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THERMOCHEMISTRY OF GASEOUS TRANSITION METAL COMPLEXES OF GROUP V AND VI LIGANDS

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CONTENTS

A. INTRODUCTION

Transition metal complexes, in which the metal is bonded to ligand atoms of Groups V and VI, are of great importance in certain biological processes. One thinks readily of haemoglobin, where Fe–N bonds hold the iron atom in and above the nitrogen atoms of the porphyrin ring; of nitrogenase, the enzyme involved in nitrogen fixation in plants, where Mo–S–Fe bonds are found; and of DNA polymerase, the function of which in the replication of DNA molecules depends on the formation of Zn–O bonds. In therapy, where transition metals are involved, cure depends on the formation of metal–ligand bonds. Thus, the use of certain platinum compounds in anti-tumour therapy results from the formation of Pt–N and Pt–O bonds

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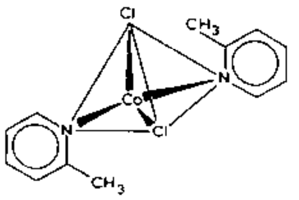
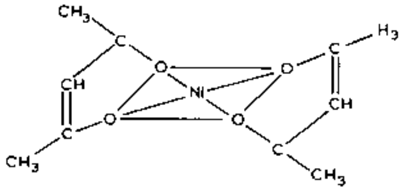
between platinum and the bases cytosine and adenine. Removal of excess copper in the treatment of Wilson's disease is achieved efficiently by use of glycylglycylhistidine *N*-methylamide, to which copper coordinates through both Cu–N and Cu–O bonding. For a better understanding of processes of this type, we need more information about the strengths of bonds between metals and these Group V and VI atoms.

Few thermochemical data have been reported for these complexes, and even for simpler model systems, such as the amino-acid complexes of transition metals, the available information refers mainly to reactions in solution. Reviews of these data are available [1,2]. However, without values for the enthalpies of formation of the gaseous complexes, it is not possible to calculate metal–ligand bond dissociation energies. The purpose of this review is to draw together data on complexes for which we have values for ΔH_f^0(complex, cryst.) and a measured, or reliably estimated value for ΔH(sublimation) so that mean bond dissociation energies of metal–ligand bonds can be calculated.

The structure of the two complexes $Co(2Mepy)_2Cl_2$, where 2Mepy is the 2-methylpyridine molecule, and $Ni(pd)_2$, where pd is the pentanedionato radical, are shown. The enthalpies of the gas-phase dissociation reactions (1) and (2) are measures of the strengths of the metal–ligand mean bond dissociation energies in these particular complexes and we write





$$2\,\overline{D}(\mathrm{Co{-}N}) = \Delta H(1), \text{ and } 4\,\overline{D}(\mathrm{Ni{-}O}) = \Delta H(2)$$

$$\mathrm{Co(2Mepy)_2Cl_2(g)} \rightarrow \mathrm{CoCl_2(g)} + 2\ \mathrm{(2Mepy)(g)} \qquad (1)$$

$$\mathrm{Ni(pd)_2(g)} \rightarrow \mathrm{Ni(g)} + 2\ \mathrm{pd(g)} \qquad (2)$$

In general, the mean bond dissociation energies, $\overline{D}$(M–L), can be derived from the enthalpy, ΔH, of a gas-phase dissociation reaction

$$\mathrm{ML}_n\mathrm{X}_m(\mathrm{g}) \rightarrow \mathrm{MX}_m(\mathrm{g}) + n\ \mathrm{L(g)}$$

and can be calculated from the relationship

$$n\,\overline{D}(\mathrm{M{-}L}) = \Delta H = \Delta H_f^0(\mathrm{MX}_m,\mathrm{g}) + n\,\Delta H_f^0(\mathrm{L},\mathrm{g}) - \Delta H_f^0(\mathrm{ML}_n\mathrm{X}_m,\mathrm{g})$$

Values for $\Delta H_f^0(\mathrm{MX}_m, \mathrm{g})$ and $\Delta H_f^0(\mathrm{L}, \mathrm{g})$ are often available, so that it is necessary only to obtain $\Delta H_f^0(\mathrm{ML}_n\mathrm{X}_m, \mathrm{g})$. Since the majority of these complexes are solid, two separate experiments are carried out, determination of: (i) the enthalpy of formation of the crystalline complex, $\Delta H_f^0(ML_nX_m, c)$; and (ii) the enthalpy of sublimation, $\Delta H_{sub}(ML_nX_m)$. In some cases it is possible to avoid determination of $\Delta H_f^0(ML_nX_m, c)$, for example in a direct measurement of the enthalpy of the following thermal decomposition reaction.

$$Co(2Mepy)_2Cl_2(c) \rightarrow CoCl_2(c) + 2\ (2Mepy)(g) \qquad (3)$$

In this case the only additional datum needed to obtain $\overline{D}(Co{-}N)$ is $\Delta H_{sub}(Co(2Mepy)_2Cl_2)$ since the value for $\Delta H_{sub}(CoCl_2)$ is known. In the sections which follow, we summarise the calorimetric measurements which have been made on crystalline transition metal complexes, list the enthalpies of sublimation, measured or estimated, and provide values for the mean metal–ligand bond dissociation energies.

B. ML_nX_2 COMPLEXES, WHERE L IS A LIGAND MOLECULE

(i) Differential scanning calorimetry

This technique is especially suited to measurement of the enthalpies, ΔH_d, of thermal decomposition reactions of the type shown in the lower line of the enthalpy cycle. On raising the temperature, the crystalline

$$\begin{tikzcd}
ML_2X_2(g) \arrow[r, "\Delta H_g"] & MX_2(g) + 2\,L(g) \\
ML_2X_2(c) \arrow[u, "\Delta H_{sub}(ML_2X_2)"] \arrow[r, "\Delta H_d"] & MX_2(c) + 2\,L(g) \arrow[u, "\Delta H_{sub}(MX_2)"']
\end{tikzcd}$$

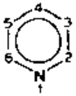
complex dissociates to crystalline MX_2, generally a metal halide, and gaseous ligand L. A number of transition metal complexes have been studied by use of this technique. Those shown in Tables 1 and 2 have been selected because values of $\Delta H_{sub}(ML_2X_2)$ are also known. Since values for $\Delta H_{sub}(MX_2)$ are also available (Appendix 3) the enthalpy, ΔH_g, of the gas-phase dissociation reaction, the upper line of the cycle, can be derived and values for $\overline{D}(M{-}L)$ calculated. It is important to note that the ΔH_d values refer to temperatures well above 298 K. Where heat capacity data for ML_2X_2, MX_2 and L are known, it is possible to refer the ΔH_d value to 298 K. There is some difficulty in obtaining heat capacity data for the complexes ML_2X_2 up to the appropriate temperatures because of the onset of decomposition. The values quoted for $\Delta H_{sub}(ML_2X_2)$ refer to temperatures between 298 K and the decomposition temperature.

TABLE 1

Enthalpies of decomposition of methyl- and halogen-substituted pyridine complexes (kJ mol^{-1})

Complex	ΔH_d [b]	Temp. (K)	Ref.	ΔH_{sub}	Temp. (K)	Ref.	ΔH_g [c]	$\bar{D}$(M–N)
$Co(py)_2Cl_2$ [a]	119.7 ± 2.1	510	3	(100 ± 10) [d]			254 ± 12	127 ± 6
$Co(py)_2Br_2$	114.2 ± 1.7	520	3	(87 ± 4) [d]			249.2 ± 6	124.6 ± 3
$Co(2Mepy)_2Cl_2$	109.6 ± 2.1	520	3	86.6 ± 3.8	347	4	257.0 ± 6	128.5 ± 3
$Co(2Mepy)_2Br_2$	88.7 ± 3.8	500	3	69.5 ± 2.9	363	4	241.2 ± 6	120.6 ± 3
$Co(2Clpy)_2Cl_2$	115.1 ± 1.3	480	4	101.2 ± 6.7	352	4	247.9 ± 8	124.0 ± 4
$Co(2Brpy)_2Cl_2$	126.4 ± 1.3	495	4	120.5 ± 4.6	363	4	240.0 ± 6	120.0 ± 3
$Co(2Brpy)_2Br_2$	129.3 ± 1.7	510	4	100.8 ± 2.1	365	4	250.5 ± 4	125.3 ± 2
$Co(3Clpy)_2Cl_2$	134.7 ± 2.5	540	4	95.8 ± 3.3	375	4	272.9 ± 6	136.5 ± 3
$Co(3Brpy)_2Cl_2$	134.3 ± 1.3	560	4	77.0 ± 4.2	365	4	291.3 ± 6	145.7 ± 3
$Ni(3Clpy)_2Cl_2$	142.2 ± 2.5	560	5	72.0 ± 7.1	370	5	316.2 ± 10	158.1 ± 5
$Ni(3Brpy)_2Cl_2$	147.3 ± 2.1	575	5	76.1 ± 5.0	390	5	317.2 ± 8	158.6 ± 4
$Cu(3Brpy)_2Cl_2$	146.4 ± 1.7	560	5	56.9 ± 5.4	375	5	283.5 ± 6	141.8 ± 3

(py) pyridine



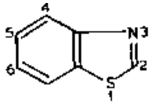
[a] Blue tetrahedral form of $Co(py)_2Cl_2$. [b] $ML_2X_2(c) \rightarrow MX_2(c) + 2\ L(g)$. [c] $ML_2X_2(g) \rightarrow MX_2(g) + 2\ L(g)$. [d] Values in parentheses estimated.

TABLE 2

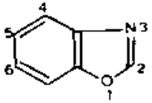
Enthalpies of decomposition of benzothiazole [6] and benzoxazole [7] complexes (kJ mol^{-1})

Complex [a]	ΔH_d [b]	Temp. (K)	ΔH_{sub} [d]	Temp. (K)	ΔH_g [c]	$\bar{D}$(M–N)	$\bar{D}$(M–O)
$Co(bt)_2Br_2$	160.2 ± 1.7	550	124.2 ± 4.2	390	258.2 ± 6	129.1 ± 3	
$Co(2Mebt)_2Cl_2$	167.8 ± 2.5	500	122.6 ± 1.3	344	279.2 ± 4	139.6 ± 2	
$Co(2Mebt)_2Br_2$	161.1 ± 1.7	525	113.8 ± 4.2	345	269.3 ± 6	134.7 ± 3	
$Co(2Mebo)_2Cl_2$	146.9 ± 1.2	520	92.4 ± 2.5	338	288.5 ± 4		144.3 ± 2
$Co(2Mebo)_2Br_2$	160.2 ± 3.3	540	111.3 ± 4.2	355	270.9 ± 8		135.5 ± 4
$Co(2,5diMebo)_2Cl_2$	156.6 ± 2.1	515	95.4 ± 4.6	338	295.1 ± 6		147.5 ± 3
$Co(2,5\text{-}diMebo)_2Br_2$	138.9 ± 2.9	530	104.6 ± 5.8	335	256.3 ± 8		128.2 ± 4

[a] (bt) benzothiazole



(bo) benzoxazole



[b] $ML_2X_2(c) \rightarrow ML_2(c) + 2\ L(g)$. [c] $ML_2X_2(g) \rightarrow ML_2(g) + 2\ L(g)$.

Using this approach it is clearly not necessary, when deriving values for $\bar{D}$(M–L), to obtain a value for the enthalpy of formation of the crystalline complex, although this could be obtained from the relationship

$$\Delta H_f^0(ML_2X_2, c) = \Delta H_f^0(MX_2, c) + \Delta H_f^0(L, g) - \Delta H_d$$

This has not been done because (a) there are insufficient data to refer values of ΔH_d and ΔH_{sub} to 298 K and (b) of the ligands listed, only the enthalpy of formation of pyridine is available from the literature.

For the pyridine and 2-substituted pyridine complexes, the $\bar{D}$(Co–N) values lie in the range 120 to 128 kJ mol^{-1}. With benzothiazoles as ligands the values are in the range 129–139 kJ mol^{-1}. Substitution in the 3-position of pyridine increases the values of $\bar{D}$(Co–N) by about 20 kJ mol^{-1} to the range 137–146 kJ mol^{-1}.

This has been explained [8] in electronic terms. The electronic withdrawing Cl atom in the 3-position reduces electron density on the pyridine ring, thus strengthening the Co → py π-bonding to a greater extent than the py → Co σ-bond is weakened.

For the series of complexes $M(3Clpy)_2Cl_2$, the $\bar{D}$(M–N) values are Co = 136 ± 3, with an increase to Ni = 158 ± 5 and a decrease to Cu = 142 ± 3 kJ mol^{-1}. Values of $\bar{D}$(Co–O) in the benzoxazole complexes, 128–148 kJ mol^{-1}, are very similar to the values of $\bar{D}$(Co–N) noted previously. To equate these bond dissociation energies with the strength of the Co–O and Co–N bonds in the complexes CoL_2X_2 is to assume that the strengths of the Co–X bonds are the same in CoL_2X_2 and CoX_2.

Table 3 shows the enthalpies of decomposition reactions of the cobalt and nickel complexes $M(py)_2X_2$, where X = Cl, Br, I

$$M(py)_2X_2(c) \rightarrow MX_2(c) + 2\,py(g) \qquad (4)$$

Data which have been obtained by differential scanning calorimetry refer to temperatures in the region 495–535 K, whilst those at 298 K have been calculated from enthalpies of formation of the complexes, which have been obtained by solution calorimetry, to be described in the next section. In each case, the values at 298 K are greater than those at the higher temperatures by some 40–60 kJ mol^{-1}. The $\bar{D}$(Ni–N) values which could be calculated from these enthalpies would be between 20 and 30 kJ mol^{-1} greater at 298 K than at ca. 500 K. This probably a real difference which could be confirmed by a temperature correction of ΔH_d.

(ii) Solution calorimetry

An alternative to measuring the enthalpy of the dissociation of a complex ML_nX_2 is to determine the enthalpy of the reaction in which it forms from

TABLE 3

Enthalpies of the reaction $M(py)_2X_2(c) \rightarrow MX_2(c) + 2\ py(g)$ (kJ mol^{-1})

Complex	ΔH_d	Temp. (K)	Ref.	ΔH_d(298 K)	Ref.	ΔH_d(298 K)− ΔH_d(ca. 500 K)
$Ni(py)_2Cl_2$	136.4 ± 2.1	500	9	198.7 ± 0.2	10	62.3
$Ni(py)_2Br_2$	139.3 ± 2.1	535	9	194.1 ± 0.2	10	54.8
$Ni(py)_2I_2$	132.2 ± 3.5	495	9	173.2 ± 0.2	10	41.0
$Co(py)_2Cl_2$ [a]	132.2 ± 2.1	510	3	189.5 ± 0.2	11	57.3
				188.7 ± 0.2	12	56.5

[a] Violet octahedral form of $Co(py)_2Cl_2$.

TABLE 4

Enthalpies of formation of thiourea complexes [13] (kJ mol^{-1})

$M(tu)_4Cl_2$ [a]	ΔH_R [b]	ΔH_f^0(complex, c)	ΔH_{sub}(complex)	Temp. (K)	ΔH_g [c]	$\bar{D}$(M–S)
$Mn(tu)_4Cl_2$	$-(31.4 \pm 0.4)$	$-(865.9 \pm 1.0)$	133.1	390	−490.7	122.7
$Fe(tu)_4Cl_2$	$-(46.0 \pm 0.8)$	$-(741.0 \pm 1.3)$	109.6	385	−504.5	126.1
$Co(tu)_4Cl_2$	$-(44.4 \pm 0.8)$	$-(710.1 \pm 1.3)$	128.9	370	−524.3	131.1
$Ni(tu)_4Cl_2$	$-(44.3 \pm 0.2)$	$-(702.5 \pm 0.8)$	73.6	430	−591.5	147.9
$Zn(tu)_4Cl_2$	$-(50.2 \pm 0.4)$	$-(818.5 \pm 1.2)$	90.4	365	−483.6	120.9
$Cd(tu)_4Cl_2$	$-(29.3 \pm 2.8)$	$-(774.0 \pm 3.0)$	73.3	290	−512.0	128.0
$Hg(tu)_4Cl_2$	$-(4.1 \pm 5.0)$	$-(579.9 \pm 5.0)$	101.7	375	−368.0	92.0
tu			93.7	360		

[a] (tu) thiourea $(NH_2)_2C{=}S$. [b] $MCl_2(c) + 4\ tu(c) \rightarrow M(tu)_4Cl_2(c)$ [c] $MCl_2(g) + 4\ tu(g) \rightarrow M(tu)_4Cl_2(g)$

the metal halide and ligand. This is conveniently done by using a precision solution calorimeter to measure the enthalpies of solution of metal halide, ligand and complex in some suitable solvent, $\Delta H(\mathrm{a})$, $\Delta H(\mathrm{b})$ and $\Delta H(\mathrm{c})$.

$$\begin{tikzcd}
MX_2(c) \arrow[d, "|\Delta H(a) \\ \text{solvent}"] & + & n\,L(c \text{ or } l) \arrow[rr, "\Delta H_R"] \arrow[d, "|\Delta H(b) \\ \text{solution A}"] & & ML_nX_2(c) \arrow[d, "|\Delta H(c) \\ \text{solvent}"] \\
\text{solution A} & & \text{solution B} & & \text{solution B}
\end{tikzcd}$$

The enthalpy, ΔH_R is then given by $\Delta H_R = \Delta H(\mathrm{a}) + \Delta H(\mathrm{b}) - \Delta H(\mathrm{c})$. This approach has been used by a number of workers and their results are shown in Tables 4–11. The enthalpies of reactions refer to 298 K, as do the derived $\bar{D}$ values.

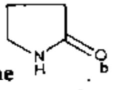
Ashcroft [13] has determined the enthalpies of the formation reactions, ΔH_R, of the thiourea complexes $\mathrm{M(tu)_4Cl_2}$, by use of 0.1 M HCl as solvent for the reactants and products. He has determined the enthalpies of sublimation of the complexes and of thiourea by use of a thermogravimetric analytical technique. Data are shown in Table 4; values of ΔH_f^0 (complex, c), ΔH_{sub}(complex), ΔH_g, for the gas phase formation reaction, together with the derived $\bar{D}$(M–S) values, are plotted in Fig. 1. This figure also shows values of $\bar{D}$(M–N) for the complexes $\mathrm{M(3Brpy)_2Cl_2}$, where M = Co, Ni and Cu, together with $\bar{D}$(M–O) for the pyrrolidone complexes $\mathrm{M(pyrr)_2Cl_2}$.

Data for these latter compounds are shown in Table 5. They were obtained by Barvinok and Lukina [14], who measured the enthalpies of

TABLE 5

Enthalpies of formation of 2-pyrrolidone complexes [14] (kJ mol^{-1})

Complex [a]	ΔH_R [b]	ΔH_f^0(complex, c) [c]	ΔH_g [d]	$\bar{D}$(M–O)(?)
$\mathrm{Mn(pyrr)_2Cl_2}$	−(70.3 ± 0.4)	−(1155.6 ± 2.0)	−(356 ± 6)	178 ± 3
$\mathrm{Co(pyrr)_2Cl_2}$	−(50.2 ± 0.3)	−(966.7 ± 2.0)	−(352 ± 6)	176 ± 3
$\mathrm{Ni(pyrr)_2Cl_2}$	−(49.5 ± 0.3)	−(958.8 ± 2.0)	−(364 ± 6)	182 ± 3
$\mathrm{Cu(pyrr)_2Cl_2}$	−(58.3 ± 0.2)	−(802.4 ± 2.0)	−(320 ± 6)	160 ± 3
$\mathrm{Zn(pyrr)_2Cl_2}$	−(74.4 ± 0.2)	−(1093.5 ± 2.0)	−(291 ± 6)	146 ± 3



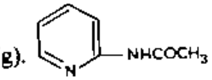
[a] (pyrr) 2-pyrrolidone . [b] $\mathrm{MCl_2(c) + 2\,(pyrr)(c) \rightarrow M(pyrr)_2Cl_2(c)}$. [c] Based on ΔH_f^0(pyrr, c) = −(302 ± 1) kJ mol^{-1}. [d] $\mathrm{MCl_2(g) + 2\,(pyrr)(g) \rightarrow M(pyrr)_2Cl_2(g)}$, calculated using $\Delta H_{\mathrm{sub}}^{298}$(pyrr) = 68 ± 4 kJ mol^{-1} derived from the relation $\Delta H_{\mathrm{sub}}^{298}(\mathrm{pyrr}) = \Delta H_{\mathrm{fusion}}^{298}(\mathrm{pyrr}) + \Delta H_{\mathrm{vap}}(\mathrm{pyrrolidine}) + \Delta H_{\mathrm{vap}}(\mathrm{cyclopentanone}) - \Delta H_{\mathrm{vap}}(\mathrm{cyclopentane})$, and the assumption that $\Delta H_{\mathrm{sub}}^{298}(\mathrm{M(pyrr)_{\mathit{n}}Cl_2}) = \Delta H_{\mathrm{sub}}^{298}(\mathrm{pyrr})$; values used are ΔH_{vap}(pyrrolidine) 37.6 ± 0.1, ΔH_{vap}(cyclopentanone) 42.7 ± 0.2, ΔH_{vap}(cyclopentane) 28.7 ± 2 kJ mol^{-1} [74] and $\Delta H_{\mathrm{fusion}}$(pyrr) = 16 kJ mol^{-1} (estimated).

TABLE 6

Enthalpies of formation of N-(2-pyridyl)acetamide complexes [16] (kJ mol^{-1})

Complex [a]	ΔH_R [b]	ΔH_f^0(complex, c)	ΔH_g [c]	$\bar{D}$(M–N)
$Zn(pa)_2Cl_2$	$-(72.8 \pm 0.6)$	$-(785 \pm 22)$	-325	163
$Zn(pa)_2Br_2$	$-(76.5 \pm 0.8)$	$-(702 \pm 22)$	-310	155
$Zn(pa)_2I_2$	$-(74.4 \pm 0.8)$	$-(580 \pm 22)$	-312	156
$Cd(pa)_2Cl_2$	$-(35.0 \pm 0.7)$	$-(724 \pm 22)$	-319	160
$Cd(pa)_2Br_2$	$-(36.7 \pm 0.8)$	$-(650 \pm 22)$	-304	152
$Cd(pa)_2I_2$	$-(40.2 \pm 0.4)$	$-(541 \pm 21)$	-290	145
$Hg(pa)_2Cl_2$	$-(22.9 \pm 1.1)$	$-(544 \pm 23)$	-211	106
$Hg(pa)Br_2$	$-(10.7 \pm 0.7)$	$-(330 \pm 22)$	-119	119

[a] (pa) N-(2-pyridyl)acetamide



[b] $MX_2(c) + n(pa)(c) \rightarrow M(pa)_nX_2(c)$.
[c] $MX_2(g) + n\ (pa)(g) \rightarrow M(pa)_n(X_2(g)$.

solution of the complexes, metal halides and ligands in 2 M HCl solution. It is uncertain whether pyrrolidone bonds to the metal via an oxygen or a nitrogen atom. The mean metal–ligand bond dissociation energy for the cobalt complex, 176 ± 3 kJ mol^{-1} is considerably greater than either the $\bar{D}$(Co–N) values for the pyridine and benzothiazole complexes (120–146 kJ mol^{-1}) or the $\bar{D}$(Co–O) values in the benzoxazole complexes of cobalt (128 to 148 kJ mol^{-1}) shown in Table 2. Possibly, the pyrrolidone molecule is bidentate, with both the nitrogen and oxygen atoms bonding to give a six-coordinate metal complex.

The shape of the plot for the octahedral $M(tu)_4Cl_2$ complexes is readily

TABLE 7

Enthalpies of formation of phosphine oxide complexes [17,18] (kJ mol^{-1})

Complex [a]	ΔH_R [b]	ΔH_f^0(complex, c)	ΔH_g [c]	$\bar{D}$(M–O)
$Zn(tepo)_2Cl_2$	$-(75.1 \pm 0.7)$		-318	159
$Cd(tepo)_2Cl_2$	$-(31.8 \pm 0.1)$		-307	154
$Hg(tepo)_2Cl_2$	$-(28.6 \pm 0.1)$		-206	103
$Zn(tppo)_2Cl_2$	$-(51.1 \pm 2.2)$	$-(586.6 \pm 50)$	-261	131
$Cd(tppo)_2Cl_2$	$-(16.3 \pm 0.5)$	$-(528.3 \pm 50)$	-258	129
$Hg(tppo)_2Cl_2$	$-(12.3 \pm 0.6)$	$-(357.7 \pm 50)$	-156	78
$Zn(tbpo)_2Cl_2$	$-(33.6 \pm 1.4)$		-287	144

[a] (tepo) triethylphosphine oxide, $OPEt_3$; (tppo) triphenylphosphine oxide, $OPPh_3$; (tbpo) tribenzylphosphine oxide, $OP(CH_2C_6H_5)_3$. [b] $MCl_2(c) + 2\ L(c) \rightarrow ML_2Cl_2(c)$. [c] $MCl_2(g) + 2\ L(g) \rightarrow ML_2Cl_2(g)$, calculated using the ΔH_{sub}^{298} values: tepo 94 kJ mol^{-1}, tppo 66 kJ mol^{-1} and tbpo 104 kJ mol^{-1}; together with the assumption that $\Delta H_{sub}^{298}(ML_2Cl_2) = \Delta H_{sub}^{298}(L)$.

TABLE 8

Enthalpies of formation of diacetamide complexes [19] (kJ mol^{-1})

Complex [a]	ΔH_R [b]	ΔH_f^0(complex, c)	ΔH_g [c]	$\bar{D}$(M–O)
$Zn(da)Cl_2$	$-(32.2\pm0.6)$	$-(945.7\pm0.5)$	−181	91
$Zn(da)Br_2$	$-(22.5\pm0.7)$	$-(849.7\pm1.2)$	−154	77
$Zn(da)I_2$	$-(12.8\pm0.8)$	$-(719.3\pm1.3)$	−133	67
$Cd(da)Cl_2$	$-(11.3\pm0.5)$	$-(901.2\pm1.0)$	−192	96
$Cd(da)Br_2$	$-(9.6\pm0.6)$	$-(824.3\pm1.1)$	−161	81
$Cd(da)I_2$	$-(10.6\pm0.9)$	$-(712.4\pm1.4)$	−148	74
$Hg(da)_2Cl_2$	$-(21.8\pm0.7)$	$-(1242.9\pm1.7)$	−176	88 [d]
$Hg(da)_2Br_2$	$-(15.4\pm0.5)$	$-(1182.9\pm1.5)$	−172	85 [d]

[a] (da) diacetamide, $CH_3CONHCOCH_3$, complexes in *trans–trans* form except $Hg(da)_2Cl_2$ and $Hg(da)_2Br_2$ which are *cis–trans*. [b] $MX_2(c)+n\ (da)(c) \rightarrow M(da)_nX_2(c)$. [c] $MX_2(g)+n\ (da)(g) \rightarrow M(da)_nX_2(g)$ calculated using $\Delta H_{sub}^{298}(da) = 72.2\pm0.6$ kJ mol^{-1} (ref. 18) and the assumption that $\Delta H_{sub}^{298}(M(da)_n(X_2) = \Delta H_{sub}^{298}(da)$. [d] Ligand assumed monodentate.

explained in terms of the Angular Overlap Model [15], a simplified molecular orbital description of the bonding in transition metal complexes, which considers only the interaction between metal *d*-orbitals and ligand group-orbitals. The relative energies of the antibonding orbitals are shown in Fig. 2. The antibonding electrons in the $Fe^{II}(d^6)$, $Co^{II}(d^7)$, $Ni^{II}(d^8)$ and $Cu^{II}(d^9)$ complexes are not spherically distributed between the σ^* and π^* antibonding orbitals, but occupy the lower energy π^* orbitals preferentially. As a result the antibonding energy is less, per electron, than for the $Mn^{II}(d^5)$ or $Zn^{II}(d^{10})$ cases. This "stabilization" energy, E, is given by the expression $E = [3n_{\sigma^*} - 2n_{\pi^*}]\Delta_0/5$, where Δ_0 is the energy separation between the σ^*

TABLE 9

Enthalpies of formation of tetramethylurea complexes [20] (kJ mol^{-1})

Complex [a]	ΔH_R [b]	ΔH_f^0(complex, c)	ΔH_g [c]	$\bar{D}$(M–O)
$Zn(tmu)_2Cl_2$	$-(83.1\pm1.0)$	$-(1006\pm2)$	−283	142
$Zn(tmu)_2Br_2$	$-(88.7\pm2.1)$	$-(926\pm3)$	−272	136
$Zn(tmu)_2I_2$	$-(127.8\pm2.9)$	$-(844\pm4)$	−299	150
$Cd(tmu)Cl_2$	$-(44.7\pm0.6)$	$-(690\pm2)$	−226	226
$Cd(tmu)Br_2$	$-(32.1\pm0.3)$	$-(602\pm1)$	−184	184
$Cd(tmu)_2I_2$	$-(63.0\pm0.7)$	$-(775\pm2)$	−252	126
$Hg(tmu)Cl_2$	$-(36.5\pm0.5)$	$-(515\pm2)$	−119	119
$Hg(tmu)Br_2$	$-(29.4\pm0.2)$	$-(454\pm1)$	−114	114

[a] (tmu) tetramethylurea, $(CH_3)_2NCON(CH_3)_2$. [b] $MX_2(c)+n\ (tmu)(l) \rightarrow M(tmu)_nX_2(c)$. [c] $MX_2(g)+n\ (tmu)(g) \rightarrow M(tmu)_nX_2(g)$ calculated using $\Delta H_{vap}^{298}(tmu) = 51.7\pm0.7$ kJ mol^{-1} and the assumption that $\Delta H_{sub}^{298}(M(tmu)_nX_2) = \Delta H_{sub}^{298}(tmu)$.

TABLE 10

Enthalpies of formation of amine complexes [22] (kJ mol^{-1})

Complex	ΔH_R [a]	ΔH_f^0(complex, c)	ΔH_g [b]	$\bar{D}$(Cu–N)
$Cu(Et_2NH)_2Cl_2$	$-(119.2 \pm 2.5)$	$-(547 \pm 5)$	$-(328 \pm 5)$	164
$Cu(Pr_2NH)_2Cl_2$	$-(126.8 \pm 2.9)$	$-(659 \pm 5)$	$-(344 \pm 5)$	172
$Cu(n\text{-}Bu_2NH)_2Cl_2$	$-(119.7 \pm 2.5)$	$-(752 \pm 5)$	$-(346 \pm 5)$	173
$Cu(Et_2NH)_2Br_2$	$-(142.7 \pm 2.5)$	$-(492 \pm 5)$	$-(346 \pm 5)$	173
$Cu(Pr_2NH)_2Br_2$	$-(150.2 \pm 3.3)$	$-(604 \pm 5)$	$-(362 \pm 5)$	181
$Cu(n\text{-}Bu_2NH)_2Br_2$	$-(144.3 \pm 2.9)$	$-(698 \pm 5)$	$-(364 \pm 5)$	182

[a] $CuX_2(c) + 2\ R_2NH(l) \rightarrow Cu(R_2NH)_2X_2(c)$. [b] $CuX_2(g) + 2\ R_2NH(g) \rightarrow Cu(R_2NH)_2X_2(g)$, calculated using ΔH_{vap}^{298} values, $Et_2NH = 31.8$, $Pr_2NH = 40.1$ and $n\text{-}Bu_2NH = 49.4$ kJ mol^{-1} and the assumption that $\Delta H_{sub}^{298}(M(R_2NH)_2X_2) = \Delta H_{vap}^{298}(R_2NH) + 17$ kJ mol^{-1}.

and π^* orbitals, which are occupied by a number n_{σ^*} and n_{π^*} of electrons, respectively. For high spin complexes, this stabilization energy rises to a maximum at Ni and then falls to Cu, which is consistent with the experimental values of $\bar{D}$(M–S) and $\bar{D}$(M–N).

Airoldi and co-workers [16–20] have measured the enthalpies of formation, from metal halide and ligand, of a number of zinc, cadmium and

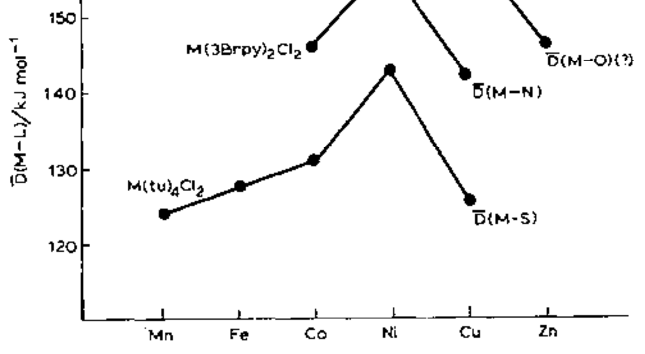


Fig. 1. $\bar{D}$(M–S) in $M(tu)_4Cl_2$, $\bar{D}$(M–N) in $M(3Brpy)_2Cl_2$ and $\bar{D}$(M–O) in $M(pyrr)_2Cl_2$.

TABLE 11

Enthalpies of formation (kJ mol^{-1}) of *trans*-Pd(AEt$_2$)$_2$Cl$_2$(c) [23] where A = S, Se or Te

Complex	ΔH_R	ΔH_f^0(complex, c)	ΔH_g	$\bar{D}$(Pd–A)
Pd(SEt$_2$)$_2$Cl$_2$	−(103.8 ± 0.4)	−(563.7 ± 3.9)	233 ± 15	117 ± 8 ($\bar{D}$(Pd–S))
Pd(SeEt$_2$)$_2$Cl$_2$	−(115.3 ± 0.9)	−(529.2 ± 9.5)	251 ± 20	126 ± 10 ($\bar{D}$(Pd–Se))
Pd(TeEt$_2$)$_2$Cl$_2$	−(175.7 ± 4.8)	−(763.8 ± 14.6)	308 ± 20	154 ± 10 ($\bar{D}$(Pd–Te))

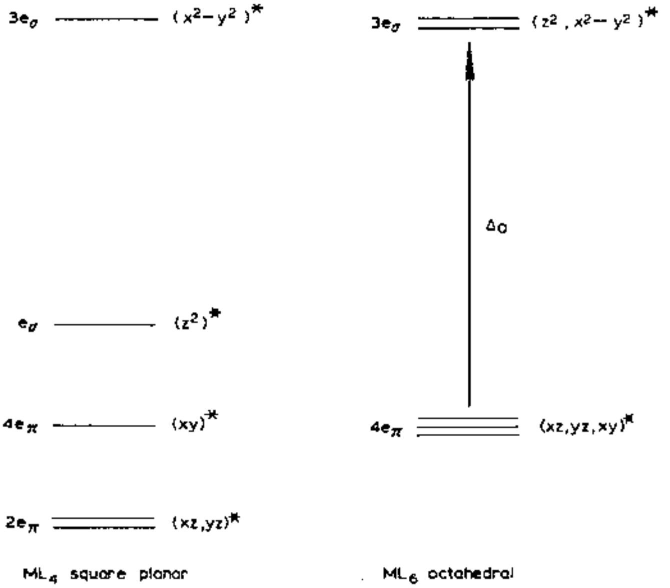


Fig. 2. Relative energy levels of antibonding orbitals in the Angular Overlap Model description of ML_4 square planar and ML_6 octahedral complexes.

mercury complexes (Tables 5–8). The ligands were *N*-(2-pyridyl)acetamide, which probably bonds to the metal through the pyridine N atom, some phosphine oxides, diacetamide (which is a bidentate ligand), and tetramethylurea, all of which form metal–oxygen bonds. Values for ΔH_f^0(complex, c) have been calculated by use of enthalpies of formation of metal halide and ligand given in Appendix 1.

It has not been possible to determine the enthalpies of sublimation of any of these metal complexes, because they dissociate when heated to temperatures at which it is possible to measure their vapour pressures. Airoldi and co-workers [16–20] make the assumption that ΔH_{sub}^{298}(complex) = ΔH_{sub}^{298}(ligand) in order to calculate a value for ΔH_g, the gas-phase formation of complex from metal halide and ligand. There is some justification for this assumption. Thus, the values of ΔH_{sub} for the complexes $M(tu)_4Cl_2$ lie in the range 73–133 kJ mol, compared with ΔH_{sub}(tu) = 94 kJ mol^{-1}. The values of ΔH_{sub} for the metal complexes of the substituted pyridines, benzothiazoles and benzoxazoles also lie in the band 70–125 kJ mol^{-1} (with the exception of $Cu(3Brpy)_2Cl_2$ for which we have $\Delta H_{sub} = 57$ kJ mol^{-1}) although the values of ΔH_{sub}(ligand) are not available for comparison. Moreover, for complexes ML_nX_2, with n ligands L, the error in the calculated value of $\bar{D}$(M–L) is only $^1/n$th of the error in the estimated value of ΔH_{sub}(complex).

The derived values for $\bar{D}$(M–N) and $\bar{D}$(M–O) in the metal chloride complexes are plotted in Fig. 3. For comparison, values of $\bar{D}$(M–S) from the thiourea complexes $M(tu)_4Cl_2$ are also shown. For the complexes of *N*-(2-pyridyl)acetamide, $\bar{D}$(M–N), triethylphosphine oxide, and triphenylphosphine oxide, $\bar{D}$(M–O), there is a slight fall in value of $\bar{D}$, from Zn to Cd, followed by a considerable drop to the much less strongly bonded Hg atom. This weaker bonding for mercury is also found for diacetamide, $\bar{D}$(M–O), and thiourea, $\bar{D}$(M–S), although in these two cases cadmium is bonded slightly more strongly than zinc. The iodide and bromide complexes follow similar patterns. In general, for any particular ligand and metal, the $\bar{D}$ values decrease along the series Cl > Br > I. Thus, for the complexes Zn(diacetamide)X_2, the values of $\bar{D}$(M–O) are as follows: Zn(da)Cl_2, 91; Zn(da)Br_2, 77; and Zn(da)I_2 67 kJ mol^{-1}. There are, however, a few exceptions to this general rule.

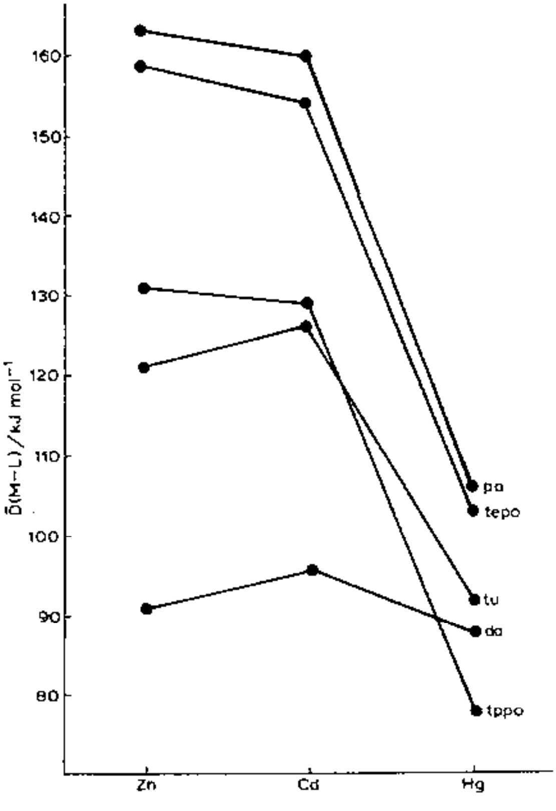


Fig. 3. $\bar{D}$(M–S) in $M(tu)_4Cl_2$; $\bar{D}$(M–N) in $M(pa)_2Cl_2$ and $\bar{D}$(M–O) in $M(tepo)_2Cl_2$, $M(tppo)_2Cl_2$ and $M(da)Cl_2$.

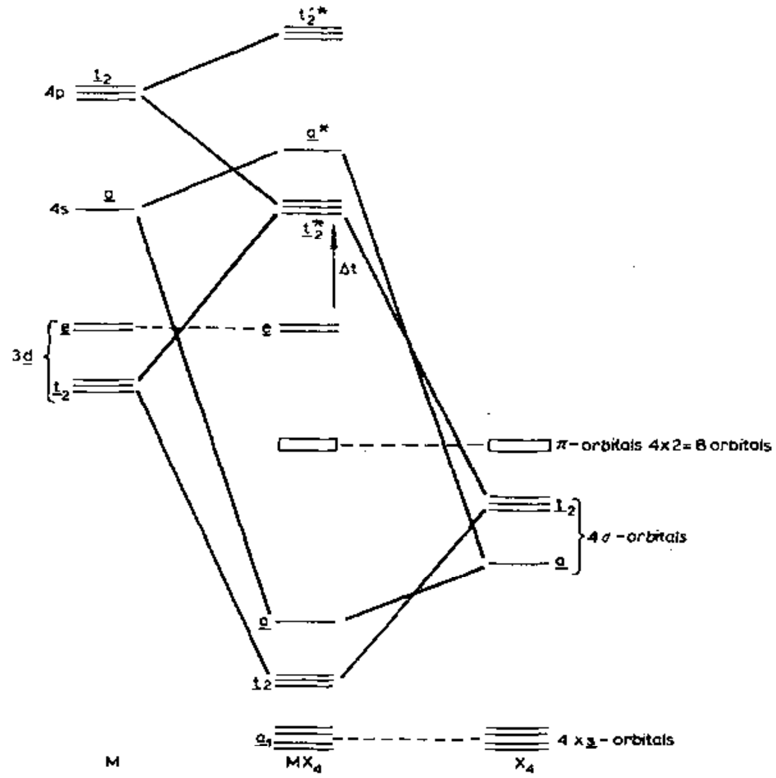


Fig. 4. Molecular orbital energy diagram of tetrahedral complex MX_4, σ-bonding only.

A more rigorous molecular orbital description [21] of the bonding in a tetrahedral complex of a transition metal, MX_4, also takes into account interactions between metal *s*- and *p*-orbitals and ligand group orbitals, in addition to the metal *d*-orbital interaction with ligand orbitals of the simpler Angular Overlap Model. An energy diagram, which shows the σ-bonding only, is given in Fig. 4. The separation of *e* and $t_2{}^*$ orbitals is the same as that derived from the simpler model, although here the *e* MO is non-bonding and the $t_2{}^*$ MO is antibonding. For Zn(II), Cd(II) and Hg(II), which have a d^{10} configuration, all of the orbitals up to and including the $t_2{}^*$ MO will be filled. Effectively, metal–ligand bonding results from overlap between the metal *s*-orbital and the *a* σ-orbital of the four ligands. Along the series Zn, Cd, Hg the increasing radial diffuseness of the 4*s*, 5*s*, to 6*s* orbital decreases the effective overlap and efficiency of the single bonding *a* molecular orbital. As a result, the *s*-component of the M–X bond is expected to decrease. The observation that the $\overline{D}$(M–X) values decrease along this series implies that it is the σ-bonding which is dominant in these molecules.

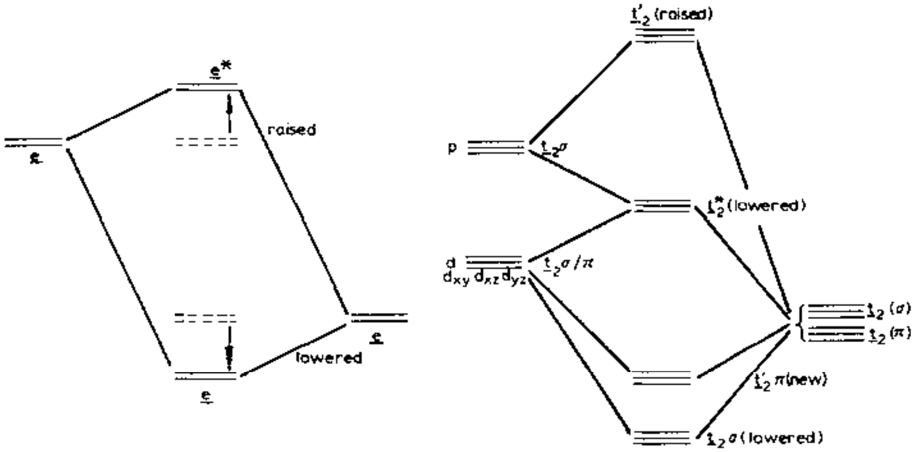
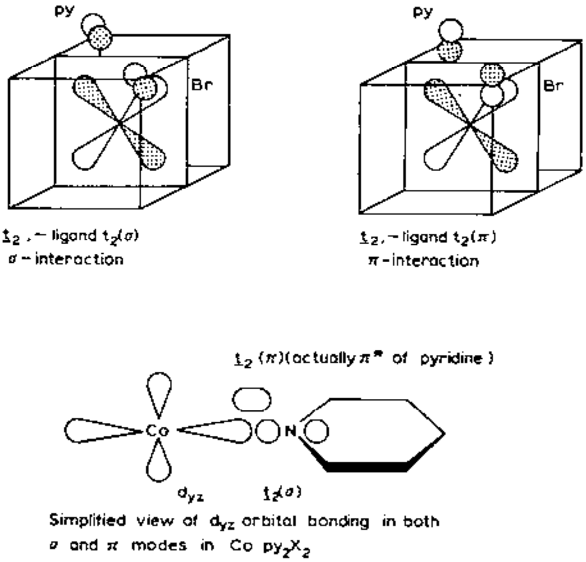


Fig. 5. Molecular orbital energy diagram of tetrahedral complex MX_4, π bonding only.

Incorporation of π-bonding between ligands and metal (Fig. 5) results in a lowering of the *e* non-bonding MO, which now becomes weakly bonding. Also, there is interaction between the t_2* and $t_2\pi$-orbitals of the ligands. The four main effects of this are: (i) to lower the energy level of t_2 bonding orbital (which now acts in both a σ- and π-bonding capacity); (ii) to lower the level of the $t_2\pi$-orbital of the ligands, which now becomes the t'_2 orbital; (iii) to lower the energy of the t_2* orbital; and finally (iv) to raise the energy level of the t'^*_2 orbital.

Since the t_2 metal orbitals (d_{xz} d_{yz} and d_{xy}) are involved in bonding to both the $t_2(\sigma)$ and $t_2(\pi)$ orbitals of the ligand, illustrated diagrammatically in Fig. 6, the two types of bonding are mutually dependant. If, for example, substitution of pyridine affects the σ-donor bonding of the N atom, the extent of bonding between the Co(d_{yz}) orbital and the pyridine $t_2(\pi)$ orbital, which in this case is a vacant π^* antibonding pyridine orbital, will be affected. In the same way bonding of the ligand X, in $Co(py)_2X_2$, will also influence the value of $\overline{D}$(Co–N) through the d_{yz} orbital, which is used to bond both the halogen and pyridine to the cobalt.

Adeosun and Nwanze [22] have measured the enthalpies of the formation of some secondary amine complexes of copper. The solvent used was 2 M HCl. Enthalpy data are shown in Table 10, together with the derived $\overline{D}$(Cu–N) values of ca. 170 kJ mol^{-1}, which refer to 298 K. We have previously noted a value $\overline{D}$(Cu–N) = 142 kJ mol^{-1}, at 560 K, in $Cu(3Brpy)_2Cl_2$. Also, for pyridine complexes of nickel and cobalt, the $\overline{D}$ values at ca. 500 K are about 30 kJ lower than at 298 K. It is likely, therefore, that the values of $\overline{D}$(Cu–N amine) and $\overline{D}$(Cu–N pyridine) are very similar.



t_2, – ligand $t_2(\sigma)$
σ – interaction

t_2, – ligand $t_2(\pi)$
π – interaction

Simplified view of d_{yz} orbital bonding in both σ and π modes in Co py_2X_2

Fig. 6. Orbital overlap in tetrahedral complex MX_4.

Evans and Mortimer [23] have determined the enthalpies, ΔH_R, of the following reactions, where A = S, Se or Te, by measuring enthalpies of solution in aqueous acetone.

$$(NH_4)_2PdCl_4(c) + Et_2A(l) \rightarrow \textit{trans}\text{-}Pd(AEt_2)_2Cl_2(c) + 2\ NH_4Cl(c)$$

Using ΔH_f^0 values for $(NH_4)_2PdCl_4$(c), Et_2S(l), Et_2Se(l), Et_2Te(l) and NH_4Cl(c) given in Appendix 1, values for $\Delta H_f^0\{\textit{trans}\text{-}Pd(AEt_2)_2Cl_2, c\}$ are derived and shown in Table 11. The enthalpies, ΔH_g, of the gas-phase dissociation reactions (5)–(7)

$$\textit{trans}\text{-}Pd(SEt_2)_2Cl_2(g) \rightarrow PdCl_2(g) + 2\ Et_2S(g) \quad (5)$$

$$\textit{trans}\text{-}Pd(SeEt_2)_2Cl_2(g) \rightarrow PdCl_2(g) + 2\ Et_2Se(g) \quad (6)$$

$$\textit{trans}\text{-}Pd(TeEt_2)_2Cl_2(g) \rightarrow PdCl_2(g) + 2\ Et_2Te(g) \quad (7)$$

can be equated to 2 $\bar{D}$(Pd–S), 2 $\bar{D}$(Pd–Se) and 2 $\bar{D}$(Pd–Te), respectively. Incorporating the value for $\Delta H_f^0(PdCl_2, c)$ given in Appendix 1, using the enthalpies of vaporisation $Et_2S = 35.86 \pm 0.04$ kJ mol^{-1} [85] $Et_2Se = 38.9 \pm 4$ kJ mol^{-1} [86] and $Et_2Te = 41.8 \pm 2$ kJ mol^{-1} [84] and the assumption $\Delta H_{sub}(PdCl_2) = \Delta H_{sub}\{\textit{trans}\text{-}Pd(AEt_2)_2Cl_2\}$, we obtain the values of ΔH_g and $\bar{D}$(Pd–A) shown in Table 10. The trend in values is $\bar{D}$(Pd–S) < $\bar{D}$(Pd–Se) < $\bar{D}$(Pd–Te).

In the square-planar, d^8, complexes PdL_4, bonding between metal and ligand depends on four molecular orbitals, for although there are other

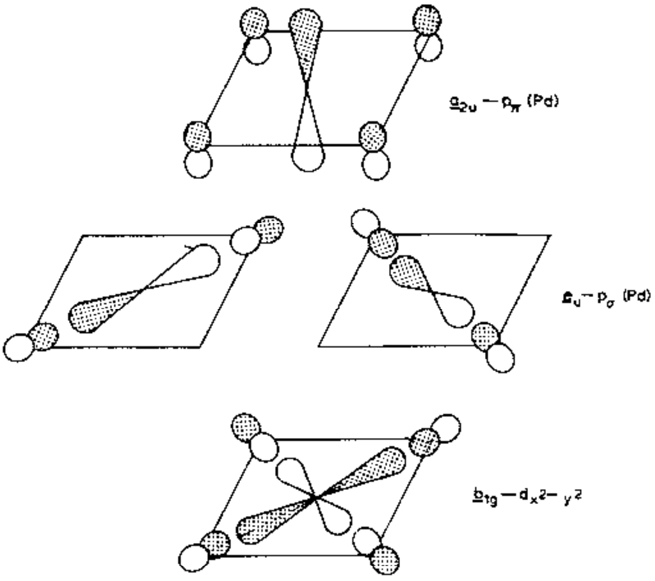
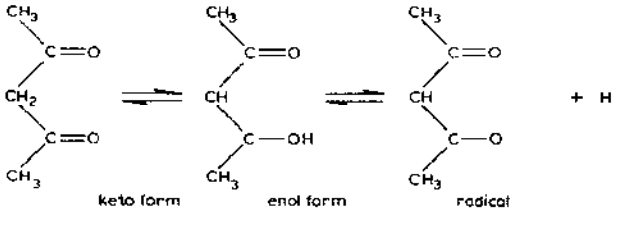


Fig. 7. Orbital overlap in square-planar d^8 complex, PdL_4.

bonding orbitals, their effect is offset by filled antibonding orbitals. The four ligand group-orbitals, b_{1g}, e_u(degenerate) and a_{2u}, overlap with the metal $d_{x^2-y^2}$, p_σ(Pd) and p_π(Pd) orbitals, respectively, as shown in Fig. 7. Of these molecular orbitals, the $b_{1g} - d_{x^2-y^2}$ is the lowest in energy and most effective. Because of the radial distribution of nodes in the $d_{x^2-y^2}$ orbital, overlap with the b_{1g} ligand-group orbital is expected to become better as the size of the $d_{x^2-y^2}$ orbital increases from $3d$(Ni) through $4d$(Pd) to $5d$(Pt), and we therefore expect metal–ligand binding to become stronger along the series $\bar{D}(\text{Ni–L}) < \bar{D}(\text{Pd–L}) < \bar{D}(\text{Pt–L})$. Similarly, if the ligand-group orbitals, a_{2u} and e_u, have a d component then the $a_{2u} - p_\pi$ and $e_u - p_\pi$ should also become more strongly bonding along the ligand series $\bar{D}(\text{Pd–S}) < \bar{D}(\text{Pd–Se}) < \bar{D}(\text{Pd–Te})$, a trend which is observed.

C. ML$_n$ COMPLEXES, WHERE L IS A LIGAND RADICAL

The complexes M(pentane-2,4-dionato)$_n$, where $n = 2$ or 3, are typical representatives of this group of compounds. They are formed from the



pentane-2,4-dionato radical, which results from the dissociation of a hydrogen atom from the enol form of pentane-2,4-dione (pd), or acetylacetone.

(i) Dionato complexes

Metal dionato complexes, ML_2 and ML_3, decompose into metal and free ligand in sulphuric, hydrochloric, or perchloric acid, although complexes of low water solubility react slowly. For these particular complexes the rate of reaction can be increased by using a mixture of hydrochloric acid and 1,4-dioxan.

This approach to the determination of enthalpies of formation of these complexes has been used by the following separate groups of workers: R.J. Irving et al., University of Surrey; M.A.V. Ribeiro da Silva et al., University of Oporto, Portugal; E. Giera et al., University of Wroclaw, Poland; J.O. Hill et al., La Trobe University, Bundoora, Victoria, Australia; G. Pilcher and H.A. Skinner, University of Manchester.

The enthalpies, ΔH_R, of the following reactions were obtained by measuring the enthalpies of solution of ML_2 in the solvent.

$$\begin{aligned} ML_2(c) + [H_2SO_4, 53.54\ H_2O](l) \rightarrow {} & (53.54 - n)H_2O(l) \\ & + 2\ HL(\text{stand. state}) + MSO_4 \cdot nH_2O(c) \end{aligned} \tag{8}$$

$$\begin{aligned} ML_2(c) + 2[HCl, 11.60\ H_2O](l) \rightarrow {} & (23.20 - n)H_2O(l) \\ & + 2\ HL(\text{stand. state}) + MCl_2 \cdot nH_2O(c) \end{aligned} \tag{9}$$

Then, in a fresh sample of solvent, the successive enthalpies of solution of the reaction products were measured. The solvent used was either $[H_2SO_4, 53.54\ H_2O]$, $[HCl, 11.60\ H_2O]$, $[HClO_4, 3.57\ H_2O]$, or a mixture of 25% by volume $[HCl, 11.60\ H_2O]$ and 75% of 1,4-dioxan.

The procedure is illustrated in more detail for the particular case of bis(pentane-2,4-dionato)copper(II), $Cu(pd)_2$.

$$\begin{tikzcd}
{[H_2SO_4, 53.54\ H_2O](l)} \arrow[d, "\Delta H(a)"] & {+\ Cu(pd)_2(c)} \arrow[dl, "\Delta H(b)"] \arrow[r, "\Delta H_R"] & {48.54\ H_2O(l)} \arrow[d, "\Delta H(c)"] & {+\ 2\ Hpd(l)} \arrow[dl, "\Delta H(d)"] & {+\ CuSO_4 \cdot 5\ H_2O(c)} \arrow[dll, "\Delta H(e)"] \\
{\text{Solvent } [H_2SO_4, 53.54\ H_2O]} \arrow[rr, "\Delta H(f)"] & & {\text{Solvent } [H_2SO_4, 53.54\ H_2O]} & & \\
{\text{Final solution } A_2} & & {\text{Final solution } B_3} & &
\end{tikzcd}$$

The following enthalpies of solution were determined:

$$\text{Solvent} + [H_2SO_4, 53.54\ H_2O](l) \xrightarrow{\Delta H(a)} \text{Solution } A_1$$

$$\text{Solution } A_1 + Cu(pd)_2(c) \xrightarrow{\Delta H(b)} \text{Solution } A_2$$

$$\text{Solvent} + H_2O(l) \xrightarrow{\Delta H(c)} \text{Solution } B_1$$

$$\text{Solution } B_1 + Hpd(l) \xrightarrow{\Delta H(d)} \text{Solution } B_2$$

$$\text{Solution } B_2 + CuSO_4 \cdot 5\ H_2O(c) \xrightarrow{\Delta H(e)} \text{Solution } B_3$$

Provided that the precise stoichiometry is realised and solution A_2 is the same as solution B_3, then the value of $\Delta H(f)$ is zero and we can write

$$\Delta H_R = \Delta H(a) + \Delta H(b) - 48.54\ \Delta H(c) - 2\Delta H(d) - \Delta H(e)$$

Since care has been taken in setting up the stoichiometry of the reaction so that the sulphuric acid used in the reaction is of the same concentration as the solvent, $[H_2SO_4, 53.54\ H_2O]$, then $\Delta H(a) = 0$. The value $\Delta H(c) = -0.121$ kJ mol^{-1} is calculated from published data [50]. By measuring the values $\Delta H(b) = -21.75$ kJ mol^{-1}, $\Delta H(d) = +6.19$ kJ mol^{-1}, $\Delta H(e) = 22.61$ kJ mol^{-1} we obtain $\Delta H_R = 50.6 \pm 0.4$ kJ mol^{-1}. Using the relationship $\Delta H_f^0\{Cu(pd)_2, c\} = 2\ \Delta H_f^0(Hpd, l) + \Delta H_f^0(CuSO_4 \cdot 5\ H_2O) - \Delta H_f^0[H_2SO_4, \text{in } 53.54] - 5\ \Delta H_f^0(H_2O, l) - \Delta H_R$
and incorporating the enthalpies of formation shown in Appendix 1, we obtain the value $\Delta H_f^0\{Cu(pd)_2, c\} = -(760.7 \pm 4)$ kJ mol^{-1}.

A similar approach has been used for $\{Co(pd)_2\}_4$ and $\{Ni(pd)_2\}_3$. The relevant thermochemical equations are as follows

$$4\,[H_2SO_4, 53.54\ H_2O](l) + \{Co(pd)_2\}_4(c) \xrightarrow{\Delta H_R} 190.16\ H_2O(l) + 8\ Hpd(c) + 4\ CoSO_4 \cdot 6\ H_2O(c) \qquad (10)$$

$$3\,[H_2SO_4, 53.54\ H_2O](l) + \{Ni(pd)_2\}_2(c) \rightarrow 142.53\ H_2O(l) + 6\ Hpd(c) + 3\ NiSO_4 \cdot 6\ H_2O(c) \qquad (11)$$

In these cases the solvent used was $[H_2SO_4, 53.54\ H_2O]$. For the study of Ni(tmhd)$_2$* the solvent used was a mixture of 25% by volume of [HCl, 11.60 H_2O] and 75% by volume of 1,4-dioxan. A mixed HCl/dioxan solvent was

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* See Table 13 for meanings of abbreviations.

TABLE 12

Thermochemical decomposition reactions of metal-dionato complexes

Eqn. no.	Reaction	Solvent [a]	Ref.
10	$4\ [H_2SO_4,\ 53.54\ H_2O](l)+\{Co(pd)_2\}_4(c) \rightarrow 190.16\ H_2O(l)+8\ Hpd(l)+4\ CoSO_4\cdot 6\ H_2O(c)$	1	24
11	$3\ [H_2SO_4,\ 53.54\ H_2O](l)+\{Ni(pd_2)\}_3(c) \rightarrow 142.62\ H_2O(l)+6\ Hpd(l)+3\ NiSO_4\cdot 6\ H_2O(c)$	1	25
12	$2\ [HCl,\ 11.60\ H_2O](l)+Ni(tmhd)_2(c) \rightarrow 17.2\ H_2O(l)+2\ Htmhd(l)+NiCl_2\cdot 6\ H_2O(c)$	5	25
13	$[H_2SO_4,\ 53.54\ H_2O](l)+Cu(pbd)_2(c) \rightarrow 48.54\ H_2O(l)+2\ Hpbd(l)+CuSO_4\cdot 5\ H_2O(c)$	5	26
14	$[H_2SO_4,\ 53.54\ H_2O](l)+Cu(pd)_2(c) \rightarrow 48.54\ H_2O(l)+2\ Hpd(l)+CuSO_4\cdot 5\ H_2O(c)$	1	24
15	$3\ [HCl,\ \infty\ H_2O](l)+Cr(pd)_3(c) \rightarrow \infty\ H_2O(l)+3\ Hpd(l)+CrCl_3\cdot 6\ H_2O(c)$	4	27
16	$3\ [HCl,\ \infty\ H_2O](l)+Mn(pd)_3(c)+FeCl_2(c) \rightarrow \infty\ H_2O(l)+FeCl_3(c)+3\ Hpd(l)+MnCl_2\cdot 4\ H_2O(c)$	2	28
17	$3\ [HCl,\ \infty\ H_2O](l)+Fe(pd)_3(c) \rightarrow \infty\ H_2O(l)+3\ Hpd(l)+FeCl_3(c)$	2	29
18	$43.85\ H_2O(l)+2\ NaCl(c)+FeCl_3(c)+Mo(pd)_3(c) \rightarrow$ $5\ [HCl,\ 7.97\ H_2O](l)+3\ Hpd(l)+3\ FeCl_2(c)+Na_2[MoO_4](c)$	3	30
19	$2\ [HCl,\ \infty\ H_2O](l)+Mn(pd)_2(c) \rightarrow \infty\ H_2O(l)+2\ Hpd(l)+MnCl_2\cdot 4\ H_2O(c)$	2	31
20	$8\ [HCl,\ \infty\ H_2O](l)+\{Co(pd)_2\}_4(c) \rightarrow \infty\ H_2O(l)+8\ Hpd(l)+4\ CoCl_2\cdot 6\ H_2O(c)$	2	31
21	$6\ [HCl,\ \infty\ H_2O](l)+\{Ni(pd)_2\}_3(c) \rightarrow \infty\ H_2O(l)+6\ Hpd(l)+3\ NiCl_2\cdot 6\ H_2O(c)$	2	31, 32
22	$2\ [HCl,\ \infty\ H_2O](l)+Cu(pd)_2(c) \rightarrow \infty\ H_2O(l)+2\ Hpd(l)+CuCl_2\cdot 2\ H_2O(c)$	2	31
23	$2\ [HCl,\ \infty\ H_2O](l)+Zn(pd)_2(c) \rightarrow \infty\ H_2O(l)+2\ Hpd(l)+ZnCl_2(c)$	2	31
24	$2\ [HCl,\ \infty\ H_2O](l)+Ni(pbd)_2(c) \rightarrow \infty\ H_2O(l)+2\ Hpbd(c)+NiCl_2\cdot 6\ H_2O(c)$	2	31, 32
25	$2\ [HCl,\ \infty\ H_2O](l)+Zn(pbd)_2(c) \rightarrow \infty\ H_2O(l)+2\ Hpbd(c)+ZnCl_2(c)$	2	31
26	$2\ [HCl,\ \infty\ H_2O](l)+Ni(dppd)_2(c) \rightarrow \infty\ H_2O(l)+2\ Hdppd(c)+NiCl_2\cdot 6\ H_2O(c)$	5	32

[a] 1, $[H_2SO_4,\ 53.54\ H_2O]$; 2, $[HCl,\ 11.60\ H_2O]$; 3, $[HCl,\ 7.97\ H_2O]$; 4, $[HClO_4,\ 3.57\ H_2O]$; 5, mixture of 25% by volume HCl, 11.60 H_2O and 25% by volume 1,4-dioxan.

TABLE 13

Enthalpies of formation of dionato complexes (kJ mol^{-1})

Reaction	Complex [a]	ΔH_R [b]	ΔH_f^0(complex, c)	ΔH_{sub}	ΔH_f^0(complex, g)	$\overline{D}$(M–O)
10	$(Co(pd)_2)_4$	−(259.4 ± 2.0)	−(3458.5 ± 9.2)	344.8 [c]	−778.4 ± 4 [e]	183 ± 4
11	$(Ni(pd)_2)_3$	−(212.9 ± 1.0)	−(2572.8 ± 9.2)	383.1 [c]	−729.9 ± 4 [f]	172 ± 4
12	$Ni(tmhd)_2$	−(62.8 ± 1.5)	−(1225.0 ± 9.5)	145.1	−1080.9 ± 12	187 ± 9
13	$Cu(pbd)_2$	−(42.4 ± 1.3)	−(600.8 ± 9.2)	(67) [d]	−533.8 ± 12	159 ± 8
14	$Cu(pd)_2$	−(50.6 ± 0.4)	−(760.7 ± 4.1)	57.1	−703.6 ± 6	143 ± 4
15	$Cr(pd)_3$	(46.3 ± 0.3)	−(1554.2 ± 5.7)	123.0	−1431.2 ± 18	187 ± 6
16	$Mn(pd)_3$	1.3 ± 0.6	−(1373.3 ± 6.0)	77.8	−1295.5 ± 8	145 ± 4
17	$Fe(pd)_3$	139.3 ± 0.5	−(1309.8 ± 5.5)	65.3	−1244.5 ± 8	159 ± 4
18	$Mo(pd)_3$	−(76.7 ± 1.5)	−(1323.7 ± 5.9)	(123) [d]	−1200.7 ± 10	192 ± 4
19	$Mn(pd)_2$	−(36.1 ± 0.2)	−(1021.5 ± 3.7)	(63) [d]	−958.5 ± 8	190 ± 4
20	$(Co(pd)_2)_4$	−(216.4 ± 0.8)	−(3439.2 ± 14.7)	344.8 [c]	−733.6 ± 5 [e]	182 ± 4
21	$(Ni(pd)_2)_3$	−(44.1 ± 0.6)	−(2661.0 ± 11.4)	383.1 [c]	−759.3 ± 6 [f]	179 ± 4
22	$Cu(pd)_2$	20.7 ± 0.2	−(783.8 ± 3.7)	57.1	−726.7 ± 6	148 ± 4
23	$Zn(pd)_2$	8.0 ± 0.2	−(936.6 ± 3.7)	(45) [d]	−891.6 ± 8	138 ± 4
24	$Ni(pbd)_2$	−(87.8 ± 0.4)	−(645.7 ± 10.2)	42.2	−603.5 ± 12	197 ± 4
25	$Zn(pbd)_2$	−(13.3 ± 0.2)	−(747.7 ± 9.7)	(55) [d]	−692.7 ± 14	145 ± 4
26	$Ni(dppd)_2$	−(208.8 ± 1.2)	−(293.9 ± 3.5)	(52) [d]	−241.9 ± 8	165 ± 8

[a] (pd) pentane-2,4-dionato, $CH_3COCH{=}CO\cdot CH_3$, acetylacetonato; (pbd) 1-phenyl-1,3-butanedionato, $C_6H_5COCH{=}CO\cdot CH_3$, benzoylacetonato; (dppd) 1,3-diphenyl-1,3-propanedionato, $C_6H_5COCH{=}CO\cdot C_6H_5$, dibenzoylmethanato; (tmhd) 2,2,6,6-tetramethylheptane-3,5-dionato, $(CH_3)_3CCOCH{=}CO\cdot C(CH_3)_3$. [b] See Table 12 for reaction to which ΔH_R refers. [c] Refers to reaction $(ML_2)_n(c) \rightarrow n\ ML_2(g)$. [d] Values in parentheses estimated. [e] $\Delta H_f^0(Co(pd)_2, g)$. [f] $\Delta H_f^0(Ni(pd)_2, g)$.

also used for $\mathrm{Cu(pbd)_2}$. The thermochemical equations are

$$2\,[\mathrm{HCl},\ 11.60\ \mathrm{H_2O}]\,(\mathrm{l}) + \mathrm{Ni(tmhd)_2(c)} \rightarrow 17.2\ \mathrm{H_2O(l)} + 2\ \mathrm{Htmhd(l)} + \mathrm{NiCl_2 \cdot 6\,H_2O(c)} \qquad (12)$$

$$[\mathrm{H_2SO_4},\ 53.54\ \mathrm{H_2O}]\,(\mathrm{l}) + \mathrm{Cu(pbd)_2(c)} \rightarrow 48.54\ \mathrm{H_2O(l)} + 2\ \mathrm{Hpd(l)} + \mathrm{CuSO_4 \cdot 5\,H_2O(c)} \qquad (13)$$

In these two cases, it was also necessary to measure the enthalpies of solution, $\Delta H(\mathrm{a})$, of [HCl, 11.60 $\mathrm{H_2O}$] and [$\mathrm{H_2SO_4}$, 53.54 $\mathrm{H_2O}$] in the mixed solvent. Values of ΔH_R and the enthalpies of formation calculated from them are shown in Table 13. The relevant reactions are given in Table 12.

In a series of three papers published in 1967 and 1968, Hill and Irving [27–29] have reported measurement of the enthalpies of decomposition of the bis(pentane-2,4-dionato)metal(III) complexes $\mathrm{Cr(pd)_3}$, $\mathrm{Mn(pd_3)}$ and $\mathrm{Fe(pd)_3}$. For the iron complex the solvent was again [HCl, 11.60 $\mathrm{H_2O}$], but the reaction scheme differed from that shown above in that the metal complex was assumed to react with hydrochloric acid at infinite dilution, as illustrated in the following scheme.

$$\begin{tikzcd}[column sep=small]
3\,[\mathrm{HCl},\ \infty\mathrm{H_2O}](\mathrm{l}) \arrow[d, "\Delta H(\mathrm{a})"] & + \mathrm{Fe(pd)_3(c)} \arrow[r, "\Delta H_\mathrm{R}"] \arrow[dl, "\Delta H(\mathrm{b})"] & \mathrm{FeCl_3(c)} \arrow[d, "\Delta H(\mathrm{c})"] & + 3\ \mathrm{Hpd(l)} \arrow[dl, "\Delta H(\mathrm{d})"] & + \infty\ \mathrm{H_2O(l)} \\
\text{Solvent } [\mathrm{HCl},\ 11.60\ \mathrm{H_2O}] & & \text{Solvent } [\mathrm{HCl},\ 11.60\ \mathrm{H_2O}] & &
\end{tikzcd}$$

The enthalpies of solution $\Delta H(\mathrm{b})$, $\Delta H(\mathrm{c})$ and $\Delta H(\mathrm{d})$ were measured and the enthalpy $\Delta H(\mathrm{a})$ was calculated. A similar approach was used for $\mathrm{Cr(pd)_3}$, although in this case the solvent was [$\mathrm{HClO_4}$, 3.57 $\mathrm{H_2O}$].

$$3\,[\mathrm{HCl},\ \infty\mathrm{H_2O}]\,(\mathrm{l}) + \mathrm{Cr(pd)_3(c)} \xrightarrow{\Delta H_\mathrm{R}} \mathrm{CrCl_3 \cdot 6\,H_2O(c)} + 3\ \mathrm{Hpd(l)} + \infty\ \mathrm{H_2O(l)} \qquad (14)$$

$$3\,[\mathrm{HCl},\ \infty\mathrm{H_2O}]\,(\mathrm{l}) + \mathrm{Mn(pd)_3(c)} + \mathrm{FeCl_2(c)} \rightarrow \mathrm{MnCl_2 \cdot 4\,H_2O(c)} + \mathrm{FeCl_3(c)} + 3\ \mathrm{Hpd(l)} + \infty\mathrm{H_2O(l)} \qquad (15)$$

In the reaction between $\mathrm{Mn(pd)_3}$ and [HCl, $\infty\mathrm{H_2O}$], where the solvent used was [HCl, 11.60 $\mathrm{H_2O}$], the $\mathrm{MnCl_3}$ which is produced is partially reduced to $\mathrm{MnCl_2}$, with the evolution of chlorine. The reduction of $\mathrm{MnCl_3}$ to $\mathrm{MnCl_2}$ occurs quantitatively in the presence of excess ferrous salt, which is oxidized to the ferric state. Values of ΔH_R and $\Delta H_\mathrm{f}^0(\mathrm{M(pd)_3, c})$ are shown in Table 13 for these complexes and also for $\mathrm{Mo(pd)_3}$. For this last compound Pilcher et al. [30] used [HCl, 7.97 H_2O] as solvent and the relevant thermochemical reaction is

$$43.85\ H_2O(l) + 2\ NaCl(c) + 3\ FeCl_3(c) + Mo(pd)_3(c) \xrightarrow{\Delta H_R}$$

$$5\,[HCl, 7.97\ H_2O]\,(l) + 3\ Hpd(l) + 3\ FeCl_2(c) + Na_2[MoO_4]\,(c) \qquad (16)$$

Two points are noteworthy. First, the stoichiometry has been arranged so that the [HCl, 7.97 H_2O] produced in the reaction has the same concentration as the solvent. Secondly, addition of $FeCl_3$ ensured oxidation of Mo(III) to Mo(IV), which appears as $Na_2[MoO_4]$. It is worth emphasising that calculated value of ΔH_f^0(Mo(pd)$_3$, c) depends on the enthalpies of formation of $Na_2[MoO_4]$(c), $FeCl_2$(c), $FeCl_3$(c), NaCl(c), [HCl, 7.97 H_2O], Hpd(l) and H_2O(l).

Kakołowicz and Giera [31,32] have published measurements of the enthalpies, ΔH_R, of the following decomposition reactions of ML_2 complexes

$$2\,[HCl, \infty H_2O]\,(l) + ML_2(c) \xrightarrow{\Delta H_R} MCl_2 \cdot nH_2O(c) + 2\ HL(l) + \infty\ H_2O(l) \qquad (17)$$

where $MCl_2 \cdot nH_2O$ is $MnCl_2 \cdot 4\ H_2O$, $CoCl_2 \cdot 6\ H_2O$, $NiCl_2 \cdot 6\ H_2O$, $CuCl_2 \cdot 2\ H_2O$, or $ZnCl_2$(anhydrous) and L is pd, pbd, or dppd. The solvent was either [HCl, 11.60 H_2O] for all of these complexes except Ni(dppd)$_2$, for which a mixture of 25% by volume of [HCl, 11.60 H_2O] and 75% by volume of 1,4-dioxan was used.

The thermochemical reactions for all of these complexes are listed in Table 12, whilst the respective values of ΔH_R are shown in Table 13. The values of ΔH_f^0(ML_2, c) which are also shown in this table are calculated from the ΔH_R values aand enthalpies of formation shown in Appendix 1.

In three cases, {Co(pd)$_2$}$_4$, {Ni(pd)$_2$}$_3$ and Cu(pd)$_2$, there are two values of ΔH_f^0(cryst), although agreement between results from different sources is not good.

Enthalpies of sublimation of the metal–dionato complexes, listed in Table 13 are shown again in Table 14, with more information. Except for one direct measurement of the enthalpy of sublimation of Cr(pd)$_3$, obtained by differential scanning calorimetry, enthalpies of sublimation have been calculated from the variation of vapour pressure with temperature. This has been determined by use of (a) the isoteniscope, (b) Knudsen effusion techniques or (c) thermogravimetric analysis. Direct measurement of vapour pressure with the isoteniscope is reliable only for highly purified samples and where a choice is available, we have preferred to select a value obtained by Knudsen effusion techniques. Where no experimental value for the enthalpy of sublimation is available, estimated values have been used. Thus, to use the same

TABLE 14

Enthalpies of sublimation of metal-dionato complexes (kJ mol^{-1})

Complex	ΔH_{sub}	T (K)	Method [b]	Ref.
$(Co(pd)_2)_4$	251	345	Isoteniscope	33
	345 [a]	350	TGA	34
$(Ni(pd)_2)_3$	287	?	Knudsen effusion	35
	207	300	Isoteniscope	33
	383 ± 30 [a]	390	Knudsen effusion	34
$Ni(tmhd)_2$	145	?	Knudsen effusion	33
$Cu(pd)_2$	57	298	Knudsen torsion/effusion	37
$Ni(pbd)_2$	145 ± 10	?	Knudsen effusion	35
$Cr(pd)_3$	123 [a]	?	Knudsen effusion	37
	125	540	DSC	38
	86	340	TGA	34
$Mn(pd)_3$	78	?	Isoteniscope	37
$Fe(pd)_3$	65	?	?	39
$Ni-(pbd)_2$	42	?	Isoteniscope	33

[a] Preferred value. [b] TGA = thermogravimetric analysis; DSC = differential scanning calorimetry.

value of 123.0 kJ mol^{-1} for both $Cr(pd)_3$ and $Mo(pd)_3$ seems reasonable when it has been shown that the enthalpies of sublimation of $Ni(pd)_2 = 127.7 \pm 10$ (390 K), $Pd(pd)_2 = 127.8 \pm 16$ (375 K) and $Pt(pd)_2 = 129.4 \pm 9$ (370 K) kJ mol^{-1} are so similar [36].

The remaining values for enthalpies of sublimation have been estimated on a somewhat arbitrary basis. The tetrahedral $Zn(pb)_2$ is assumed to have a smaller enthalpy of sublimation than the square planar $Cu(pb)_2$ by 12 kJ mol^{-1}. Replacement of a methyl group of pd by a phenyl group to give pbd is taken to increase the value of ΔH_{sub} by about 10 kJ mol^{-1}; thus $Cu(pd)_2 = 57.1$, $Cu(pbd)_2 = (67)$ kJ mol^{-1}; $Zn(pd)_2 = 45$, $Zn(pbd)_2 = (55)$ kJ mol^{-1}, and similarly $Ni(pbd)_2 = 42.2$, $Ni(dppd)_2 = (52)$ kJ mol^{-1}. Calculation of accurate metal–ligand bond dissociation energies requires reliable values for the sublimation enthalpies of the complexes. Appendix 3 summarises the current experimental approach to the determination of these enthalpies of sublimation.

The mean metal–oxygen bond dissociation energies in the metal dionato complexes ML_2 and ML_3, $\bar{D}(M–O)$, corresponding to the gas-phase dissociation reactions

$$ML_2(g) \rightarrow M(g) + 2\,L(g) \qquad (18)$$

and

$$ML_3(g) \rightarrow M(g) + 3\,L(g) \qquad (19)$$

can be calculated from the relationships

$$\overline{D}(\mathrm{M{-}O}) = \tfrac{1}{4}\,\{\Delta H_f^0(\mathrm{M,\,g}) + 2\,\Delta H_f^0(\mathrm{L,\,g}) - \Delta H_f^0(\mathrm{ML_2,\,g})\} \tag{20}$$

and

$$\overline{D}(\mathrm{M{-}O}) = \tfrac{1}{6}\,\{\Delta H_f^0(\mathrm{M,\,g}) + 3\,\Delta H_f^0(\mathrm{L,\,g}) - \Delta H_f^0(\mathrm{ML_3,\,g})\} \tag{21}$$

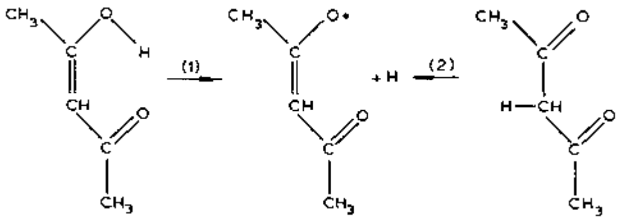
To calculate these $\overline{D}$(M–O) values, we require ΔH_f^0(M, g) and ΔH_f^0(L, g), values for which are shown in the Appendices. However, we give here the derivation of the enthalpy of formation of the pentanedionato radical in some detail.

(ii) ΔH_f^0*(pentanedionato, g)*

The enthalpy of formation of the pentane-2,4-dionato radical, $CH_3COCH{=}COCH_3$ (pd), has been calculated by Cavell and Pilcher [41] and what follows is a summary of their approach.

The enthalpy of combustion of acetylacetone, $-\Delta H_c^0(\mathrm{Hpd,\,l}) = 2687 \pm 1.5$ kJ mol^{-1}, measured by Nicholson [42] which leads to $\Delta H_f^0(\mathrm{Hpd,\,l}) = -(423.8 \pm 1.5)$ kJ mol^{-1} was made on the liquid equilibrium mixture, 18.6% keto + 81.4% enol form [43]. The enthalpy of enolisation has been reported, in the liquid phase [43] to be -11.3 ± 0.4 kJ mol^{-1}, and in the gaseous phase [44] -10.0 ± 0.8 kJ mol^{-1}. The enthalpy of vaporisation of the enol was determined by Irving and Wadsö [45] as 43.2 ± 0.1 kJ mol^{-1}. These data permit derivation of the enthalpy of formation of Hpd(g) in both the keto and enol forms: $\Delta H_f^0(\mathrm{Hpd,\,keto,\,g}) = -372.7 \pm 1.7$ kJ mol^{-1} and $\Delta H_f^0(\mathrm{Hpd,\,enol,\,g}) = -382.7 \pm 1.7$ kJ mol^{-1}. Application of the Allen bond-energy scheme [46] to these structures yields the estimated values, $\Delta H_f^0(\mathrm{Hpd,\,keto,\,g,\,calc.}) = -370.7$ kJ mol^{-1}, $\Delta H_f^0(\mathrm{Hpd,\,enol,\,g,\,calc.}) = -272.7$ kJ mol^{-1}; i.e. there is agreement for the keto form, but the enol form is stabilised by 110 kJ mol^{-1}, probably due to internal hydrogen bonding and π-electron delocalisation.

The pentanedionato radical, pd, results from the enol form by dissociation from the hydroxyl group, and from the keto form by dissociation of the methylene/hydrogen atom i.e. by routes (1) or (2). From the enthalpy of



enolisation in the gaseous state it follows that, $D(\text{O–H, enol}) - D(\text{C–H, keto}) = 10$ kJ mol^{-1}. An upper limit for the (C–H) dissociation energy in acetone has been given by Kerr [47], $D(\text{CH}_3\text{COCH}_2\text{–H}) = 385$ kJ mol^{-1}. D(C–H, keto) should be less than this because (a) the dissociation is from a secondary, not a primary carbon atom, and (b) the delocalisation stabilisation in the pd radical will be greater than that in the $\text{CH}_3\text{COCH}_2\cdot$ radical. Accurate calculation of these differences is not possible but from comparison with changes in dissociation energies produced by similar effects in other molecules [47], a reasonable estimate is $D(\text{C–H, keto}) = 355$ kJ mol^{-1}, whence it follows that $D(\text{O–H, enol}) = 365$ kJ mol^{-1}, although this is a lower value than used previously [48].

The estimated dissociation energies with $\Delta H_f^0(\text{H, g}) = 218.00 \pm 0.01$ kJ mol^{-1} [50] lead to $\Delta H_f^0(\text{pd, g}) = -235.7$ kJ mol^{-1}.

A plot of $\bar{D}$(M–O) values is shown in Fig. 8. Values for M(pd)_3 complexes indicate a fall in the value of $\bar{D}$(M–O) from Cr to Mn. The higher value for $\bar{D}$(Fe–O) in Fe(pd)_3 may be due to this complex being low spin. For the complexes M(pd)_2, the values fall along the series Mn > Co > Ni > Cu > Zn, which is contrary to the normal plot of enthalpies of complexation in solution, where the bond strength increases from Mn to a maximum at Ni or Cu, before falling to Zn. Substitution of a CH_3 group in pd by a C_6H_5 group to give pbd increases the value of $\bar{D}$(M–O), considerably for Ni, less so for

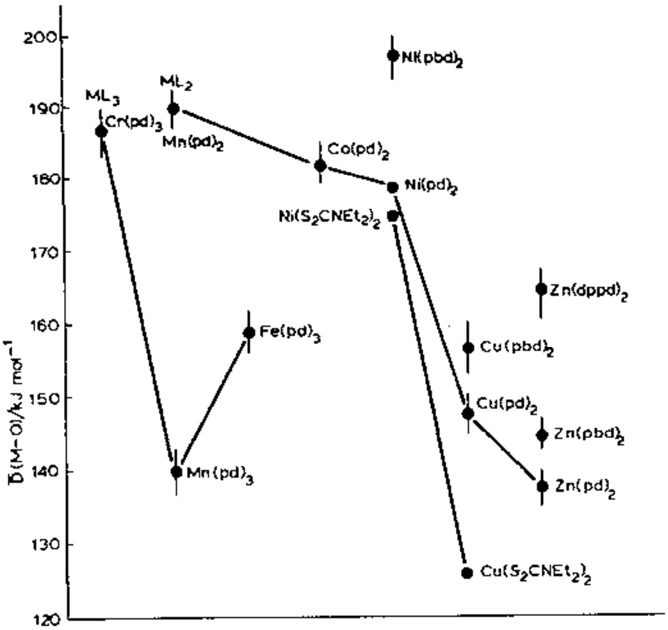


Fig. 8. $\bar{D}$(M–O) in dionato and thiocarbamato complexes.

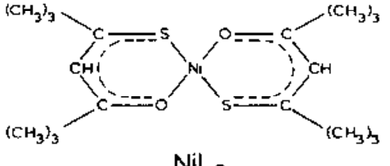
Cu and to a yet smaller extent for Zn complexes. The value of $\bar{D}$(Ni–O) is marginally lowered by substitution of a CH_3 group in pd by $(CH_3)_2CH$ in the Ni complex (not shown in Fig. 8).

It should be noted that these $\bar{D}$(M–O) values are not dependent on the enthalpies of formation of the ligands Hpb, Hpbd, Hdppd and Htmhd, since the term appears in the calculation of both ΔH_f^0(complex, c) and also of the ligand radical, e.g. ΔH_f^0(pd, g). Calculations of the enthalpies of formation ΔH_f^0(dppd, g) and ΔH_f^0(tmhd, g) are shown in Appendix 2.

(iii) Mercapto-onato complexes

Using a procedure similar to that outlined for determination of the enthalpies of formation of the metal dionato complexes, Irving and Lockyer [40] have found the enthalpy, $\Delta H_R = -(5.5 \pm 1.2)$ kJ mol^{-1}, of the following reaction, where L is 5-mercapto-2,2,6,6-tetramethylhept-4-en-3-onato, $(CH_3)_3CCOCH{=}CS^{\cdot}C(CH_3)_3$.

$$NiL_2(c) + 2\left[HClO_4, 3\ H_2O\right](l) \rightarrow 2\ HL(l) + Ni(ClO_4)_2 \cdot 6\ H_2O(c) \qquad (22)$$



NiL_2

The solvent used was a mixture of butan-2-one and $[HClO_4, 3.03\ H_2O]$ in a 9 : 1 ratio. Using the values $\Delta H_f^0(Ni(ClO_4)_2 \cdot 6\ H_2O, c) = -2035.9$ kJ mol^{-1} and $\Delta H_f^0[HClO_4$ in $3.03\ H_2O](l) = -(119.1 \pm 0.4)$ kJ mol^{-1}, given in Appendix 1, we calculate the difference $2\ \Delta H_f^0(HL, l) - \Delta H_f^0(NiL_2, c) = 77.2 \pm 2$ kJ mol^{-1}. Incorporating a value for the enthalpy of sublimation of NiL_2, $\Delta H_{sub} = 117.7 \pm 8$ kJ mol^{-1} (measured by a Knudsen effusion technique) and a latent heat of vaporisation $\Delta H_{vap}(HL) = 64.4 \pm 0.4$ kJ mol^{-1}, estimated by Irving and Lockyer [40] on the basis of differences between values for several esters and their thio analogues, the difference is calculated $2\ \Delta H_f^0(HL, g) – \Delta H_f^0(NiL_2, g) = +88.3 \pm 10$ kJ mol^{-1}.

For the two gas-phase dissociation reactions

$$HL \rightarrow H + L \qquad (23)$$

$$NiL_2 \rightarrow Ni + 2\ L \qquad (24)$$

we write

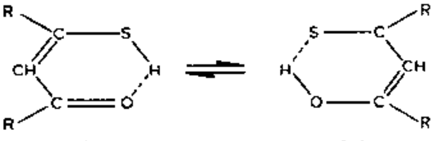
$$\bar{D}(H–L) = \Delta H_f^0(H, g) + \Delta H_f^0(L, g) - \Delta H_f^0(HL, g)$$

$$2\ D(Ni–L) = \Delta H_f^0(Ni, g) + 2\ \Delta H_f^0(L, g) - \Delta H_f^0(NiL_2, g) \qquad (25)$$

hence

$$2\,D(\text{Ni–L}) = \Delta H_f^0(\text{Ni, g}) + 2\,D(\text{H–L}) - 2\,\Delta H_f^0(\text{H, g}) + 2\,\Delta H_f^0(\text{HL, g}) - \Delta H_f^0(\text{NiL}_2\text{, g}) \qquad (26)$$

It is a matter of conjecture whether the structure of gaseous monothio-β-diketones show the predominance of either of the two possible intramolecular hydrogen-bonded forms, i.e. the keto-thioenol (**I**) or the thioketo-enol (**II**), and consequently whether D(L–H) refers mainly to dissociation of the O–H or the S–H bond. For pentane-dione we have used the value D(O–H) = 365 kJ mol^{-1}, whilst Kerr [47] has given a value of D(S–H) = 377 ± 20 kJ mol^{-1}. We select a value of 370 ± 20 kJ mol^{-1} for D(L–H).

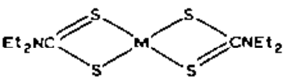


(I) (II)

This leads to 2 D(Ni–L) = 822 ± 50 kJ mol^{-1}, which is the sum of the mean dissociation energies 2 $\{\bar{D}(\text{Ni–O}) + \bar{D}(\text{Ni–S})\}$. Assuming that $\bar{D}$(Ni–O) = 175 ± 9 kJ mol^{-1} as in the 2,2,6,6-tetramethylheptane-3,5-dionato complex, Ni(tmhd)$_2$, leads to the value $\bar{D}$(Ni–S) = 236 ± 16 kJ mol^{-1}. It is noted that the Ni–S bond in this monothio-β-diketone complex is considerably stronger than that found by Ashcroft [13] in the thiourea complex, Ni(tu)$_4$Cl$_2$, where D(Ni–S) = 148 kJ mol^{-1}.

(iv) Diethyldithiocarbonato complexes

In the bis(diethyldithiocarbamato)nickel(II) and copper(II) complexes, all four of the sulphur atoms are assumed to bond to the metal. Cavell et al. [51] have determined the enthalpies of formation of these complexes, by measuring the enthalpies, ΔH_R, of the following ligand replacement reactions.



$$\tfrac{1}{3}\,\{\text{Ni(pd)}_2\}_3\text{(c)} + 2\,[\text{NEt}_2\text{H}_2][\text{S}_2\text{CNEt}_2]\text{(c)} \rightarrow \text{Ni(S}_2\text{CNEt}_2)_2\text{(c)} + 2\,\text{NEt}_2\text{H(l)} + 2\text{Hpd(l)} \qquad (27)$$

$$\text{Cu(pd)}_2\text{(c)} + 2\,[\text{NEt}_2\text{H}_2][\text{S}_2\text{CNEt}_2]\text{(c)} \rightarrow \text{Cu(S}_2\text{CNEt}_2)_2\text{(c)} + 2\,\text{NEt}_2\text{H(l)} + 2\,\text{Hpd(l)} \qquad (28)$$

In these reactions, the pentane-2,4-dionato group in the complex $M(pd)_2$ is replaced by the diethyldithiocarbamato group to give $M(S_2CNEt_2)_2$, where M is Ni or Cu. For the nickel complex dioxan was used as solvent, whilst for the copper complex dimethylformamide was used. Using a direct calorimetric technique involving differential scanning calorimetry Cavell et al. [52] obtained ΔH_{sub} values for $Ni(SCNEt_2)_2$ of 102.6 ± 1.5 kJ mol^{-1} and $Cu(S_2CNEt_2)_2$ of 116.2 ± 1.3 kJ mol^{-1}, which are much higher than those obtained by D'Ascenzo and Wendlandt [53] based on isoteniscope vapour pressure/temperature data, viz. $Ni(SCNEt_2)_2 = 61.1 \pm 1.7$ and $Cu(SCNEt_2)_2 = 87 \pm 1.7$ kJ mol^{-1}. Incomplete outgassing of the sample appears to give low results by the isoteniscope method.

In order to calculate the enthalpy of the following gas-phase dissociation reaction, a value for $\Delta H_f^0(S_2CNEt_2, g)$ is required. A value

$$M(S_2CNEt_2)(g) \rightarrow M(g) + 2\ S_2CNEt_2(g)$$

for the enthalpy of formation of gaseous diethyldithiocarbamic acid has been calculated by Cavell et al. [51] using the Allen [54] bond-energy scheme, as $\Delta H_f^0(\text{acid, g}) = 35.13$ kJ mol^{-1}. The S–H bond dissociation energy D(S–H) for diethyldithiocarbamic acid is assumed to be 316 ± 25 kJ mol^{-1}, some 60 kJ mol^{-1} less than $D(\text{HS–H}) = 376.6$ kJ mol^{-1} in H_2S, because $D(\text{O–H}) = 433 \pm 10$ kJ mol^{-1} in CH_3COOH [55] is 60 kJ mol^{-1} less than $D(\text{HO–H}) = 498.3$ kJ mol^{-1} in H_2O. This leads to $\Delta H_f^0(S_2CNEt_2, g) = 133 \pm 25$ kJ mol^{-1}. Using this value leads to those for $\bar{D}$(M–S) in Table 15.

(v) Amino acid complexes

Bernard et al. [56] have measured enthalpies of solution of the amino acid complexes $M(NH_2RCO_2)_2$, $M(NH_2RCO_2) \cdot 2\ NH_3$ and $M(NH_2RCO_2) \cdot H_2O$ in 2 M HNO_3 at 298 K, eqns. (29)–(31)

$$M(NH_2RCO_2)_2(c) + 4\ H^+(aq) \rightarrow M^{2+}(aq) + 2\ NH_3^+RCOOH(aq) \qquad (29)$$

$$M(NH_2RCO_2)_2 \cdot 2\ NH_3(c) + 6\ H^+(aq) \rightarrow M^{2+}(aq) + 2\ NH_3^+RCOOH(aq) + 2\ NH_4^+(aq) \qquad (30)$$

$$M(NH_2RCO_2)_2 \cdot H_2O(c) + 4\ H^+(aq) \rightarrow M^{2+}(aq) + 2\ NH_3^+RCOOH(aq) + H_2O(l) \qquad (31)$$

Experimental details are not given in their paper, nor are the values of enthalpies of formation used in the calculations, except that their source of these ancillary data is the National Bureau of Standards Circular 500 [57]. Their derived ΔH_f^0 values are shown in Tables 16 and 17, together with other values, either obtained by Ribeiro da Silva [10], who used a similar ap-

TABLE 15

Enthalpies of formation of diethyldithiocarbamato complexes [51] (kJ mol^{-1})

Complex	ΔH_R(298 K)	ΔH_f^0(complex, c)	ΔH_{sub}	ΔH_f^0(complex, g)	$\bar{D}$(M–S)
$Ni(S_2CNEt_2)_2$	94.5 ± 2.0	-105.5 ± 20	102.6 ± 1.5	-2.9 ± 21	175 ± 18
$Cu(S_2CNEt_2)_2$	97.6 ± 1.1	-5.4 ± 18	116.2 ± 1.3	$+110.8 \pm 19$	123 ± 17

TABLE 16

Enthalpies of formation (kJ mol^{-1}) of amino acid complexes [56] $Ni(NH_2RCO_2)_2 \cdot xH_2O \cdot yNH_3$,

Complex		x	y	ΔH_f^0(complex, c)
R = CH_2	Glycine	0	0	−(966.8 ± 2.9)
$CHCH_3$		0	2	−(1180.4 ± 3.5)
		2	0	−(1559.6 ± 4.7)
$CHCH_3$	α-Alanine	0	0	−(1065.9 ± 3.2)
		0	2	−(1285.4 ± 3.8)
		4	0	−(2243.4 ± 6.7)
$CHCH(CH_3)_2$	Valine	0	0	−(1208.0 ± 3.6)
		0	2	−(1412.8 ± 4.3)
		2	0	−(1804.1 ± 5.4)
$CHCH(CH_3)CH_2CH_3$	Isoleucine	0	0	−(1272.8 ± 3.8)
		0	2	−(1479.6 ± 4.4)
		2	0	−(1858.8 ± 5.6)
$CH(CH_2)_3CH_3$	Norleucine	0	0	−(1312.5 ± 3.9)

proach, or taken from N.B.S. Circular 500 [57].

Enthalpies of sublimation of only two of these metal amino-acid complexes have been measured experimentally: ΔH_{sub}^{298}Ni(gly)$_2$ = 120 ± 10 kJ mol^{-1} and ΔH_{sub}^{298}Cu(gly)$_2$ = 105 ± 12 kJ mol^{-1} [36]. Incorporating these values we calculate ΔH_f^0(Ni(gly)$_2$, g) = −(846.8 ± 13) and ΔH_f^0(Cu(gly)$_2$,

TABLE 17

Enthalpies of formation (kJ mol^{-1}) of amino acid complexes [56] $Cu(NH_2RCO_2)_2 \cdot xH_2O \cdot yNH_3$

Complex		x	y	ΔH_f^0(complex, c)
R=CH_2	Glycine	0	0	−(937.5) [57], −(948.1 ± 1.2) [10]
		0	2	−(1125.3 ± 3.4)
		1	0	−(1235.2) [57]
$CHCH_3$	α-Alanine	0	0	−(1016.6 ± 3.4), −(1010.4 ± 1.3) [10]
		0	2	−(1203.4 ± 3.6)
		1	0	−(1307.1 ± 3.9)
$CHCH(CH_3)_2$	Valine	0	0	−(1098.1 ± 3.3), −(1115.7 ± 1.3) [10]
		0	2	−(1295.8 ± 3.8)
		1	0	−(1395.3 ± 4.2)
$CHCH(CH_3)CH_2CH_3$	Isoleucine	0	0	−(1162.9 ± 3.5)
		0	2	−(1347.9 ± 4.1)
		1	0	−(1459.7 ± 4.4)
$CH(CH_2)_3CH_3$	Norleucine	0	0	−(1203.8 ± 3.6)

g) = $-(843.1 \pm 13)$ kJ mol^{-1}. Using the value $\Delta H_f^0(\mathrm{NH_2CH_2CO_2},\ g) = -178.9 \pm 3.5$ kJ mol^{-1}, calculated in Appendix 2, we obtained the sums $[\bar{D}(\mathrm{Ni{-}O}) + \bar{D}(\mathrm{Ni{-}N})] = 459 \pm 11$ and $[\bar{D}(\mathrm{Cu{-}O}) + \bar{D}(\mathrm{Cu{-}N})] = 412 \pm 10$ kJ mol^{-1}. It is difficult to apportion the sum between the two bonds. However, we note that these sums are both greater than $2\bar{D}(\mathrm{Ni{-}O}) = 350 \pm 8$ kJ mol^{-1} in $\mathrm{Ni(pd)_2}$ or $2\bar{D}(\mathrm{Cu{-}O}) = 290 \pm 8$ kJ mol^{-1} in $\mathrm{Cu(pd)_2}$, so that the bonding of an amino acid radical is certainly stronger than the bonding of a pentanedionato radical by ca. 100 kJ mol^{-1}.

The enthalpies of the dissociation reactions

$$\mathrm{M(NH_2RCO_2)_2 \cdot \mathit{x}H_2O(c) \rightarrow M(NH_2RCO_2)_2(c) + \mathit{x}H_2O(g)}$$

$$\mathrm{M(NH_2RCO_2)_2 \cdot \mathit{y}NH_3(c) \rightarrow M(NH_2RCO_2)_2(c) + \mathit{y}NH_3(g)}$$

have been calculated from the enthalpies of formation at 298 K and have also been measured directly, using differential scanning calorimetry, at temperatures between 400 and 420 K. Assuming that $\Delta H_{\mathrm{sub}}\mathrm{M(NH_2RCO_2)_2 \cdot \mathit{x}H_2O} = \Delta H_{\mathrm{sub}}\mathrm{M(NH_2RCO_2)_2}$ for a given metal and R group, the mean bond dissociation energies $\bar{D}(\mathrm{M{-}O})$ and $\bar{D}(\mathrm{M{-}N})$, corresponding to the

TABLE 18

Mean bond dissociation energies (kJ mol^{-1}) for dissociation of two axial ligands [56]

Complex	$\bar{D}(\mathrm{M{-}O})$	
	From ΔH_f^0(298 K)	DSC (ca. 400 K)
$\mathrm{Ni(gly)_2 \cdot 2\ H_2O}$	54.8	55.6 ± 1.7
$\mathrm{Ni(ala)_2 \cdot 2\ H_2O}$	52.7	50.6 ± 1.5
$\mathrm{Ni(val)_2 \cdot 2\ H_2O}$	56.4	58.9 ± 1.8
$\mathrm{Ni(isol)_2 \cdot 2\ H_2O}$	51.4	53.1 ± 1.6
$\mathrm{Cu(gly)_2 \cdot H_2O}$	56.0	
$\mathrm{Cu(ala)_2 \cdot H_2O}$	48.5	46.4 ± 1.4
$\mathrm{Cu(val)_2 \cdot H_2O}$	55.6	58.1 ± 1.7
$\mathrm{Cu(isol)_2 \cdot H_2O}$	55.2	57.3 ± 1.7
	$\bar{D}(\mathrm{M{-}N})$	
$\mathrm{Ni(gly)_2 \cdot 2\ NH_3}$	60.2	62.3 ± 1.9
$\mathrm{Ni(ala)_2 \cdot 2\ NH_3}$	63.5	61.5 ± 1.8
$\mathrm{Ni(val)_2 \cdot 2\ NH_3}$	56.4	58.1 ± 1.7
$\mathrm{Ni(isol)_2 \cdot 2\ NH_3}$	57.3	55.5 ± 1.6
$\mathrm{Cu(gly)_2 \cdot 2\ NH_3}$	58.3	56.8 ± 1.7
$\mathrm{Cu(ala)_2 \cdot 2\ NH_3}$	47.2	48.1 ± 1.4
$\mathrm{Cu(val)_2 \cdot 2\ NH_3}$	52.7	52.2 ± 1.6
$\mathrm{Cu(isol)_2 \cdot 2\ NH_3}$	46.4	47.8 ± 1.4

removal of the axial water or ammonia molecules, can be calculated. These values are shown in Table 18. They lie in the range 46–62 kJ mol^{-1} and for a particular metal–amino-acid complex the $\bar{D}$(M–O) and $\bar{D}$(M–N) values are very similar. These values are less than one-half of those for $\bar{D}$(M–O) and $\bar{D}$(M–N) which we noted for the bonding of pyridine or benzoxazole in the complexes ML_2X_2.

The loss of two axial ligands changes the configuration of the complex from octahedral to square planar. According to the Angular Overlap Model description [15] of bonding in these complexes, the relative energy levels of the antibonding orbitals will be those shown in Fig. 2. (The levels of the bonding orbitals will be of the same pattern, mirrored about the zero energy level.) Metal–ligand bonding, due to filled bonding orbitals, is offset by the effect of antibonding electrons. This simplified description of bonding gives the same total σ-bonding energy for the octahedral and square planar complexes, $6e_\sigma$ for Ni(II)d^8 complexes, and $3e_\sigma$ for Cu(II)d^9 complexes, and implies that no energy is required to remove the two axial ligands. This molecular orbital description is slightly modified by the inclusion of metal s- and p-orbitals in the bonding. However, as the resultant additional molecular orbitals are only weakly bonding the mean bond dissociation energies of axial bond are predicted to be low. Igumenov et al. [58] have determined the enthalpies of the gas-phase dissociation reactions

$$\tfrac{1}{2}\ \mathrm{Co(pd)_2B_2(g)} \rightarrow \tfrac{1}{2}\ \mathrm{Co(pd)_2(g)} + \mathrm{B(g)}$$

where the base B is NH_3 (57.7 kJ mol^{-1}), pyridine (63.2 kJ mol^{-1}), $^{n}BuNH_2$ (77.0 kJ mol^{-1}) and H_2O (50.2 kJ mol^{-1}). They assume a value $\Delta H_{sub}\mathrm{Co(pd)_2B_2} = 105$ kJ mol^{-1}, which is ca. 20 kJ mol^{-1} greater than $\frac{1}{4}$ $\Delta H_{sub}\{\mathrm{Co(pd)_2}\}_4 = 334.8$ kJ mol^{-1}. Incidentally, if in an octahedral complex, it is generally easier to remove the fifth and sixth axial ligands, than the remaining four, then the value of $\bar{D}$(M–thiourea) calculated for the complexes $\mathrm{M(tu)_4X_2}$ is likely to be a lower value than $\bar{D}$(M–thiourea) in the four-coordinate complexes $\mathrm{M(tu)_2X_2}$.

(vi) Trifluoroacetato and benzoato complexes

Calado et al. [59] have obtained values for the enthalpies of formation of the metallocene complexes $\mathrm{M(\eta\text{-}C_5H_5)_2(O_2CR)_2}$, where M = Mo, W or Ti, and R = C_6H_5 or CF_3. The enthalpies, ΔH_R, of reactions (32) and (33) were determined by measuring the enthalpies of solution of reactants and products in a mixture of acetone and either 8.3 M or 10.0 M HCl.

$$\mathrm{Mn(\eta\text{-}C_5H_5)_2(O_2CC_6H_5)_2(c)} + 2\,[\mathrm{HCl},\ 5.55\ \mathrm{H_2O}]\,(\mathrm{l}) \rightarrow \mathrm{M(\eta\text{-}C_5H_5)_2Cl_2(c)} + 2\ \mathrm{C_6H_5COOH(c)} \qquad (32)$$

TABLE 19

Enthalpies of formation of $M(\eta\text{-}C_5H_5)_2(O_2CR)_2$ [59] (kJ mol^{-1})

Complex	ΔH_R	ΔH_f^0(complex, c)	ΔH_{sub} [a]	ΔH_f^0(complex, g)	$\bar{D}(M-O)_{O_2CR}$
$Mo(\eta\text{-}C_5H_5)_2(O_2CC_6H_5)_2$	−(65.8 ± 3.9)	−(486.2 ± 3.4)	(94 ± 10)	−(392.2 ± 14)	305 ± 9
$W(\eta\text{-}C_5H_5)_2(O_2CC_6H_5)_2$	−(78.4 ± 4.4)	−(448.9 ± 3.7)	(98 ± 10)	−(350.9 ± 14)	341 ± 9
$Ti(\eta\text{-}C_5H_5)_2(O_2CC_6H_5)_2$	−(64.2 ± 5.3)	−(775.2 ± 8.1)	(112 ± 8)	−(663.2 ± 23)	432 ± 10
$Mo(\eta\text{-}C_5H_5)_2(O_2CCF_3)_2$	+26.0 ± 4.1	−(1952.0 ± 3.9)	(90 ± 10)	−(1862.0 ± 14)	327 ± 26
$W(\eta\text{-}C_5H_5)_2(O_2CCF_3)_2$	+13.2 ± 3.4	−(1914.5 ± 3.8)	(94 ± 10)	−(1820.5 ± 13)	310 ± 26
$Ti(\eta\text{-}C_5H_5)_2(O_2CCF_3)_2$	+5.6 ± 3.8	−(2219.0 ± 8.0)	108 ± 8	−(2111.0 ± 12)	443 ± 26

[a] Estimated values in parentheses.

TABLE 20

Enthalpies of formation of $Mo(\eta\text{-}C_5H_5)_2(SR)_2$ [60] (kJ mol^{-1})

	ΔH_R	ΔH_f^0(complex, c)	ΔH_{sub} [a]	ΔH_f^0(complex, g)	$\bar{D}(M-S)$
$Mo(\eta\text{-}C_5H_5)_2(S^nC_3H_7)_2$	14.2 ± 7.3	4.6 ± 7.3	(90 ± 10)	94.6 ± 17	237 ± 18
$Mo(\eta\text{-}C_5H_5)_2(S^iC_3H_7)_2$	−(50.3 ± 6.7)	57.1 ± 10.5	(90 ± 10)	147.1 ± 20	202 ± 18
$Mo(\eta\text{-}C_5H_5)_2(S^nC_4H_9)_2$	−(44.8 ± 6.4)	14.0 ± 11.4	(92 ± 10)	106.0 ± 21	211 ± 19
$Mo(\eta\text{-}C_5H_5)_2(S^tC_4H_9)_2$	−(69.6 ± 4.8)	6.9 ± 9.0	(92 ± 10)	98.9 ± 20	193 ± 18

[a] Estimated values.

$$M(\eta\text{-}C_5H_5)_2(O_2CCF_3)_2(c) + 2\,[HCl, 4.40\,H_2O]\,(l) \rightarrow M(\eta\text{-}C_5H_5)_2Cl_2(c) + 2\,CF_3COOH(l) \quad (33)$$

Values of ΔH_R and the derived ΔH_f^0(complex, c) are shown in Table 19. It is noted that the values for the enthalpies of formation of the complexes depend on $\Delta H_f^0(M(\eta\text{-}C_5H_5)_2Cl_2$, c) and on ΔH_f^0(RCOOH, c or l) given in Appendix 1.

The mean bond dissociation of the acid radicals, $\bar{D}(M\text{-}O)_{O_2CR}$ is one half of the enthalpy of the gas-phase dissociation reaction

$$M(\eta\text{-}C_5H_5)_2(O_2CR)_2(g) \rightarrow M(\eta\text{-}C_5H_5)_2(g) + 2\,RCO_2(g)$$

To calculate this enthalpy, the enthalpies of formation of the radicals $M(C_5H_5)_2$, where M = Mo, W and Ti, and of the radicals RCO_2(g), where $R = C_6H_5$ and CF_3 must first be calculated. Using the values derived in Appendix 2, the mean bond dissociation energies, $\bar{D}(M\text{-}O)_{O_2CR}$, shown in Table 18 are derived.

A very similar approach has been used by Dias et al. [60] in a determination of the mean bond dissociation energies, $\bar{D}$(M–S), in the metallocene complexes $Mo(\eta\text{-}C_5H_5)_2(SR)_2$, where R = n-$C_3H_7$, i-$C_3H_7$, n-$C_4H_9$, and t-$C_4H_9$. Enthalpies of reaction (34) are shown in Table 20, together with ΔH_f^0 values and the derived $\bar{D}$(M–S). These latter depend on enthalpies of formation of the radicals, RS, which are given in Appendix 2.

$$Mo(\eta\text{-}C_5H_5)_2(SR)_2(c) + 2\,[HCl, 5.55\,H_2O]\,(l) \rightarrow Mo(\eta\text{-}C_5H_5)_2Cl_2(c) + 2\,RSH(l) \quad (34)$$

(vii) Alkoxide and alkylamino complexes

Bradley and Hillyer [61] have determined the enthalpy of hydrochlorination of $Ti(OEt)_4$ (reaction (35)) and also the enthalpies of reactions in which the ethoxy group of this complex is replaced by either another alkoxy group, such as tertiary butoxy, or the diethylamino group. Enthalpies of acid hydrolysis of the complexes $V(O^tBu)_4$ and $Cr(O^tBu)_4$ in 0.1 M HCl and 1 M H_2SO_4, respectively, were also measured.

$$Ti(OEt)_4(l) + 4\,HCl(g) \rightarrow TiCl_4(g) + 2\,EtOH(l) \quad (35)$$

$$Ti(OEt)_4(l) + 4\,{}^tBuOH(l) \rightarrow Ti(O^tBu)_4(l) + 4\,EtOH(l) \quad (36)$$

$$Ti(OEt)_4(l) + 4\,Et_2NH(l) \rightarrow Ti(NEt_2)_4(l) + 4\,EtOH(l) \quad (37)$$

$$V(O^tBu)_4(l) + 4\,[HCl, 51.3\,H_2O] \rightarrow VCl_4(l) + 4\,{}^tBuOH(l) \quad (38)$$

$$Cr(O^tBu)_4(l) + 4\,H^+(aq) \rightarrow 2\,Cr(H_2O)_6^{3+}(aq) + CrO_4^{2-}(aq) + 12\,{}^tBuOH(l) \quad (39)$$

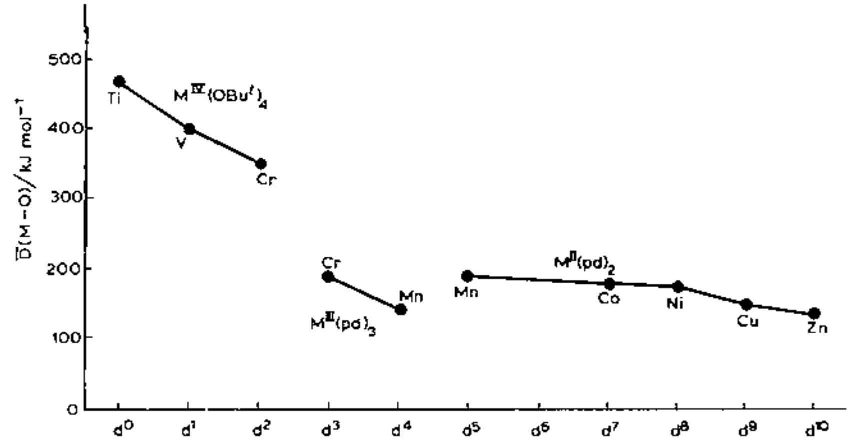


Fig. 9. Plot of $\bar{D}$(M–O) against the number of metal *d* electrons.

$$\mathrm{Mo(NMe_2)_4(c)} + \tfrac{1}{2}\,\mathrm{N_2(g)} + 4\,\mathrm{H_2O(l)} + \mathrm{Na_2SO_4(c)} \rightarrow \mathrm{Na_2MoO_4(c)}$$
$$+\,[\,H_2SO_4,\ 108\ H_2O] + \tfrac{1}{2}\,N_2H_4(l) + 4\ MeNH(l) \qquad (40)$$

The hydrolysis of $\mathrm{Cr(O^tBu)_4}$ is not well-defined thermochemically because of uncertainty of the extent to which $\mathrm{HCrO_4^-}$ and $\mathrm{Cr_2O_7^{2-}}$ has also formed. The reader is referred to the original paper for details of the calculation of ΔH_f^0. The enthalpy of hydrolysis of $\mathrm{Mo(NMe_2)_4(c)}$ has been measured by Adedeji et al. [65]. Enthalpies of reactions (35–40) are shown in Table 21, together with the derived enthalpies of formation and mean bond dissociation energies. Values of $\bar{D}$(M–O) for the complexes $\mathrm{M^{IV}(O^tBu)_4}$, $\mathrm{M^{III}(pd)_3}$ and $\mathrm{M^{II}(pd)_2}$ are plotted in Fig. 9 against the number of metal *d* electrons.

Values of $\bar{D}$(M–O) in the octahedral complexes $\mathrm{Cr(pd)_3}$ and $\mathrm{Mn(pd)_3}$ are depressed, as compared with $\bar{D}$(M–O) values in the other 4-coordinate complexes, because of the relative weakness of the two axial bonds in the 6-coordinate $\mathrm{M(pd)_3}$ complexes. Taking account of this, it seems likely that there is a steady fall in $\bar{D}$(M–O) values along the series Ti → Zn. Increase in the nuclear charge of the metal atom results in a contraction of the *s*, *p* and *d* orbitals and a lowering of their energies. This will result in stronger metal–oxygen bonding. Clearly, this effect is more than offset by the antibonding effect of the increasing number of metal *d*-electrons.

D. BINUCLEAR COMPLEXES WITH RADICAL LIGANDS

Tetra-μ-acetato dichromium(II), $\mathrm{Cr_2(O_2CMe)_4}$, and the corresponding molybdenum compound, $\mathrm{Mo_2(O_2CMe)_4}$, have the structure shown. These,

TABLE 21

Enthalpies of formation of alkoxide and alkylamino complexes (kJ mol^{-1})

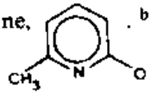
Complex	ΔH_R	ΔH_f^0(complex, l or c)	ΔH_{sub}	ΔH_f^0(complex, g)	$\bar{D}$(M–O)	$\bar{D}$(M–N)
$Ti(OEt)_4$	81.6 ± 3.8	−(1462.7 ± 7.5) (l)	100.4 [b]	−(1359.8 ± 8)	431	
$Ti(O^tBu)_4$	66.1 ± 0.4	−(1719.6 ± 6) (l)	66	−(1654 ± 8)	464	
$Ti(NEt_2)_4$	278.7 ± 2.0	−(485 ± 8) (l)	(67) [a]	−(418 ± 8)		291
$V(O^tBu)_4$	95.0 ± 3.7	−(1439 ± 3) (l)	(67) [a]	−(1372 ± 8)	405	
$Cr(O^tBu)_4$	−(177.8 ± 3.8)	−(1342 ± 3) (l)	(66) [a]	−(1276 ± 8)	351	
$Mo(NMe_2)_4$	−(109.6 ± 3.8)	59 ± 5 (c)	72 ± 6	131 ± 8		255

[a] Estimated. [b] To monomeric gas.

TABLE 22

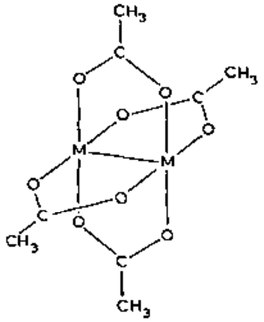
Enthalpies of formation of binuclear Cr and Mo complexes [62–65] (kJ mol^{-1})

Complex [a]	ΔH_R [b]	ΔH_f^0(complex, c)	ΔH_{sub}	ΔH_f^0(complex, g)
$Cr_2(O_2CMe)_4$	−(429.5 ± 3.5)	−(2297.5 ± 6)	314 ± 27	−(1984.5 ± 34)
$Cr_2(mhp)_4$	−(119.8 ± 6.6)	−(948.2 ± 9)	150 ± 4	−(798 ± 10)
$Mo_2(O^iPr)_6$	−(504 ± 5)	−(1662 ± 9)	113 ± 10	−(1549 ± 14)
$Mo_2(O_2CMe)_4$	144.5 ± 3.4	−(1970.7 ± 8)	163 ± 5	−(1805.7 ± 13)
$Mo_2(O_2CMe)_2(pd)_2$	−(474.2 ± 3.6)	−(1805.0 ± 9)	163 ± 5	−(1645.4 ± 10)
$Mo_2(NMe_2)_6$		17 ± 10	111 ± 8	128 ± 13
$Mo_2(mhp)_4$	−(561.3 ± 5.2)	−(754.0 ± 9)	157 ± 3	−(597 ± 10)
$Mo_2(mhp)_2(O_2CMe)_2$	−(490.9 ± 9.8)	−(1366.8 ± 12)	(161 ± 4) [c]	−(1206 ± 13)

[a] (mhp) 2-hydroxy-6-methylpyridine,  . [b] Refers to reactions (41–47). [c] Estimated.

and the other dimetal compounds, listed in Table 22, have metal–metal bonds, the length and strength of which vary from one compound to another.

$M_2(O_2CMe)_4$



Cavell et al. [62] have plotted the mean bond dissociation energies, $\bar{D}$(Cr–Cr) and $\bar{D}$(Mo–Mo) against interatomic distance, r, shown in Fig. 10. The enthalpy of atomization of chromium metal, $\Delta H_a^{298} = 396.6$ kJ mol^{-1}, is attributed to the bonding with neighbour and nearest-neighbour atoms, i.e.

$$\Delta H_a^{298} = 4\,\bar{D}(\text{Cr–Cr})(2.498\ \text{Å}) + 3\,\bar{D}(\text{Cr–Cr})(2.884\ \text{Å})$$

from which the values $\bar{D}(2.498\ \text{Å}) = 84.7$ kJ mol^{-1} and $\bar{D}(2.884\ \text{Å}) = 19.3$ kJ mol^{-1} are calculated.

Similarly for molybdenum, $\Delta H_a^{298} = 658.1$ kJ mol^{-1}, the values $\bar{D}(2.725\ \text{Å}) = 143$ kJ mol^{-1} and $\bar{D}(3.14\ \text{Å}) = 29$ kJ mol^{-1} are derived. Two additional points are included for this metal. One is a theoretically calculated value r(Mo–Mo) = 2.214 Å, D(Mo–Mo) = 526 ± 63 kJ mol^{-1}. The second is the experimental dissociation energy $D_{298}^0 = 406 \pm 20$ kJ mol^{-1} for Mo$_2$, in

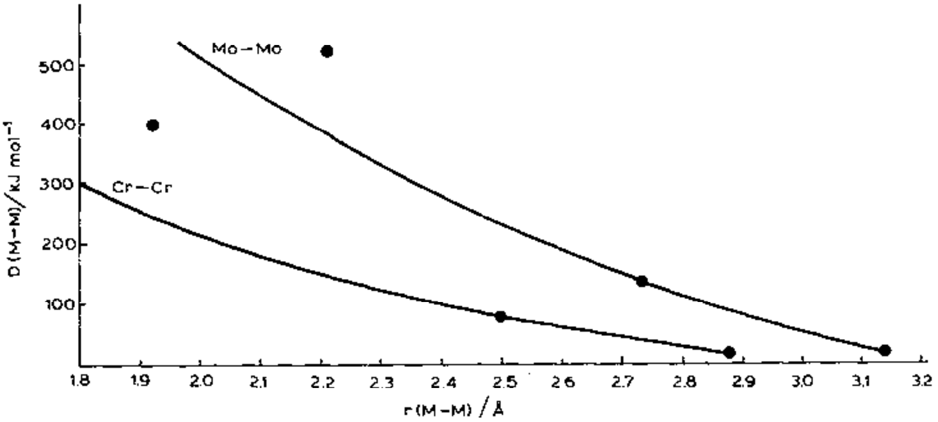


Fig. 10. Bond energy/bond length for Mo–Mo and Cr–Cr bonds.

which $r(\mathrm{Mo{-}Mo}) = 1.929$ Å. The plot passes between these two points. The enthalpies of formation of the compounds listed in Table 22 have been determined by Pilcher and co-workers [62–65] from enthalpies of reactions (41–47). These were obtained by measured enthalpies of solution of the reactants and products in a solvent composed of $FeCl_3$, HCl, $HClO_4$ and H_2O in the ratio 1 : 15 : 30 : 1000. Enthalpies of these reactions are also listed in Table 22.

$$\begin{aligned}&\mathrm{Cr_2(O_2CMe)_4(c) + 8\,FeCl_3(c) + 4\,NaCl(c) + 8\,H_2O(l)}\\&\quad\rightarrow \mathrm{12\,[HCl, 7.97\,H_2O]\,(l) + 4\,MeCO_2H(l) + 8\,FeCl_2(c) + 2\,Na_2CrO_4(c)}\end{aligned}\tag{41}$$

$$\begin{aligned}&\mathrm{Cr_2(mhp)_4(c) + 8\,FeCl_3(c) + 4\,NaCl(c) + 8\,H_2O(l)}\\&\quad\rightarrow \mathrm{12\,[HCl, 7.97\,H_2O]\,(l) + 4\,Hmhp(c) + 8\,FeCl_2(c) + 2\,Na_2CrO_4(c)}\end{aligned}\tag{42}$$

$$\begin{aligned}&\mathrm{Mo_2(O_2CMe)_4(c) + 8\,FeCl_3(c) + 4\,NaCl(c) + 8\,H_2O(l)}\\&\quad\rightarrow \mathrm{12\,[HCl, 7.97\,H_2O]\,(l) + 4\,MeCO_2H(l) + 8\,FeCl_2(c) + 2\,Na_2MoO_4(c)}\end{aligned}\tag{43}$$

$$\begin{aligned}&\mathrm{Mo_2(O_2CMe)_4(pd)_2(c) + 8\,FeCl_3(c) + 4\,NaCl(c) + 8\,H_2O(l)}\\&\quad\rightarrow \mathrm{12\,[HCl, 7.97\,H_2O]\,(l) + 2\,MeCO_2H(l) + 2\,Hpd(l) + 8\,FeCl_2(c)}\\&\quad\mathrm{+ 2\,Na_2MoO_4(l)}\end{aligned}\tag{44}$$

$$\begin{aligned}&\mathrm{Mo_2(mhp)_4(c) + 8\,FeCl_3(c) + 4\,NaCl(c) + 8\,H_2O(l)}\\&\quad\rightarrow \mathrm{12\,[HCl, 7.97\,H_2O]\,(l) + 4\,Hmhp(c) + 8\,FeCl_2(c)}\\&\quad\mathrm{+ 2\,Na_2MoO_4(c)}\end{aligned}\tag{45}$$

$$\begin{aligned}&\mathrm{Mo_2(mhp)_2(O_2CMe)_2(c) + 8\,FeCl_3(c) + 4\,NaCl(c) + 8\,H_2O(l)}\\&\quad\rightarrow \mathrm{12\,[HCl, 7.97\,H_2O](l) + 2\,MeCO_2H(l) + 2\,Hmhp(c)}\\&\quad\mathrm{+ 9\,FeCl_2(c) + 2\,Na_2MoO_4(c)}\end{aligned}\tag{46}$$

$$\begin{aligned}&\mathrm{Mo_2(O^iPr)_6(c) + 6\,FeCl_3(c) + 4\,NaCl(c) + 8\,H_2O(l)}\\&\quad\rightarrow \mathrm{10\,[HCl, 7.97\,H_2O]\,(l) + 6\,{}^iPrOH(l) + 6\,FeCl_2(c)}\\&\quad\mathrm{+ 2\,Na_2MoO_4(c)}\end{aligned}\tag{47}$$

Reactions involved in the oxidative hydrolysis of both $Mo_2(NMe)_6$ are complex and the reader is referred to the original paper [65] for details.

The enthalpies of the gas-phase disruption reactions

$$\mathrm{Mo}_n\mathrm{L}_m(\mathrm{g}) \rightarrow n\,\mathrm{Mo(g)} + m\,\mathrm{L(g)}$$

can be calculated and equated to the sum of mean bond dissociation as

TABLE 23

Bond lengths (Å) and dissociation energies (kJ mol^{-1}) in Cr and Mo complexes

	r(M–M)	$\bar{D}$(Mo–Mo)	r(M–O)	r(M–N)	$\bar{D}$(M–O)	$\bar{D}$(M–N)
$Cr_2(O_2CMe)_4$	(1.89)[a]	257	1.969		206	
$Cr_2(mhp)_4$	1.889	257	(1.969)[a]	2.067	206	150
$Mo_2(O^iPr)_6$	2.222	395	(1.878)[b]		385	
$Mo_2(O_2CMe)_4$	2.093	480	2.12		221	
$Mo_2(O_2CMe)_2(pd)_2$	2.13	455	2.106(O_2CMe)		224	
			2.095(pd)		192	
$Mo(pd)_3$			2.041		192	
$Mo_2(NMe_2)_6$	2.214	425		1.98		251
$Mo_2(mhp)_4$	2.065	505	2.086	2.167	220	155
$Mo_2(mhp)_2(O_2CMe)_2$	(2.080)[a]	495	(2.10)[a]		220	158
$Mo(NMe_2)_4$				1.926		255

[a] Estimated. [b] Assumed to be as in $Mo_2(OCH_2^tBu)_6$.

follows:

Compound	Mean bond dissociation	Enthalpy (kJ mol^{-1})
$Cr_2(O_2CMe)_4$	$\bar{D}(Cr-Cr)+8\,\bar{D}(Cr-O)_{O_2CMe}$	1903 ± 48
$Cr_2(mhp)_4$	$\bar{D}(Cr-Cr)+4\,\bar{D}(Cr-O)+4\bar{D}(Cr-N)$	1683 ± 45
$Mo_2(O^iPr)_6$	$\bar{D}(Mo-Mo)+6\,\bar{D}(Mo-O)_{O^iPr}$	2703 ± 14
$Mo_2(O_2CMe)_4$	$\bar{D}(Mo-Mo)+8\,\bar{D}(Mo-O)_{O_2CMe}$	2249 ± 41
$Mo_2(O_2CMe)_2(pd)_2$	$\bar{D}(Mo-Mo)+4\,\bar{D}(Mo-O)_{O_2CMe}+4\,\bar{D}(Mo-O)_{pd}$	2120 ± 45
$Mo(pd)_3$	$6\,\bar{D}(Mo-O)_{pd}$	1148 ± 61
$Mo_2(NMe_2)_6$	$\bar{D}(Mo-Mo)+6\,\bar{D}(Mo-N)$	1929 ± 28
$Mo_2(mhp)_4$	$\bar{D}(Mo-Mo)+4\,\bar{D}(Mo-O)+4\,\bar{D}(Mo-N)$	2005 ± 45
$Mo_2(mhp)_2(O_2CMe)_2$	$\bar{D}(Mo-Mo)+6\,\bar{D}(Mo-O)+2\,\bar{D}(Mo-N)$	2131 ± 44
$Mo(NMe_2)_4$	$4\,\bar{D}(Mo-N)$	1022 ± 19

Lengths of the Cr–Cr and Mo–Mo bonds in these compounds are shown in Table 23. Using the plot of bond energy against bond length, shown in Fig. 10, values of $\bar{D}$(Cr–Cr) and $\bar{D}$(Mo–Mo) can be obtained. With this information $\bar{D}$(Cr–O), $\bar{D}$(Cr–N), $\bar{D}$(Mo–O) and $\bar{D}$(Mo–N) values are obtained. It is interesting that $\bar{D}$(Cr–N) = 150 and $\bar{D}$(Mo–N) = 155 kJ mol^{-1} in the complexes $Cr_2(mhp)_4$ and $Mo_2(mhp)_4$, values which are very close to $\bar{D}$(Co–N) = 142–159 kJ mol^{-1}, in the substituted pyridine complexes $M(3Brpy)_2Cl_2$, where M is Co, Ni or Cu.

Figure 11 shows a plot of $\bar{D}$(Mo–O) against r(Mo–O). Two additional

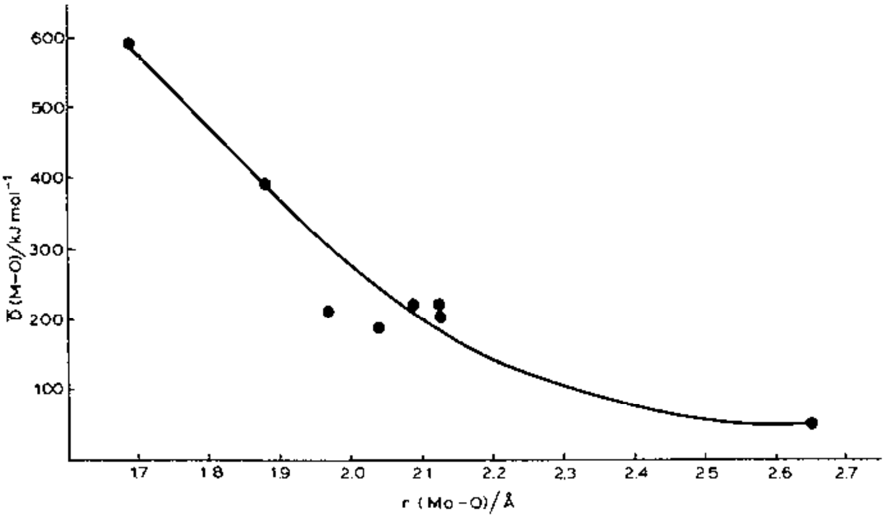


Fig. 11. Bond energy plot for Mo–O bonds.

points are included by the authors of the paper from which this figure is taken [64]; $\overline{D}$(Mo–O) = 589 ± 7 kJ mol^{-1}, r(Mo–O) = 1.69 Å in MoO_3 and $\overline{D}$(Mo–O) = 50 kJ mol^{-1}, r(Mo–O) = 2.64 Å, which is a measure of the intermolecular Mo–O contracts in $Mo_2(O_2CMe)_4$, estimated from enthalpy of sublimation data.

This very elegant piece of work by Skinner and co-workers [62–65] shows that it is now possible to relate the strengths of metal–ligand bonds to their length in a useful way.

APPENDIX 1

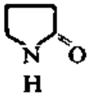
Enthalpies of formation (kJ mol^{-1})

Compound	Enthalpy of formation	Ref.
H(g)	218.00 ± 0.01	50
Cl(g)	121.302 ± 0.0008	79
Ti(g)	470.7	99
V(g)	514.6	99
Cr(g)	396.0	50
Mn(g)	280.7	50
Fe(g)	416.3	50
Co(g)	424.7	50
Ni(g)	429.7	50
Cu(g)	338.3	50
Zn(g)	130.7	50
Mo(g)	658.1	50
H_2O(l)	−(285.83 ± 0.01)	66
NH_3(g)	−(46.11 ± 0.001)	50
NH_4Cl(c)	−(314.43 ± 0.05)	50
N_2H_4(l)	50.63 ± 0.05	50
[HCl, in 4.40 H_2O](l)	−(154.106 ± 0.004)	67
[HCl, in 5.55 H_2O](l)	−(156.824 ± 0.004)	67
[HCl, in 7.97 H_2O](l)	−(159.971 ± 0.001)	67
[HCl, in 11.60 H_2O](l)	−(161.920 ± 0.001)	67
[HCl, in 51.3 H_2O](l)	−(165.295 ± 0.001)	67
[HCl, in ∞H_2O](l)	−(167.059 ± 0.001)	67
[H_2SO_4, in 53.54 H_2O](l)	−(886.87 ± 0.01)	50
[H_2SO_4, in 108 H_2O](l)	−(887.74 ± 0.01)	50
[$HClO_4$, in 3.03 H_2O](l)	−(119.1 ± 0.4)	67
$TiCl_4$(l)	−(804.6 ± 2.0)	95
VCl_4(l)	−(569.9 ± 1.6)	96
$CrCl_3 \cdot 6\ H_2O$(c)	−(2452.7 ± 0.8)	50
$MnCl_2$(c)	−(481.3 ± 0.5)	50
$MnCl_2 \cdot 4\ H_2O$(c)	−(1687.4 ± 0.5)	50
$FeCl_2$(c)	−(341.8 ± 0.5)	50
$FeCl_3$(c)	−(399.5 ± 0.5)	50
$CoCl_2$(c)	−(312.5 ± 0.5)	50

APPENDIX 1 (continued)

Compound	Enthalpy of formation	Ref.
$CoCl_2\cdot 6\,H_2O$(c)	−(2115.4 ± 0.5)	50
$CoSO_4\cdot 6\,H_2O$(c)	−(2683.6 ± 0.5)	50
$NiCl_2$(c)	−(305.3 ± 0.1)	50
$NiCl_2\cdot 6\,H_2O$(c)	−(2103.2 ± 0.5)	50
$NiSO_4\cdot 6\,H_2O$(c)	−(2682.8 ± 0.5)	50
$Ni(ClO_4)_2\cdot 6\,H_2O$(c)	−(2035.9 ± 0.5)	50
$CuCl_2$(c)	−(220.1 ± 0.5)	50
$CuCl_2\cdot 2\,H_2O$(c)	−(821.3 ± 0.5)	50
$CuBr_2$(c)	−(141.8 ± 0.5)	50
$CuSO_4\cdot 5\,H_2O$(c)	−(2279.6 ± 0.5)	50
$ZnCl_2$(c)	−(415.1 ± 0.5)	50
$ZnBr_2$(c)	−(328.7 ± 0.5)	50
ZnI_2(c)	−(208.0 ± 0.5)	50
$CdCl_2$(c)	−(391.5 ± 0.5)	50
$CdBr_2$(c)	−(316.2 ± 0.5)	50
CdI_2(c)	−(203.2 ± 0.5)	50
$HgCl_2$(c)	−(224.3 ± 0.5)	50
$HgBr_2$(c)	−(170.9 ± 0.5)	50
$PdCl_2$(c)	−(163.2 ± 10)	87
NaCl(c)	−(411.0 ± 0.01)	50
Na_2SO_4(c)	−(1387.9 ± 0.9)	96
$Na_2(CrO_4)$(c)	−(1344.0 ± 2.1)	68
$Na_2(MoO_4)$(c)	−(1467.6 ± 3.3)	68
$Ti(\eta\text{-}C_5H_5)_2Cl_2$(c)	−(383.2 ± 7.5)	69
$Mo(\eta\text{-}C_5H_5)_2Cl_2$(c)	−(95.8 ± 2.5)	69
$W(\eta\text{-}C_5H_5)_2Cl_2$(c)	−(71.1 ± 2.5)	69
$(NH_4)_2PdCl_2$(c)	−(841.0 ± 1.7)	83
$(CH_3)_2NH$(l)	−(43.9 ± 0.4)	74
$(C_2H_5)_2NH$(l)	−(103.8 ± 1.1)	74
$(n\text{-}C_3H_7)_2NH$(l)	−(156.1 ± 1.0)	74
$(n\text{-}C_4H_9)_2NH$(l)	−(206.0 ± 0.9)	74
C_2H_5OH(l)	−(277.1 ± 0.2)	74
$i\text{-}C_3H_7OH$(l)	−(317.9 ± 0.4)	74
$t\text{-}C_4H_9OH$(l)	−(359.2 ± 1.4)	74
$n\text{-}C_3H_7SH$(l)	−(99.9 ± 0.6)	74
$i\text{-}C_3H_7SH$(l)	−(105.8 ± 0.6)	74
$n\text{-}C_4H_9SH$(l)	−(124.7 ± 1.2)	74
$t\text{-}C_4H_9SH$(l)	−(140.5 ± 0.8)	74
CH_3COOH(l)	−(484.3 ± 0.2)	74
CF_3COOH(l)	−(1069.2 ± 1.1)	74
C_6H_5COOH(c)	−(384.9 ± 0.6)	74
$[(C_2H_5)_2NH_2][S_2CN(C_2H_5)_2]$(c) (diethylammonium diethyldithiocarbamate)	−(198.8 ± 4.1)	82
$CH_2(NH_2)COOH$(c) (glycine)	−(530.3 ± 3.5)	74
$(C_2H_5)_2S$(l)	−(119.4 ± 0.8)	74

APPENDIX 1 (continued)

Compound	Enthalpy of formation	Ref.
$(C_2H_5)_2Se(l)$	$-(96.4 \pm 3.4)$	74
$(C_2H_5)_2Te(l)$	$-(188.0 \pm 4)$	84
$(NH_2)_2C{=}S(c)$ (thiourea)	$-(88.3 \pm 0.1)$	50
$(CH_3)_2NCON(CH_3)_2(l)$ (tetramethylurea)	$-(254.4 \pm 0.5)$	70
$(C_5H_5N)NHCOCH_3(c)$ (*N*-(2-pyridyl)acetamide)	$-(149 \pm 21)$	71
$CH_3CONHCOCH_3(c)$ (diacetamide)	$-(498.4 \pm 0.5)$	72
$(C_6H_5)_3PO$ (triphenylphosphine oxide)	$-(61 \pm 25)$	73
$CH_3COCH_2COCH_3(l)$ (pentane-2,4-dione (Hpd))	$-(423.8 \pm 1.5)$	74
$C_6H_5COCH_2COCH_3(c)$ (1-phenyl-1,3-butanedione (Hpbd))	$-(335.1 \pm 2.8)$	75
$C_6H_5COCH_2COC_6H_5(c)$ (1,3-diphenyl-1,3-propanedione (Hdppd))	$-(224.3 \pm 1.5)$	74
$(CH_3)_2CHCOCH_2COCH(CH_3)_2(l)$ (2,2,6,6-tetramethylheptane-3,5-dione (Htmhd)	$-(587.7 \pm 3.8)$	75
$(CH_3)(OH)C_5H_3N(c)$ (2-hydroxy-6-methylpyridine(l) (Hmhp))	$-(213.05 \pm 2.3)$	61
 (2-pyrrolidone (pyrr))(c)	$-(286 \pm 0.4)$	74

APPENDIX 2

Enthalpies of formation of radicals

$\Delta H_f^0(C_6H_5COCH{=}COCH_3, g) = \Delta H_f^0(pbd, g) = -(117.3 \pm 9)$ kJ mol^{-1}

$$C_6H_5COCH{=}C(OH)CH_3(g) \xrightarrow{D(O-H)} C_6H_5COCH{=}COCH_3(g) + H(g)$$

$D(O{-}H) = 352 \pm 6$ kJ mol^{-1} as calculated for phenol [46,49].
$\Delta H_f^0(C_6H_5COCH_2COCH_3, c) = -(335.1 \pm 2.8)$ kJ mol^{-1}
$\Delta H_{sub}(C_6H_5COCH_2COCH_3, c) = 83.8 \pm 0.4$ kJ mol^{-1} (ref. 76).
$\Delta H_f^0(C_6H_5COCH{=}C(OH)CH_3, g) = -(251.3 \pm 3.2)$ kJ mol^{-1}
Hpbd(g) is assumed to be entirely in the enolic form.

$\Delta H_f^0(C_6H_5COCH{=}CO_6^CH_5, g) = \Delta H_f^0(dppd, g) = -(5.3 \pm 13)$ kJ mol^{-1}

$$C_6H_5COCH{=}C(OH)C_6H_5(g) \xrightarrow{D(O-H)} C_6H_5COCH{=}COC_6H_5(g) + H(g)$$

$D(O{-}H) = 352 \pm 6$ kJ mol^{-1} as calculated for phenol.
$\Delta H_f^0(C_6H_5COCH_2COC_6H_5, c) = -(224.3 \pm 1.5)$ kJ mol^{-1}
$\Delta H_{sub}(C_6H_5COCH_2COC_6H_5) = (85 \pm 5)$ kJ mol^{-1} (estimated).

$\Delta H_f^0(\mathrm{C_6H_5COCH{=}C(OH)C_6H_5},\ \mathrm{g}) = -(139.3 \pm 6.5)\ \mathrm{kJ\ mol^{-1}}$
Hdppd(g) is assumed to be entirely in the enolic form.

$\Delta H_f^0(\mathit{(CH_3)_3CCOCH{=}COC(CH_3)_3},\ \mathit{g}) = \Delta H_f^0(\mathit{tmhd},\ \mathit{g}) = -381.4 \pm 12\ \mathrm{kJ\ mol^{-1}}$

$\mathrm{(CH_3)_2CHCOCH{=}CO(OH)CH(CH_3)_2(g)}$

$\rightarrow \mathrm{(CH_3)_2COCH{=}COCH(CH_3)_2(g) + H(g)}$

$D(\mathrm{O{-}H}) = 365 \pm 6\ \mathrm{kJ\ mol^{-1}}$ as assumed in the enolic form of pentane-2,4-dione.
$\Delta H_f^0(\mathrm{(CH_3)_2CHCOCH_2COCH(CH_3)_2},\ \mathrm{c}) = -(587.7 \pm 3.8)\ \mathrm{kJ\ mol^{-1}}$
$\Delta H_{\mathrm{sub}}\mathrm{(CH_3)_2CHCOCH_2COCH(CH_3)_2} = 59.3 \pm 2\ \mathrm{kJ\ mol^{-1}}$ (ref. 75) to 100% enol form.
$\Delta H_f^0(\mathrm{(CH_3)_2CHCOCH{=}C(OH)CH(CH_3)_2},\ \mathrm{g}) = -(528.4 \pm 6)\ \mathrm{kJ\ mol^{-1}}$

$\Delta H_f^0(\mathit{CH_3COO},\ \mathit{g}) = -(217 \pm 10)\ \mathrm{kJ\ mol^{-1}}$

$$\mathrm{CH_3CO_2H(g)} \xrightarrow{D(\mathrm{CH_3COO{-}H})} \mathrm{CH_3CO_2(g) + H(g)}$$

$D(\mathrm{CH_3COO{-}H}) = 433 \pm 10\ \mathrm{kJ\ mol^{-1}}$ (ref. 55).
$\Delta H_f^0(\mathrm{CH_3CO_2H},\ \mathrm{g}) = -(432.1 \pm 0.4)\ \mathrm{kJ\ mol^{-1}}$ (ref. 74).

$\Delta H_f^0(\mathit{C_6H_5COO},\ \mathit{g}) = -(76.3 \pm 3.0)\ \mathrm{kJ\ mol^{-1}}$

$$\mathrm{C_6H_5COO{-}OOC_6H_5(g)} \xrightarrow{D(\mathrm{O{-}O})} 2\ \mathrm{C_6H_5COO(g)}$$

$D(\mathrm{O{-}O}) = 125.5 \pm 4.2\ \mathrm{kJ\ mol^{-1}}$ (ref. 77).
$\Delta H_f^0(\mathrm{[C_6H_5COO]_2},\ \mathrm{g}) = -(278.2 \pm 4.2)\ \mathrm{kJ\ mol^{-1}}$ (ref. 74).

$\Delta H_f^0(\mathit{CF_3COO},\ \mathit{g}) = -(815.7 \pm 10)\ \mathrm{kJ\ mol^{-1}}$ (based on $D(\mathrm{O{-}H}) = 433 \pm 10$).
$-(788.7 \pm 17)\ \mathrm{kJ\ mol^{-1}}$ (based on $D(\mathrm{O{-}H}) = 460 \pm 17$).

$$\mathrm{CF_3COOH(g)} \xrightarrow{D(\mathrm{O{-}H})} \mathrm{CF_3COO(g) + H(g)}$$

$D(\mathrm{O{-}H})$ assumed to be equal to $D(\mathrm{CH_3COO{-}H}) = 433 \pm 10\ \mathrm{kJ\ mol^{-1}}$ (ref. 55).
$D(\mathrm{RCOO{-}H})$ in carboxylic acids ca. $460 \pm 17\ \mathrm{kJ\ mol^{-1}}$ (ref. 78).
$\Delta H_f^0(\mathrm{CF_3COOH},\ \mathrm{g}) = -(1030.7 \pm 1.4)\ \mathrm{kJ\ mol^{-1}}$ (ref. 74).
$\Delta H_f^0(\mathrm{H},\ \mathrm{g}) = 218.00 \pm 0.01\ \mathrm{kJ\ mol^{-1}}$ (ref. 50).

$\Delta H_f^0(\mathit{C_2H_5O},\ \mathit{g}) = -(26 \pm 10)\ \mathrm{kJ\ mol^{-1}}$

$$\mathrm{C_2H_5OH(g)} \xrightarrow{D(\mathrm{O{-}H})} \mathrm{C_2H_5O(g) + H(g)}$$

$D(\mathrm{O{-}H}) = 427$ kJ mol^{-1} (ref. 47).
$\Delta H_f^0(\mathrm{C_2H_5OH, g}) = -(234.8 \pm 0.2)$ kJ mol^{-1} (ref. 74).

$\Delta H_f^0({}^{i}C_3H_7O, g) = -(27 \pm 10)\ \mathrm{kJ\ mol^{-1}}$

$\mathrm{i\text{-}C_3H_7OH(g)} \xrightarrow{D({}^{i}\mathrm{PrO{-}H})} \mathrm{iso\text{-}C_3H_7O(g) + H(g)}$
$D({}^{i}\mathrm{PrO{-}H}) = 464$ kJ mol^{-1} (ref. 100).
$\Delta H_f^0(\mathrm{i\text{-}C_3H_7OH, g}) = -(272.5 \pm 0.4)$ kJ mol^{-1} (ref. 74).

$\Delta H_f^0({}^{t}C_4H_9O, g) = -(67 \pm 10)\ \mathrm{kJ\ mol^{-1}}$

${}^{t}\mathrm{C_4H_9OH(g)} \xrightarrow{D(\mathrm{O{-}H})} \mathrm{C_4H_9O(g) + H(g)}$
$D(\mathrm{O{-}H}) = 464$ kJ mol^{-1} (ref. 100).
$\Delta H_f^0(\mathrm{t\text{-}C_4H_9OH, g}) = -(312.4 \pm 2.8)$ kJ mol^{-1} (ref. 74).

$\Delta H_f^0((CH_3)_2N, g) = 123.4 \pm 4\ \mathrm{kJ\ mol^{-1}}$

$\mathrm{(CH_3)_2NH(g)} \xrightarrow{D(\mathrm{N{-}H})} \mathrm{(CH_3)_2N(g) + H(g)}$
$D(\mathrm{N{-}H}) = 360$ kJ mol^{-1} (ref. 97).
$\Delta H_f^0(\mathrm{(CH_3)_2NH, g}) = -(18.5 \pm 0.4)$ (ref. 74).

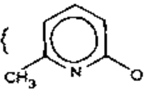
$\Delta H_f^0((C_2H_5)_2N, g) = 69 \pm 5\ \mathrm{kJ\ mol^{-1}}$

$\mathrm{(C_2H_5)_2NH(g)} \xrightarrow{D(\mathrm{N{-}H})} \mathrm{(C_2H_5)_2N(g) + H(g)}$
$D(\mathrm{N{-}H}) =$ ca. 360 kJ mol^{-1} (assumed same as $D(\mathrm{Me_2N{-}H})$).
$\Delta H_f^0(\mathrm{(C_2H_5)_2NH, g}) = -(72.6 \pm 1.9)$ kJ mol^{-1} (ref. 74).

$\Delta H_f^0(RS, g)$

$\mathrm{RSH(g)} \xrightarrow{D(\mathrm{S{-}H})} \mathrm{RS(g) + H(g)}$
$D(\mathrm{S{-}H}) = 384.9 \pm 8.4$ kJ mol^{-1} (assumed to be the same for each thiol (ref. 80)).

	n-C_3H_7	i-C_3H_7	n-C_4H_9	t-C_4H_9
ΔH_f^0(RSH, g) (kJ mol^{-1})	$-(67.9 \pm 0.6)$	$-(76.2 \pm 0.6)$	$-(88.1 \pm 1.2)$	$-(109 \pm 0.8)$
ΔH_f^0(RS, g) (kJ mol^{-1})	99.0 ± 9	90.7 ± 9	78.8 ± 10	57.3 ± 9

ΔH_f^0{  , g} = ΔH_f^0(mhp, g) = 23 ± 13 kJ mol^{-1}

D(O–H) = 362 ± 10 kJ mol^{-1}
ΔH_f^0(Hmhp, c) = −(213.05 ± 2.3) kJ mol^{-1}
ΔH_{sub}(Hmhp) = (92 ± 1.5) kJ mol^{-1} (estimated).
ΔH_f^0(Hmhp, g) = −(121.0 ± 3.0) kJ mol^{-1}

$\Delta H_f^0(NH_2CH_2COO, g) = -(178.9 \pm 13.5)$

$NH_2CH_2COOH(g) \xrightarrow{D(O-H)} NH_2CH_2CO_2(g) + H(g)$
D(O–H) = 433 ± 10 kJ mol^{-1} as in CH_3COOH (ref. 55).
ΔH_f^0(NH_2CH_2COOH, c) = −(530.3 ± 3.5) kJ mol^{-1}
ΔH_{sub}(NH_2CH_2COOH) = 136.5 (419 K) (ref. 81).
ΔH_f^0(NH_2CH_2COOH, g) = −(393.8 ± 3.5) kJ mol^{-1}

$\Delta H_f^0[Mo(n\text{-}C_5H_5)_2, g]$ = 369.6 ± 7 kJ mol^{-1}

$Mo(\eta\text{-}C_5H_5)_2Cl_2(g) \xrightarrow{2\bar{D}(Mo-Cl)} Mo(\eta\text{-}C_5H_5)_2(g) + 2\,Cl(g)$
$\bar{D}$(Mo–Cl) assumed to be equal to the mean bond dissociation energy.
$\bar{D}$(Mo–Cl) = 303.8 kJ mol^{-1} in $MoCl_6$.
$\Delta H_f^0[Mo(\eta\text{-}C_5H_5)_2Cl_2, c]$ = −(95.8 ± 2.5) kJ mol^{-1} (ref. 69).
$\Delta H_{sub}[Mo(\eta\text{-}C_5H_5)_2Cl_2]$ = (100.4 ± 4.1) kJ mol^{-1} (estimated).
$\Delta H_f^0[Mo(\eta\text{-}C_5H_5)Cl_2, g]$ = 4.6 ± 6.6 kJ mol^{-1}
ΔH_f^0(Cl, g) = 121.302 ± 0.008 kJ mol^{-1}

$\Delta H_f^0[W(\eta\text{-}C_5H_5)_2, g]$ = 484.5 ± 7 kJ mol^{-1}

$W(\eta\text{-}C_5H_5)_2Cl_2(g) \xrightarrow{2\bar{D}(W-Cl)} W(\eta\text{-}C_5H_5)_2(g) + 2\,Cl(g)$
$\bar{D}$(W–Cl) assumed to be equal to mean bond dissociation energy.
$\bar{D}$(W–Cl) = 347.3 kJ mol^{-1} in WCl_6.
$\Delta H_f^0[W(\eta\text{-}C_5H_5)_2Cl_2, c]$ = −(71.1 ± 2.5) kJ mol^{-1} (ref. 69).
$\Delta H_{sub}[W(\eta\text{-}C_5H_5)_2Cl_2]$ = 104.6 ± 4.1 kJ mol^{-1} (ref. 69).
$\Delta H_f^0[W(\eta\text{-}C_5H_5)_2Cl_2, g]$ = 33.5 ± 6.6 kJ mol^{-1}
ΔH_f^0(Cl, g) = 121.302 ± 0.08 kJ mol^{-1}

$\Delta H_f^0[Ti(\eta\text{-}C_5H_5)_2, g]$ = +352.4 ± 10 kJ mol^{-1}

$Ti(\eta\text{-}C_5H_5)_2Cl_2(g) \xrightarrow{2\bar{D}(Ti-Cl)} Ti(\eta\text{-}C_5H_5)_2 + Cl(g)$

$\overline{D}$(Ti–Cl) assumed to be equal to mean bond dissociation energy.
$\overline{D}$(Ti–Cl) = 430.5 kJ mol^{-1} in $TiCl_4$.
$\Delta H_f^0[Ti(\eta\text{-}C_5H_5)_2Cl_2, c] = -(383.2 \pm 7.5)$ kJ mol^{-1} (ref. 69).
$\Delta H_{sub}[Ti(\eta\text{-}C_5H_5)_2Cl_2] = 117.2 \pm 2.0$ kJ mol^{-1} (ref. 69).
$\Delta H_f^0[Ti(\eta\text{-}C_5H_5)_2Cl_2, g] = -(266.0 \pm 9.5)$ kJ mol^{-1}
$\Delta H_f^0(Cl, g) = 121.302 \pm 0.008$ kJ mol^{-1}

APPENDIX 3

Enthalpies of sublimation of metal halides (kJ mol^{-1})

	ΔH_{sub}	Ref.
$MnCl_2$	217.6 ± 2	50
$FeCl_2$	193.3 ± 2	50
$CoCl_2$	234 ± 1.7	88
$CoBr_2$	222 ± 2	89
CoI_2	209 ± 2	89
$NiCl_2$	246 ± 2	89
NiI_2	214 ± 2	90
$CuCl_2$	194 ± 2	91
$CuBr_2$	188 ± 2	89
$ZnCl_2$	149.0 ± 2	50
$ZnBr_2$	131 ± 2	92
ZnI_2	120 ± 2	92
$CdCl_2$	181.2 ± 2	93
$CdBr_2$	151.5 ± 2	92
CdI_2	137.7 ± 2	92
$HgCl_2$	82.8 ± 2	94
$HgBr_2$	84.1 ± 2	94
HgI_2(yellow)	85.8 ± 2	50

Procedures for determining the enthalpy of sublimation of transition metal complexes

To obtain reliable values of the metal–ligand bond strengths in a given coordination compound it is necessary to determine accurately the enthalpy of hypothetical gas phase dissociation reactions of the type

$$ML_n(g) \rightarrow M(g) + nL(g)$$

In practice this means that two different types of measurement will have to be made; an enthalpy of reaction measurement for the reaction when carried out using reagents in the condensed phase; and enthalpy of vaporisation measurements for each of the species involved in the gas phase reaction. In most cases, the enthalpies of sublimation or vaporisation of the simple organic and inorganic species generated by the dissociation reaction will have been measured by earlier workers using well established methods [46,98,101] and the experimentalist will be faced with the task of measuring the enthalpy of sublimation of the coordination compound.

The great majority of coordination compounds are not appreciably volatile at standard temperature and pressure and so specialised techniques are required involving high vacuum apparatus operating at elevated temperatures [102]. The methods commonly used may be classified as dynamic methods (e.g. Knudsen effusion, torsion effusion, Langmuir evaporation) or static methods (e.g. sublimation bulb, isoteniscope, spoon gauge). Although each of these methods has particular strengths and weaknesses the following considerations apply to all.

(a) Sample purity

As with all thermochemical measurements reliable results will only be obtained if the substrate is of high purity. This is particularly true if a static method of vapour pressure measurement is used since volatile impurities, even when present in trace amounts, will produce large systematic errors in the derived vapour pressure relationships. All samples should be rigorously degassed in vacuo prior to use in vapour pressure measurements.

(b) Apparatus construction and calibration

When working at elevated temperatures it is important that the sample cell is at a uniform temperature since thermal gradients may seriously bias vapour pressure measurements. It is also essential that the sample or its vapour does not come into contact with reactive materials (this is especially important when manometer fluids are present). If an effusion apparatus is used the orifice area must be carefully calibrated by use of suitable standards such as naphthalene or cadmium [103], the vapour pressures of which are known, to ensure that absolute vapour pressures of the sample under investigation can be reliably calculated.

(c) Analysis of the sample vapour

It is essential that the sublimation process is rigorously characterised both to distinguish a true vaporisation process from a decomposition reaction and to determine the relative molecular masses of the gas phase species for use in the calculation of vapour pressures. When dynamic methods are used analysis of the vapour phase is usually carried out by mass spectroscopy under conditions similar to those employed during the thermochemical measurement. An extension of this technique involves measurement of vaporisation enthalpies by means of a mass spectrometer equipped with a multiple effusion cell as the source. The ion current, I^+, is measured at a series of different temperatures and the vaporisation enthalpy is then calculated from a plot of $\ln(I^+T)$ against T^{-1} [104]. The mass spectroscopic method is applicable to equilibrium mixtures of gas phase species and is extensively used for the study of the metathetical reactions of inorganic species at high temperatures [105]. De Kruif has used a combined Knudsen effusion/torsion effusion apparatus to determine the relative molecular mass of the vapour phase during a vaporisation measurement [106].

In principle the mass spectroscopic method of analysis can also be applied to static vaporisation methods. When the sublimation bulb technique is used the electronic spectrum of the gas phase species is employed both as a method of determining the vapour pressure of the substrate and as a means of product identification [107].

If the vapour species can be condensed onto a suitable receiver the condensate may be examined by microanalysis or, in the case of small amounts of material, by atomic absorption spectroscopy (which will indicate the approximate metal content).

The results of the measurement are generally reported as $\Delta H_{\mathrm{vap}}^{\mathrm{T}}$ with an uncertainty based on the fit of the data to the chosen vapour pressure, temperature model. Analysis of literature data on coordination compounds reveals that measurements by different workers on the same substrate seldom agree within the quoted uncertainties suggesting that the authors' own estimates of experimental uncertainty are almost invariably too small. In this regard it should be noted that a number of isoteniscope measurements made in the 1960s [108] appear to be subject to large systematic errors, probably due to outgassing of volatile impurities from samples of inadequate purity.

Conversion of $\Delta H_{\mathrm{vap}}^{\mathrm{T}}$ to $\Delta H_{\mathrm{vap}}^{298\mathrm{K}}$ presents special problems in the case of coordination complexes. The low volatility of the substrates precludes the measurement of vapour phase heat capacities and therefore calculation of the necessary ΔCp correction to 298 K. The alternative approach is the calculation of the correction on the basis of spectroscopically derived thermal functions, a method used for a large number of simple inorganic compounds. However the complexity of the spectra of coordination compounds makes this method impractical at present and for this reason the majority of workers apply no ΔCp correction to their data and make the assumption that $\Delta H_{\mathrm{vap}}^{\mathrm{T}} = \Delta H_{\mathrm{vap}}^{298\mathrm{K}}$ within the experimental uncertainty of the measurement.

As yet there is no accepted standard compound for use under the conditions encountered in measuring the enthalpies of sublimation of coordination compounds, although a recent review by Sachinidis and Hill [109] indicates that certain metal pentanedionate complexes, which are readily available, yield consistent results when analysed by a variety of different techniques. In this regard it is interesting that careful work carried out by differential scanning calorimetry yields values similar to those obtained by more sophisticated methods [110]. There can be little doubt that reliable vaporisation measurements can be carried out on coordination complexes and that the precision obtainable is comparable with that for simple inorganic compounds though rather less than that for accurate work on organic species. However, in view of the low thermal decomposition temperatures of many coordination compounds it is essential to carry out a careful analysis of the gas phase species present under the conditions of the vapour pressure measurements.

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