# Energetics of metal–ligand binding in copper(II) and nickel(II) complexes of two Schiff bases

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The standard molar enthalpies of formation, at 298.15 K, of crystalline copper(II) and nickel(II) complexes with 4,4′-ethylenedinitrilobis(pentan-2-one) ($H_2$acacen) and with 1,1′-diphenyl-3,3′-ethylenedinitrilobis(butan-1-one) ($H_2$bzacen), were determined from solution-reaction calorimetric measurements as, respectively, $\Delta_f H^\circ_m$[Cu(acacen), cr] = −385.1 ± 3.2, $\Delta_f H^\circ_m$[Cu(bzacen), cr] = − 203.4 ± 5.1, $\Delta_f H^\circ_m$[Ni(acacen), cr] = −472.6 ± 3.1 and $\Delta_f H^\circ_m$[Ni(bzacen), cr] = −292.2 ± 5.1 kJ $mol^{-1}$. The standard molar enthalpies of sublimation of the same metal complexes, at 298.15 K, were obtained by effusion methods as: $\Delta^g_{cr} H^\circ_m$[Cu(acacen) = 127.6 ± 0.7, $\Delta^g_{cr} H^\circ_m$[Ni(acacen)] = 129.1 ± 0.9, $\Delta^g_{cr} H^\circ_m$[Cu(bzacen)] = 205.6 ± 3.0 and $\Delta^g_{cr} H^\circ_m$[Ni(bzacen) = 201.7 ± 2.8 kJ $mol^{-1}$. The differences between the mean metal–ligand and hydrogen–ligand bond-dissociation enthalpies were derived.

Metal complexes derived from Schiff bases[1] have been known for over 100 years, since 1840 when Ettling[2] isolated bis(salicylideneamido)copper(II). Since then they have occupied a central role in the development of co-ordination chemistry, resulting in a large number of publications ranging from pure synthetic work to modern physicochemical and biochemically relevant studies of these complexes. A considerable number of Schiff-base complexes have potential biological interest, being used as more or less successful models of biological compounds.[3] On the other hand, the use of these compounds in catalytic reactions has been considered.[4] These studies dealing mainly with synthesis, spectroscopic, structural, electrochemical and magnetic properties, photo- and thermo-chroism have been extensively reviewed.[5–8]

In view of recent interest in the energetics of metal–ligand binding in metal chelates involving bidentate N,O-donor ligands,[9–11] we started to study Schiff-base complexes derived from N,N′-bridged tetradentate ligands involving an $N_2O_2$ donor atom set. Despite some stability constant studies[12–14] and recent investigations of the thermal behaviour of such complexes,[15–17] information on their thermochemical aspects is still very scarce.

In the present paper we report the standard molar enthalpies of formation of two four-co-ordinated copper(II) and two four-co-ordinated nickel(II) complexes with 4,4′-ethylenedinitrilobis(pentan-2-one), $H_2$acacen, and 1,1′-diphenyl-3,3′-ethylenedinitrolobis(butan-1-one), $H_2$bzacen. These results are used to provide a direct measure of the differences in the metal–ligand and hydrogen–ligand binding enthalpies.

## Experimental and Results

### Materials

The compound $H_2$acacen was prepared as described by McCarthy *et al.*[18] using stoichiometric amounts (1:2) of recently distilled ethane-1,2-diamine (Merck, for synthesis), dried over sodium hydroxide and freshly distilled acetylacetone (Merck, p.a.). The compound $H_2$bzacen was prepared also according to the McCarthy procedure,[18] adding recently distilled ethane-1,2-diamine (Merck, for synthesis), dried over sodium hydroxide, to a solution of recrystallized benzoylacetone (Merck, for synthesis) in hot ethanol. Both compounds were stored in desiccators over phosphorus(V) oxide. The purities of the samples were checked by IR spectroscopy and microanalysis (C, H, N) (Microanalytical Services of the University of Manchester). The microanalytical results are given in Table 1.

**Table 1** Elemental analytical data (%)

| | Found | | | Calculated | | |
|---|---|---|---|---|---|---|
| Compound | C | H | N | C | H | N |
| $H_2$acacen | 64.6 | 9.3 | 12.6 | 64.3 | 9.0 | 12.5 |
| $H_2$bzacen | 75.8 | 7.1 | 8.0 | 75.8 | 6.9 | 8.0 |
| [Cu(acacen)] | 49.7 | 6.6 | 9.4 | 50.4 | 6.4 | 9.8 |
| [Ni(acacen)] | 50.6 | 6.7 | 9.4 | 51.3 | 6.5 | 10.0 |
| [Cu(bzacen)] | 64.1 | 5.3 | 6.7 | 64.4 | 5.4 | 6.8 |
| [Ni(bzacen)] | 65.1 | 5.5 | 6.7 | 65.2 | 5.5 | 6.9 |

**[Cu(acacen)].** This complex was prepared as described by Martell *et al.*[19] Copper(II) acetate monohydrate (Merck, p.a.) in warm 1,4-dioxane was added to a stoichiometric amount of $H_2$acacen: the red solution was heated on a steam-bath, diluted with water and allowed to stand overnight. Dark red needles which crystallized were filtered off, and more product was recovered after evaporation of the mother-liquor to a smaller volume. The combined product thus obtained was about 49% of the theoretical yield, and its purity was confirmed by elemental analysis and infrared spectroscopy. M.p. 141 °C (lit., 142[18] and 145 °C[19]). The compound was stored in a desiccator over phosphorus(V) oxide.

**[Ni(acacen)].** This complex was prepared according to the above procedure, using nickel(II) acetate tetrahydrate (BDH, Laboratory Reagent) in 1,4-dioxane and $H_2$acacen in stoichiometric quantities. The brownish crystals were recrystallized from water–acetone (1:10), giving about 42% of the theoretical yield. M.p. 193 °C (lit.,[18] 195–196 °C). Other details as above.

**[Cu(bzacen)].** The complex was prepared as described by Martell *et al.*[19] for the acetylacetonate derivative. The red-brown compound was recrystallized from chloroform and dried at 100 °C, giving 74% of the theoretical yield. The product did not melt until 274 °C, but decomposes at this temperature as described.[18] Other details as above.

**Table 2** Solution calorimetry results for the copper(II) complexes

| Reactant | Solvent | Solution | $\Delta_i H_m$/kJ mol$^{-1}$ |
|---|---|---|---|
| Water (l) | $HCl\cdot12.61H_2O$–1,4-dioxane (1:2) | $A_1$ | −0.958 ± 0.002 |
| $MeCO_2H$ (l) | $A_1$ | $A_2$ | −0.879 ± 0.009 |
| [Cu(acacen)] (cr) | $A_2$ | $F_1$ | −12.34 ± 0.02 |
| [Cu(bzacen)] (cr) | $A_2$ | $F_{1a}$ | 21.53 ± 0.02 |
| $Cu(O_2CMe)_2\cdot H_2O$ (cr) | $HCl\cdot12.61H_2O$–1,4-dioxane (1:2) | $B_1$ | 14.87 ± 0.02 |
| $H_2$acacen (cr) | $B_1$ | $F_1$ | 10.94 ± 0.02 |
| $H_2$bzacen (cr) | $B_1$ | $F_{1a}$ | 38.56 ± 0.04 |

**Table 3** Solution calorimetry results for the nickel(II) complexes

| Reactant | Solvent | Solution | $\Delta_i H_m$/kJ mol$^{-1}$ |
|---|---|---|---|
| Water | $HCl\cdot12.61H_2O$–1,4-dioxane (1:2) | $A_1$ | −0.958 ± 0.002 |
| $NiCl_2\cdot6H_2O$ (cr) | $A_1$ | $A_2$ | 4.66 ± 0.07 |
| $H_2$acacen (cr) | $A_2$ | $F_1$ | 8.27 ± 0.02 |
| $H_2$bzacen (cr) | $A_2$ | $F_{1a}$ | 41.63 ± 0.02 |
| $HCl\cdot12.61H_2O$ (l) | $HCl\cdot12.61H_2O$–1,4-dioxane (1:2) | $B_1$ | −20.05 ± 0.02 |
| [Ni(acacen)] (cr) | $B_1$ | $F_1$ | −47.52 ± 0.05 |
| [Ni(bzacen)] (cr) | $B_1$ | $F_{1a}$ | −6.62 ± 0.05 |

**[Ni(bzacen)].** This complex was prepared according to the procedure described above, using nickel(II) acetate tetrahydrate in 1,4-dioxane and $H_2$bzacen in stoichiometric quantities. The brown-red compound was recrystallized from acetone, in 50% of the theoretical yield. The product melted above 285 °C (lit.,[18] 288–289 °C). Other details as above.

Copper(II) acetate monohydrate (Aldrich, gold label) and nickel(II) chloride hexahydrate (Aldrich, gold label) were used in calorimetric measurements without any purification, being handled under nitrogen, to keep the well established degrees of hydration. Acetic acid (Fluka A.G., puriss. p.a. ACS) was also handled under nitrogen. 1,4-Dioxane (BDH, pure) was purified according to the literature procedure.[20] Concentrated HCl (Merck, p.a.) was diluted with distilled water to prepare solutions of concentration near 4 mol dm$^{-3}$; its concentration was determined by titration against $Na_2B_4O_7\cdot10H_2O$ and found to be 4.053 ± 0002 mol dm$^{-3}$ (which corresponds to the composition $HCl\cdot12.61H_2O$.[21] A 2:1 v/v mixture of 1,4-dioxane and 4.053 mol dm$^{-3}$ HCl was used as calorimetric solvent.

## Solution-reaction calorimetry

The reaction and solution enthalpies were measured in a reaction-solution calorimeter with an all-glass reaction vessel, containing 120.0 cm$^3$ of solvent, the auxiliary equipment and technique used being described previously.[22,23] 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 calibration and experimental procedure were tested by measuring the molar enthalpy of a solution of tris(hydroxymethyl)aminomethane (BDH, Thermochemical Standard) in 0.1000 mol dm$^{-3}$ HCl(aq) at 298.15 K, six independent measurements giving $\Delta_{sol}H = -29.72 \pm 0.03$ kJ mol$^{-1}$ in good agreement with the value reported by Kilday and Prosen,[24] −29.77 ± 0.31 kJ mol$^{-1}$.

The relative atomic masses used are as recommended by the IUPAC Commission.[25]

The general thermochemical reactions (1) and (2) were used

$$Cu(O_2CMe)_2\cdot H_2O\ (cr) + H_2L\ (cr) \longrightarrow H_2O\ (l) + 2MeCO_2H\ (l) + [CuL]\ (cr) \quad (1)$$

$$NiCl_2\cdot6H_2O\ (cr) + H_2L\ (cr) + (2n-6)\ H_2O\ (l) \longrightarrow [NiL]\ (cr) + 2HCl\cdot nH_2O\ (l) \quad (2)$$

for determining the enthalpies of formation of the [CuL] and [NiL] complexes. The standard enthalpy of each reaction, $\Delta_r H^\circ_m$, was determined by successively measuring the enthalpy of solution, $\Delta_i H_m$, of the stoichiometric amount of each reactant or product in the calorimetric solvent, so that the final solution from the dissolution of the reactants had the same composition as that resulting from the dissolution of the products. As a check of the validity of this, ampoules of the final solution resulting from the dissolution of all the reactants were broken into the final solution obtained upon dissolution of all the products in the calorimeter and no enthalpy change was detected.

The molar enthalpies of solution and reaction, using $HCl\cdot12.61H_2O(l)$–1,4-dioxane (1:2) as solvent, are listed in Tables 2 and 3, and are the means of at least five independent determinations for each enthalpy of solution; the uncertainties given are twice the standard deviation of the mean, in accordance with normal thermochemical practice.

The standard molar enthalpies of the thermochemical reactions (1) and (2), listed in Table 4, were calculated by means of equations (3) and (4) in which $\Delta_i H_m$ are the molar enthalpies of

$$\Delta_r H^\circ_m(\mathrm{CuL}) = -\Delta_1 H_m - 2\Delta_2 H_m - \Delta_3 H_m + \Delta_4 H_m + \Delta_5 H_m \quad (3)$$

$$\Delta_r H^\circ_m(\mathrm{NiL}) = 19.22\Delta_1 H_m + \Delta_2 H_m + \Delta_3 H_m - 2\Delta_4 H_m - \Delta_5 H_m \quad (4)$$

solution and reaction of each chemical species, as defined in Tables 2 and 3. The standard enthalpies of formation of the complexes in the crystalline state are listed in Table 4 and were derived from the enthalpies of the thermochemical reactions and the auxiliary data also listed in Table 4.

## Enthalpies of sublimation

The enthalpies of sublimation of [M(acacen)] (M = Cu or Ni) were derived from measurements of vapour pressures as functions of temperature using a mass-loss Knudsen-effusion apparatus. The detailed description of the apparatus, procedure, technique, and the results obtained with test substances (ferrocene and benzoic acid) have been previously reported.[29] This apparatus enables the simultaneous operation of three Knudsen cells with three different effusion holes. In each effusion experiment the mass losses, $\Delta m$, of the crystalline samples were measured by weighing the cells with the samples to ±0.01 mg, before and after a convenient effusion time, $t$, in an evacuated system at pressures lower than $1 \times 10^{-4}$ Pa. The cells were

**Table 4** Derived standard molar values (kJ mol$^{-1}$) at 298.15 K

| Complex | $\Delta_f H^\circ_m$ (cr) | $-\Delta_f H^\circ_m$ (cr) | $\Delta^g_{cr} H^\circ_m$ | $-\Delta_f H^\circ_m$ (g) |
|---|---|---|---|---|
| [Cu(acacen)] | 40.866 ± 0.039 | 385.1 ± 3.2 | 127.6 ± 0.7 | 257.5 ± 3.3 |
| [Cu(bzacen)] | 34.616 ± 0.052 | 203.4 ± 5.1 | 205.6 ± 3.0 | −2.2 ± 5.9 |
| [Ni(acacen)] | 82.13 ± 0.10 | 472.6 ± 3.1 | 129.1 ± 0.9 | 343.5 ± 3.2 |
| [Ni(bzacen)] | 74.59 ± 0.10 | 292.2 ± 5.1 | 201.7 ± 2.8 | 90.5 ± 5.8 |

Auxiliary data: $\Delta_f H^\circ_m(H_2O, l) = -285.83 \pm 0.04$ kJ mol$^{-1}$;[26] $\Delta_f H^\circ_m$(HCl in 12.61 $H_2O$, l) $= -162.352 \pm 0.005$ kJ mol$^{-1}$;[26] $\Delta_f H^\circ_m(MeCO_2H, l) = -484.3 \pm 0.2$ kJ mol$^{-1}$;[27] $\Delta_f H^\circ_m(NiCl{\cdot}6H_2O, cr) = -2103.17 \pm 0.21$ kJ mol$^{-1}$;[26] $\Delta_f H^\circ_m[Cu(O_2CMe)_2{\cdot}H_2O, cr] = -1189.1 \pm 0.5$ kJ mol$^{-1}$;[26] $\Delta_f H^\circ_m(H_2acacen, cr) = -491.3 \pm 3.1$ kJ mol$^{-1}$;[28] $\Delta_f H^\circ_m(H_2bzacen, cr) = -303.3 \pm 5.1$ kJ mol$^{-1}$.[28]

**Table 5** Experimental results and residuals of the Clausius–Clapeyron equation for [Cu(acacen)] and for [Ni(acacen)]

|  | $p$/Pa |  |  | 100 Δ ln ($p$/Pa) |  |  |
|---|---|---|---|---|---|---|
| $T$/K | hole 1 | hole 2 | hole 3 | hole 1 | hole 2 | hole 3 |
| [Cu(acacen)] |  |  |  |  |  |  |
| 384.17 | 0.1940 | 0.1858 | 0.1878 | 2.34 | −1.20 | 0.51 |
| 385.18 | 0.2111 | 0.2136 | 0.2076 | 0.67 | 2.61 | 0.52 |
| 387.14 | 0.2628 | 0.2567 | 0.2532 | 3.08 | 1.49 | 1.09 |
| 388.29 | 0.2792 | 0.2815 | 0.2732 | −2.21 | −0.64 | −2.53 |
| 389.14 | 0.3083 | 0.3068 | 0.3106 | −0.63 | −0.38 | 2.05 |
| 391.08 | 0.3749 | 0.3673 | 0.3660 | 0.03 | −1.30 | −0.24 |
| 391.15 | 0.3837 | 0.3826 | 0.3736 | 1.67 | 2.10 | 1.14 |
| 392.23 | 0.4134 | 0.4105 | 0.4086 | −1.31 | −1.31 | −0.23 |
| 393.15 | 0.4407 | 0.4590 | 0.4451 | −3.77 | 1.00 | −0.43 |
| 394.16 | 0.4823 | 0.4890 | 0.4775 | −4.41 | −2.34 | −2.96 |
| 394.24 | 0.4977 | 0.4935 | 0.4887 | −2.03 | −2.18 | −1.40 |
| 395.39 | 0.5633 | 0.5569 | 0.5493 | −0.59 | −1.05 | −0.53 |
| 397.22 | 0.6851 | 0.6638 | 0.6585 | 1.71 | −0.78 | 0.50 |
| 398.29 | 0.7483 | 0.7435 | 0.7231 | 0.51 | 0.53 | −0.06 |
| 399.21 | 0.8245 | 0.8195 | 0.7928 | 1.63 | 1.67 | 0.65 |
| 400.18 | 0.8982 | 0.8916 | 0.8749 | 1.19 | 1.09 | 1.60 |
| 400.37 | 0.9228 | 0.9037 | 0.8788 | 2.13 | 0.68 | 0.30 |
| [Ni(acacen)] |  |  |  |  |  |  |
| 389.25 | 0.0807 | 0.0762 |  | 0.85 | −1.56 |  |
| 393.40 | 0.1169 | 0.1160 |  | −2.09 | −0.37 |  |
| 399.58 | 0.2169 | 0.2179 |  | 1.70 | 3.49 |  |
| 405.24 | 0.3598 | 0.3574 |  | 0.76 | 0.40 |  |
| 411.37 | 0.5884 | 0.6054 |  | −2.62 | −2.23 |  |
| 415.75 | 0.9088 | 0.9126 |  | 1.39 | 0.28 |  |

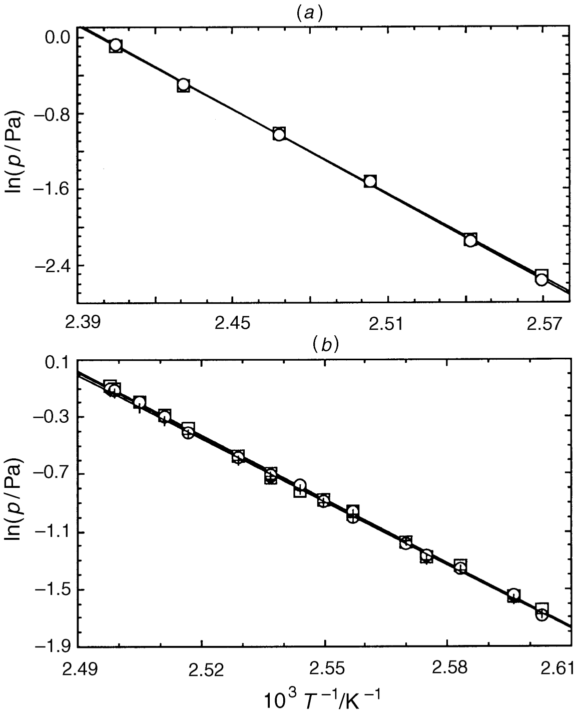

**Fig. 1** Plots of ln $p$ against $1/T$ for ($a$) [Ni(acacen)] and ($b$) [Cu(acacen)]. □, hole 1; ○, hole 2; +, hole 3

immersed in a thermostatically controlled oil-bath. At the temperature, $T$, of the effusion experiment, the vapour pressure, $p$, was calculated by equation (5) in which $M$ is the molar mass of

$$p = (\Delta m/A_0 w_0 t)(2\pi RT/M)^{\frac{1}{2}} \qquad (5)$$

the effusing vapour, $R$ the gas constant, $A_0$ the area of the effusion hole and $w_0$ the respective Clausing factor $[1 + (3l/8r)]^{-1}$ where $l$ is the thickness of the effusion hole and $r$ its radius. The thickness $l$ was 0.049 mm and the areas and Clausing factors were: hole 1, $A_0 = 0.596$ mm$^2$, $w_0 = 0.959$; hole 2, $A_0 = 0.813$ mm$^2$, $w_0 = 0.965$; hole 3, $A_0 = 0.862$ mm$^2$, $w_0 = 0.966$.

The integrated form of Clausius–Clapeyron equation (6) was

$$\ln(p/\text{Pa}) = a - (bT^{-1}/\text{K}^{-1}) \qquad (6)$$

used to derive the standard molar enthalpies of sublimation, at the mean temperature $\langle T \rangle$ of the experimental range, by least-squares fitting of the experimental results obtained with the three different cells, for [Cu(acacen)] and with the cells with holes 1 and 2 for [Ni(acacen)].

The experimental results obtained from each cell, for both complexes, together with the residuals of equation (6) are given in Table 5. These results and the global ones obtained with the three cells used were fitted by equation (6) using a least-squares computer program. The plots of ln $p = f(1/T)$, for the individual effusion holes are represented in Fig. 1.

Table 6 presents, for each complex and hole used, the detailed parameters of equation (6), the mean temperatures of the experiments, $\langle T \rangle$, and the standard molar enthalpies of sublimation at $\langle T \rangle$, $\Delta^g_{cr} H^\circ_m(\langle T \rangle)$; the standard molar enthalpies of sublimation at 298.15 K, $\Delta^g_{cr} H^\circ_m$ (298.15), calculated from the global treatment of all the experimental ($p$, $T$) points obtained for both complexes are also given. These values were calculated using relation (7) with $\Delta^g_{cr} C^\circ_{p,m} = -50$ J K$^{-1}$ mol$^{-1}$ estimated for

$$\Delta^g_{cr} H^\circ_m(298.15) = \Delta^g_{cr} H^\circ_m(\langle T \rangle) + \Delta^g_{cr} C^\circ_{p,m}(298.15 - \langle T \rangle) \qquad (7)$$

all the studied complexes, in accordance with similar estimations made by other authors.[30]

Table 7 lists the ($p$, $T$) values calculated from the ($p$, $T$) overall treatment equations, within 0.1–1 Pa.

The enthalpies of sublimation of [M(bzacen)] (M = Cu or Ni) were also derived from measurements using a Knudsen-effusion method, as described by Burkinshaw and Mortimer,[30] since these two complexes were too involatile to be measured by the mass-loss Knudsen-effusion apparatus at its range of working temperatures. The vapour effusing from the Knudsen cell was allowed to condense on a quartz crystal positioned above the effusion hole and changes in the frequency of oscillation of the quartz plate were proportional to the mass condensed.

Measurements were made using an Edward 306 vacuum-coating unit providing a minimum pressure of 7 × 10$^{-5}$ Pa fitted with the FTM3 film-thickness monitor incorporating a quartz-crystal oscillator (6 MHz), but with some modifications from

**Table 6** Parameters of the Clausius–Clapeyron equation and standard enthalpies of sublimation for [Cu(acacen)] and for [Ni(acacen)]

| Hole number | *a* | *b* | $\langle T\rangle$/K | $\Delta^{g}_{cr}H^{\circ}_{m}(\langle T\rangle)$/kJ mol$^{-1}$ | $\Delta^{g}_{cr}H^{\circ}_{m}$(298.15 K)/kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| [Cu(acacen)] | | | | | |
| 1 | 36.932 ± 0.430 | 14 827 ± 169 | | 123.3 ± 1.4 | |
| 2 | 36.957 ± 0.300 | 14 840 ± 118 | | 123.4 ± 1.0 | |
| 3 | 36.513 ± 0.264 | 14 672 ± 104 | | 122.0 ± 0.9 | |
| Global results | 36.800 ± 0.219 | 14 779 ± 86 | 392.27 | 122.9 ± 0.7 | 127.6 ± 0.7 |
| [Ni(acacen)] | | | | | |
| 1 | 35.376 ± 0.364 | 14 753 ± 147 | | 122.7 ± 1.2 | |
| 2 | 36.096 ± 0.391 | 15 046 ± 157 | | 125.1 ± 1.3 | |
| Global results | 35.736 ± 0.271 | 14 900 ± 109 | 402.50 | 123.9 ± 0.9 | 129.1 ± 0.9 |

**Table 7** Mean *T*, *p* values from vapour-pressure equations for [Cu(acacen)] and [Ni(acacen)]

| | *T*/K | |
|---|---|---|
| *p*/Pa | [Cu(acacen)] | [Ni(acacen)] |
| 0.1 | 377.95 | 391.71 |
| 0.2 | 384.78 | 398.98 |
| 0.3 | 388.88 | 403.36 |
| 0.4 | 391.85 | 406.52 |
| 0.5 | 394.18 | 409.01 |
| 0.6 | 396.11 | 411.07 |
| 0.7 | 397.75 | 412.83 |
| 0.8 | 399.18 | 414.36 |
| 0.9 | 400.46 | 415.72 |
| 1.0 | 401.60 | 416.95 |

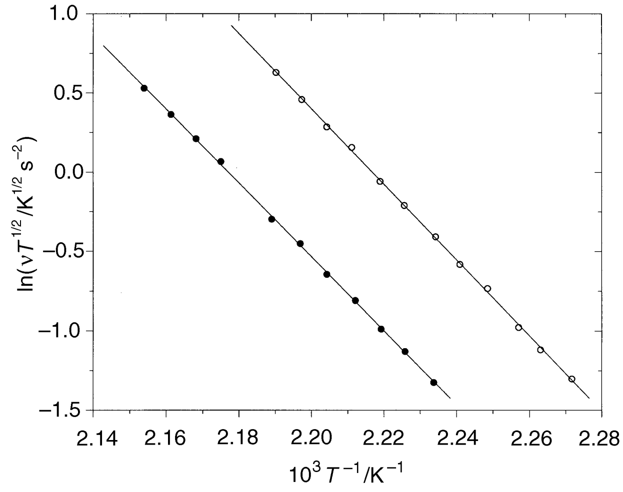

**Fig. 2** Plots of $\ln(\nu T^{\frac{1}{2}}/\mathrm{K}^{\frac{1}{2}}\ \mathrm{s}^{-2})$ against $1/T$ for [Ni(bzacen)] (●) and [Cu(bzacen)] (○)

the apparatus described by Burkinshaw and Mortimer. The cylindrical Knudsen cell was made of steel, external diameter 13 mm, internal diameter 6 mm and depth 8 mm. The lid with an effusion-hole diameter of 0.8 mm was screwed on to the cell. The complete cell was screwed into an electrically heated cylindrical steel block, and the temperature was controlled to ±0.1 K by a proportional integral derivative controller, Eurotherm 815. Temperatures were measured by a Lab Facility P100/0620 platinum sensing detector screwed into the effusion cell. Frequency changes in the quartz-crystal oscillator circuit were measured with a Philips PM 6685 frequency counter connected to the FTM3 film-thickness monitor. The equipment was tested with several compounds of known standard molar enthalpy of sublimation {7*H*-benz[*d*,*e*]anthracen-7-one (benzanthrone), 3,4-dihydroxycyclobut-3-ene-1,2-dione (squaric acid), 4-hydroxy-2-methylquinoline}.

The relationship between the change in frequency of a quartz crystal, $\Delta f$, and the mass of the substance deposited on its surface, *m*, was developed by Sauerbrey.[31] This relationship was derived for AT-cut quartz crystals, vibrating in thickness shear mode and can be expressed as in equation (8) where *f* is the

$$\Delta f = (f^2/ArN)m \qquad (8)$$

average resonance frequency, *A* and *r* the surface area and the density of the quartz crystal and *N* is the crystal constant. The change in frequency, $\Delta f$, is directly proportional to the mass deposited on the crystal, assuming that the total frequency change is small when compared with *f*, *i.e.* $f \gg \Delta f$. The experimental measured rate, ν, of resonance frequency change in time, *t*, for the quartz crystal, $\nu = \Delta f/t$, is proportional to the rate of sublimed mass of the crystalline sample, $\Delta m/t$, which can be related to the vapour pressure according to equation (5).

Thus we obtain expressions (9) and (10). Hence $\Delta^{g}_{cr}H^{\circ}_{m}$ may

$$\nu = \Delta f/t = c\Delta m/t = cpA_0w_0(M/2\pi RT)^{\frac{1}{2}} \qquad (9)$$

$$p = \nu T^{\frac{1}{2}}[(2\pi R/M)^{\frac{1}{2}}/(cA_0w_0)^2] \qquad (10)$$

be derived from the slope of $\ln(\nu T^{\frac{1}{2}})$ *versus* $T^{-1}$ by applying the integrated form of the Clausius–Clapeyron equation. The enthalpy of sublimation thus calculated corresponds to the mean temperature of the experimental temperature range, and was also corrected to $T = 298.15$ K by means of equation (7).

For the [Cu(bzacen)] complex, twelve experimental measurements of the change in frequency of the quartz oscillator at different temperatures were made, over the temperature range 440.18–456.56 K. For [Ni(bzacen)] similar measurements were made over the range 447.67–464.25 K. Fig. 2 shows that the plots of $\ln(\nu T^{\frac{1}{2}}/\mathrm{K}^{\frac{1}{2}}\ \mathrm{s}^{-2})$ against $T^{-1}$ for these measurements yield straight lines, from the slopes of which the standard molar enthalpy of sublimation, at the weighted mean temperatures of the experimental ranges, is derived as $\Delta^{g}_{cr}H^{\circ}_{m}(448.4\ \mathrm{K}) = 198.07 \pm 2.96$ kJ mol$^{-1}$ for [Cu(bzacen)] and as $\Delta^{g}_{cr}H^{\circ}_{m}(455.9\ \mathrm{K}) = 198.85 \pm 2.80$ kJ mol$^{-1}$ for [Ni(bzacen)]. These values were corrected to 298.15 K by means of equation (7) giving $\Delta^{g}_{cr}H^{\circ}_{m}$ [Cu(bzacen), 298.15 K] = 205.5 ± 3.0 kJ mol$^{-1}$ and $\Delta^{g}_{cr}H^{\circ}_{m}$ [Ni(bzacen), 298.15 K] = 201.7 ± 2.88 kJ mol$^{-1}$.

## Discussion

Dissociation enthalpies have relevance in considering reactivity, *e.g.* in a thermal decomposition the most probable initial step is the rupture of that bond in the molecule with smallest dissociation enthalpy. For a metal complex ML, L being the dianion of the tetradentate ligand $H_2L$, the metal–ligand dissociation enthalpy *D*(M−L) is defined as the enthalpy of the disruption reaction (11) and for $H_2L$ the mean bond-dissociation enthalpy, $2\langle D(\mathrm{H{-}L})\rangle$, is the enthalpy of the dissociation (12).

$$\mathrm{ML\ (g)} \longrightarrow \mathrm{M\ (g) + L\ (g)} \qquad (11)$$

$$\mathrm{H_2L\ (g)} \longrightarrow \mathrm{2H\ (g) + L\ (g)} \qquad (12)$$

The dissociation enthalpy *D*(M−L) includes the radical

**Table 8** Comparison of $D(\mathrm{M{-}L}) - 2\langle D(\mathrm{H{-}L})\rangle$ values (kJ mol$^{-1}$) for ML complexes and $\langle D(\mathrm{M{-}L})\rangle - D(\mathrm{H{-}L})$ for ML$_2$ complexes

| Complex* | $D(\mathrm{M{-}L}) - 2\langle D(\mathrm{H{-}L})\rangle$ | $2\langle D(\mathrm{M{-}L})\rangle - 2D(\mathrm{H{-}L})$ |
|---|---|---|
| [Cu(acacen)] | −200.6 ± 4.7 | |
| [Cu(bzacen)] | −205.1 ± 9.5 | |
| [Cu(quin)$_2$] | | −150 ± 8[33] |
| [Cu(glyO)$_2$] | | −39 ± 10[10] |
| [Ni(acacen)] | −22.5 ± 4.7 | |
| [Ni(bzacen)] | −20.3 ± 9.4 | |
| [Ni(quin)$_2$] | | −6 ± 10[33] |
| [Ni(glyO)$_2$] | | 132 ± 10[11] |

* Hquin = Quinolin-8-ol, glyOH = glycine.

reorganization energy (*i.e.* the energy associated with the difference in structure of the ligand when bound and free), hence it does not, in itself, give a fair picture of the strength of chemical binding. The question arises as to whether the variations in $D(\mathrm{M{-}L})$ fairly reflect changes in binding energies or are due to variations in reorganization energies. The effect of reorganization energies can, to a first approximation, be eliminated by considering the dissociation enthalpy of the ligand relative to the binding to hydrogen, *i.e.* the difference $D(\mathrm{M{-}L}) - 2\langle D(\mathrm{H{-}L})\rangle$. This value is effective for considering relative binding energies but there is another, and more important, motive for taking this approach: the values of $\langle D(\mathrm{H{-}L})\rangle$ for these ligands are unknown.

Hence, from equations (11) and (12), the difference between the mean metal–ligand dissociation enthalpy and the mean dissociation enthalpy of the ligand–hydrogen bond is given by equation (13) with the following auxiliary data for $\Delta_\mathrm{f}H^\circ_\mathrm{m}$/kJ

$$D(\mathrm{M{-}L}) - 2\langle \mathrm{D(H{-}L)}\rangle = \Delta_\mathrm{f}H^\circ_\mathrm{m}(\mathrm{M, g}) - 2\Delta_\mathrm{f}H^\circ_\mathrm{m}(\mathrm{H, g}) + \Delta_\mathrm{f}H^\circ_\mathrm{m}(\mathrm{H_2L, g}) - \Delta_\mathrm{f}H^\circ_\mathrm{m}(\mathrm{ML, g}) \quad (13)$$

mol$^{-1}$: Cu(g), 337.6 ± 1.2;[32] Ni(g), 429.7 ± 1.2;[32] H(g), 218.00 ± 0.01;[32] H$_2$acacen(g), −359.7 ± 3.2;[28] H$_2$bzacen(g), −104.5 ± 7.3.[28]

Values of $D(\mathrm{M{-}L}) - 2\langle D(\mathrm{H{-}L})\rangle$ for the complexes studied in this paper are given in Table 8. At the moment there are no other thermochemical data for metal complexes in which the ligand is bound through two nitrogen and two oxygen atoms, so comparison of the corresponding metal–ligand bond strengths is not possible. However, in Table 8, we report the values for the energetics of the binding of copper and nickel quinolin-8-olates and glycinates, as $2\langle D(\mathrm{M{-}L})\rangle - 2D(\mathrm{H{-}L})$, where HL represents the bidentate ligand both of which have one oxygen and one nitrogen co-ordinating atoms.

The results in Table 8 confirm other studies[34] which show that for the same metal bound to a similar type of ligand there is a constancy of the values of $D(\mathrm{M{-}L}) - 2\langle D(\mathrm{H{-}L})\rangle$. Indeed, these values for [Cu(acacen)] and for [Cu(bzacen)] are equal, within the uncertainties ascribed to them; the same is also true for [Ni(acacen)] and [Ni(bzacen)]. This constancy demonstrates that, for a particular type of ligand, the effects influencing $D(\mathrm{H{-}L})$ are compensated in $D(\mathrm{M{-}L})$. However, it is not possible to make such comparisons when different types of ligands are involved, as can be seen from the results for the metal quinolin-8-olates and glycinates. From Table 8 it can be seen that the average value of $D(\mathrm{M{-}L}) - 2\langle D(\mathrm{H{-}L})\rangle$ for [Cu(acacen)] and [Cu(bzacen)] is −202.9 ± 7.1 kJ mol$^{-1}$ whereas the average for the corresponding nickel complexes is −21.4 ± 7.1 kJ mol$^{-1}$, a difference of 182 ± 10 kJ mol$^{-1}$. The appropriate comparison with the metal glycinates is of $2\langle D(\mathrm{M{-}L})\rangle - 2D(\mathrm{H{-}L})$ and for copper this value is −39 ± 10 kJ mol$^{-1}$,[10] whereas for Ni it is 132 ± 10 kJ mol$^{-1}$,[11] the difference being 171 ± 15 kJ mol$^{-1}$. A similar comparison for the corresponding quinolin-8-olates[33] is for Cu −150 ± 8 kJ mol$^{-1}$ and for Ni −6 ± 10 kJ ml$^{-1}$, the difference being 144 ± 14 kJ mol$^{-1}$, slightly less but in the same direction. It is apparent that the relative binding energies of the ligands bound through nitrogen and oxygen to copper and nickel follow a similar pattern irrespective of whether the N and O atoms are positioned *cis* or *trans*.

The previous results also show that the binding of the metal quinolin-8-olates and glycinates, which are five-membered ring complexes, is stronger than that of the studied six-membered ring Schiff-base complexes. This can also be due to the effect of the ethylene bridge forcing these complexes to adopt a *cis* planar configuration at the metal which, in some rare cases, can be slightly distorted towards the tetrahedral form. The flexibility in the molecular structure will grow as the number of methylene groups in the N,N′ bridge increases, which will imply a lower steric strain.

The present solution calorimetric investigation represents the first detailed thermochemical contribution to the study of metal–ligand bond enthalpies in bridged Schiff-base complexes. It does not allow the determination of absolute metal–ligand bond-dissociation enthalpies in the MO$_2$N$_2$ system, mainly since the value of $D(\mathrm{H{-}L})$ is not known. If this were to be the case the enthalpy of formation of the ligand radical would allow calculation of the sums $2[\langle D(\mathrm{M{-}O})\rangle + \langle D(\mathrm{M{-}N})\rangle]$, although there is no unambiguous way of apportioning $\langle D(\mathrm{M{-}L})\rangle$ between $\langle D(\mathrm{M{-}O})\rangle$ and $\langle D(\mathrm{M{-}N})\rangle$ and little value in attempting to do so, since these bonds occur together and must interact.

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