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MEAN COPPER–LIGAND BINDING ENTHALPIES IN COPPER(II) COMPLEXES OF DIMETHYLGLYOXIME, GLYCINE, ACETIC ACID AND 4-PHENYLAMINO-3-PENTEN-2-ONE

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ABSTRACT

The standard enthalpies of formation of some crystalline copper(II) complexes were obtained from solution-reaction calorimetric measurements and the enthalpies of sublimation of $Cu_2(acetate)_4$, $Cu(dmg)_2$ and $Cu(PhNacac)_2$ were obtained from torsion–Knudsen vapour pressure measurements. The differences between the mean Cu–ligand and H–ligand dissociation enthalpies were derived and are given below.

Complex [a]	$\Delta_f H_m^{\ominus}$(cr) (kJ mol^{-1})	$\Delta H_m^{\ominus}$(sub) (kJ mol^{-1})	$\bar{D}$(Cu–L) – D(H–L) (kJ mol^{-1})
$Cu_2(acetate)_4$	-1765.8 ± 2.7	106.1 ± 0.9	-67.1 ± 1.8
$Cu(dmg)_2$	-171.5 ± 2.3	93.1 ± 0.8	-63.7 ± 1.8
$Cu(PhNacac)_2$	-174.3 ± 2.7	128.1 ± 0.8	-92.3 ± 3.7
$Cu(gly)_2$	-940.8 ± 1.7	111 ± 15	-26.3 ± 7.7

[a] Hdmg, Dimethylglyoxime; Hgly, glycine; PhNacacH, 4-phenylamino-3-penten-2-one.

INTRODUCTION

For a metal complex ML_n, the mean metal–ligand dissociation enthalpy $\bar{D}$(M–L) is defined as $1/n$ of the enthalpy of disruption

$$ML_n(g) \rightarrow M(g) + nL(g) \tag{1}$$

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and as $D(\text{H–L})$ is the enthalpy of dissociation

$$\text{HL(g)} \rightarrow \text{H(g)} + \text{L(g)} \tag{2}$$

then

$$\bar{D}(\text{M–L}) - D(\text{H–L}) = (1/n)\left[\Delta_f H_m^{\ominus}(\text{M, g}) - \Delta_f H_m^{\ominus}(\text{ML}_n\text{, g})\right] - \Delta_f H_m^{\ominus}(\text{H, g}) + \Delta_f H_m^{\ominus}(\text{HL, g}) \tag{3}$$

The quantities on the right-hand side of eqn. (3) are relatively easy to measure but for most ligands, experimental values for $D(\text{H–L})$ are not available. It has been shown for a series of Cu^{II} β-diketonate complexes that $\bar{D}(\text{Cu–L}) - D(\text{H–L})$ is constant within experimental error [1,2]. Any effect on $\bar{D}(\text{Cu–L})$ caused by altering the ligand structure appears to be counterbalanced by a corresponding change in $D(\text{H–L})$. If the constancy of $\bar{D}(\text{M–L}) - D(\text{H–L})$ is assumed to be of general application, then for a particular metal and ligand of a particular type, if $D(\text{H–L})$ is assumed constant then the derived value of $\bar{D}(\text{M–L})$ will be constant. Constant metal–ligand binding enthalpies derived based on these assumptions have been reported for the β-diketonate complexes of Fe^{III} [3], Mn^{III} [4], Co^{III} [5,6], Cr^{III} [7], Al^{III} [8–11], Be^{II} [9,12], Mn^{II} [13–15], Co^{II} [13,15,16] and Ni^{II} [15,17,18]; hence, in all these cases $\bar{D}(\text{M–L}) - D(\text{H–L})$ will be constant.

In this paper we report the enthalpies of formation of a series of Cu^{II} complexes with ligands of different types. Attention is focussed on $\bar{D}(\text{Cu–L}) - D(\text{H–L})$ because values for $D(\text{H–L})$ in these ligands are not available. This quantity however, gives the difference in the binding enthalpy of the ligand to copper relative to that to hydrogen, and so permits some elucidation of the specificity of the binding of the ligand to the metal.

EXPERIMENTAL

Materials

Bis(dimethylglyoxime)copper(II), Cu(dmg)_2, was prepared as described by Frasson et al. [19]. Dimethylglyoxime in ethanol was reacted with a hot aqueous solution of cupric acetate: the red needles produced were recrystallised from ethanol and dried in vacuo. Bis(glycinato)copper(II), Cu(gly)_2, was prepared by adding an excess of an aqueous solution of glycine to aqueous cupric sulphate: the deep blue precipitate was recrystallised from ethanol and dried in vacuo at 100 °C. Tetrakis(acetato)dicopper(II), $\text{Cu}_2\text{(acetate)}_4$, was prepared by recrystallising a general purpose reagent (Hopkins and Williams) from water followed by drying in vacuo. 4-Phenylamino-3-penten-2-one, PhNacacH, was prepared as described by Roberts and Turner [20]. Aniline plus acetylacetone were boiled under reflux for 2 h, cooled, and then refluxed with water. A benzene extract was dried over

TABLE 1

Mass percentage analyses of complexes

Complex	Expected			Found		
	C	H	N	C	H	N
$Cu(dmg)_2$	32.7	4.8	19.1	33.2	4.7	19.3
$Cu(gly)_2$	22.7	3.8	13.2	22.3	3.9	12.8
$Cu_2(acetate)_4$	26.5	3.3		26.2	3.2	
$Cu(PhNacac)_2$	64.1	5.9	6.8	64.3	6.0	6.7
PhNacacH	75.4	7.5	7.9	75.6	7.5	7.8

anhydrous sodium sulphate and the benzene removed by distillation. The product was then purified by repeated sublimation in vacuo. Bis(4-phenylamino-3-penten-2-onato)-copper(II), $Cu(PhNacac)_2$, was prepared as described by Holtzclaw et al. [21]. A solution of PhNacacH in acetone was added to $Cu_2(acetate)_4$ dissolved in dilute ammonia, sodium hydroxide (0.1 mol dm^{-3}) was added with stirring and the precipitate recrystallised from ethanol to give black rhombic crystals. The microanalysis results for the samples are given in Table 1.

For the remaining compounds, AnalaR materials were used when available, and for salts such as $CuSO_4 \cdot 5H_2O$, analyses were made to establish the exactness of the degree of hydration. When AnalaR materials were not available, laboratory reagent grade samples were recrystallised and dried in vacuo before use.

Solution–reaction calorimetry

Solution–reaction calorimetric measurements were made in Manchester and in Porto. The description, method of use, and the performance testing of these calorimeters have been previously reported for the Manchester calorimeter [22,23] and the Porto calorimeter [6,17]. The general thermochemical reaction for determining the enthalpies of formation of the CuL_2 complexes was

$$\begin{aligned}&CuL_2(cr) + H_2SO_4 \cdot nH_2O(l)\\&\quad = CuSO_4 \cdot 5H_2O(cr) + 2HL(cr/l) + (n-5)H_2O(l) \qquad (4)\end{aligned}$$

The standard enthalpy of this reaction was determined by successively measuring, or calculating from reference data [24], the enthalpy of solution of each reactant or product in the acidic calorimetric solvent, so that the final solution resulting from the dissolution of the reactants was of the same composition as that resulting from the dissolution of the products.

The molar enthalpies of reaction and solution when using $H_2SO_4 \cdot 9.02H_2O(l)$ as the calorimetric solvent are listed in Table 2, where, in

TABLE 2

Molar enthalpies of reaction and solution in $H_2SO_4 \cdot 9.02H_2O(l)$ at 298.15 K

i	Reactant	Solvent	Solution	No. of experiments	$\Delta_i H$ (kJ mol^{-1})
1	$H_2O(l)$	$H_2SO_4 \cdot 9.02H_2O$	A_1	2	-1.14 ± 0.02
2	$CuSO_4 \cdot 5H_2O(cr)$	A_1	A_2	5	34.71 ± 0.48
3	Glycine(cr)	A_2	F_1	5	-0.96 ± 0.04
4	$Cu(gly)_2(cr)$	$H_2SO_4 \cdot 9.02H_2O$	F_1	5	-59.09 ± 0.42
5	Acetic acid (l)	A_2	F_2	5	1.67 ± 0.04
6	$Cu_2(acetate)_4(cr)$	$H_2SO_4 \cdot 9.02H_2O$	F_2	5	-46.74 ± 0.87
7	PhNacacH(cr)	A_2	F_3	5	19.96 ± 0.18
8	$Cu(PhNacac)_2(cr)$	$H_2SO_4 \cdot 9.02H_2O$	F_3	5	-39.34 ± 0.34

accordance with normal thermochemical practice, uncertainties are given as twice the standard deviation of the mean. The thermochemical reactions and corresponding standard enthalpies of reaction derived from the data in Table 2 were

$$\begin{aligned} &Cu(gly)_2(cr) + H_2SO_4 \cdot 9.02H_2O(l) \\ &\quad = CuSO_4 \cdot 5H_2O(cr) + 2Hgly(cr) + 4.02H_2O(l) \end{aligned} \tag{5}$$

$$\begin{aligned} \Delta_r H_m^\ominus(Cu(gly)_2)\ (kJ\ mol^{-1}) &= \Delta_4 H - \Delta_2 H - 2\Delta_3 H - 4.02\Delta_1 H \\ &= -87.30 \pm 0.65 \end{aligned} \tag{6}$$

$$\begin{aligned} &Cu_2(acetate)_4(cr) + 2H_2SO_4 \cdot 9.02H_2O(l) \\ &\quad = CuSO_4 \cdot 5H_2O(cr) + 4Hacetate(l) + 8.04H_2O(l) \end{aligned} \tag{7}$$

$$\begin{aligned} \Delta_r H_m^\ominus(Cu_2(acetate)_4)\ (kJ\ mol^{-1}) &= \Delta_6 H - 2\Delta_2 H - 4\Delta_5 H - 8.04\Delta_1 H \\ &= -113.67 \pm 1.32 \end{aligned} \tag{8}$$

$$\begin{aligned} &Cu(PhNacac)_2(cr) + H_2SO_4 \cdot 9.02H_2O(l) \\ &\quad = CuSO_4 \cdot 5H_2O(cr) + 2PhNacacH(cr) + 4.02H_2O(l) \end{aligned} \tag{9}$$

$$\begin{aligned} \Delta_r H_m^\ominus(Cu(PhNacac)_2)\ (kJ\ mol^{-1}) &= \Delta_8 H - \Delta_2 H - 2\Delta_7 H - 4.02\Delta_1 H \\ &= -109.39 \pm 0.69(A) \end{aligned} \tag{10}$$

A satisfactory rate of hydrolysis of $Cu(dmg)_2$ required an acidic water + methanol mixture as the initial calorimetric solvent; the relevant molar enthalpies of reaction and solution are listed in Table 3. The thermochemical reaction and standard enthalpy of reaction derived from the data in Table 3 were

$$Cu(dmg)_2(cr) + H_2SO_4 \cdot 5H_2O(l) = CuSO_4 \cdot 5H_2O(cr) + 2Hdmg(cr) \tag{11}$$

$$\begin{aligned} \Delta_r H_m^\ominus(Cu(dmg)_2)(kJ\ mol^{-1}) &= \Delta_9 H + \Delta_{10} H - 2\Delta_{11} H - \Delta_{12} H \\ &= -105.38 \pm 0.77 \end{aligned} \tag{12}$$

TABLE 3

Molar enthalpies of reaction and solution in an initial calorimetric solvent of H_2SO_4 (3 mol dm^{-3}) + methanol, 30/70 by volume, at 298.15 K

i	Reactant	Solvent	Solution	No. of experiments	$\Delta_i H$ (kJ mol^{-1})
9	$H_2SO_4 \cdot 5H_2O(l)$	Initial	A_3	5	-13.90 ± 0.50
10	$Cu(dmg)_2(cr)$	A_3	F_4	4	-2.03 ± 0.16
11	Hdmg(cr)	Initial	A_4	5	30.33 ± 0.26
12	$CuSO_4 \cdot 5H_2O(cr)$	A_4	F_4	5	28.79 ± 0.23

$Cu(PhNacac)_2$ was measured independently in the Porto calorimeter with an acidic water + dioxan mixture as the initial calorimetric solvent; the molar enthalpies of reaction and solution are listed in Table 4. The thermochemical reaction and standard enthalpy of reaction derived from the data in Table 4 were

$$\mathrm{Cu(PhNacac)_2(cr)} + \mathrm{H_2SO_4 \cdot 53.54H_2O(l)} = \mathrm{CuSO_4 \cdot 5H_2O(cr)} + \mathrm{2PhNacacH(cr)} + \mathrm{48.54H_2O(l)} \tag{13}$$

$$\begin{aligned}\Delta_r H_m^{\ominus}(\mathrm{Cu(PhNacac)_2})\ (\mathrm{kJ\ mol^{-1}}) &= \Delta_{16}H + \Delta_{17}H - \Delta_{14}H - 2\Delta_{15}H - 48.54\Delta_{13}H \\ &= 100.99 \pm 1.25(B)\end{aligned} \tag{14}$$

The standard enthalpies of formation of the complexes in the crystalline state were derived, and are listed in Table 5, from the enthalpies of the thermochemical reactions and the following auxiliary data for $\Delta_f H_m^{\ominus}$ (kJ mol^{-1}):

H_2SO_4 in $5H_2O(l)$, -871.48 ± 0.40 [24];
H_2SO_4 in $9.02H_2O(l)$, -879.43 ± 0.40 [24];
H_2SO_4 in $53.54H_2O(l)$, -886.85 ± 0.40 [24];
$CuSO_4 \cdot 5H_2O(cr)$, -2279.7 ± 1.1 [24]; $H_2O(l)$, -285.83 ± 0.04 [24];
$CH_3CO_2H(l)$, -484.3 ± 0.2 [25]; glycine(cr), -528.5 ± 0.5 [25];
PhNacacH(cr), -156.1 ± 1.8 [26]; and Hdmg(cr), -148.9 ± 0.8 [27].

TABLE 4

Molar enthalpies of reaction and solution in an initial calorimetric solvent of HCl(4.322 mol dm^{-3}) + dioxane, 25/75 by volume, at 298.15 K

i	Reactant	Solvent	Solution	No. of experiments	$\Delta_i H$ (kJ mol^{-1})
13	$H_2O(l)$	Initial	A_5	5	-0.98 ± 0.02
14	$CuSO_4 \cdot 5H_2O(cr)$	A_5	A_6	5	47.40 ± 0.59
15	PhNacacH(cr)	A_6	F_5	5	28.49 ± 0.08
16	$H_2SO_4 \cdot 53.54H_2O(l)$	Initial	A_7	5	-53.97 ± 0.50
17	$Cu(PhNacac)_2(cr)$	A_7	F_5	5	9.79 ± 0.08

TABLE 5

Derived molar values at 298.15 K

Complex	$\Delta_f H_m^{\ominus}$(cr) (kJ mol^{-1})	$\Delta_{sub} H_m^{\ominus}$ (kJ mol^{-1})	$\Delta_f H_m^{\ominus}$(g) (kJ mol^{-1})	$\Delta_f H_m^{\ominus}$(HL, g) (kJ mol^{-1})	$\bar{D}$(Cu–L) − D(H–L) (kJ mol^{-1})
$Cu_2(acetate)_4$	−1765.8 ± 2.7	106.1 ± 0.9	−1659.7 ± 2.8	−432.8 ± 1.5 [25]	−67.1 ± 1.8
$Cu(dmg)_2$	−171.5 ± 2.3	93.1 ± 0.8	−78.4 ± 2.4	−53.7 ± 1.3 [27]	−63.7 ± 1.9
$Cu(PhNacac)_2$	−174.3 ± 2.7	128.1 ± 0.8	−46.2 ± 2.8	−66.2 ± 3.0 [26]	−92.3 ± 3.4
$Cu(gly)_2$	−940.8 ± 1.7	111 ± 15 [41]	−830 ± 15	−392.1 ± 0.6 [25]	−26.3 ± 7.7
$Cu(acac)_2$	−809.9 ± 1.3 [1]	109.9 ± 3.4 [1]	−700.0 ± 3.8	−384.4 ± 1.3 [42]	−83.6 ± 2.4
$Cu(BZAC)_2$	−591.4 ± 5.8 [43]	159.6 ± 2.0	−431.8 ± 6.1	−251.3 ± 2.9 [25]	−84.6 ± 4.2
$Cu(TROP)_2$	−414.8 ± 1.8 [44]	167 ± 21	−248 ± 21	−155.6 ± 1.2 [25]	−80.8 ± 10.6
$Cu(ox)_2$	−107.7 ± 2.9 [23]	170 ± 3 [41]	62 ± 4	6.5 ± 1.7 [45]	−44 ± 3

For Cu(PhNacac)$_2$(cr), $\Delta_f H_m^\ominus$(kJ mol^{-1}) derived from $\Delta_r H_m^\ominus$(A) was -173.9 ± 3.8, and from $\Delta_r H_m^\ominus$(B), -174.9 ± 4.0; Table 5 lists the weighted mean value. $\Delta_f^\ominus H_m$(Cu$_2$(acetate)$_4$, cr) was previously reported by Thomsen in 1983 [28] to be -1763.1 kJ mol^{-1}, in agreement with the value reported here: the NBS tables [24] give -1786.6 kJ mol^{-1}, in marked disagreement. A series of Cu^{II} amino acid complexes have been studied by Ribeiro da Silva et al. [29]: for Cu(gly)$_2$(cr) they obtained -943.7 ± 1.6 kJ mol^{-1}, agreeing with the value reported here but, again, in disagreement with the NBS tables which gives α as -938.5 and β as -932.6 kJ mol^{-1}. The sources of the NBS values are not given and no conclusion can be made about these discrepancies.

Enthalpies of sublimation

The enthalpies of sublimation of Cu$_2$(acetate)$_4$, Cu(dmg)$_2$ and Cu(PhNacac)$_2$ were derived from measurements of vapour pressure as functions of temperature. The vapour pressures were measured using the Leeds combined mass-loss and torsion–Knudsen effusion apparatus [30]. The effusion cell was suspended in a metal vacuum chamber (1.3×10^{-5} Pa) by a tungsten wire (diameter 0.0025 cm) from an automatic microbalance (Sartorius Model 4104) which continuously recorded the mass loss from the cell throughout the experiment. The deflection of the cell was determined using a beam of light reflected from a mirror attached to the suspension; the deflection was continuously recorded by a light-spot follower (Photodyne, Sefram, Paris Ltd.). The effusion cell was heated in a thermostatically controlled furnace and the temperature was determined by measuring with thermistors the temperature of a dummy cell also mounted within the furnace.

For each complex, two series of measurements were made using cells with effusion hole diameters of 200 μm and 400 μm. Because of the small area of the effusion holes, the low vapour pressures were derived using the Knudsen equation

$$p = (\mathrm{d}W/\mathrm{d}t)(1/K_c A)(2\pi RT/M)^{1/2} \qquad (15)$$

where $\mathrm{d}W/\mathrm{d}t$ is the rate of mass loss, K_c is the Clausing factor, A is the hole area and M is the molar mass of the effusing species. Pressures were also derived from the angle of torsion deflection ϕ by

$$p = D\phi/f\lambda A \qquad (16)$$

where D is the torsional constant of the wire, f is the recoil force correction factor, A is the hole area and λ is the distance of the holes from the suspension. Close agreement between the pressures derived from the rate of mass loss and the angular deflection of the cell demonstrates the correctness of the molar mass assumed for the effusing species.

TABLE 6

Enthalpies of sublimation of benzoic acid and of 4-nitroaniline at 298.15 K

Benzoic acid			4-Nitroaniline		
Ref.	Method	$\Delta_{\text{sub}}H_{\text{m}}^{\ominus}$ (kJ mol^{-1})	Ref.	Method	$\Delta_{\text{sub}}H_{\text{m}}^{\ominus}$ (kJ mol^{-1})
Morawetz [32]	Calorimetry	89.5 ±0.2	Malaspina et al. [37]	Calorimetry	101.67±0.70
Malaspina et al. [33]	Calorimetry	89.26±0.40	Ferro and Piacente [38]	Torsion	105.2 ±3.7
Colomina et al. [34]	Knudsen	90.60±0.20	Malaspina et al. [37]	Knudsen	100.9 ±0.6
de Kruif and Block [35]	Knudsen	92.1 ±0.3	Franklin [39]	Knudsen	100.4 ±2.1
de Kruif [36]	Torsion	90.4 ±1.0	This work	Knudsen	101.4 ±1.3
This work	Knudsen	90.35±1.27	This work	Torsion	101.5 ±1.7
This work	Torsion	91.07±0.91			

Enthalpies of sublimation were derived at the mean temperature of the experiment by applying the Clausius–Clapeyron equation

$$\mathrm{d}\ln p/\mathrm{d}(1/T) = -\Delta_{\text{sub}}H_{\text{m}}^{\ominus}/R \tag{17}$$

to the linear plot of ln p versus T^{-1}. Values were corrected to 298.15 K using either $\{C_p(\text{g}) - C_p(\text{cr})\}$ when values for these heat capacities were available, or by assuming this heat capacity difference to be $-2R$ [31].

TABLE 7

Vapour pressure of $Cu_2(\text{acetate})_4$ with cells having 200 μm effusion holes

Mass loss [a]				Torsion [b]	
T (K)	10^3K (T)	$\mathrm{d}W/\mathrm{d}t \times 10^{11}$ (kg s^{-1})	p (Pa)	Φ (deg)	p (Pa)
321.84	3.107	0.3095	0.0113	0.0052	0.0138
323.37	3.092	0.4233	0.0155	0.0084	0.0220
325.96	3.068	0.4726	0.0173	0.0084	0.0220
329.18	3.038	0.6785	0.0250	0.0125	0.0331
333.74	2.996	1.1769	0.0437	0.0209	0.0551
338.13	2.957	1.8351	0.0686	0.0418	0.1102
343.40	2.912	3.2137	0.1210	0.0627	0.1654
348.08	2.873	5.2249	0.1981	0.1044	0.2757
351.56	2.844	8.1034	0.3088	0.1567	0.4135
355.81	2.810	12.6698	0.4857	0.2403	0.6342
359.64	2.781	18.9622	0.7308	0.3553	0.9378

[a] $p = 2.0323 \times 10^3 (\mathrm{d}W/\mathrm{d}t)\, T^{1/2}$.

[b] $p = 26394\Phi$.

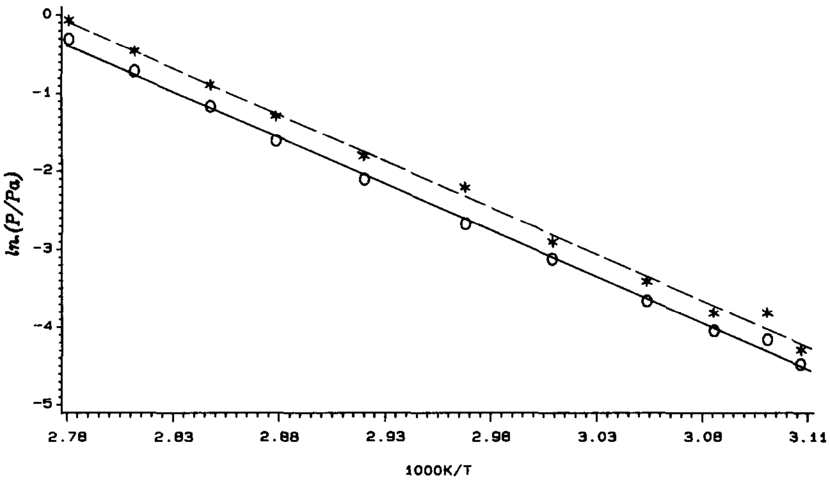

Fig. 1. Vapour pressure of cupric acetate: ○, mass loss; *, torsion.

Tests of the apparatus and technique were made by measuring the enthalpies of sublimation of benzoic acid and of 4-nitroaniline: comparison of the values obtained with some of the most recently reported reliable values is made in Table 6.

The vapour pressure measurements on $Cu_2(acetate)_4$ using the cell with 200 μm effusion holes are given as a typical example in Table 7. The results are expressed as

$$\ln p\ (\mathrm{Pa}) = A - B/T \qquad (18)$$

and the values of A and B, derived by least-squares analysis of the vapour pressure data, are given in Table 8. Curves of ln p versus T^{-1} are shown for $Cu_2(acetate)_4$ (Fig. 1), $Cu(dmg)_2$ (Fig. 2) and $Cu(PhNacac)_2$ (Fig. 3). The enthalpies of sublimation derived from the measurements using cells of different effusion hole diameters are listed in Table 9. The weighted mean values together with the standard entropy and standard Gibbs energy of sublimation at 298.15 K are given in Table 10.

DISCUSSION

By applying eqn. (3), the difference between the mean copper–ligand dissociation enthalpy and the dissociation enthalpy of the ligand–hydrogen bond is given by

$$\{\bar{D}(\mathrm{Cu{-}L}) - D(\mathrm{H{-}L})\} = 0.5\{\Delta_f H_m^\ominus(\mathrm{Cu, g}) - \Delta_f H_m^\ominus(\mathrm{CuL_2, g})\} - \Delta_f H_m^\ominus(\mathrm{H, g}) + \Delta_f H_m^\ominus(\mathrm{HL, g}) \qquad (19)$$

TABLE 8

Vapour pressure equations: $\ln p$ (Pa) $= A - B/T$

Complex		200 μm cell			400 μm cell		
		Mean T (K)	A	$-B$	Mean T (K)	A	$-B$
$Cu_2(acetate)_4$	ML	339.16	34.634 ± 0.577	12569 ± 195	338.05	33.969 ± 0.700	12420 ± 251
	DF	339.16	35.131 ± 0.789	12666 ± 267	338.05	35.794 ± 0.528	12911 ± 180
$Cu(dmg)_2$	ML	337.12	30.534 ± 0.428	11162 ± 144	341.00	29.615 ± 0.622	10919 ± 211
	DF	343.90	31.032 ± 0.913	11218 ± 313	340.12	31.167 ± 0.657	11179 ± 223
$Cu(PhNacac)_2$	ML	351.09	40.722 ± 0.615	15097 ± 216	347.42	41.065 ± 0.602	15316 ± 209
	DF	353.33	41.641 ± 0.437	15338 ± 154	348.09	42.499 ± 0.902	15596 ± 313

ML, Knudsen mass loss; DF, torsion deflection.

TABLE 9

Results for enthalpies of sublimation at 298.5 K in kJ mol^{-1}

Complex	Knudsen		Torsion	
Hole diameter =	200 μm	400 μm	200 μm	400 μm
$Cu_2(acetate)_4$	105.2 ± 1.6	103.9 ± 2.1	106.0 ± 2.2	108.0 ± 1.5
$Cu(dmg)_2$	93.5 ± 1.2	91.5 ± 1.8	94.0 ± 2.6	93.6 ± 1.9
$Cu(PhNacac)_2$	126.4 ± 1.8	128.2 ± 1.7	128.4 ± 1.3	130.5 ± 2.6

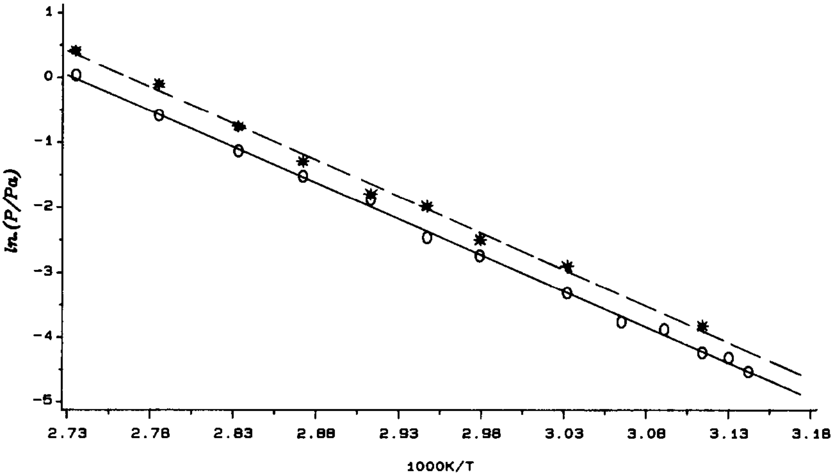

Fig. 2. Vapour pressure of copper bis(dimethylglyoxinate): o, mass loss; *, torsion.

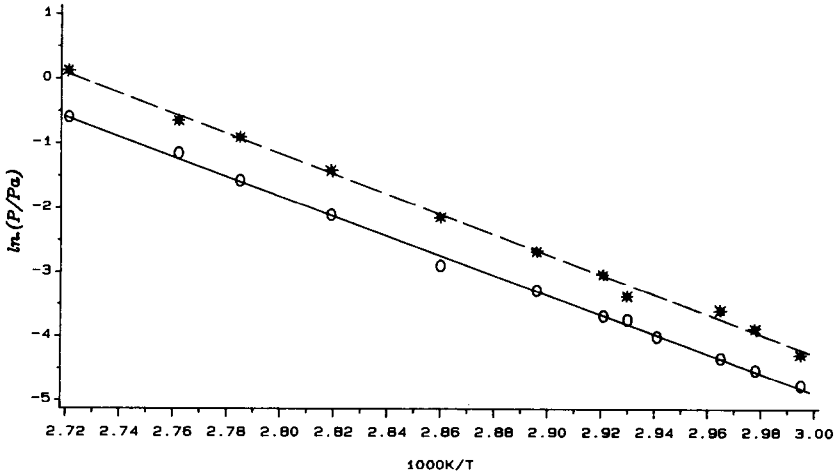

Fig. 3. Vapour pressure of bis(4-phenyl-amino-3-penten-2-onato)copper(II): o, mass loss; *, torsion.

TABLE 10

Thermodynamic quantities for sublimation at 298.15 K

Complex	$\Delta_{\text{sub}}H_{\text{m}}^{\ominus}$ (kJ mol^{-1})	$\Delta_{\text{sub}}S_{\text{m}}^{\ominus}$ (J K^{-1} mol^{-1})	$\Delta_{\text{sub}}G_{\text{m}}^{\ominus}$ (kJ mol^{-1})
Cu_2(acetate)$_4$	106.1 ± 0.9	200.0 ± 0.6	46.5 ± 1.0
Cu(dmg)$_2$	93.1 ± 0.8	157.7 ± 1.5	46.1 ± 0.9
Cu(PhNacac)$_2$	128.1 ± 0.8	248.2 ± 1.7	54.1 ± 1.0

with $\Delta_f H_m^{\ominus}$(Cu, g) (kJ mol^{-1}) = 337.6 ± 1.2 and $\Delta_f H_m^{\ominus}$(H, g) (kJ mol^{-1}) = 218.00 ± 0.01 [40]. Values of $\bar{D}$(Cu–L) – D(H–L) for the complexes studied in this paper, together with values for some other CuL_2 complexes, are given in Table 5.

In effect, $\bar{D}$(Cu–L) – D(H–L) is a measure of the enthalpy of transfer of the ligand from Cu to H, and in the event that the ligand structure is unchanged, it provides a direct measure of the difference in binding enthalpies. For those cases where the ligand binding is through oxygen atoms, Cu(acac)$_2$, Cu(BZAC)$_2$, Cu(TROP)$_2$ and Cu_2(acetate)$_4$, the latter shows the greatest increase in the relative binding enthalpy for the ligand bound to Cu. The existence of a (Cu–Cu) bond in Cu_2(acetate)$_4$ is controversial. With the estimated D(O–H)-(acetylacetone, enol) = 400 ± 20 kJ mol^{-1} [1] and D(O–H)-(acetic acid) = 433 ± 10 kJ mol^{-1} [46], then $\bar{D}$(Cu–O) in Cu(acac)$_2$ = 158 ± 10 kJ mol^{-1} and, making the assumption that there is no (Cu–Cu) bond in Cu_2(acetate)$_4$, $\bar{D}$(Cu–O) in Cu_2(acetate)$_4$ = 183 ± 5 kJ mol^{-1}. From the data presented by Cavell et al. [47], in Mo(acac)$_3$, $\bar{D}$(Mo–O) = 209 ± 10 kJ mol^{-1}, and in Mo_2(acetate)$_4$, after allowance for the energy of the (Mo–Mo) bond, $\bar{D}$(Mo–O) = 242 ± 10 kJ mol^{-1}. Moreover for the corresponding chromium compounds [48], $\bar{D}(\text{Cr–O})_{\text{acetate}} - \bar{D}(\text{Cr–O})_{\text{acac}}$ = 33 ± 15 kJ mol^{-1}. Hence the difference, $\bar{D}(\text{Cu–O})_{\text{acetate}} - \bar{D}(\text{Cu–O})_{\text{acac}}$ = 25 ± 15 kJ mol^{-1} appears to be reasonable. Whilst thermochemistry cannot provide an answer to the question of the existence of this (Cu–Cu) bond, it does suggest that if such a bond is postulated, it will be energetically very weak.

The relative binding enthalpy in Cu(dmg)$_2$ is greater than that for Cu(acac)$_2$ and this is expected because the crystal structure [19] shows the presence of two intramolecular hydrogen bonds of 2.53 Å and 2.70 Å between the two dmg ligands attached to Cu. Moreover, in Cu(dmg)$_2$ the ligand is bound to Cu through N atoms, i.e. there are (Cu–N) bonds which appear to be stronger than (Cu–O) bonds, whereas the hydrogen in the free ligand is bound to oxygen. The weakening observed for Cu(PhNacac)$_2$ is expected because of the steric hindrance between the two bulky attached ligands. The relative binding enthalpy increase in Cu(ox)$_2$ compared with Cu(acac)$_2$ is in line with that observed for a series of M(ox)$_2$ complexes [23].

The relative binding enthalpy increase for $Cu(gly)_2$ over that for $Cu(acac)_2$ is surprisingly large especially in view of the fact that the ligand is attached to Cu in a 5-membered ring whereas the other complexes contain 6-membered rings. Part of the increase may be because the (Cu–O) bond arises from an acetate group and also because the force constants [49], $\nu_{Cu-N} = 439$ cm^{-1} and $\nu_{Cu-O} = 360$ cm^{-1}, show that the (Cu–N) bond appears to be stronger than the (Cu–O). Further studies on other amino acid complexes of Cu^{II} and of other metals would be desirable to provide an explanation as to why aminoacids in particular should be bound so strongly to metals.

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