_2$, cr] = $-898.6 \pm 3.0$ kJ mol$^{-1}$.

A linear correlation between the standard molar enthalpies of formation of the crystalline nickel(II) amino acid complexes and the crystalline amino acids is established. Estimations of the standard molar enthalpies of sublimation of the nickel(II) amino acid complexes are presented. The total binding energies in nickel(II) complexes of amino acids and of $\beta$-diketonate ligands are compared.

## INTRODUCTION

The transition metal amino acid and peptide complexes are convenient models for the metal-binding sites on proteins and enzymes and so, in recent years, many studies of solution equilibrium between metal ions and amino acid ligands have acted as models for biochemical systems. The enormous amount of research work on the thermodynamics of the formation of transition metal complexes with several different amino acid ligands [1] has been done mainly in aqueous solution, and very little has been done on the thermochemistry of the crystalline metal amino acid complexes.

In a previous paper [2] we reported the determination of the standard molar enthalpies of formation, at 298.15 K, of the crystalline copper(II)

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complexes with seven simple amino acid ligands. In the present paper we report the thermochemical investigation of the crystalline complexes of nickel(II) with the same amino acids.


EXPERIMENTAL


*Materials*


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

The nickel(II) complexes with the seven amino acids were prepared by a method similar to that described by Nakamoto et al. [3]. All the chemicals used in the preparation of these complexes were of analytical grade. The complexes were filtered off, washed with distilled water and dried first in a vacuum desiccator over phosphorus(V) pentoxide. As the complexes obtained by this process were hydrated, all of them were dehydrated by heating them in vacuum for between 5 and 8 h at 120–140°C. The IR spectra were recorded for all the complexes, showing the absence of water bands and the presence of the characteristic bands of these complexes [3].


TABLE 1

Mass percentage analyses

| | Found (%) | | | | Expected (%) | | | |
|---|---|---|---|---|---|---|---|---|
| | C | H | N | Ni | C | H | N | Ni |
| 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 | |
| Ni(gly)$_2$(cr) | 22.8 | 4.0 | 13.4 | 27.5 | 23.23 | 3.90 | 13.54 | 26.38 |
| Ni(ala)$_2$(cr) | 30.5 | 5.2 | 11.8 | 24.9 | 30.68 | 5.15 | 11.92 | 24.99 |
| Ni(val)$_2$(cr) | 40.3 | 6.9 | 9.4 | 19.9 | 41.28 | 6.93 | 9.63 | 20.17 |
| Ni(leu)$_2$(cr) | 45.1 | 7.4 | 8.4 | 18.2 | 45.17 | 7.60 | 8.78 | 18.33 |
| Ni(isoleu)$_2$(cr) | 44.8 | 7.7 | 8.4 | 18.1 | 45.17 | 7.60 | 8.78 | 18.33 |
| Ni(Phgly)$_2$(cr) | 53.8 | 4.5 | 7.5 | 16.2 | 53.52 | 4.49 | 7.80 | 16.35 |
| Ni(Phala)$_2$(cr) | 53.2 | 5.1 | 6.9 | 15.2 | 55.85 | 5.20 | 7.24 | 15.17 |

The compositions of the complexes were checked by elemental microanalyses. The mass percentage analyses of the ligands and complexes are given in Table 1.

All the complexes were stored in Schlenk tubes under dry nitrogen, because they are hygroscopic.

Nickel(II) chloride hexahydrate (BDH AnalaR) was powdered and dried in a desiccator over sodium hydroxide pellets; its composition was confirmed by means of nickel volumetric analyses with EDTA solution (Merck Titrisol) at pH 10, using murexide as indicator [4]; the composition was found to be $NiCl_2 \cdot 6.00H_2O$. The nickel chloride was stored in bottles and its composition was periodically checked by metal analyses.

Concentrated HCl (Merck, p.a.) was diluted with distilled water to prepare solutions of concentration near 1 mol $dm^{-3}$. Four different solutions were prepared, their concentrations being determined by titration against $Na_2B_4O_7 \cdot 10H_2O$ and found to be (series of at least six titrations), for the different solutions, 1.007 mol $dm^{-3}$ (which corresponds [5] to the composition $HCl \cdot 53.96H_2O$ [5]), 1.016 mol $dm^{-3}$ ($HCl \cdot 53.49H_2O$ [5]), 1.011 mol $dm^{-3}$ ($HCl \cdot 53.76H_2O$ [5]) and 2.024 mol $dm^{-3}$ ($HCl \cdot 26.32H_2O$ [5]).

Carbon, hydrogen and nitrogen microanalyses were carried out at the Microanalytical Service of the University of Manchester, UK.

Nickel(II) analyses, both for the amino acid complexes and for the nickel chloride, were performed by a complexometric titration [4].
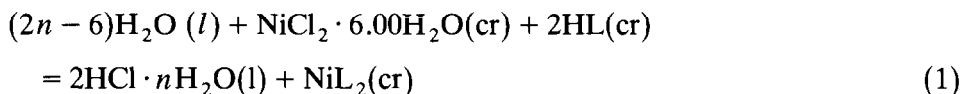
*Solution–reaction calorimeter*

A glass Dewar reaction–solution calorimeter with an all glass reaction vessel [6,7], containing 120.0 $cm^3$ of solvent, was used. The samples were sealed in thin glass ampoules which were broken into 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 auxiliary equipment and the technique used were described in the previous paper [2]. The adiabatic temperature change was calculated using the equal area method [8]. All the experiments were performed at 298.150 ± 0.001 K. 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, $\Delta_{sol}H_m^{\ominus}(cr) = -29.753 \pm 0.034$ kJ $mol^{-1}$, was in agreement with the literature value of Kilday and Prosen: $-29.770 \pm 0.032$ kJ $mol^{-1}$ [9].

The relative atomic masses used are as recommended by the IUPAC Commission [10]. All uncertainty intervals given are twice the standard deviation of the mean.

RESULTS

Preliminary tests of solubility showed that rapid hydrolysis was achieved in aqueous solutions of strong acids, 1 mol dm$^{-3}$ HCl being used for all the nickel(II) amino acid complexes except for the complex with phenylglycine, for which 2 mol dm$^{-3}$ HCl was used.

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

$$(2n - 6)H_2O \ (l) + NiCl_2 \cdot 6.00H_2O(cr) + 2HL(cr)$$

$$= 2HCl \cdot nH_2O(l) + NiL_2(cr) \tag{1}$$

As stated in the previous paper [2], the standard enthalpies of these reactions were determined by measuring, or calculating from reference data, the enthalpies of solution in the calorimetric solvent $\Delta_t H_m$ of the stoichiometric amount of each reactant, successively in the order they are written in the equation. The same procedure was followed for the products of the reaction. Special attention was paid to maintaining the control of the 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 of 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 detectable enthalpy change was detected.

Table 2 lists the molar enthalpies of solution and reaction for the study of nickel(II) complexes of glycine, alanine and valine. The solvent used for the nickel complexes of glycine and alanine was HCl $\cdot$ 53.96H$_2$O, and that for nickel(II) valinate was HCl $\cdot$ 53.49H$_2$O. It was found experimentally

TABLE 2

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

| $i$ | Reactant | Solvent | Solution | Number of expts. | $\Delta_t H_m$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| 1 | H$_2$O(l) | HCl·53.96H$_2$O | A$_1$ | 5 | $-0.019 \pm 0.001$ |
| 2 | NiCl$_2$·6.00H$_2$O(cr) | A$_1$ | A$_2$ | 5 | $+7.52 \pm 0.32$ |
| 3 | Hgly(cr) | A$_2$ | A$_3$ | 5 | $+8.89 \pm 0.13$ |
| 3a | Hala(cr) | A$_2$ | A$_{3a}$ | 5 | $+6.00 \pm 0.10$ |
| 3b | Hval(cr) | A$_2$ | A$_{3b}$ | 5 | $+5.00 \pm 0.12$ |
| 4 | HCl·53.96H$_2$O(l) | HCl·53.96H$_2$O | B$_1$ | Calc. | 0.00 |
| 5 | Ni(gly)$_2$(cr) | B$_1$ | A$_3$ | 5 | $-96.8 \pm 1.4$ |
| 5a | Ni(ala)$_2$(cr) | B$_1$ | A$_{3a}$ | 6 | $-92.1 \pm 1.9$ |
| 5b | Ni(val)$_2$(cr) | B$_1$ | A$_{3b}$ | 5 | $-102.1 \pm 1.3$ |

TABLE 3

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

| $i$ | Reactant | Solvent | Solution | Number of expts. | $\Delta_i H_m$ (kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| 1' | H$_2$O(l) | HCl·53.76H$_2$O | A'$_1$ | 7 | $-0.018 \pm 0.002$ |
| 2' | NiCl$_2$·6.00H$_2$O(cr) | A'$_1$ | A'$_2$ | 7 | $+7.19 \pm 0.42$ |
| 3' | Hleu(cr) | A'$_2$ | A'$_3$ | 6 | $+0.98 \pm 0.05$ |
| 3'c | Hisoleu(cr) | A'$_2$ | A'$_{3c}$ | 5 | $+1.53 \pm 0.04$ |
| 3'd | HPhala(cr) | A'$_2$ | A'$_{3d}$ | 6 | $+5.10 \pm 0.21$ |
| 4' | HCl·53.76H$_2$O(l) | HCl·53.76H$_2$O | B'$_1$ | Calc. | 0.000 |
| 5' | Ni(leu)$_2$(cr) | B'$_1$ | A'$_3$ | 6 | $-81.5 \pm 1.7$ |
| 5'c | Ni(isoleu)$_2$(cr) | B'$_1$ | A'$_{3c}$ | 5 | $-101.0 \pm 1.2$ |
| 5'd | Ni(Phala)$_2$(cr) | B'$_1$ | A'$_{3d}$ | 5 | $-77.0 \pm 1.6$ |
| 1" | H$_2$O(l) | HCl·26.32H$_2$O | A"$_1$ | 5 | $-0.083 \pm 0.004$ |
| 2" | NiCl$_2$·6.00H$_2$O(cr) | A"$_1$ | A"$_2$ | 5 | $+10.04 \pm 0.40$ |
| 3" | HPhgly(cr) | A"$_2$ | A"$_3$ | 5 | $+8.24 \pm 0.15$ |
| 4" | HCl·26.32H$_2$O(l) | HCl·26.32H$_2$O | B"$_1$ | Calc. | 0.000 |
| 5" | Ni(Phgly)$_2$(cr) | B"$_1$ | A"$_3$ | 7 | $-70.8 \pm 2.4$ |

that the dissolution of water in either of these solvents gave the same result within the experimental uncertainty: $\Delta_1 H_m = -0.019 \pm 0.001$ kJ mol$^{-1}$, and that the dissolution of NiCl$_2$ · 6.00 H$_2$O in the solutions A$_1$ (solution of the original HCl · $n$H$_2$O solvent plus the stoichiometric amount of water) also gave the same value, in both solvents, within the experimental uncertainty: $\Delta_2 H_m = +7.52 \pm 0.32$ kJ mol$^{-1}$. Table 3 lists the results obtained in

TABLE 4

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

| Compound | $\Delta_f H_m^{\ominus}$(l, cr) (kJ mol$^{-1}$) | $\Delta_{cr}^{g} H_m^{\ominus}$ (kJ mol$^{-1}$) | $\Delta_f H_m^{\ominus}$(g) (kJ mol$^{-1}$) |
|---|---|---|---|
| H$_2$O(l) | $-285.830 \pm 0.042$ [11] | | |
| NiCl$_2$· 6.00H$_2$O(cr) | $-2103.17 \pm 0.21$ [12] | | |
| HCl in 53.96H$_2$O(l) | $-165.414 \pm 0.006$ [12] | | |
| HCl in 53.49H$_2$O(l) | $-165.407 \pm 0.006$ [12] | | |
| HCl in 53.76H$_2$O(l) | $-165.411 \pm 0.006$ [12] | | |
| HCl in 26.32H$_2$O(l) | $-164.426 \pm 0.006$ [12] | | |
| Glycine | $-528.5 \pm 0.5$ [13] | $143.8 \pm 2.0$ [14] | $-384.7 \pm 2.1$ |
| DL-Alanine | $-562.35 \pm 0.65$ [15] | $139.7 \pm 1.0$ [14] | $-422.6 \pm 1.2$ |
| DL-Valine | $-617.0 \pm 1.0$ [16] | $171.7 \pm 1.0$ [17] | $-445.3 \pm 1.4$ |
| L-($\alpha$)-Leucine | $-637.4 \pm 1.0$ [18] | $160.0 \pm 1.0$ [17] | $-477.4 \pm 1.4$ |
| L-($\alpha$)-Isoleucine | $-638.06 \pm 0.84$ [19] | $[160.0 \pm 1.0]$ [a] | $-478.1 \pm 1.3$ |
| L-Phenylglycine | $-445.53 \pm 0.63$ [20] | $165.0 \pm 6.0$ [20] | $-280.5 \pm 6.0$ |
| L-($\alpha$)-Phenylalanine | $-466.9 \pm 1.2$ [19] | $163.7 \pm 1.0$ [17] | $-303.2 \pm 1.6$ |

[a] Estimated value (see ref. 2).

TABLE 5

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

| NiL$_2$ | $\Delta_r H_m^{\ominus}$ (kJ mol$^{-1}$) | $\Delta_f H_m^{\ominus}$(NiL$_2$,cr)(kJ mol$^{-1}$) | | $\Delta$/(expt.– calc.) (kJ mol$^{-1}$) |
|---|---|---|---|---|
| | | Expt. | Calc. | |
| Ni(gly)$_2$ | 120.2 ± 1.5 | − 994.2 ± 1.8 | − 1011.9 | 17.7 |
| Ni(ala)$_2$ | 109.7 ± 1.9 | − 1072.4 ± 2.3 | − 1077.8 | 5.4 |
| Ni(val)$_2$ | 117.7 ± 1.4 | − 1173.7 ± 2.5 | − 1184.2 | 10.5 |
| Ni(leu)$_2$ | 88.8 ± 1.8 | − 1243.4 ± 2.7 | − 1223.9 | − 19.5 |
| Ni(isoleu)$_2$ | 109.4 ± 1.3 | − 1224.1 ± 2.1 | − 1225.2 | 1.1 |
| Ni(Phgly)$_2$ | 93.4 ± 2.5 | − 857.0 ± 2.8 | − 850.4 | − 6.6 |
| Ni(Phala)$_2$ | 92.6 ± 1.7 | − 898.6 ± 3.0 | − 892.0 | − 6.6 |

the study of the nickel(II) complexes of leucine, isoleucine and phenylalanine (all in a solvent of initial composition HCl · 53.76H$_2$O) and in the study of nickel(II) phenylglycinate (in HCl · 26.32H$_2$O as initial solvent).

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

$$\Delta_r H_m^{\ominus}[\text{NiL}_2] = (2n - 6)\Delta_1 H_m + \Delta_2 H_m + 2\Delta_3 H_m - 2\Delta_4 H_m - \Delta_5 H_m \qquad (2)$$

The standard molar enthalpies of formation of the crystalline nickel(II) complexes with the different amino acids were derived with the auxiliary data of Table 4, and are listed in Table 5. Although there are in the literature several published values for the standard molar enthalpies of formation of the amino acids, which were listed in the previous paper [2], in the present work we used the same values as were given in the paper on the copper(II) amino acid complexes.

DISCUSSION

Values for the standard molar enthalpies of formation of some crystalline nickel(II) amino acid complexes have been previously reported. Wood and Jones [21] reported $\Delta_f H_m^{\ominus}[\text{Ni(gly)}_2$, cr] = − 1216 kJ mol$^{-1}$, derived from combustion calorimetry of this compound. This was pioneer work and has since been shown to be of very low accuracy [22], since insufficient attention was paid to controlling the combustion with auxiliary aids and in defining the completeness of combustion and the nature of the combustion products, accounting for the difference between Wood and Jones' and the present result. The NBS tables [12] give the value − 972.8 kJ mol$^{-1}$ for the nickel(II) glycinate, but as the sources of the NBS values are not given no conclusion can be drawn about the discrepancy of results. Bernard et al. [23] have measured enthalpies of solution of some nickel(II) amino acid complexes at 298.15 K; experimental details are not given in

their paper, neither are the values of the auxiliary enthalpies of formation used in the calculations, except that their source of these ancillary data is the NBS Circular 500 [24]. Their derived standard molar enthalpies of formation are as follows: $\Delta_f H_m^{\ominus}(\text{cr})$ (kJ mol$^{-1}$): Ni(gly)$_2$ = $-966.8 \pm 2.9$; Ni(ala)$_2$ = $-1065.9 \pm 3.2$; Ni(val)$_2$ = $-1208.0 \pm 3.6$; Ni(isoleu)$_2$ = $-1272.8 \pm 3.8$. The values cannot be directly compared 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 difference between the mean metal–ligand bond dissociation enthalpy $\langle D \rangle (\text{M–L})$ and the ligand–hydrogen dissociation enthalpy $D(\text{H–L})$ is given by:

$$\langle D \rangle (\text{M–L}) - D(\text{H–L}) = (1/n) \left[ \Delta_f H_m^{\ominus}(\text{M, g}) - \Delta_f H_m^{\ominus}(\text{ML}_n, \text{g}) \right]$$

$$- \Delta_f H_m^{\ominus}(\text{H, g}) + \Delta_f H_m^{\ominus}(\text{HL, g}) \tag{3}$$

As stated in the previous paper [2], it has been shown experimentally that, for a large number of complexes of a given metal with the same type of ligand, $\langle D \rangle (\text{M–L}) - D(\text{H–L})$ is constant. This constancy implies that $\Delta_f H_m^{\ominus}(\text{ML}_n, \text{g})$ should be linear with respect to $\Delta_f H_m^{\ominus}(\text{HL, g})$ with slope $n$, i.e.

$$\Delta_f H_m^{\ominus}(\text{ML}_n, \text{g}) = n\Delta_f H_m^{\ominus}(\text{HL, g}) + \left\{ \Delta_f H_m^{\ominus}(\text{M, g}) - n\Delta_f H_m^{\ominus}(\text{H, g}) \right.$$

$$\left. - n[\langle D \rangle (\text{M–L}) - D(\text{H–L})] \right\} \tag{4}$$

As

$$\Delta_f H_m^{\ominus}(\text{g}) = \Delta_f H_m^{\ominus}(\text{cr}) + \Delta_{cr}^{g} H_m^{\ominus} \tag{5}$$

eqn. (4) yields

$$\Delta_f H_m^{\ominus}(\text{ML}_n, \text{cr})$$

$$= n\Delta_f H_m^{\ominus}(\text{HL, cr}) + \left[ \Delta_f H_m^{\ominus}(\text{M, g}) - n\Delta_f H_m^{\ominus}(\text{H, g}) \right]$$

$$- n[\langle D \rangle (\text{M–L}) - D(\text{H–L})] - \left[ \Delta_{cr}^{g} H_m^{\ominus}(\text{ML}_n) - n \Delta_{cr}^{g} H_m^{\ominus}(\text{HL}) \right] \tag{6}$$

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

In using eqn. (6), it is convenient to distinguish the nature of the significance of the factor $n$ in the different terms: it is expected that $n$ will be exactly the number of ligands for all those terms related to the structure of the molecule, but the assumptions made and the experimental errors in the measurements imply that, for those terms depending on experimental
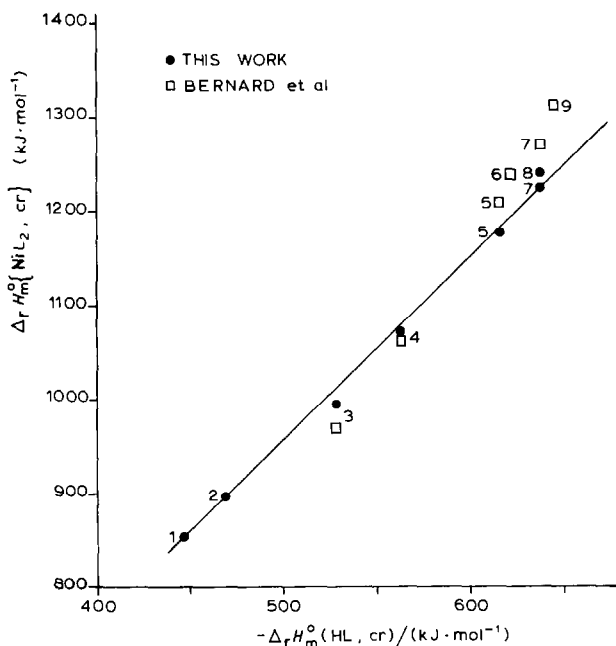
Fig. 1. Variation of the standard molar enthalpies of formation of the crystalline nickel(II)–amino acid complexes with the standard molar enthalpies of formation of the amino acid ligands in the crystalline state: 1, phenylglycine; 2, phenylalanine; 3, glycine; 4, alanine; 5, valine; 6, norvaline; 7, isoleucine; 8, leucine; 9, norleucine.

measurements, $n$ must be determined as $n'$, which is expected to be close to $n$. Hence eqn. (6) should be written as

$$\Delta_f H_m^{\ominus}(\mathrm{ML}_n, \mathrm{cr})$$

$$= n' \Delta_f H_m^{\ominus}(\mathrm{HL}, \mathrm{cr}) + \left[ \Delta_f H_m^{\ominus}(\mathrm{M}, \mathrm{g}) - n \Delta_f H_m^{\ominus}(\mathrm{H}, \mathrm{g}) \right]$$

$$- n \left[ \langle D \rangle (\mathrm{M-L}) - D(\mathrm{H-L}) \right] - \left[ \Delta_{cr}^g H_m^{\ominus}(\mathrm{ML}_n) - n' \Delta_{cr}^g H_m^{\ominus}(\mathrm{HL}) \right] \quad (7)$$

A least-squares treatment (correlation coefficient 0.994) of the standard molar enthalpies of formation data for the crystalline complexes of nickel(II) with amino acids, $\mathrm{ML}_2(\mathrm{cr})$, and for the crystalline amino acid ligands HL(cr) gives

$$\Delta_f H_m^{\ominus}(\mathrm{NiL}_2, \mathrm{cr}) = 17.09 + 1.947 \, \Delta_f H_m^{\ominus}(\mathrm{HL}, \mathrm{cr}) \quad (8)$$

Hence $n' = 2$ to within the experimental error. A comparison between the experimental and calculated values is given in Table 5: the average deviation between the experimental and the calculated values is 9.6 kJ mol$^{-1}$, in quite good concordance for such a simple relationship applied to the crystalline state.

Figure 1 shows the plot of $\Delta_f H_m^{\ominus}(\mathrm{NiL}_2, \mathrm{cr})$ versus $\Delta_f H_m^{\ominus}(\mathrm{HL}, \mathrm{cr})$; the straight line represents eqn. (8), showing good agreement with the standard

molar enthalpies of formation determined in this paper. The plot shows also the values determined by Bernard et al. [23] for the same complexes studied in this paper, as well as their values for the standard molar enthalpies of formation of the crystalline nickel(II) complexes with norvaline and with norleucine respectively: $\Delta_f H_m^{\ominus}$[Ni(norval)$_2$, cr] = $- 1238.0 \pm$ 3.7 kJ mol$^{-1}$ and $\Delta_f H_m^{\ominus}$[Ni(norleu)$_2$, cr] = $- 1312.5 \pm 3.9$ kJ mol$^{-1}$. The values of Bernard et al. do not fit this line and the slope of a line through them would be larger than two.

The only enthalpy of sublimation reported in the literature for a nickel(II) amino acid complex is that for the glycinate, $\Delta_{cr}^g H_m^{\ominus}$[Ni(gly)$_2$, cr] = $125 \pm 10$ kJ mol$^{-1}$ [25]. The selected values [2] of the standard molar enthalpies of formation of the gaseous amino acids, recorded in Table 4, will be used in the following discussion.

From the intercept, and eqns. (7) and (8), we have

$$17.09 = \left\{ \Delta_f H_m^{\ominus}(\text{Ni, g}) - 2\Delta_f H_m^{\ominus}(\text{H,g}) \right\} - 2[\langle D \rangle(\text{Ni–L}) - D(\text{H–L})]$$

$$- \left[ (\Delta_{cr}^g H_m^{\ominus})(\text{NiL}_2) - 1.947 \, \Delta_{cr}^g H_m^{\ominus}(\text{HL}) \right] \qquad (9)$$

with $\Delta_f H_m^{\ominus}(\text{Ni, g}) = 429.7 \pm 1.2$ kJ mol$^{-1}$ [11], $\Delta_f H_m^{\ominus}(\text{H, g}) = 218.00 \pm 0.01$ kJ mol$^{-1}$ [11], $\Delta_{cr}^g H_m^{\ominus}$[Ni(gly)$_2$] = $125 \pm 10$ kJ mol$^{-1}$ [24] and $\Delta_{cr}^g H_m^{\ominus}(\text{Hgly}) = 143.8 \pm 2.0$ kJ mol$^{-1}$ [14]. Assuming that $[\Delta_{cr}^g H_m^{\ominus}(\text{NiL}_2) - 1.947\Delta_{cr}^g H_m^{\ominus}(\text{HL})]$ is the same for all these complexes and equal to the experimental values for glycine, then

$$\langle D \rangle(\text{Ni–amino acid}) - D(\text{H–amino acid}) = +65.8 \text{ kJ mol}^{-1} \qquad (10)$$

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

$$\left[ \Delta_{cr}^g H_m^{\ominus}(\text{NiL}_2) - 1.947 \, \Delta_{cr}^g H_m^{\ominus}(\text{HL}) \right] = - 155.0 \text{ kJ mol}^{-1} \qquad (11)$$

TABLE 6

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

| Complex | $\Delta_f H_m^{\ominus}(\text{cr})$ (kJ mol$^{-1}$) | $\Delta_{cr}^g H_m^{\ominus}$ (kJ mol$^{-1}$) | $\Delta_f H_m^{\ominus}(\text{g})$ (kJ mol$^{-1}$) |
|---|---|---|---|
| Ni(gly)$_2$ | $-994.2 \pm 1.8$ | $125 \pm 10$ | $-869 \pm 12$ |
| Ni(ala)$_2$ | $-1072.4 \pm 2.3$ | $117 \pm 10$ | $-955 \pm 12$ |
| Ni(val)$_2$ | $-1173.7 \pm 2.5$ | $179 \pm 10$ | $-994 \pm 12$ |
| Ni(leu)$_2$ | $-1243.4 \pm 2.1$ | $157 \pm 10$ | $-1087 \pm 12$ |
| Ni(isoleu)$_2$ | $-1224.1 \pm 2.1$ | $157 \pm 10$ | $-1068 \pm 12$ |
| Ni(Phgly)$_2$ | $-857.0 \pm 2.8$ | $166 \pm 10$ | $-691 \pm 12$ |
| Ni(Phala)$_2$ | $-898.6 \pm 3.0$ | $164 \pm 10$ | $-735 \pm 12$ |

and the reported enthalpies of sublimation of the amino acids (Table 4) to derive $\Delta_f H_m^{\ominus}(NiL_2, g)$ listed in Table 6.

The derived standard molar enthalpies of formation of the nickel(II) amino acid complexes, in the gaseous state, are correlated (correlation coefficient 0.994) with the standard molar enthalpies of formation of the amino acid ligands in the gaseous state by eqn. (12)

$$\Delta_f H_m^{\ominus}(NiL_2, g) = -141.62 + 1.937 \, \Delta_f H_m(HL, g) \tag{12}$$

the slope again being two, within the experimental error.

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 Ni(gly)$_2$ from eqn. (10)

$$\langle D \rangle(Ni-gly) - D(H-gly) = +65.8 \text{ kJ mol}^{-1} \tag{13}$$

Assuming that $D(H-gly) = D(CH_3COO-H) = 433$ kJ mol$^{-1}$ [26], then $\langle D \rangle(Ni-gly) = \langle D \rangle(Ni-O) + \langle D \rangle(Ni-N) \approx 499$ kJ mol$^{-1}$. It is difficult to apportion the sum between the two bonds. However, we note that this sum is greater than $2\langle D \rangle(Ni-O) = 406$ kJ mol$^{-1}$ in Ni($\beta$-diketonate)$_2$ [27], so that the bonding of an amino acid radical is certainly stronger than the bonding of a $\beta$-diketonate radical by about 90 kJ mol$^{-1}$. The same effect has been observed [2] for the energetics of bonding of copper(II) with the amino acid and acetylacetonate radicals.

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