

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

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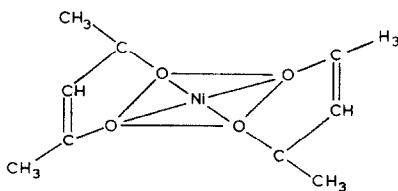
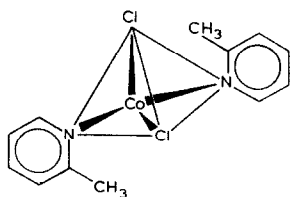
### A. INTRODUCTION

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

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.

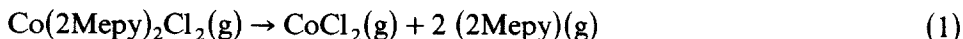
Few thermochemical data have been reported for these complexes, and even for simpler model systems, such as the amino-acid complexes of transition metals, the available information refers mainly to reactions in solution. Reviews of these data are available [1,2]. However, without values for the enthalpies 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  $\Delta H_f^0(\text{complex, cryst.})$  and a measured, or reliably estimated value for  $\Delta H(\text{sublimation})$  so that mean bond dissociation energies of metal–ligand bonds can be calculated.

The structure of the two complexes  $\text{Co}(\text{2Mepy})_2\text{Cl}_2$ , where 2Mepy is the 2-methylpyridine molecule, and  $\text{Ni}(\text{pd})_2$ , 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

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



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



and can be calculated from the relationship

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

Values for  $\Delta H_f^0(\text{MX}_m, \text{g})$  and  $\Delta H_f^0(\text{L}, \text{g})$  are often available, so that it is necessary only to obtain  $\Delta H_f^0(\text{ML}_n\text{X}_m, \text{g})$ . 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,  $\Delta H_f^0(\text{ML}_n\text{X}_m, \text{c})$ ; and (ii) the enthalpy of sublimation,  $\Delta H_{\text{sub}}(\text{ML}_n\text{X}_m)$ . In some cases it is possible to avoid determination of  $\Delta H_f^0(\text{ML}_n\text{X}_m, \text{c})$ , for example in a direct measurement of the enthalpy of the following thermal decomposition reaction.

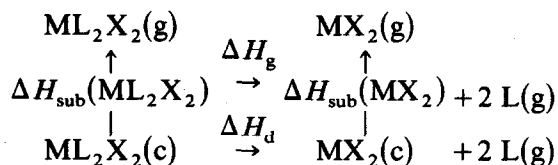


In this case the only additional datum needed to obtain  $\bar{D}(\text{Co-N})$  is  $\Delta H_{\text{sub}}(\text{Co(2Mepy)}_2\text{Cl}_2)$  since the value for  $\Delta H_{\text{sub}}(\text{CoCl}_2)$  is known. In the sections which follow, we summarise the calorimetric measurements which have been 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. $\text{ML}_n\text{X}_2$ COMPLEXES, WHERE L IS A LIGAND MOLECULE

### (i) *Differential scanning calorimetry*

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

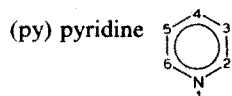


complex dissociates to crystalline  $\text{MX}_2$ , generally a metal halide, and gaseous ligand L. A number of transition metal complexes have been studied by use of this technique. Those shown in Tables 1 and 2 have been selected because values of  $\Delta H_{\text{sub}}(\text{ML}_2\text{X}_2)$  are also known. Since values for  $\Delta H_{\text{sub}}(\text{MX}_2)$  are also available (Appendix 3) the enthalpy,  $\Delta H_g$ , of the gas-phase dissociation reaction, the upper line of the cycle, can be derived and values for  $\bar{D}(\text{M-L})$  calculated. It is important to note that the  $\Delta H_d$  values refer to temperatures well above 298 K. Where heat capacity data for  $\text{ML}_2\text{X}_2$ ,  $\text{MX}_2$  and L are known, it is possible to refer the  $\Delta H_d$  value to 298 K. There is some difficulty in obtaining heat capacity data for the complexes  $\text{ML}_2\text{X}_2$  up to the appropriate temperatures because of the onset of decomposition. The values quoted for  $\Delta H_{\text{sub}}(\text{ML}_2\text{X}_2)$  refer to temperatures between 298 K and the decomposition temperature.

TABLE 1

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

Complex	$\Delta H_d^b$	Temp. (K)	Ref.	$\Delta H_{\text{sub}}$	Temp. (K)	Ref.	$\Delta H_g^c$	$\bar{D}(\text{M}-\text{N})$
$\text{Co}(\text{py})_2\text{Cl}_2^a$	$119.7 \pm 2.1$	510	3	$(100 \pm 10)^d$			$254 \pm 12$	$127 \pm 6$
$\text{Co}(\text{py})_2\text{Br}_2$	$114.2 \pm 1.7$	520	3	$(87 \pm 4)^d$			$249.2 \pm 6$	$124.6 \pm 3$
$\text{Co}(\text{2Mepy})_2\text{Cl}_2$	$109.6 \pm 2.1$	520	3	$86.6 \pm 3.8$	347	4	$257.0 \pm 6$	$128.5 \pm 3$
$\text{Co}(\text{2Mepy})_2\text{Br}_2$	$88.7 \pm 3.8$	500	3	$69.5 \pm 2.9$	363	4	$241.2 \pm 6$	$120.6 \pm 3$
$\text{Co}(\text{2Clpy})_2\text{Cl}_2$	$115.1 \pm 1.3$	480	4	$101.2 \pm 6.7$	352	4	$247.9 \pm 8$	$124.0 \pm 4$
$\text{Co}(\text{2Brpy})_2\text{Cl}_2$	$126.4 \pm 1.3$	495	4	$120.5 \pm 4.6$	363	4	$240.0 \pm 6$	$120.0 \pm 3$
$\text{Co}(\text{2Brpy})_2\text{Br}_2$	$129.3 \pm 1.7$	510	4	$100.8 \pm 2.1$	365	4	$250.5 \pm 4$	$125.3 \pm 2$
$\text{Co}(\text{3Clpy})_2\text{Cl}_2$	$134.7 \pm 2.5$	540	4	$95.8 \pm 3.3$	375	4	$272.9 \pm 6$	$136.5 \pm 3$
$\text{Co}(\text{3Brpy})_2\text{Cl}_2$	$134.3 \pm 1.3$	560	4	$77.0 \pm 4.2$	365	4	$291.3 \pm 6$	$145.7 \pm 3$
$\text{Ni}(\text{3Clpy})_2\text{Cl}_2$	$142.2 \pm 2.5$	560	5	$72.0 \pm 7.1$	370	5	$316.2 \pm 10$	$158.1 \pm 5$
$\text{Ni}(\text{3Brpy})_2\text{Cl}_2$	$147.3 \pm 2.1$	575	5	$76.1 \pm 5.0$	390	5	$317.2 \pm 8$	$158.6 \pm 4$
$\text{Cu}(\text{3Brpy})_2\text{Cl}_2$	$146.4 \pm 1.7$	560	5	$56.9 \pm 5.4$	375	5	$283.5 \pm 6$	$141.8 \pm 3$

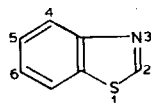
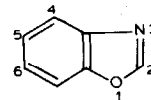


<sup>a</sup> Blue tetrahedral form of  $\text{Co}(\text{py})_2\text{Cl}_2$ . <sup>b</sup>  $\text{ML}_2\text{X}_2(\text{c}) \rightarrow \text{MX}_2(\text{c}) + 2 \text{L}(\text{g})$ . <sup>c</sup>  $\text{ML}_2\text{X}_2(\text{g}) \rightarrow \text{MX}_2(\text{g}) + 2 \text{L}(\text{g})$ . <sup>d</sup> Values in parentheses estimated.

TABLE 2

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

Complex <sup>a</sup>	$\Delta H_d$ <sup>b</sup>	Temp. (K)	$\Delta H_{\text{sub}}$ <sup>d</sup>	Temp. (K)	$\Delta H_g$ <sup>c</sup>	$\bar{D}(\text{M-N})$	$\bar{D}(\text{M-O})$
$\text{Co}(\text{bt})_2\text{Br}_2$	$160.2 \pm 1.7$	550	$124.2 \pm 4.2$	390	$258.2 \pm 6$	$129.1 \pm 3$	
$\text{Co}(\text{2Mebt})_2\text{Cl}_2$	$167.8 \pm 2.5$	500	$122.6 \pm 1.3$	344	$279.2 \pm 4$	$139.6 \pm 2$	
$\text{Co}(\text{2Mebt})_2\text{Br}_2$	$161.1 \pm 1.7$	525	$113.8 \pm 4.2$	345	$269.3 \pm 6$	$134.7 \pm 3$	
$\text{Co}(\text{2Mebo})_2\text{Cl}_2$	$146.9 \pm 1.2$	520	$92.4 \pm 2.5$	338	$288.5 \pm 4$		$144.3 \pm 2$
$\text{Co}(\text{2Mebo})_2\text{Br}_2$	$160.2 \pm 3.3$	540	$111.3 \pm 4.2$	355	$270.9 \pm 8$		$135.5 \pm 4$
$\text{Co}(\text{2,5diMebo})_2\text{Cl}_2$	$156.6 \pm 2.1$	515	$95.4 \pm 4.6$	338	$295.1 \pm 6$		$147.5 \pm 3$
$\text{Co}(\text{2,5-diMebo})_2\text{Br}_2$	$138.9 \pm 2.9$	530	$104.6 \pm 5.8$	335	$256.3 \pm 8$		$128.2 \pm 4$

<sup>a</sup> (bt) benzothiazole<sup>a</sup> (bo) benzoxazole<sup>b</sup>  $\text{ML}_2\text{X}_2(\text{c}) \rightarrow \text{ML}_2(\text{c}) + 2 \text{L}(\text{g})$ . <sup>c</sup>  $\text{ML}_2\text{X}_2(\text{g}) \rightarrow \text{ML}_2(\text{g}) + 2 \text{L}(\text{g})$ .

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

$$\Delta H_f^0(\text{ML}_2\text{X}_2, \text{c}) = \Delta H_f^0(\text{MX}_2, \text{c}) + \Delta H_f^0(\text{L}, \text{g}) - \Delta H_d$$

This has not been done because (a) there are insufficient data to refer values of  $\Delta H_d$  and  $\Delta H_{\text{sub}}$  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  $\overline{D}(\text{Co-N})$  values lie in the range 120 to 128 kJ mol<sup>-1</sup>. With benzothiazoles as ligands the values are in the range 129–139 kJ mol<sup>-1</sup>. Substitution in the 3-position of pyridine increases the values of  $\overline{D}(\text{Co-N})$  by about 20 kJ mol<sup>-1</sup> to the range 137–146 kJ mol<sup>-1</sup>.

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  $\pi$ -bonding to a greater extent than the py → Co  $\sigma$ -bond is weakened.

For the series of complexes  $\text{M}(\text{3Clpy})_2\text{Cl}_2$ , the  $\overline{D}(\text{M-N})$  values are Co =  $136 \pm 3$ , with an increase to Ni =  $158 \pm 5$  and a decrease to Cu =  $142 \pm 3$  kJ mol<sup>-1</sup>. Values of  $\overline{D}(\text{Co-O})$  in the benzoxazole complexes, 128–148 kJ mol<sup>-1</sup>, are very similar to the values of  $\overline{D}(\text{Co-N})$  noted previously. To equate these bond dissociation energies with the strength of the Co–O and Co–N bonds in the complexes  $\text{CoL}_2\text{X}_2$  is to assume that the strengths of the Co–X bonds are the same in  $\text{CoL}_2\text{X}_2$  and  $\text{CoX}_2$ .

Table 3 shows the enthalpies of decomposition reactions of the cobalt and nickel complexes  $\text{M}(\text{py})_2\text{X}_2$ , where X = Cl, Br, I



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<sup>-1</sup>. The  $\overline{D}(\text{Ni-N})$  values which could be calculated from these enthalpies would be between 20 and 30 kJ mol<sup>-1</sup> greater at 298 K than at ca. 500 K. This probably a real difference which could be confirmed by a temperature correction of  $\Delta H_d$ .

## (ii) Solution calorimetry

An alternative to measuring the enthalpy of the dissociation of a complex  $\text{ML}_n\text{X}_2$  is to determine the enthalpy of the reaction in which it forms from

TABLE 3

Enthalpies of the reaction  $M(\text{py})_2\text{X}_2(\text{c}) \rightarrow \text{MX}_2(\text{c}) + 2 \text{py}(\text{g})$  ( $\text{kJ mol}^{-1}$ )

Complex	$\Delta H_d$	Temp. (K)	Ref.	$\Delta H_d(298 \text{ K})$	Ref.	$\Delta H_d(298 \text{ K}) - \Delta H_d(\text{ca. } 500 \text{ K})$
$\text{Ni}(\text{py})_2\text{Cl}_2$	$136.4 \pm 2.1$	500	9	$198.7 \pm 0.2$	10	62.3
$\text{Ni}(\text{py})_2\text{Br}_2$	$139.3 \pm 2.1$	535	9	$194.1 \pm 0.2$	10	54.8
$\text{Ni}(\text{py})_2\text{I}_2$	$132.2 \pm 3.5$	495	9	$173.2 \pm 0.2$	10	41.0
$\text{Co}(\text{py})_2\text{Cl}_2^a$	$132.2 \pm 2.1$	510	3	$189.5 \pm 0.2$	11	57.3
				$188.7 \pm 0.2$	12	56.5

<sup>a</sup> Violet octahedral form of  $\text{Co}(\text{py})_2\text{Cl}_2$ .

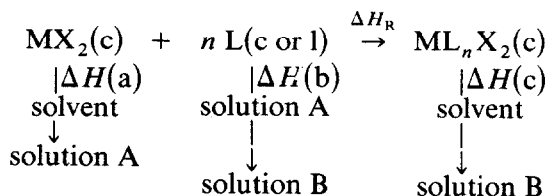
TABLE 4

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

$\text{M}(\text{tu})_4\text{Cl}_2^a$	$\Delta H_R^b$	$\Delta H_f^0(\text{complex, c})$	$\Delta H_{\text{sub}}(\text{complex})$	Temp. (K)	$\Delta H_g^c$	$\bar{D}(\text{M-S})$
$\text{Mn}(\text{tu})_4\text{Cl}_2$	$-(31.4 \pm 0.4)$	$-(865.9 \pm 1.0)$	133.1	390	-490.7	122.7
$\text{Fe}(\text{tu})_4\text{Cl}_2$	$-(46.0 \pm 0.8)$	$-(741.0 \pm 1.3)$	109.6	385	-504.5	126.1
$\text{Co}(\text{tu})_4\text{Cl}_2$	$-(44.4 \pm 0.8)$	$-(710.1 \pm 1.3)$	128.9	370	-524.3	131.1
$\text{Ni}(\text{tu})_4\text{Cl}_2$	$-(44.3 \pm 0.2)$	$-(702.5 \pm 0.8)$	73.6	430	-591.5	147.9
$\text{Zn}(\text{tu})_4\text{Cl}_2$	$-(50.2 \pm 0.4)$	$-(818.5 \pm 1.2)$	90.4	365	-483.6	120.9
$\text{Cd}(\text{tu})_4\text{Cl}_2$	$-(29.3 \pm 2.8)$	$-(774.0 \pm 3.0)$	73.3	290	-512.0	128.0
$\text{Hg}(\text{tu})_4\text{Cl}_2$	$-(4.1 \pm 5.0)$	$-(579.9 \pm 5.0)$	101.7	375	-368.0	92.0
tu			93.7	360		

<sup>a</sup> (tu) thiourea  $(\text{NH}_2)_2\text{C}=\text{S}$ . <sup>b</sup>  $\text{MCl}_2(\text{c}) + 4 \text{tu}(\text{c}) \rightarrow \text{M}(\text{tu})_4\text{Cl}_2(\text{c})$  <sup>c</sup>  $\text{MCl}_2(\text{g}) + 4 \text{tu}(\text{g}) \rightarrow \text{M}(\text{tu})_4\text{Cl}_2(\text{g})$

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,  $\Delta H(a)$ ,  $\Delta H(b)$  and  $\Delta H(c)$ .



The enthalpy,  $\Delta H_{\text{R}}$  is then given by  $\Delta H_{\text{R}} = \Delta H(a) + \Delta H(b) - \Delta H(c)$ . 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.

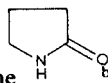
Ashcroft [13] has determined the enthalpies of the formation reactions,  $\Delta H_{\text{R}}$ , of the thiourea complexes  $\text{M}(\text{tu})_4\text{Cl}_2$ , by use of 0.1 M HCl as solvent for the reactants and products. He has determined the enthalpies of sublimation of the complexes and of thiourea by use of a thermogravimetric analytical technique. Data are shown in Table 4; values of  $\Delta H_{\text{f}}^0$  (complex, c),  $\Delta H_{\text{sub}}(\text{complex})$ ,  $\Delta H_{\text{g}}$ , for the gas phase formation reaction, together with the derived  $\bar{D}(\text{M-S})$  values, are plotted in Fig. 1. This figure also shows values of  $\bar{D}(\text{M-N})$  for the complexes  $\text{M}(\text{3Brpy})_2\text{Cl}_2$ , where  $\text{M} = \text{Co}, \text{Ni}$  and  $\text{Cu}$ , together with  $\bar{D}(\text{M-O})$  for the pyrrolidone complexes  $\text{M}(\text{pyrr})_2\text{Cl}_2$ .

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] ( $\text{kJ mol}^{-1}$ )

Complex <sup>a</sup>	$\Delta H_{\text{R}}$ <sup>b</sup>	$\Delta H_{\text{f}}^0(\text{complex, c})$ <sup>c</sup>	$\Delta H_{\text{g}}$ <sup>d</sup>	$\bar{D}(\text{M-O})(?)$
$\text{Mn}(\text{pyrr})_2\text{Cl}_2$	$-(70.3 \pm 0.4)$	$-(1155.6 \pm 2.0)$	$-(356 \pm 6)$	$178 \pm 3$
$\text{Co}(\text{pyrr})_2\text{Cl}_2$	$-(50.2 \pm 0.3)$	$-(966.7 \pm 2.0)$	$-(352 \pm 6)$	$176 \pm 3$
$\text{Ni}(\text{pyrr})_2\text{Cl}_2$	$-(49.5 \pm 0.3)$	$-(958.8 \pm 2.0)$	$-(364 \pm 6)$	$182 \pm 3$
$\text{Cu}(\text{pyrr})_2\text{Cl}_2$	$-(58.3 \pm 0.2)$	$-(802.4 \pm 2.0)$	$-(320 \pm 6)$	$160 \pm 3$
$\text{Zn}(\text{pyrr})_2\text{Cl}_2$	$-(74.4 \pm 0.2)$	$-(1093.5 \pm 2.0)$	$-(291 \pm 6)$	$146 \pm 3$



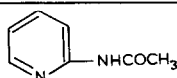
<sup>a</sup> (pyrr) 2-pyrrolidone <sup>b</sup>  $\text{MCl}_2(\text{c}) + 2 (\text{pyrr})(\text{c}) \rightarrow \text{M}(\text{pyrr})_2\text{Cl}_2(\text{c})$ . <sup>c</sup> Based on  $\Delta H_{\text{f}}^0(\text{pyrr}, \text{c}) = -(302 \pm 1) \text{ kJ mol}^{-1}$ . <sup>d</sup>  $\text{MCl}_2(\text{g}) + 2 (\text{pyrr})(\text{g}) \rightarrow \text{M}(\text{pyrr})_2\text{Cl}_2(\text{g})$ , calculated using  $\Delta H_{\text{sub}}^{298}(\text{pyrr}) = 68 \pm 4 \text{ kJ mol}^{-1}$  derived from the relation  $\Delta H_{\text{sub}}^{298}(\text{pyrr}) = \Delta H_{\text{fusion}}^{298}(\text{pyrr}) + \Delta H_{\text{vap}}(\text{pyrrolidine}) + \Delta H_{\text{vap}}(\text{cyclopentanone}) - \Delta H_{\text{vap}}(\text{cyclopentane})$ , and the assumption that  $\Delta H_{\text{sub}}^{298}(\text{M}(\text{pyrr})_n\text{Cl}_2) = \Delta H_{\text{sub}}^{298}(\text{pyrr})$ ; values used are  $\Delta H_{\text{vap}}(\text{pyrrolidine}) 37.6 \pm 0.1$ ,  $\Delta H_{\text{vap}}(\text{cyclopentanone}) 42.7 \pm 0.2$ ,  $\Delta H_{\text{vap}}(\text{cyclopentane}) 28.7 \pm 2 \text{ kJ mol}^{-1}$  [74] and  $\Delta H_{\text{fusion}}(\text{pyrr}) = 16 \text{ kJ mol}^{-1}$  (estimated).



TABLE 6

Enthalpies of formation of *N*-(2-pyridyl)acetamide complexes [16] (kJ mol<sup>-1</sup>)

Complex <sup>a</sup>	$\Delta H_R$ <sup>b</sup>	$\Delta H_f^0$ (complex, c)	$\Delta H_g$ <sup>c</sup>	$\bar{D}(\text{M}-\text{N})$
Zn(pa) <sub>2</sub> Cl <sub>2</sub>	-(72.8 ± 0.6)	-(785 ± 22)	-325	163
Zn(pa) <sub>2</sub> Br <sub>2</sub>	-(76.5 ± 0.8)	-(702 ± 22)	-310	155
Zn(pa) <sub>2</sub> I <sub>2</sub>	-(74.4 ± 0.8)	-(580 ± 22)	-312	156
Cd(pa) <sub>2</sub> Cl <sub>2</sub>	-(35.0 ± 0.7)	-(724 ± 22)	-319	160
Cd(pa) <sub>2</sub> Br <sub>2</sub>	-(36.7 ± 0.8)	-(650 ± 22)	-304	152
Cd(pa) <sub>2</sub> I <sub>2</sub>	-(40.2 ± 0.4)	-(541 ± 21)	-290	145
Hg(pa) <sub>2</sub> Cl <sub>2</sub>	-(22.9 ± 1.1)	-(544 ± 23)	-211	106
Hg(pa)Br <sub>2</sub>	-(10.7 ± 0.7)	-(330 ± 22)	-119	119

<sup>a</sup> (pa) *N*-(2-pyridyl)acetamide<sup>c</sup> MX<sub>2</sub>(g) + *n* (pa)(g) → M(pa)<sub>*n*</sub>(X<sub>2</sub>(g).<sup>b</sup> MX<sub>2</sub>(c) + *n*(pa)(c) → M(pa)<sub>*n*</sub>X<sub>2</sub>(c).

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<sup>-1</sup> is considerably greater than either the  $\bar{D}(\text{Co}-\text{N})$  values for the pyridine and benzothiazole complexes (120–146 kJ mol<sup>-1</sup>) or the  $\bar{D}(\text{Co}-\text{O})$  values in the benzoxazole complexes of cobalt (128 to 148 kJ mol<sup>-1</sup>) 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)<sub>4</sub>Cl<sub>2</sub> complexes is readily

TABLE 7

Enthalpies of formation of phosphine oxide complexes [17,18] (kJ mol<sup>-1</sup>)

Complex <sup>a</sup>	$\Delta H_R$ <sup>b</sup>	$\Delta H_f^0$ (complex, c)	$\Delta H_g$ <sup>c</sup>	$\bar{D}(\text{M}-\text{O})$
Zn(tepo) <sub>2</sub> Cl <sub>2</sub>	-(75.1 ± 0.7)		-318	159
Cd(tepo) <sub>2</sub> Cl <sub>2</sub>	-(31.8 ± 0.1)		-307	154
Hg(tepo) <sub>2</sub> Cl <sub>2</sub>	-(28.6 ± 0.1)		-206	103
Zn(tppo) <sub>2</sub> Cl <sub>2</sub>	-(51.1 ± 2.2)	-(586.6 ± 50)	-261	131
Cd(tppo) <sub>2</sub> Cl <sub>2</sub>	-(16.3 ± 0.5)	-(528.3 ± 50)	-258	129
Hg(tppo) <sub>2</sub> Cl <sub>2</sub>	-(12.3 ± 0.6)	-(357.7 ± 50)	-156	78
Zn(tbpo) <sub>2</sub> Cl <sub>2</sub>	-(33.6 ± 1.4)		-287	144

<sup>a</sup> (tepo) triethylphosphine oxide, OPEt<sub>3</sub>; (tppo) triphenylphosphine oxide, OPPh<sub>3</sub>; (tbpo) tribenzylphosphine oxide, OP(CH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>. <sup>b</sup> MCl<sub>2</sub>(c) + 2 L(c) → ML<sub>2</sub>Cl<sub>2</sub>(c). <sup>c</sup> MCl<sub>2</sub>(g) + 2 L(g) → ML<sub>2</sub>Cl<sub>2</sub>(g), calculated using the  $\Delta H_{\text{sub}}^{298}$  values: tepo 94 kJ mol<sup>-1</sup>, tppo 66 kJ mol<sup>-1</sup> and tbpo 104 kJ mol<sup>-1</sup>; together with the assumption that  $\Delta H_{\text{sub}}^{298}(\text{ML}_2\text{Cl}_2) = \Delta H_{\text{sub}}^{298}(\text{L})$ .

TABLE 8

Enthalpies of formation of diacetamide complexes [19] (kJ mol<sup>-1</sup>)

Complex <sup>a</sup>	$\Delta H_R$ <sup>b</sup>	$\Delta H_f^0$ (complex, c)	$\Delta H_g$ <sup>c</sup>	$\bar{D}(\text{M-O})$
Zn(da)Cl <sub>2</sub>	-(32.2 ± 0.6)	-(945.7 ± 0.5)	-181	91
Zn(da)Br <sub>2</sub>	-(22.5 ± 0.7)	-(849.7 ± 1.2)	-154	77
Zn(da)I <sub>2</sub>	-(12.8 ± 0.8)	-(719.3 ± 1.3)	-133	67
Cd(da)Cl <sub>2</sub>	-(11.3 ± 0.5)	-(901.2 ± 1.0)	-192	96
Cd(da)Br <sub>2</sub>	-(9.6 ± 0.6)	-(824.3 ± 1.1)	-161	81
Cd(da)I <sub>2</sub>	-(10.6 ± 0.9)	-(712.4 ± 1.4)	-148	74
Hg(da) <sub>2</sub> Cl <sub>2</sub>	-(21.8 ± 0.7)	-(1242.9 ± 1.7)	-176	88 <sup>d</sup>
Hg(da) <sub>2</sub> Br <sub>2</sub>	-(15.4 ± 0.5)	-(1182.9 ± 1.5)	-172	85 <sup>d</sup>

<sup>a</sup> (da) diacetamide, CH<sub>3</sub>CONHCOCH<sub>3</sub>, complexes in *trans-trans* form except Hg(da)<sub>2</sub>Cl<sub>2</sub> and Hg(da)<sub>2</sub>Br<sub>2</sub> which are *cis-trans*. <sup>b</sup> MX<sub>2</sub>(c) + n (da)(c) → M(da)<sub>n</sub>X<sub>2</sub>(c). <sup>c</sup> MX<sub>2</sub>(g) + n (da)(g) → M(da)<sub>n</sub>X<sub>2</sub>(g) calculated using  $\Delta H_{\text{sub}}^{298}(\text{da}) = 72.2 \pm 0.6$  kJ mol<sup>-1</sup> (ref. 18) and the assumption that  $\Delta H_{\text{sub}}^{298}(\text{M}(\text{da})_n\text{X}_2) = \Delta H_{\text{sub}}^{298}(\text{da})$ . <sup>d</sup> 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<sup>II</sup>(*d*<sup>6</sup>), Co<sup>II</sup>(*d*<sup>7</sup>), Ni<sup>II</sup>(*d*<sup>8</sup>) and Cu<sup>II</sup>(*d*<sup>9</sup>) complexes are not spherically distributed between the  $\sigma^*$  and  $\pi^*$  antibonding orbitals, but occupy the lower energy  $\pi^*$  orbitals preferentially. As a result the antibonding energy is less, per electron, than for the Mn<sup>II</sup>(*d*<sup>5</sup>) or Zn<sup>II</sup>(*d*<sup>10</sup>) cases. This "stabilization" energy, *E*, is given by the expression  $E = [3n_{\sigma^*} - 2n_{\pi^*}]\Delta_0/5$ , where  $\Delta_0$  is the energy separation between the  $\sigma^*$

TABLE 9

Enthalpies of formation of tetramethylurea complexes [20] (kJ mol<sup>-1</sup>)

Complex <sup>a</sup>	$\Delta H_R$ <sup>b</sup>	$\Delta H_f^0$ (complex, c)	$\Delta H_g$ <sup>c</sup>	$\bar{D}(\text{M-O})$
Zn(tmu) <sub>2</sub> Cl <sub>2</sub>	-(83.1 ± 1.0)	-(1006 ± 2)	-283	142
Zn(tmu) <sub>2</sub> Br <sub>2</sub>	-(88.7 ± 2.1)	-(926 ± 3)	-272	136
Zn(tmu) <sub>2</sub> I <sub>2</sub>	-(127.8 ± 2.9)	-(844 ± 4)	-299	150
Cd(tmu)Cl <sub>2</sub>	-(44.7 ± 0.6)	-(690 ± 2)	-226	226
Cd(tmu)Br <sub>2</sub>	-(32.1 ± 0.3)	-(602 ± 1)	-184	184
Cd(tmu) <sub>2</sub> I <sub>2</sub>	-(63.0 ± 0.7)	-(775 ± 2)	-252	126
Hg(tmu)Cl <sub>2</sub>	-(36.5 ± 0.5)	-(515 ± 2)	-119	119
Hg(tmu)Br <sub>2</sub>	-(29.4 ± 0.2)	-(454 ± 1)	-114	114

<sup>a</sup> (tmu) tetramethylurea, (CH<sub>3</sub>)<sub>2</sub>NCON(CH<sub>3</sub>)<sub>2</sub>. <sup>b</sup> MX<sub>2</sub>(c) + n (tmu)(l) → M(tmu)<sub>n</sub>X<sub>2</sub>(c). <sup>c</sup> MX<sub>2</sub>(g) + n (tmu)(g) → M(tmu)<sub>n</sub>X<sub>2</sub>(g) calculated using  $\Delta H_{\text{vap}}^{298}(\text{tmu}) = 51.7 \pm 0.7$  kJ mol<sup>-1</sup> and the assumption that  $\Delta H_{\text{sub}}^{298}(\text{M}(\text{tmu})_n\text{X}_2) = \Delta H_{\text{sub}}^{298}(\text{tmu})$ .

TABLE 10

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

Complex	$\Delta H_R^a$	$\Delta H_f^0(\text{complex, c})$	$\Delta H_g^b$	$\bar{D}(\text{Cu-N})$
$\text{Cu}(\text{Et}_2\text{NH})_2\text{Cl}_2$	$-(119.2 \pm 2.5)$	$-(547 \pm 5)$	$-(328 \pm 5)$	164
$\text{Cu}(\text{Pr}_2\text{NH})_2\text{Cl}_2$	$-(126.8 \pm 2.9)$	$-(659 \pm 5)$	$-(344 \pm 5)$	172
$\text{Cu}(\text{n-Bu}_2\text{NH})_2\text{Cl}_2$	$-(119.7 \pm 2.5)$	$-(752 \pm 5)$	$-(346 \pm 5)$	173
$\text{Cu}(\text{Et}_2\text{NH})_2\text{Br}_2$	$-(142.7 \pm 2.5)$	$-(492 \pm 5)$	$-(346 \pm 5)$	173
$\text{Cu}(\text{Pr}_2\text{NH})_2\text{Br}_2$	$-(150.2 \pm 3.3)$	$-(604 \pm 5)$	$-(362 \pm 5)$	181
$\text{Cu}(\text{n-Bu}_2\text{NH})_2\text{Br}_2$	$-(144.3 \pm 2.9)$	$-(698 \pm 5)$	$-(364 \pm 5)$	182

<sup>a</sup>  $\text{CuX}_2(\text{c}) + 2 \text{R}_2\text{NH}(\text{l}) \rightarrow \text{Cu}(\text{R}_2\text{NH})_2\text{X}_2(\text{c})$ . <sup>b</sup>  $\text{CuX}_2(\text{g}) + 2 \text{R}_2\text{NH}(\text{g}) \rightarrow \text{Cu}(\text{R}_2\text{NH})_2\text{X}_2(\text{g})$ , calculated using  $\Delta H_{\text{vap}}^{298}$  values,  $\text{Et}_2\text{NH} = 31.8$ ,  $\text{Pr}_2\text{NH} = 40.1$  and  $\text{n-Bu}_2\text{NH} = 49.4 \text{ kJ mol}^{-1}$  and the assumption that  $\Delta H_{\text{sub}}^{298}(\text{M}(\text{R}_2\text{NH})_2\text{X}_2) = \Delta H_{\text{vap}}^{298}(\text{R}_2\text{NH}) + 17 \text{ kJ mol}^{-1}$ .

and  $\pi^*$  orbitals, which are occupied by a number  $n_{\sigma^*}$  and  $n_{\pi^*}$  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  $\bar{D}(\text{M-S})$  and  $\bar{D}(\text{M-N})$ .

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

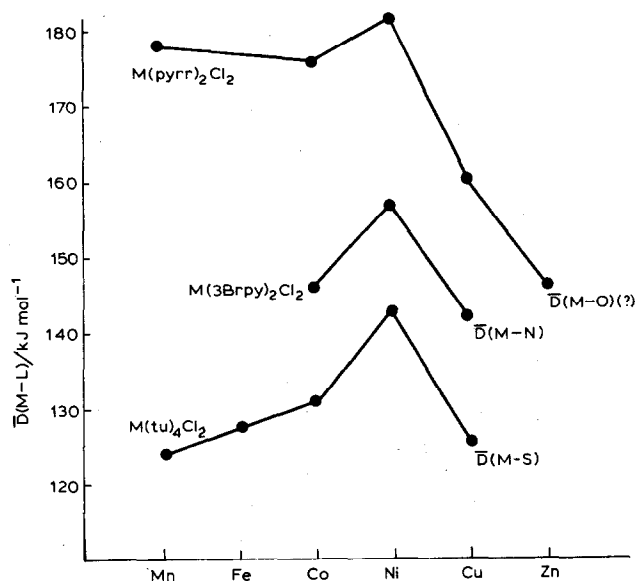


Fig. 1.  $\bar{D}(\text{M-S})$  in  $\text{M}(\text{tu})_4\text{Cl}_2$ ,  $\bar{D}(\text{M-N})$  in  $\text{M}(\text{3Brpy})_2\text{Cl}_2$  and  $\bar{D}(\text{M-O})$  in  $\text{M}(\text{pyrr})_2\text{Cl}_2$ .

TABLE 11

Enthalpies of formation ( $\text{kJ mol}^{-1}$ ) of *trans*-Pd(AEt<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>(c) [23] where A = S, Se or Te

Complex	$\Delta H_R$	$\Delta H_f^0(\text{complex, c})$	$\Delta H_g$	$\bar{D}(\text{Pd-A})$
Pd(SEt <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub>	-(103.8 ± 0.4)	-(563.7 ± 3.9)	233 ± 15	117 ± 8 ( $\bar{D}(\text{Pd-S})$ )
Pd(SeEt <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub>	-(115.3 ± 0.9)	-(529.2 ± 9.5)	251 ± 20	126 ± 10 ( $\bar{D}(\text{Pd-Se})$ )
Pd(TeEt <sub>2</sub> ) <sub>2</sub> Cl <sub>2</sub>	-(175.7 ± 4.8)	-(763.8 ± 14.6)	308 ± 20	154 ± 10 ( $\bar{D}(\text{Pd-Te})$ )

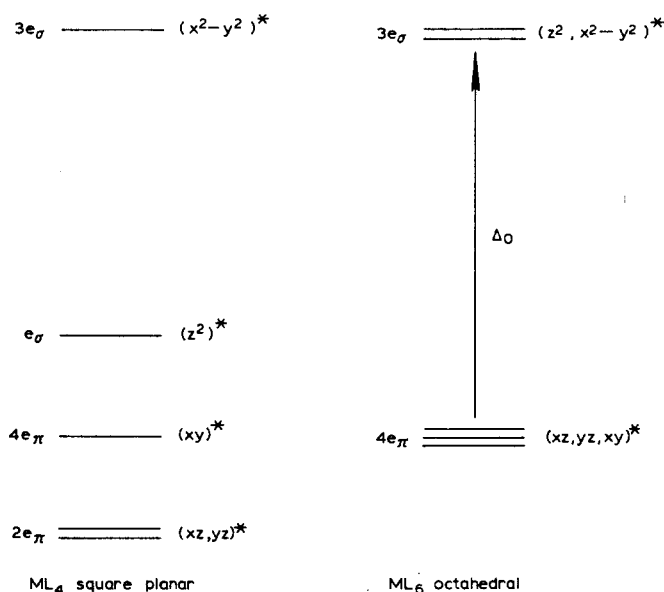


Fig. 2. Relative energy levels of antibonding orbitals in the Angular Overlap Model description of  $ML_4$  square planar and  $ML_6$  octahedral complexes.

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  $\Delta H_f^0$ (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. Airoidi and co-workers [16–20] make the assumption that  $\Delta H_{sub}^{298}$ (complex) =  $\Delta H_{sub}^{298}$ (ligand) in order to calculate a value for  $\Delta H_g$ , the gas-phase formation of complex from metal halide and ligand. There is some justification for this assumption. Thus, the values of  $\Delta H_{sub}$  for the complexes  $M(tu)_4Cl_2$  lie in the range 73–133 kJ mol, compared with  $\Delta H_{sub}(tu) = 94$  kJ mol<sup>-1</sup>. The values of  $\Delta H_{sub}$  for the metal complexes of the substituted pyridines, benzothiazoles and benzoxazoles also lie in the band 70–125 kJ mol<sup>-1</sup> (with the exception of  $Cu(3Brpy)_2Cl_2$  for which we have  $\Delta H_{sub} = 57$  kJ mol<sup>-1</sup>) although the values of  $\Delta H_{sub}$ (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  $\Delta H_{sub}$ (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  $\bar{D}(\text{M-S})$  from the thiourea complexes  $\text{M}(\text{tu})_4\text{Cl}_2$  are also shown. For the complexes of *N*-(2-pyridyl)acetamide,  $\bar{D}(\text{M-N})$ , triethylphosphine oxide, and triphenylphosphine oxide,  $\bar{D}(\text{M-O})$ , 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,  $\bar{D}(\text{M-O})$ , and thiourea,  $\bar{D}(\text{M-S})$ , 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  $\text{Cl} > \text{Br} > \text{I}$ . Thus, for the complexes  $\text{Zn}(\text{diacetamide})\text{X}_2$ , the values of  $\bar{D}(\text{M-O})$  are as follows:  $\text{Zn}(\text{da})\text{Cl}_2$ , 91;  $\text{Zn}(\text{da})\text{Br}_2$ , 77; and  $\text{Zn}(\text{da})\text{I}_2$ , 67  $\text{kJ mol}^{-1}$ . There are, however, a few exceptions to this general rule.

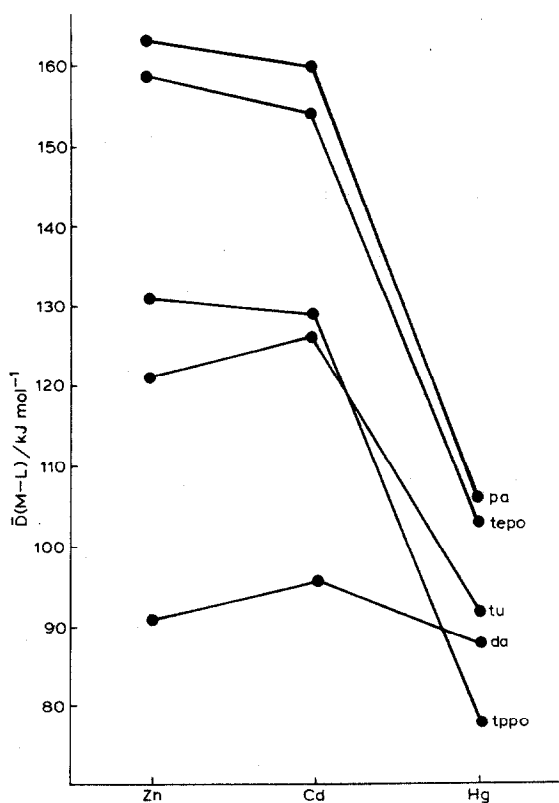


Fig. 3.  $\bar{D}(\text{M-S})$  in  $\text{M}(\text{tu})_4\text{Cl}_2$ ;  $\bar{D}(\text{M-N})$  in  $\text{M}(\text{pa})_2\text{Cl}_2$  and  $\bar{D}(\text{M-O})$  in  $\text{M}(\text{tepo})_2\text{Cl}_2$ ,  $\text{M}(\text{tppo})_2\text{Cl}_2$  and  $\text{M}(\text{da})\text{Cl}_2$ .

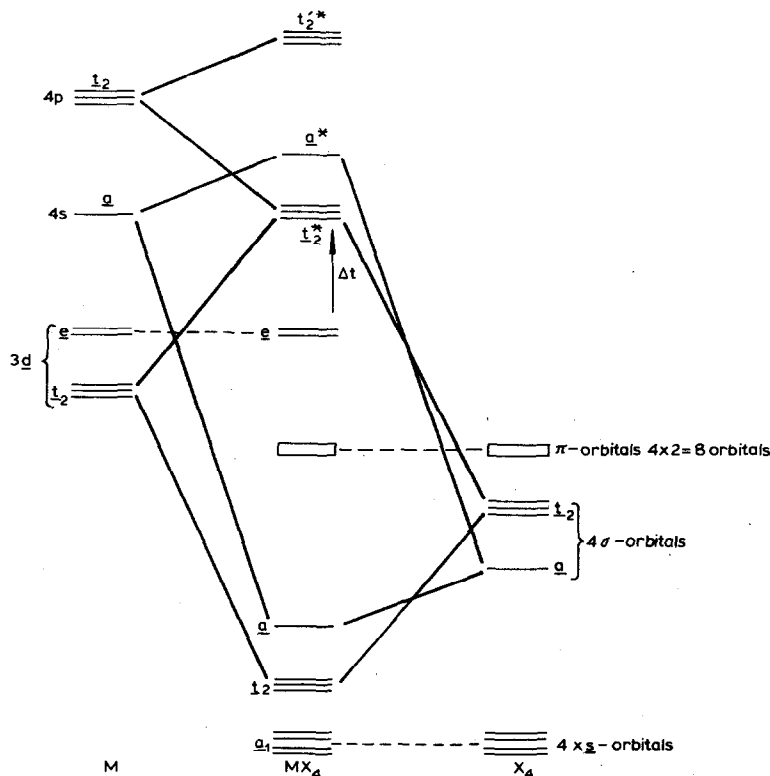


Fig. 4. Molecular orbital energy diagram of tetrahedral complex  $MX_4$ ,  $\sigma$ -bonding only.

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  $\sigma$ -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  $a_1$   $\sigma$ -orbital of the four ligands. Along the series  $Zn$ ,  $Cd$ ,  $Hg$  the increasing radial diffuseness of the  $4s$ ,  $5s$ , to  $6s$  orbital decreases the effective overlap and efficiency of the single bonding  $a_1$  molecular orbital. As a result, the  $s$ -component of the  $M-X$  bond is expected to decrease. The observation that the  $\bar{D}(M-X)$  values decrease along this series implies that it is the  $\sigma$ -bonding which is dominant in these molecules.

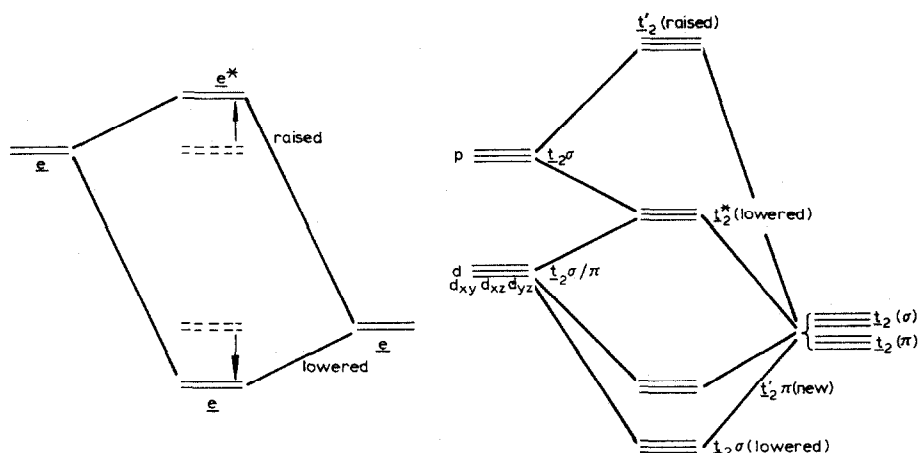


Fig. 5. Molecular orbital energy diagram of tetrahedral complex  $MX_4$ ,  $\pi$  bonding only.

Incorporation of  $\pi$ -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  $\sigma$ - and  $\pi$ -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  $\sigma$ -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  $\pi^*$  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  $\bar{D}(Co-N)$  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  $\bar{D}(Cu-N)$  values of ca.  $170 \text{ kJ mol}^{-1}$ , which refer to 298 K. We have previously noted a value  $\bar{D}(Cu-N) = 142 \text{ kJ mol}^{-1}$ , at 560 K, in  $Cu(3Brpy)_2Cl_2$ . Also, for pyridine complexes of nickel and cobalt, the  $\bar{D}$  values at ca. 500 K are about 30 kJ lower than at 298 K. It is likely, therefore, that the values of  $\bar{D}(Cu-N \text{ amine})$  and  $\bar{D}(Cu-N \text{ pyridine})$  are very similar.



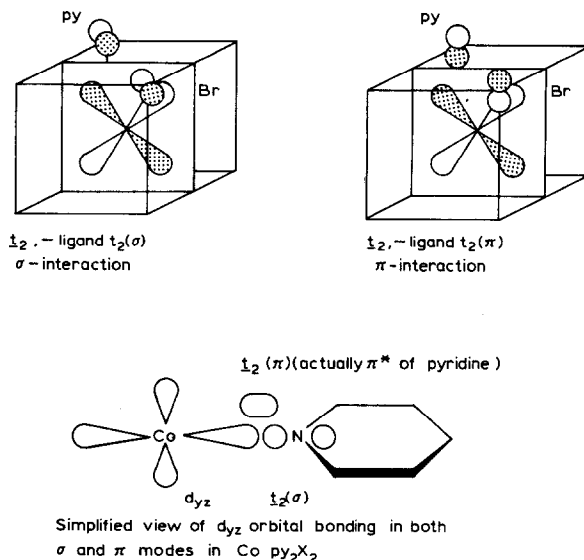
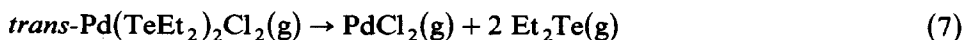
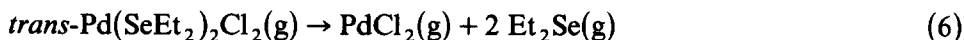
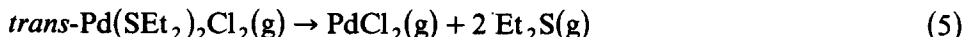


Fig. 6. Orbital overlap in tetrahedral complex  $\text{MX}_4$ .

Evans and Mortimer [23] have determined the enthalpies,  $\Delta H_R$ , of the following reactions, where  $\text{A} = \text{S}, \text{Se}$  or  $\text{Te}$ , by measuring enthalpies of solution in aqueous acetone.



Using  $\Delta H_f^0$  values for  $(\text{NH}_4)_2\text{PdCl}_4(\text{c})$ ,  $\text{Et}_2\text{S}(\text{l})$ ,  $\text{Et}_2\text{Se}(\text{l})$ ,  $\text{Et}_2\text{Te}(\text{l})$  and  $\text{NH}_4\text{Cl}(\text{c})$  given in Appendix 1, values for  $\Delta H_f^0(\text{trans-Pd}(\text{AEt}_2)_2\text{Cl}_2, \text{c})$  are derived and shown in Table 11. The enthalpies,  $\Delta H_g$ , of the gas-phase dissociation reactions (5)–(7)



can be equated to  $2 \bar{D}(\text{Pd-S})$ ,  $2 \bar{D}(\text{Pd-Se})$  and  $2 \bar{D}(\text{Pd-Te})$ , respectively. Incorporating the value for  $\Delta H_f^0(\text{PdCl}_2, \text{c})$  given in Appendix 1, using the enthalpies of vaporisation  $\text{Et}_2\text{S} = 35.86 \pm 0.04 \text{ kJ mol}^{-1}$  [85]  $\text{Et}_2\text{Se} = 38.9 \pm 4 \text{ kJ mol}^{-1}$  [86] and  $\text{Et}_2\text{Te} = 41.8 \pm 2 \text{ kJ mol}^{-1}$  [84] and the assumption  $\Delta H_{\text{sub}}(\text{PdCl}_2) = \Delta H_{\text{sub}}(\text{trans-Pd}(\text{AEt}_2)_2\text{Cl}_2)$ , we obtain the values of  $\Delta H_g$  and  $\bar{D}(\text{Pd-A})$  shown in Table 10. The trend in values is  $\bar{D}(\text{Pd-S}) < \bar{D}(\text{Pd-Se}) < \bar{D}(\text{Pd-Te})$ .

In the square-planar,  $d^8$ , complexes  $\text{PdL}_4$ , bonding between metal and ligand depends on four molecular orbitals, for although there are other



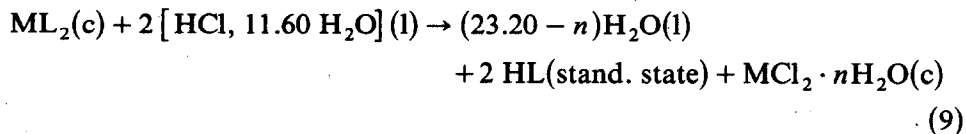
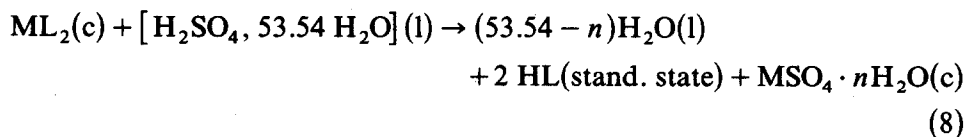
pentane-2,4-dionato radical, which results from the dissociation of a hydrogen atom from the enol form of pentane-2,4-dione (pd), or acetylacetone.

(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.

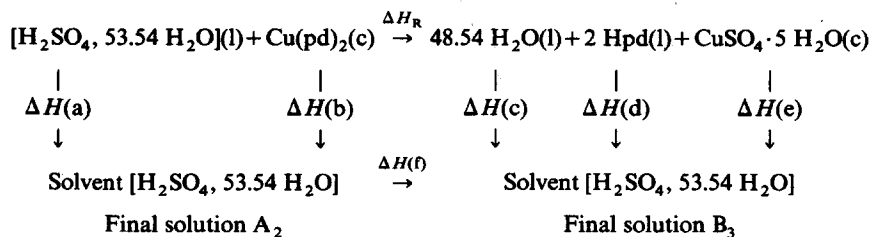
This approach to the determination of enthalpies of formation of these complexes has been used by the following separate groups of workers: R.J. Irving et al., University of Surrey; M.A.V. Ribeiro da Silva et al., University of Oporto, Portugal; E. Giera et al., University of Wroclaw, Poland; J.O. Hill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

The enthalpies,  $\Delta H_R$ , of the following reactions were obtained by measuring the enthalpies of solution of  $ML_2$  in the solvent.

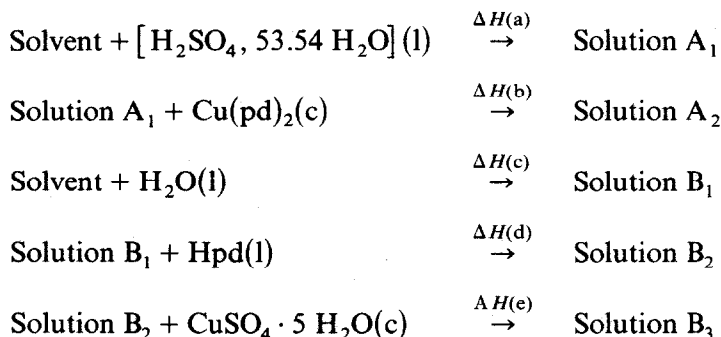


Then, in a fresh sample of solvent, the successive enthalpies of solution of the reaction products were measured. The solvent used was either  $[H_2SO_4, 53.54 H_2O]$ ,  $[HCl, 11.60 H_2O]$ ,  $[HClO_4, 3.57 H_2O]$ , or a mixture of 25% by volume  $[HCl, 11.60 H_2O]$  and 75% of 1,4-dioxan.

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



The following enthalpies of solution were determined:



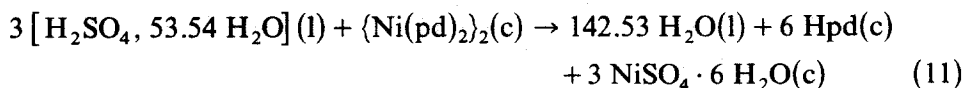
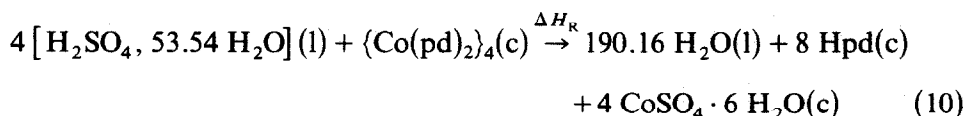
Provided that the precise stoichiometry is realised and solution A<sub>2</sub> is the same as solution B<sub>3</sub>, then the value of  $\Delta H(f)$  is zero and we can write

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

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<sub>2</sub>SO<sub>4</sub>, 53.54 H<sub>2</sub>O], then  $\Delta H(a) = 0$ . The value  $\Delta H(c) = -0.121$  kJ mol<sup>-1</sup> is calculated from published data [50]. By measuring the values  $\Delta H(b) = -21.75$  kJ mol<sup>-1</sup>,  $\Delta H(d) = +6.19$  kJ mol<sup>-1</sup>,  $\Delta H(e) = 22.61$  kJ mol<sup>-1</sup> we obtain  $\Delta H_R = 50.6 \pm 0.4$  kJ mol<sup>-1</sup>. Using the relationship  $\Delta H_f^0(\text{Cu}(\text{pd})_2, \text{c}) = 2 \Delta H_f^0(\text{Hpd}, \text{l}) + \Delta H_f^0(\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}) - \Delta H_f^0[\text{H}_2\text{SO}_4, \text{in } 53.54] - 5 \Delta H_f^0(\text{H}_2\text{O}, \text{l}) - \Delta H_R$

and incorporating the enthalpies of formation shown in Appendix 1, we obtain the value  $\Delta H_f^0(\text{Cu}(\text{pd})_2, \text{c}) = -(760.7 \pm 4)$  kJ mol<sup>-1</sup>.

A similar approach has been used for {Co(pd)<sub>2</sub>}<sub>4</sub> and {Ni(pd)<sub>2</sub>}<sub>3</sub>. The relevant thermochemical equations are as follows



In these cases the solvent used was [H<sub>2</sub>SO<sub>4</sub>, 53.54 H<sub>2</sub>O]. For the study of Ni(tmhd)<sub>2</sub>\* the solvent used was a mixture of 25% by volume of [HCl, 11.60 H<sub>2</sub>O] and 75% by volume of 1,4-dioxan. A mixed HCl/dioxan solvent was

\* See Table 13 for meanings of abbreviations.

TABLE 12

Thermochemical decomposition reactions of metal-dionato complexes

Eqn. no.	Reaction	Solvent <sup>a</sup>	Ref.
10	$4 [\text{H}_2\text{SO}_4, 53.54 \text{ H}_2\text{O}](\text{l}) + \{\text{Co}(\text{pd})_2\}_4(\text{c}) \rightarrow 190.16 \text{ H}_2\text{O}(\text{l}) + 8 \text{ Hpd}(\text{l}) + 4 \text{ CoSO}_4 \cdot 6 \text{ H}_2\text{O}(\text{c})$	1	24
11	$3 [\text{H}_2\text{SO}_4, 53.54 \text{ H}_2\text{O}](\text{l}) + \{\text{Ni}(\text{pd})_2\}_3(\text{c}) \rightarrow 142.62 \text{ H}_2\text{O}(\text{l}) + 6 \text{ Hpd}(\text{l}) + 3 \text{ NiSO}_4 \cdot 6 \text{ H}_2\text{O}(\text{c})$	1	25
12	$2 [\text{HCl}, 11.60 \text{ H}_2\text{O}](\text{l}) + \text{Ni}(\text{tmhd})_2(\text{c}) \rightarrow 17.2 \text{ H}_2\text{O}(\text{l}) + 2 \text{ Htmhd}(\text{l}) + \text{NiCl}_2 \cdot 6 \text{ H}_2\text{O}(\text{c})$	5	25
13	$[\text{H}_2\text{SO}_4, 53.54 \text{ H}_2\text{O}](\text{l}) + \text{Cu}(\text{pbd})_2(\text{c}) \rightarrow 48.54 \text{ H}_2\text{O}(\text{l}) + 2 \text{ Hpbd}(\text{l}) + \text{CuSO}_4 \cdot 5 \text{ H}_2\text{O}(\text{c})$	5	26
14	$[\text{H}_2\text{SO}_4, 53.54 \text{ H}_2\text{O}](\text{l}) + \text{Cu}(\text{pd})_2(\text{c}) \rightarrow 48.54 \text{ H}_2\text{O}(\text{l}) + 2 \text{ Hpd}(\text{l}) + \text{CuSO}_4 \cdot 5 \text{ H}_2\text{O}(\text{c})$	1	24
15	$3 [\text{HCl}, \infty \text{ H}_2\text{O}](\text{l}) + \text{Cr}(\text{pd})_3(\text{c}) \rightarrow \infty \text{ H}_2\text{O}(\text{l}) + 3 \text{ Hpd}(\text{l}) + \text{CrCl}_3 \cdot 6 \text{ H}_2\text{O}(\text{c})$	4	27
16	$3 [\text{HCl}, \infty \text{ H}_2\text{O}](\text{l}) + \text{Mn}(\text{pd})_3(\text{c}) + \text{FeCl}_2(\text{c}) \rightarrow \infty \text{ H}_2\text{O}(\text{l}) + \text{FeCl}_3(\text{c}) + 3 \text{ Hpd}(\text{l}) + \text{MnCl}_2 \cdot 4 \text{ H}_2\text{O}(\text{c})$	2	28
17	$3 [\text{HCl}, \infty \text{ H}_2\text{O}](\text{l}) + \text{Fe}(\text{pd})_3(\text{c}) \rightarrow \infty \text{ H}_2\text{O}(\text{l}) + 3 \text{ Hpd}(\text{l}) + \text{FeCl}_3(\text{c})$	2	29
18	$43.85 \text{ H}_2\text{O}(\text{l}) + 2 \text{ NaCl}(\text{c}) + \text{FeCl}_3(\text{c}) + \text{Mo}(\text{pd})_3(\text{c}) \rightarrow$ $5 [\text{HCl}, 7.97 \text{ H}_2\text{O}](\text{l}) + 3 \text{ Hpd}(\text{l}) + 3 \text{ FeCl}_2(\text{c}) + \text{Na}_2[\text{MoO}_4](\text{c})$	3	30
19	$2 [\text{HCl}, \infty \text{ H}_2\text{O}](\text{l}) + \text{Mn}(\text{pd})_2(\text{c}) \rightarrow \infty \text{ H}_2\text{O}(\text{l}) + 2 \text{ Hpd}(\text{l}) + \text{MnCl}_2 \cdot 4 \text{ H}_2\text{O}(\text{c})$	2	31
20	$8 [\text{HCl}, \infty \text{ H}_2\text{O}](\text{l}) + \{\text{Co}(\text{pd})_2\}_4(\text{c}) \rightarrow \infty \text{ H}_2\text{O}(\text{l}) + 8 \text{ Hpd}(\text{l}) + 4 \text{ CoCl}_2 \cdot 6 \text{ H}_2\text{O}(\text{c})$	2	31
21	$6 [\text{HCl}, \infty \text{ H}_2\text{O}](\text{l}) + \{\text{Ni}(\text{pd})_2\}_3(\text{c}) \rightarrow \infty \text{ H}_2\text{O}(\text{l}) + 6 \text{ Hpd}(\text{l}) + 3 \text{ NiCl}_2 \cdot 6 \text{ H}_2\text{O}(\text{c})$	2	31, 32
22	$2 [\text{HCl}, \infty \text{ H}_2\text{O}](\text{l}) + \text{Cu}(\text{pd})_2(\text{c}) \rightarrow \infty \text{ H}_2\text{O}(\text{l}) + 2 \text{ Hpd}(\text{l}) + \text{CuCl}_2 \cdot 2 \text{ H}_2\text{O}(\text{c})$	2	31
23	$2 [\text{HCl}, \infty \text{ H}_2\text{O}](\text{l}) + \text{Zn}(\text{pd})_2(\text{c}) \rightarrow \infty \text{ H}_2\text{O}(\text{l}) + 2 \text{ Hpd}(\text{l}) + \text{ZnCl}_2(\text{c})$	2	31
24	$2 [\text{HCl}, \infty \text{ H}_2\text{O}](\text{l}) + \text{Ni}(\text{pbd})_2(\text{c}) \rightarrow \infty \text{ H}_2\text{O}(\text{l}) + 2 \text{ Hpbd}(\text{c}) + \text{NiCl}_2 \cdot 6 \text{ H}_2\text{O}(\text{c})$	2	31, 32
25	$2 [\text{HCl}, \infty \text{ H}_2\text{O}](\text{l}) + \text{Zn}(\text{pbd})_2(\text{c}) \rightarrow \infty \text{ H}_2\text{O}(\text{l}) + 2 \text{ Hpbd}(\text{c}) + \text{ZnCl}_2(\text{c})$	2	31
26	$2 [\text{HCl}, \infty \text{ H}_2\text{O}](\text{l}) + \text{Ni}(\text{dppd})_2(\text{c}) \rightarrow \infty \text{ H}_2\text{O}(\text{l}) + 2 \text{ Hdppd}(\text{c}) + \text{NiCl}_2 \cdot 6 \text{ H}_2\text{O}(\text{c})$	5	32

<sup>a</sup> 1,  $[\text{H}_2\text{SO}_4, 53.54 \text{ H}_2\text{O}]$ ; 2,  $[\text{HCl}, 11.60 \text{ H}_2\text{O}]$ ; 3,  $[\text{HCl}, 7.97 \text{ H}_2\text{O}]$ ; 4,  $[\text{HClO}_4, 3.57 \text{ H}_2\text{O}]$ ; 5, mixture of 25% by volume  $\text{HCl}$ , 11.60  $\text{H}_2\text{O}$  and 25% by volume 1,4-dioxan.

TABLE 13

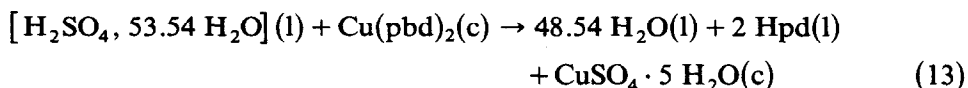
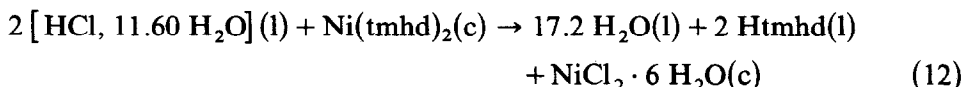
Enthalpies of formation of dionato complexes ( $\text{kJ mol}^{-1}$ )

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

<sup>a</sup> (pd) pentane-2,4-dionato,  $\text{CH}_3\text{COCH}=\text{CO}\cdot\text{CH}_3$ , acetylacetonato; (pbd) 1-phenyl-1,3-butanedionato,  $\text{C}_6\text{H}_5\text{COCH}=\text{CO}\cdot\text{CH}_3$ , benzoylacetonato; (dppd) 1,3-diphenyl-1,3-propanedionato,  $\text{C}_6\text{H}_5\text{COCH}=\text{CO}\cdot\text{C}_6\text{H}_5$ , dibenzoylmethanato; (tmhd) 2,2,6,6-tetramethylheptane-3,5-dionato,  $(\text{CH}_3)_3\text{CCOCH}=\text{CO}\cdot\text{C}(\text{CH}_3)_3$ . <sup>b</sup> See Table 12 for reaction to which  $\Delta H_R$  refers. <sup>c</sup> Refers to reaction  $(\text{ML}_2)_n(\text{c}) \rightarrow n \text{ML}_2(\text{g})$ .

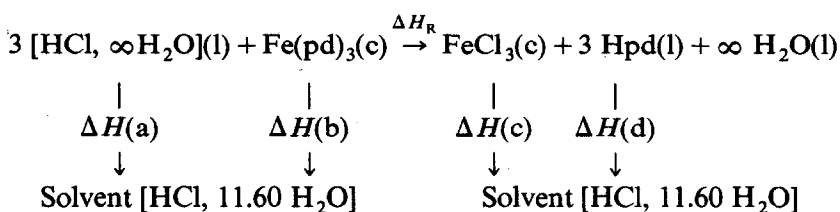
<sup>d</sup> Values in parentheses estimated. <sup>e</sup>  $\Delta H_f^0(\text{Co}(\text{pd})_2, \text{g})$ . <sup>f</sup>  $\Delta H_f^0(\text{Ni}(\text{pd})_2, \text{g})$ .

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

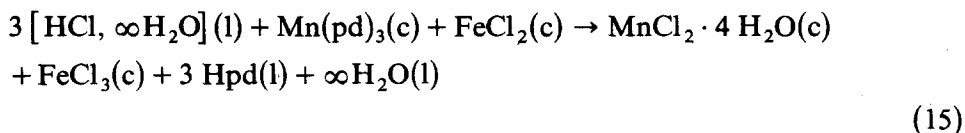
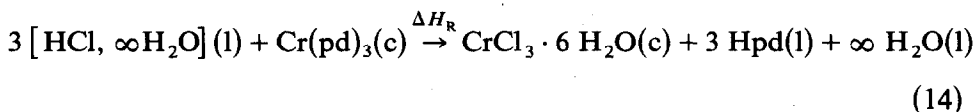


In these two cases, it was also necessary to measure the enthalpies of solution,  $\Delta H(\text{a})$ , of  $[\text{HCl}, 11.60 \text{ H}_2\text{O}]$  and  $[\text{H}_2\text{SO}_4, 53.54 \text{ H}_2\text{O}]$  in the mixed solvent. Values of  $\Delta H_{\text{R}}$  and the enthalpies of formation calculated 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  $\text{Cr}(\text{pd})_3$ ,  $\text{Mn}(\text{pd})_3$  and  $\text{Fe}(\text{pd})_3$ . For the iron complex the solvent was again  $[\text{HCl}, 11.60 \text{ H}_2\text{O}]$ , 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.

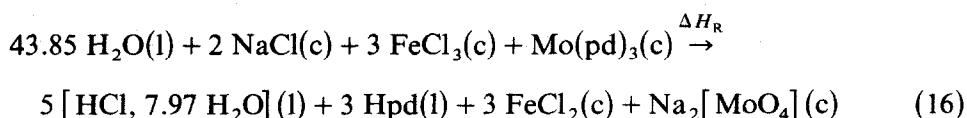


The enthalpies of solution  $\Delta H(\text{b})$ ,  $\Delta H(\text{c})$  and  $\Delta H(\text{d})$  were measured and the enthalpy  $\Delta H(\text{a})$  was calculated. A similar approach was used for  $\text{Cr}(\text{pd})_3$ , although in this case the solvent was  $[\text{HClO}_4, 3.57 \text{ H}_2\text{O}]$ .



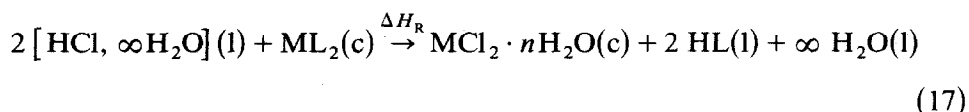
In the reaction between  $\text{Mn}(\text{pd})_3$  and  $[\text{HCl}, \infty \text{ H}_2\text{O}]$ , where the solvent used was  $[\text{HCl}, 11.60 \text{ H}_2\text{O}]$ , the  $\text{MnCl}_3$  which is produced is partially reduced to  $\text{MnCl}_2$ , with the evolution of chlorine. The reduction of  $\text{MnCl}_3$  to  $\text{MnCl}_2$  occurs quantitatively in the presence of excess ferrous salt, which is oxidized to the ferric state. Values of  $\Delta H_{\text{R}}$  and  $\Delta H_{\text{f}}^0(\text{M}(\text{pd})_3, \text{c})$  are shown in Table 13 for these complexes and also for  $\text{Mo}(\text{pd})_3$ . For this last compound Pilcher et

al. [30] used [HCl, 7.97 H<sub>2</sub>O] as solvent and the relevant thermochemical reaction is



Two points are noteworthy. First, the stoichiometry has been arranged so that the [HCl, 7.97 H<sub>2</sub>O] produced in the reaction has the same concentration as the solvent. Secondly, addition of FeCl<sub>3</sub> ensured oxidation of Mo(III) to Mo(IV), which appears as Na<sub>2</sub>[MoO<sub>4</sub>]. It is worth emphasising that calculated value of  $\Delta H_f^0(\text{Mo(pd)}_3, \text{c})$  depends on the enthalpies of formation of Na<sub>2</sub>[MoO<sub>4</sub>](c), FeCl<sub>2</sub>(c), FeCl<sub>3</sub>(c), NaCl(c), [HCl, 7.97 H<sub>2</sub>O], Hpd(l) and H<sub>2</sub>O(l).

Kakołowicz and Giera [31,32] have published measurements of the enthalpies,  $\Delta H_R$ , of the following decomposition reactions of ML<sub>2</sub> complexes



where  $\text{MCl}_2 \cdot n\text{H}_2\text{O}$  is  $\text{MnCl}_2 \cdot 4 \text{ H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6 \text{ H}_2\text{O}$ ,  $\text{NiCl}_2 \cdot 6 \text{ H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2 \text{ H}_2\text{O}$ , or  $\text{ZnCl}_2$ (anhydrous) and L is pd, pbd, or dppd. The solvent was either [HCl, 11.60 H<sub>2</sub>O] for all of these complexes except Ni(dppd)<sub>2</sub>, for which a mixture of 25% by volume of [HCl, 11.60 H<sub>2</sub>O] 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  $\Delta H_R$  are shown in Table 13. The values of  $\Delta H_f^0(\text{ML}_2, \text{c})$  which are also shown in this table are calculated from the  $\Delta H_R$  values and enthalpies of formation shown in Appendix 1.

In three cases, {Co(pd)<sub>2</sub>}<sub>4</sub>, {Ni(pd)<sub>2</sub>}<sub>3</sub> and Cu(pd)<sub>2</sub>, there are two values of  $\Delta H_f^0(\text{cryst})$ , 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)<sub>3</sub>, 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 ( $\text{kJ mol}^{-1}$ )

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

<sup>a</sup> Preferred value. <sup>b</sup> TGA = thermogravimetric analysis; DSC = differential scanning calorimetry.

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

The remaining values for enthalpies of sublimation have been estimated on a somewhat arbitrary basis. The tetrahedral  $\text{Zn}(\text{pb})_2$  is assumed to have a smaller enthalpy of sublimation than the square planar  $\text{Cu}(\text{pb})_2$  by  $12 \text{ kJ mol}^{-1}$ . Replacement of a methyl group of pd by a phenyl group to give pbd is taken to increase the value of  $\Delta H_{\text{sub}}$  by about  $10 \text{ kJ mol}^{-1}$ ; thus  $\text{Cu}(\text{pd})_2 = 57.1$ ,  $\text{Cu}(\text{pbd})_2 = (67) \text{ kJ mol}^{-1}$ ;  $\text{Zn}(\text{pd})_2 = 45$ ,  $\text{Zn}(\text{pbd})_2 = (55) \text{ kJ mol}^{-1}$ , and similarly  $\text{Ni}(\text{pbd})_2 = 42.2$ ,  $\text{Ni}(\text{dppd})_2 = (52) \text{ kJ mol}^{-1}$ . 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 donato complexes  $\text{ML}_2$  and  $\text{ML}_3$ ,  $\bar{D}(\text{M}-\text{O})$ , corresponding to the gas-phase dissociation reactions



and



can be calculated from the relationships

$$\bar{D}(\text{M-O}) = \frac{1}{4} \{ \Delta H_f^0(\text{M, g}) + 2 \Delta H_f^0(\text{L, g}) - \Delta H_f^0(\text{ML}_2, \text{g}) \} \quad (20)$$

and

$$\bar{D}(\text{M-O}) = \frac{1}{6} \{ \Delta H_f^0(\text{M, g}) + 3 \Delta H_f^0(\text{L, g}) - \Delta H_f^0(\text{ML}_3, \text{g}) \} \quad (21)$$

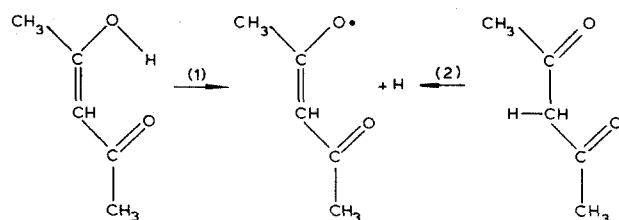
To calculate these  $\bar{D}(\text{M-O})$  values, we require  $\Delta H_f^0(\text{M, g})$  and  $\Delta H_f^0(\text{L, g})$ , values for which are shown in the Appendices. However, we give here the derivation of the enthalpy of formation of the pentanedionato radical in some detail.

(ii)  $\Delta H_f^0(\text{pentanedionato, g})$

The enthalpy of formation of the pentane-2,4-dionato radical,  $\text{CH}_3\text{COCH}=\text{COCH}_3$  (pd), has been calculated by Cavell and Pilcher [41] and what follows is a summary of their approach.

The enthalpy of combustion of acetylacetone,  $-\Delta H_c^0(\text{Hpd, l}) = 2687 \pm 1.5$   $\text{kJ mol}^{-1}$ , measured by Nicholson [42] which leads to  $\Delta H_f^0(\text{Hpd, l}) = -(423.8 \pm 1.5)$   $\text{kJ mol}^{-1}$  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  $-11.3 \pm 0.4$   $\text{kJ mol}^{-1}$ , and in the gaseous phase [44]  $-10.0 \pm 0.8$   $\text{kJ mol}^{-1}$ . The enthalpy of vaporisation of the enol was determined by Irving and Wadsö [45] as  $43.2 \pm 0.1$   $\text{kJ mol}^{-1}$ . These data permit derivation of the enthalpy of formation of Hpd(g) in both the keto and enol forms:  $\Delta H_f^0(\text{Hpd, keto, g}) = -372.7 \pm 1.7$   $\text{kJ mol}^{-1}$  and  $\Delta H_f^0(\text{Hpd, enol, g}) = -382.7 \pm 1.7$   $\text{kJ mol}^{-1}$ . Application of the Allen bond-energy scheme [46] to these structures yields the estimated values,  $\Delta H_f^0(\text{Hpd, keto, g, calc.}) = -370.7$   $\text{kJ mol}^{-1}$ ,  $\Delta H_f^0(\text{Hpd, enol, g, calc.}) = -272.7$   $\text{kJ mol}^{-1}$ ; i.e. there is agreement for the keto form, but the enol form is stabilised by 110  $\text{kJ mol}^{-1}$ , probably due to internal hydrogen bonding and  $\pi$ -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,  $D(\text{O}-\text{H}, \text{enol}) - D(\text{C}-\text{H}, \text{keto}) = 10 \text{ kJ mol}^{-1}$ . An upper limit for the  $(\text{C}-\text{H})$  dissociation energy in acetone has been given by Kerr [47],  $D(\text{CH}_3\text{COCH}_2-\text{H}) = 385 \text{ kJ mol}^{-1}$ .  $D(\text{C}-\text{H}, \text{keto})$  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  $\text{pd}$  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  $D(\text{C}-\text{H}, \text{keto}) = 355 \text{ kJ mol}^{-1}$ , whence it follows that  $D(\text{O}-\text{H}, \text{enol}) = 365 \text{ kJ mol}^{-1}$ , although this is a lower value than used previously [48].

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

A plot of  $\bar{D}(\text{M}-\text{O})$  values is shown in Fig. 8. Values for  $\text{M}(\text{pd})_3$  complexes indicate a fall in the value of  $\bar{D}(\text{M}-\text{O})$  from Cr to Mn. The higher value for  $\bar{D}(\text{Fe}-\text{O})$  in  $\text{Fe}(\text{pd})_3$  may be due to this complex being low spin. For the complexes  $\text{M}(\text{pd})_2$ , the values fall along the series  $\text{Mn} > \text{Co} > \text{Ni} > \text{Cu} > \text{Zn}$ , 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  $\text{CH}_3$  group in  $\text{pd}$  by a  $\text{C}_6\text{H}_5$  group to give  $\text{pbd}$  increases the value of  $\bar{D}(\text{M}-\text{O})$ , considerably for Ni, less so for

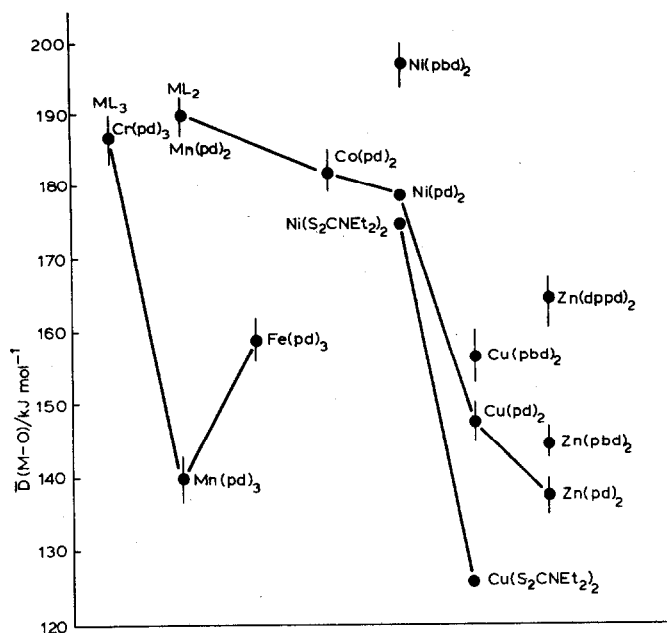


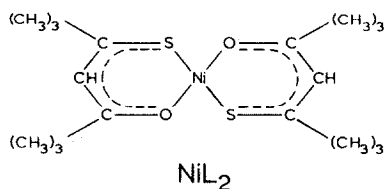
Fig. 8.  $\bar{D}(\text{M}-\text{O})$  in dionato and thiocarbamato complexes.

Cu and to a yet smaller extent for Zn complexes. The value of  $\bar{D}(\text{Ni}-\text{O})$  is marginally lowered by substitution of a  $\text{CH}_3$  group in pd by  $(\text{CH}_3)_2\text{CH}$  in the Ni complex (not shown in Fig. 8).

It should be noted that these  $D(\text{M}-\text{O})$  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  $\Delta H_f^0(\text{complex}, \text{c})$  and also of the ligand radical, e.g.  $\Delta H_f^0(\text{pd}, \text{g})$ . Calculations of the enthalpies of formation  $\Delta H_f^0(\text{dppd}, \text{g})$  and  $\Delta H_f^0(\text{tmhd}, \text{g})$  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,  $\Delta H_R = -(5.5 \pm 1.2) \text{ kJ mol}^{-1}$ , of the following reaction, where L is 5-mercapto-2,2,6,6-tetramethylhept-4-en-3-onato,  $(\text{CH}_3)_3\text{CCOCH}=\text{CS} \cdot \text{C}(\text{CH}_3)_3$ .



The solvent used was a mixture of butan-2-one and  $[\text{HClO}_4, 3.03 \text{H}_2\text{O}]$  in a 9:1 ratio. Using the values  $\Delta H_f^0(\text{Ni}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}, \text{c}) = -2035.9 \text{ kJ mol}^{-1}$  and  $\Delta H_f^0[\text{HClO}_4 \text{ in } 3.03 \text{H}_2\text{O}](\text{l}) = -(119.1 \pm 0.4) \text{ kJ mol}^{-1}$ , given in Appendix 1, we calculate the difference  $2 \Delta H_f^0(\text{HL}, \text{l}) - \Delta H_f^0(\text{NiL}_2, \text{c}) = 77.2 \pm 2 \text{ kJ mol}^{-1}$ . Incorporating a value for the enthalpy of sublimation of  $\text{NiL}_2$ ,  $\Delta H_{\text{sub}} = 117.7 \pm 8 \text{ kJ mol}^{-1}$  (measured by a Knudsen effusion technique) and a latent heat of vaporisation  $\Delta H_{\text{vap}}(\text{HL}) = 64.4 \pm 0.4 \text{ kJ mol}^{-1}$ , estimated by Irving and Lockyer [40] on the basis of differences between values for several esters and their thio analogues, the difference is calculated  $2 \Delta H_f^0(\text{HL}, \text{g}) - \Delta H_f^0(\text{NiL}_2, \text{g}) = +88.3 \pm 10 \text{ kJ mol}^{-1}$ .

For the two gas-phase dissociation reactions



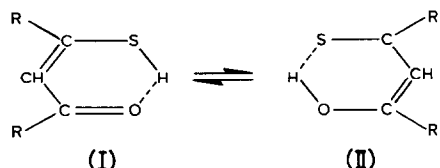
we write

$$\begin{aligned} \bar{D}(\text{H}-\text{L}) &= \Delta H_f^0(\text{H}, \text{g}) + \Delta H_f^0(\text{L}, \text{g}) - \Delta H_f^0(\text{HL}, \text{g}) \\ 2 D(\text{Ni}-\text{L}) &= \Delta H_f^0(\text{Ni}, \text{g}) + 2 \Delta H_f^0(\text{L}, \text{g}) - \Delta H_f^0(\text{NiL}_2, \text{g}) \end{aligned} \quad (25)$$

hence

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

It is a matter of conjecture whether the structure of gaseous monothio- $\beta$ -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  $D(\text{L-H})$  refers mainly to dissociation of the O-H or the S-H bond. For pentane-dione we have used the value  $D(\text{O-H})$

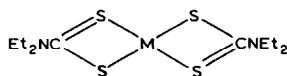


=  $365 \text{ kJ mol}^{-1}$ , whilst Kerr [47] has given a value of  $D(\text{S-H}) = 377 \pm 20 \text{ kJ mol}^{-1}$ . We select a value of  $370 \pm 20 \text{ kJ mol}^{-1}$  for  $D(\text{L-H})$ .

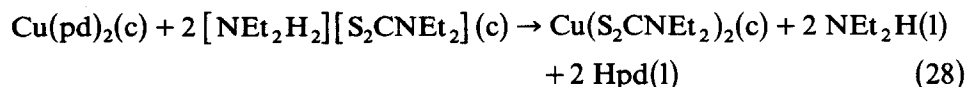
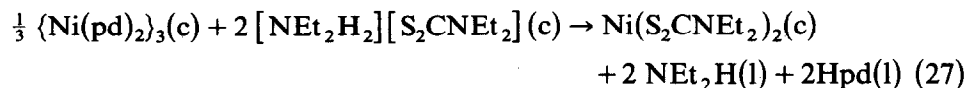
This leads to  $2 D(\text{Ni-L}) = 822 \pm 50 \text{ kJ mol}^{-1}$ , which is the sum of the mean dissociation energies  $2 \{ \bar{D}(\text{Ni-O}) + \bar{D}(\text{Ni-S}) \}$ . Assuming that  $\bar{D}(\text{Ni-O}) = 175 \pm 9 \text{ kJ mol}^{-1}$  as in the 2,2,6,6-tetramethylheptane-3,5-dionato complex,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

#### (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,  $\Delta H_R$ , of the following ligand replacement reactions.



In these reactions, the pentane-2,4-dionato group in the complex  $M(\text{pd})_2$  is replaced by the diethyldithiocarbamato group to give  $M(\text{S}_2\text{CNEt}_2)_2$ , 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  $\Delta H_{\text{sub}}$  values for  $\text{Ni}(\text{SCNEt}_2)_2$  of  $102.6 \pm 1.5 \text{ kJ mol}^{-1}$  and  $\text{Cu}(\text{S}_2\text{CNEt}_2)_2$  of  $116.2 \pm 1.3 \text{ kJ mol}^{-1}$ , which are much higher than those obtained by D'Ascenzo and Wendlandt [53] based on isoteniscope vapour pressure/temperature data, viz.  $\text{Ni}(\text{SCNEt}_2)_2 = 61.1 \pm 1.7$  and  $\text{Cu}(\text{SCNEt}_2)_2 = 87 \pm 1.7 \text{ kJ mol}^{-1}$ . Incomplete outgassing of the sample appears to give low results by the isoteniscope method.

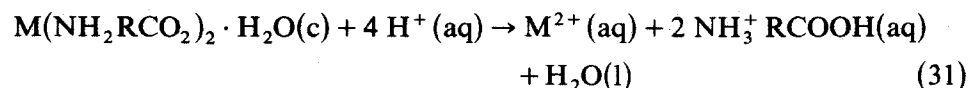
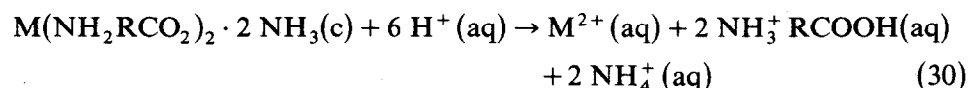
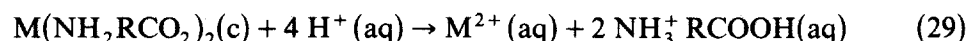
In order to calculate the enthalpy of the following gas-phase dissociation reaction, a value for  $\Delta H_f^0(\text{S}_2\text{CNEt}_2, \text{g})$  is required. A value



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  $\Delta H_f^0(\text{acid}, \text{g}) = 35.13 \text{ kJ mol}^{-1}$ . The S–H bond dissociation energy  $D(\text{S–H})$  for diethyldithiocarbamic acid is assumed to be  $316 \pm 25 \text{ kJ mol}^{-1}$ , some  $60 \text{ kJ mol}^{-1}$  less than  $D(\text{HS–H}) = 376.6 \text{ kJ mol}^{-1}$  in  $\text{H}_2\text{S}$ , because  $D(\text{O–H}) = 433 \pm 10 \text{ kJ mol}^{-1}$  in  $\text{CH}_3\text{COOH}$  [55] is  $60 \text{ kJ mol}^{-1}$  less than  $D(\text{HO–H}) = 498.3 \text{ kJ mol}^{-1}$  in  $\text{H}_2\text{O}$ . This leads to  $\Delta H_f^0(\text{S}_2\text{CNEt}_2, \text{g}) = 133 \pm 25 \text{ kJ mol}^{-1}$ . Using this value leads to those for  $\bar{D}(\text{M–S})$  in Table 15.

#### (v) Amino acid complexes

Bernard et al. [56] have measured enthalpies of solution of the amino acid complexes  $\text{M}(\text{NH}_2\text{RCO}_2)_2$ ,  $\text{M}(\text{NH}_2\text{RCO}_2) \cdot 2 \text{NH}_3$  and  $\text{M}(\text{NH}_2\text{RCO}_2) \cdot \text{H}_2\text{O}$  in 2 M  $\text{HNO}_3$  at 298 K, eqns. (29)–(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  $\Delta H_f^0$  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 diethyldithiocarbamate complexes [51] ( $\text{kJ mol}^{-1}$ )

Complex	$\Delta H_{\text{R}}(298 \text{ K})$	$\Delta H_{\text{f}}^0(\text{complex, c})$	$\Delta H_{\text{sub}}$	$\Delta H_{\text{f}}^0(\text{complex, g})$	$\bar{D}(\text{M-S})$
$\text{Ni}(\text{S}_2\text{CNEt}_2)_2$	$94.5 \pm 2.0$	$-105.5 \pm 20$	$102.6 \pm 1.5$	$-2.9 \pm 21$	$175 \pm 18$
$\text{Cu}(\text{S}_2\text{CNEt}_2)_2$	$97.6 \pm 1.1$	$-5.4 \pm 18$	$116.2 \pm 1.3$	$+110.8 \pm 19$	$123 \pm 17$

TABLE 16

Enthalpies of formation ( $\text{kJ mol}^{-1}$ ) of amino acid complexes [56]  $\text{Ni}(\text{NH}_2\text{RCO}_2)_2 \cdot x\text{H}_2\text{O} \cdot y\text{NH}_3$ ,

Complex		x	y	$\Delta H_f^0(\text{complex, c})$
$\text{R} = \text{CH}_2$ $\text{CHCH}_3$	Glycine	0	0	$-(966.8 \pm 2.9)$
		0	2	$-(1180.4 \pm 3.5)$
		2	0	$-(1559.6 \pm 4.7)$
$\text{CHCH}_3$	$\alpha$ -Alanine	0	0	$-(1065.9 \pm 3.2)$
		0	2	$-(1285.4 \pm 3.8)$
		4	0	$-(2243.4 \pm 6.7)$
$\text{CHCH}(\text{CH}_3)_2$	Valine	0	0	$-(1208.0 \pm 3.6)$
		0	2	$-(1412.8 \pm 4.3)$
		2	0	$-(1804.1 \pm 5.4)$
$\text{CHCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	Isoleucine	0	0	$-(1272.8 \pm 3.8)$
		0	2	$-(1479.6 \pm 4.4)$
		2	0	$-(1858.8 \pm 5.6)$
$\text{CH}(\text{CH}_2)_3\text{CH}_3$	Norleucine	0	0	$-(1312.5 \pm 3.9)$

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:  $\Delta H_{\text{sub}}^{298} \text{Ni}(\text{gly})_2 = 120 \pm 10 \text{ kJ mol}^{-1}$  and  $\Delta H_{\text{sub}}^{298} \text{Cu}(\text{gly})_2 = 105 \pm 12 \text{ kJ mol}^{-1}$  [36]. Incorporating these values we calculate  $\Delta H_f^0(\text{Ni}(\text{gly})_2, \text{g}) = -(846.8 \pm 13)$  and  $\Delta H_f^0(\text{Cu}(\text{gly})_2,$

TABLE 17

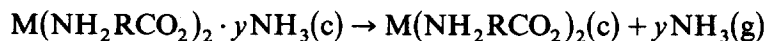
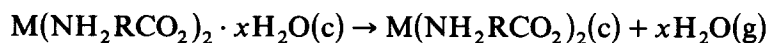
Enthalpies of formation ( $\text{kJ mol}^{-1}$ ) of amino acid complexes [56]  $\text{Cu}(\text{NH}_2\text{RCO}_2)_2 \cdot x\text{H}_2\text{O} \cdot y\text{NH}_3$

Complex		x	y	$\Delta H_f^0(\text{complex, c})$
$\text{R} = \text{CH}_2$	Glycine	0	0	$-(937.5)$ [57], $-(948.1 \pm 1.2)$ [10]
		0	2	$-(1125.3 \pm 3.4)$
		1	0	$-(1235.2)$ [57]
$\text{CHCH}_3$	$\alpha$ -Alanine	0	0	$-(1016.6 \pm 3.4)$ , $-(1010.4 \pm 1.3)$ [10]
		0	2	$-(1203.4 \pm 3.6)$
		1	0	$-(1307.1 \pm 3.9)$
$\text{CHCH}(\text{CH}_3)_2$	Valine	0	0	$-(1098.1 \pm 3.3)$ , $-(1115.7 \pm 1.3)$ [10]
		0	2	$-(1295.8 \pm 3.8)$
		1	0	$-(1395.3 \pm 4.2)$
$\text{CHCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	Isoleucine	0	0	$-(1162.9 \pm 3.5)$
		0	2	$-(1347.9 \pm 4.1)$
		1	0	$-(1459.7 \pm 4.4)$
$\text{CH}(\text{CH}_2)_3\text{CH}_3$	Norleucine	0	0	$-(1203.8 \pm 3.6)$



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

The enthalpies of the dissociation reactions



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  $\Delta H_{\text{sub}}\text{M}(\text{NH}_2\text{RCO}_2)_2 \cdot x\text{H}_2\text{O} = \Delta H_{\text{sub}}\text{M}(\text{NH}_2\text{RCO}_2)_2$  for a given metal and R group, the mean bond dissociation energies  $\bar{D}(\text{M}-\text{O})$  and  $\bar{D}(\text{M}-\text{N})$ , corresponding to the

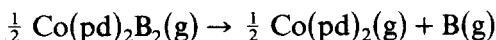
TABLE 18

Mean bond dissociation energies (kJ mol<sup>-1</sup>) for dissociation of two axial ligands [56]

Complex	$\bar{D}(\text{M}-\text{O})$	
	From $\Delta H_f^0(298 \text{ K})$	DSC (ca. 400 K)
Ni(gly) <sub>2</sub> ·2 H <sub>2</sub> O	54.8	55.6 ± 1.7
Ni(ala) <sub>2</sub> ·2 H <sub>2</sub> O	52.7	50.6 ± 1.5
Ni(val) <sub>2</sub> ·2 H <sub>2</sub> O	56.4	58.9 ± 1.8
Ni(isol) <sub>2</sub> ·2 H <sub>2</sub> O	51.4	53.1 ± 1.6
Cu(gly) <sub>2</sub> ·H <sub>2</sub> O	56.0	
Cu(ala) <sub>2</sub> ·H <sub>2</sub> O	48.5	46.4 ± 1.4
Cu(val) <sub>2</sub> ·H <sub>2</sub> O	55.6	58.1 ± 1.7
Cu(isol) <sub>2</sub> ·H <sub>2</sub> O	55.2	57.3 ± 1.7
	$\bar{D}(\text{M}-\text{N})$	
Ni(gly) <sub>2</sub> ·2 NH <sub>3</sub>	60.2	62.3 ± 1.9
Ni(ala) <sub>2</sub> ·2 NH <sub>3</sub>	63.5	61.5 ± 1.8
Ni(val) <sub>2</sub> ·2 NH <sub>3</sub>	56.4	58.1 ± 1.7
Ni(isol) <sub>2</sub> ·2 NH <sub>3</sub>	57.3	55.5 ± 1.6
Cu(gly) <sub>2</sub> ·2 NH <sub>3</sub>	58.3	56.8 ± 1.7
Cu(ala) <sub>2</sub> ·2 NH <sub>3</sub>	47.2	48.1 ± 1.4
Cu(val) <sub>2</sub> ·2 NH <sub>3</sub>	52.7	52.2 ± 1.6
Cu(isol) <sub>2</sub> ·2 NH <sub>3</sub>	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<sup>-1</sup> and for a particular metal–amino-acid complex the  $\bar{D}(\text{M}-\text{O})$  and  $\bar{D}(\text{M}-\text{N})$  values are very similar. These values are less than one-half of those for  $\bar{D}(\text{M}-\text{O})$  and  $\bar{D}(\text{M}-\text{N})$  which we noted for the bonding of pyridine or benzoxazole in the complexes  $\text{ML}_2\text{X}_2$ .

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  $\sigma$ -bonding energy for the octahedral and square planar complexes,  $6e_g$  for  $\text{Ni(II)}d^8$  complexes, and  $3e_g$  for  $\text{Cu(II)}d^9$  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



where the base  $\text{B}$  is  $\text{NH}_3$  (57.7 kJ mol<sup>-1</sup>), pyridine (63.2 kJ mol<sup>-1</sup>),  $n\text{BuNH}_2$  (77.0 kJ mol<sup>-1</sup>) and  $\text{H}_2\text{O}$  (50.2 kJ mol<sup>-1</sup>). They assume a value  $\Delta H_{\text{sub}}\text{Co}(\text{pd})_2\text{B}_2 = 105 \text{ kJ mol}^{-1}$ , which is ca. 20 kJ mol<sup>-1</sup> greater than  $\frac{1}{4} \Delta H_{\text{sub}}(\text{Co}(\text{pd})_2)_4 = 334.8 \text{ kJ mol}^{-1}$ . 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  $\bar{D}(\text{M}-\text{thiourea})$  calculated for the complexes  $\text{M}(\text{tu})_4\text{X}_2$  is likely to be a lower value than  $\bar{D}(\text{M}-\text{thiourea})$  in the four-coordinate complexes  $\text{M}(\text{tu})_2\text{X}_2$ .

(vi) *Trifluoroacetato and benzoato complexes*

Calado et al. [59] have obtained values for the enthalpies of formation of the metallocene complexes  $\text{M}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{CR})_2$ , where  $\text{M} = \text{Mo}, \text{W}$  or  $\text{Ti}$ , and  $\text{R} = \text{C}_6\text{H}_5$  or  $\text{CF}_3$ . The enthalpies,  $\Delta H_{\text{R}}$ , 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  $\text{HCl}$ .

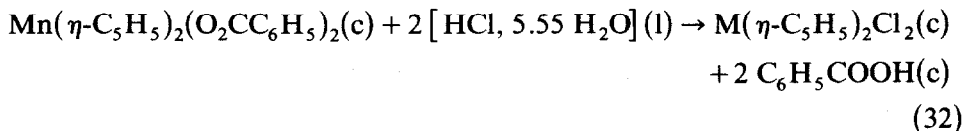


TABLE 19

Enthalpies of formation of  $M(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{CR})_2$  [59] ( $\text{kJ mol}^{-1}$ )

Complex	$\Delta H_R$	$\Delta H_f^0(\text{complex, c})$	$\Delta H_{\text{sub}}^a$	$\Delta H_f^0(\text{complex, g})$	$\bar{D}(\text{M-O})_{\text{O}_2\text{CR}}$
$\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{CC}_6\text{H}_5)_2$	$-(65.8 \pm 3.9)$	$-(486.2 \pm 3.4)$	$(94 \pm 10)$	$-(392.2 \pm 14)$	$305 \pm 9$
$\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{CC}_6\text{H}_5)_2$	$-(78.4 \pm 4.4)$	$-(448.9 \pm 3.7)$	$(98 \pm 10)$	$-(350.9 \pm 14)$	$341 \pm 9$
$\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{CC}_6\text{H}_5)_2$	$-(64.2 \pm 5.3)$	$-(775.2 \pm 8.1)$	$(112 \pm 8)$	$-(663.2 \pm 23)$	$432 \pm 10$
$\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{CCF}_3)_2$	$+26.0 \pm 4.1$	$-(1952.0 \pm 3.9)$	$(90 \pm 10)$	$-(1862.0 \pm 14)$	$327 \pm 26$
$\text{W}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{CCF}_3)_2$	$+13.2 \pm 3.4$	$-(1914.5 \pm 3.8)$	$(94 \pm 10)$	$-(1820.5 \pm 13)$	$310 \pm 26$
$\text{Ti}(\eta\text{-C}_5\text{H}_5)_2(\text{O}_2\text{CCF}_3)_2$	$+5.6 \pm 3.8$	$-(2219.0 \pm 8.0)$	$108 \pm 8$	$-(2111.0 \pm 12)$	$443 \pm 26$

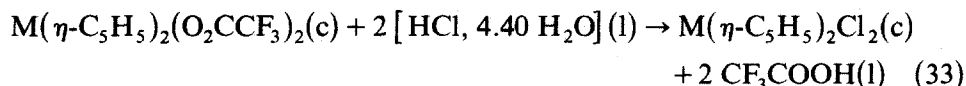
<sup>a</sup> Estimated values in parentheses.

TABLE 20

Enthalpies of formation of  $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{SR})_2$  [60] ( $\text{kJ mol}^{-1}$ )

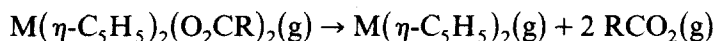
	$\Delta H_R$	$\Delta H_f^0(\text{complex, c})$	$\Delta H_{\text{sub}}^a$	$\Delta H_f^0(\text{complex, g})$	$\bar{D}(\text{M-S})$
$\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{S}^n\text{C}_3\text{H}_7)_2$	$14.2 \pm 7.3$	$4.6 \pm 7.3$	$(90 \pm 10)$	$94.6 \pm 17$	$237 \pm 18$
$\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{S}^i\text{C}_3\text{H}_7)_2$	$-(50.3 \pm 6.7)$	$57.1 \pm 10.5$	$(90 \pm 10)$	$147.1 \pm 20$	$202 \pm 18$
$\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{S}^n\text{C}_4\text{H}_9)_2$	$-(44.8 \pm 6.4)$	$14.0 \pm 11.4$	$(92 \pm 10)$	$106.0 \pm 21$	$211 \pm 19$
$\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{S}^i\text{C}_4\text{H}_9)_2$	$-(69.6 \pm 4.8)$	$6.9 \pm 9.0$	$(92 \pm 10)$	$98.9 \pm 20$	$193 \pm 18$

<sup>a</sup> Estimated values.



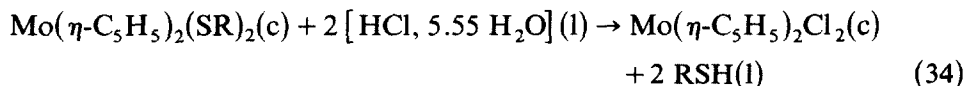
Values of  $\Delta H_{\text{R}}$  and the derived  $\Delta H_{\text{f}}^0(\text{complex}, \text{c})$  are shown in Table 19. It is noted that the values for the enthalpies of formation of the complexes depend on  $\Delta H_{\text{f}}^0(\text{M}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2, \text{c})$  and on  $\Delta H_{\text{f}}^0(\text{RCOOH}, \text{c or l})$  given in Appendix 1.

The mean bond dissociation of the acid radicals,  $\bar{D}(\text{M-O})_{\text{O}_2\text{CR}}$  is one half of the enthalpy of the gas-phase dissociation reaction



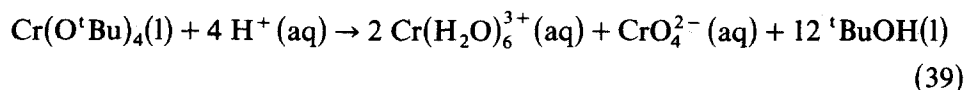
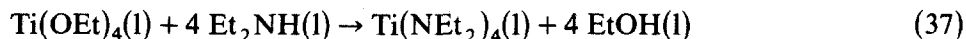
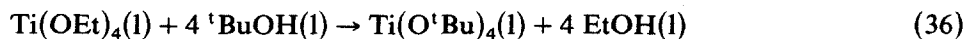
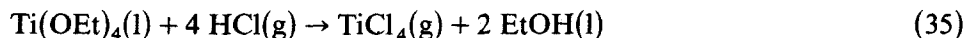
To calculate this enthalpy, the enthalpies of formation of the radicals  $\text{M}(\text{C}_5\text{H}_5)_2$ , where  $\text{M} = \text{Mo}, \text{W}$  and  $\text{Ti}$ , and of the radicals  $\text{RCO}_2(\text{g})$ , where  $\text{R} = \text{C}_6\text{H}_5$  and  $\text{CF}_3$  must first be calculated. Using the values derived in Appendix 2, the mean bond dissociation energies,  $\bar{D}(\text{M-O})_{\text{O}_2\text{CR}}$ , 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,  $\bar{D}(\text{M-S})$ , in the metallocene complexes  $\text{Mo}(\eta\text{-C}_5\text{H}_5)_2(\text{SR})_2$ , where  $\text{R} = \text{n-C}_3\text{H}_7$ ,  $\text{i-C}_3\text{H}_7$ ,  $\text{n-C}_4\text{H}_9$ , and  $\text{t-C}_4\text{H}_9$ . Enthalpies of reaction (34) are shown in Table 20, together with  $\Delta H_{\text{f}}^0$  values and the derived  $\bar{D}(\text{M-S})$ . These latter depend on enthalpies of formation of the radicals,  $\text{RS}$ , which are given in Appendix 2.



*(vii) Alkoxide and alkylamino complexes*

Bradley and Hillyer [61] have determined the enthalpy of hydrochlorination of  $\text{Ti}(\text{OEt})_4$  (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  $\text{V}(\text{O}^t\text{Bu})_4$  and  $\text{Cr}(\text{O}^t\text{Bu})_4$  in 0.1 M  $\text{HCl}$  and 1 M  $\text{H}_2\text{SO}_4$ , respectively, were also measured.



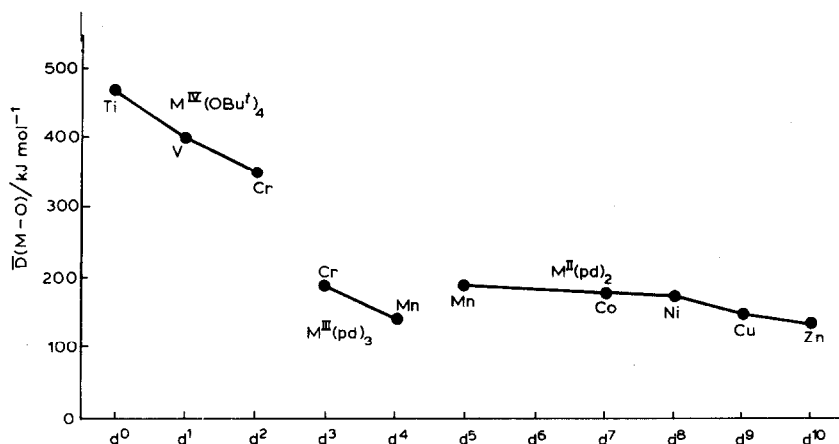
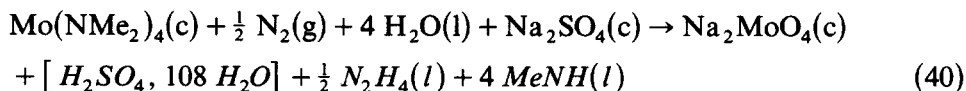


Fig. 9. Plot of  $\bar{D}(\text{M-O})$  against the number of metal  $d$  electrons.



The hydrolysis of  $\text{Cr}(\text{O}^t\text{Bu})_4$  is not well-defined thermochemically because of uncertainty of the extent to which  $\text{HCrO}_4^-$  and  $\text{Cr}_2\text{O}_7^{2-}$  has also formed. The reader is referred to the original paper for details of the calculation of  $\Delta H_f^\circ$ . The enthalpy of hydrolysis of  $\text{Mo}(\text{NMe}_2)_4(\text{c})$  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  $\bar{D}(\text{M-O})$  for the complexes  $\text{M}^{\text{IV}}(\text{O}^t\text{Bu})_4$ ,  $\text{M}^{\text{III}}(\text{pd})_3$  and  $\text{M}^{\text{II}}(\text{pd})_2$  are plotted in Fig. 9 against the number of metal  $d$  electrons.

Values of  $\bar{D}(\text{M-O})$  in the octahedral complexes  $\text{Cr}(\text{pd})_3$  and  $\text{Mn}(\text{pd})_3$  are depressed, as compared with  $\bar{D}(\text{M-O})$  values in the other 4-coordinate complexes, because of the relative weakness of the two axial bonds in the 6-coordinate  $\text{M}(\text{pd})_3$  complexes. Taking account of this, it seems likely that there is a steady fall in  $\bar{D}(\text{M-O})$  values along the series  $\text{Ti} \rightarrow \text{Zn}$ . 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- $\mu$ -acetato dichromium(II),  $\text{Cr}_2(\text{O}_2\text{CMe})_4$ , and the corresponding molybdenum compound,  $\text{Mo}_2(\text{O}_2\text{CMe})_4$ , have the structure shown. These,

TABLE 21

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

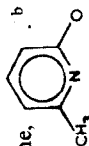
Complex	$\Delta H_R$	$\Delta H_f^\circ(\text{complex, l or c})$	$\Delta H_{\text{sub}}$	$\Delta H_f^\circ(\text{complex, g})$	$\bar{D}(\text{M-O})$	$\bar{D}(\text{M-N})$
$\text{Ti}(\text{OEt})_4$	$81.6 \pm 3.8$	$-(1462.7 \pm 7.5)$ (l)	$100.4^b$	$-(1359.8 \pm 8)$	431	
$\text{Ti}(\text{O}^i\text{Bu})_4$	$66.1 \pm 0.4$	$-(1719.6 \pm 6)$ (l)	66	$-(1654 \pm 8)$	464	
$\text{Ti}(\text{NEt}_2)_4$	$278.7 \pm 2.0$	$-(485 \pm 8)$ (l)	$(67)^a$	$-(418 \pm 8)$		291
$\text{V}(\text{O}^i\text{Bu})_4$	$95.0 \pm 3.7$	$-(1439 \pm 3)$ (l)	$(67)^a$	$-(1372 \pm 8)$	405	
$\text{Cr}(\text{O}^i\text{Bu})_4$	$-(177.8 \pm 3.8)$	$-(1342 \pm 3)$ (l)	$(66)^a$	$-(1276 \pm 8)$	351	
$\text{Mo}(\text{NMe}_2)_4$	$-(109.6 \pm 3.8)$	$59 \pm 5$ (c)	$72 \pm 6$	$131 \pm 8$		255

<sup>a</sup> Estimated. <sup>b</sup> To monomeric gas.

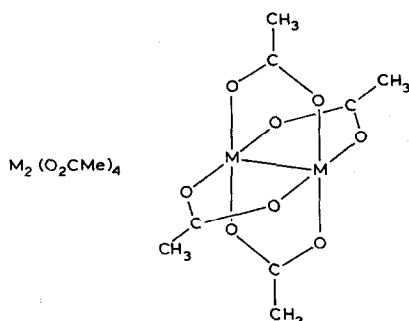
TABLE 22

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

Complex <sup>a</sup>	$\Delta H_R^b$	$\Delta H_f^\circ(\text{complex, c})$	$\Delta H_{\text{sub}}$	$\Delta H_f^\circ(\text{complex, g})$
$\text{Cr}_2(\text{O}_2\text{CMe})_4$	$-(429.5 \pm 3.5)$	$-(2297.5 \pm 6)$	$314 \pm 27$	$-(1984.5 \pm 34)$
$\text{Cr}_2(\text{mhp})_4$	$-(119.8 \pm 6.6)$	$-(948.2 \pm 9)$	$150 \pm 4$	$-(798 \pm 10)$
$\text{Mo}_2(\text{O}^i\text{Pr})_6$	$-(504 \pm 5)$	$-(1662 \pm 9)$	$113 \pm 10$	$-(1549 \pm 14)$
$\text{Mo}_2(\text{O}_2\text{CMe})_4$	$144.5 \pm 3.4$	$-(1970.7 \pm 8)$	$163 \pm 5$	$-(1805.7 \pm 13)$
$\text{Mo}_2(\text{O}_2\text{CMe})_2(\text{pd})_2$	$-(474.2 \pm 3.6)$	$-(1805.0 \pm 9)$	$163 \pm 5$	$-(1645.4 \pm 10)$
$\text{Mo}_2(\text{NMe}_2)_6$		$17 \pm 10$	$111 \pm 8$	$128 \pm 13$
$\text{Mo}_2(\text{mhp})_4$	$-(561.3 \pm 5.2)$	$-(754.0 \pm 9)$	$157 \pm 3$	$-(597 \pm 10)$
$\text{Mo}_2(\text{mhp})_2(\text{O}_2\text{CMe})_2$	$-(490.9 \pm 9.8)$	$-(1366.8 \pm 12)$	$(161 \pm 4)^c$	$-(1206 \pm 13)$

<sup>a</sup> (mhp) 2-hydroxy-6-methylpyridine,<sup>b</sup> Refers to reactions (41-47). <sup>c</sup> 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.



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

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

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

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

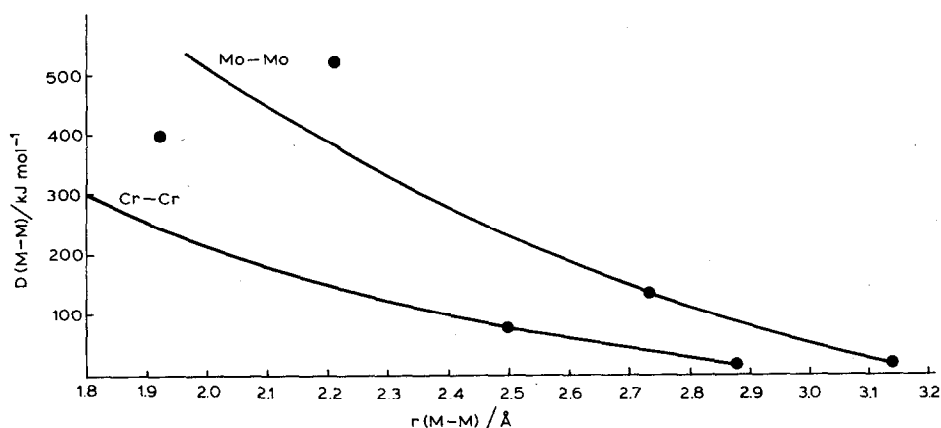
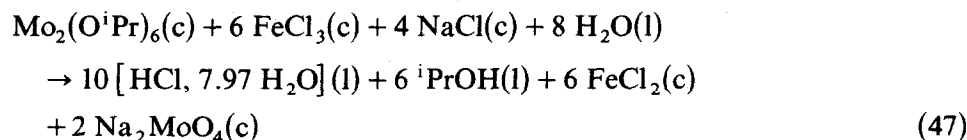
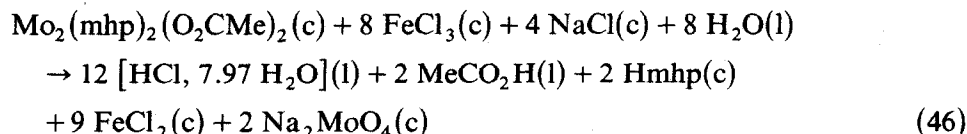
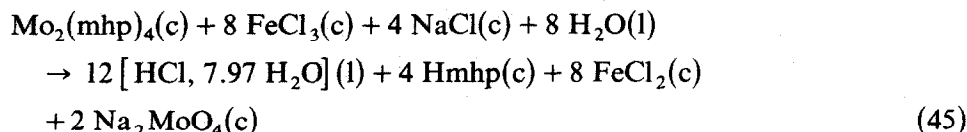
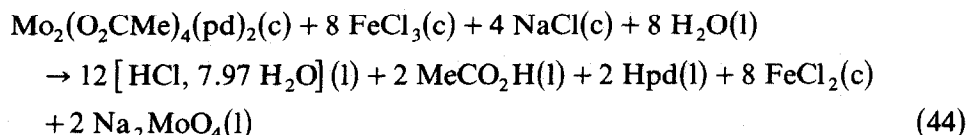
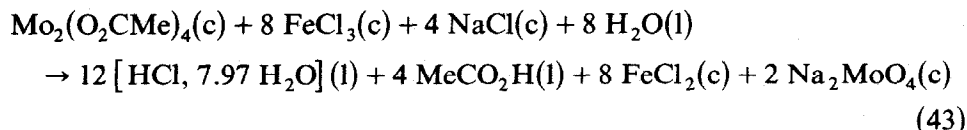
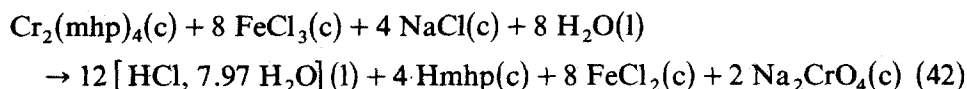
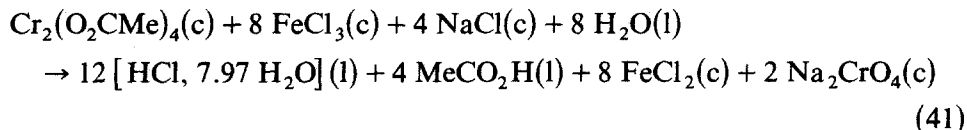


Fig. 10. Bond energy/bond length for Mo-Mo and Cr-Cr bonds.

which  $r(\text{Mo-Mo}) = 1.929 \text{ \AA}$ . 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  $\text{FeCl}_3$ ,  $\text{HCl}$ ,  $\text{HClO}_4$  and  $\text{H}_2\text{O}$  in the ratio 1 : 15 : 30 : 1000. Enthalpies of these reactions are also listed in Table 22.



Reactions involved in the oxidative hydrolysis of both  $\text{Mo}_2(\text{NMe})_6$  are complex and the reader is referred to the original paper [65] for details.

The enthalpies of the gas-phase disruption reactions



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



TABLE 23

Bond lengths (Å) and dissociation energies (kJ mol<sup>-1</sup>) in Cr and Mo complexes

	$r(\text{M-M})$	$\bar{D}(\text{Mo-Mo})$	$r(\text{M-O})$	$r(\text{M-N})$	$\bar{D}(\text{M-O})$	$\bar{D}(\text{M-N})$
$\text{Cr}_2(\text{O}_2\text{CMe})_4$	(1.89) <sup>a</sup>	257	1.969		206	
$\text{Cr}_2(\text{mhp})_4$	1.889	257	(1.969) <sup>a</sup>	2.067	206	150
$\text{Mo}_2(\text{O}^i\text{Pr})_6$	2.222	395	(1.878) <sup>b</sup>		385	
$\text{Mo}_2(\text{O}_2\text{CMe})_4$	2.093	480	2.12		221	
$\text{Mo}_2(\text{O}_2\text{CMe})_2(\text{pd})_2$	2.13	455	2.106( $\text{O}_2\text{CMe}$ )		224	
			2.095(pd)		192	
$\text{Mo}(\text{pd})_3$			2.041		192	
$\text{Mo}_2(\text{NMe}_2)_6$	2.214	425		1.98		251
$\text{Mo}_2(\text{mhp})_4$	2.065	505	2.086	2.167	220	155
$\text{Mo}_2(\text{mhp})_2(\text{O}_2\text{CMe})_2$	(2.080) <sup>a</sup>	495	(2.10) <sup>a</sup>		220	158
$\text{Mo}(\text{NMe}_2)_4$				1.926		255

<sup>a</sup> Estimated. <sup>b</sup> Assumed to be as in  $\text{Mo}_2(\text{OCH}_2^t\text{Bu})_6$ .

follows:

Compound	Mean bond dissociation	Enthalpy (kJ mol <sup>-1</sup> )
Cr <sub>2</sub> (O <sub>2</sub> CMe) <sub>4</sub>	$\bar{D}(\text{Cr}-\text{Cr}) + 8 \bar{D}(\text{Cr}-\text{O})_{\text{O}_2\text{CMe}}$	1903 ± 48
Cr <sub>2</sub> (mhp) <sub>4</sub>	$\bar{D}(\text{Cr}-\text{Cr}) + 4 \bar{D}(\text{Cr}-\text{O}) + 4 \bar{D}(\text{Cr}-\text{N})$	1683 ± 45
Mo <sub>2</sub> (O <sup>i</sup> Pr) <sub>6</sub>	$\bar{D}(\text{Mo}-\text{Mo}) + 6 \bar{D}(\text{Mo}-\text{O})_{\text{O}^i\text{Pr}}$	2703 ± 14
Mo <sub>2</sub> (O <sub>2</sub> CMe) <sub>4</sub>	$\bar{D}(\text{Mo}-\text{Mo}) + 8 \bar{D}(\text{Mo}-\text{O})_{\text{O}_2\text{CMe}}$	2249 ± 41
Mo <sub>2</sub> (O <sub>2</sub> CMe) <sub>2</sub> (pd) <sub>2</sub>	$\bar{D}(\text{Mo}-\text{Mo}) + 4 \bar{D}(\text{Mo}-\text{O})_{\text{O}_2\text{CMe}} + 4 \bar{D}(\text{Mo}-\text{O})_{\text{pd}}$	2120 ± 45
Mo(pd) <sub>3</sub>	$6 \bar{D}(\text{Mo}-\text{O})_{\text{pd}}$	1148 ± 61
Mo <sub>2</sub> (NMe <sub>2</sub> ) <sub>6</sub>	$\bar{D}(\text{Mo}-\text{Mo}) + 6 \bar{D}(\text{Mo}-\text{N})$	1929 ± 28
Mo <sub>2</sub> (mhp) <sub>4</sub>	$\bar{D}(\text{Mo}-\text{Mo}) + 4 \bar{D}(\text{Mo}-\text{O}) + 4 \bar{D}(\text{Mo}-\text{N})$	2005 ± 45
Mo <sub>2</sub> (mhp) <sub>2</sub> (O <sub>2</sub> CMe) <sub>2</sub>	$\bar{D}(\text{Mo}-\text{Mo}) + 6 \bar{D}(\text{Mo}-\text{O}) + 2 \bar{D}(\text{Mo}-\text{N})$	2131 ± 44
Mo(NMe <sub>2</sub> ) <sub>4</sub>	$4 \bar{D}(\text{Mo}-\text{N})$	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  $\bar{D}(\text{Cr}-\text{Cr})$  and  $\bar{D}(\text{Mo}-\text{Mo})$  can be obtained. With this information  $\bar{D}(\text{Cr}-\text{O})$ ,  $\bar{D}(\text{Cr}-\text{N})$ ,  $\bar{D}(\text{Mo}-\text{O})$  and  $\bar{D}(\text{Mo}-\text{N})$  values are obtained. It is interesting that  $\bar{D}(\text{Cr}-\text{N}) = 150$  and  $\bar{D}(\text{Mo}-\text{N}) = 155$  kJ mol<sup>-1</sup> in the complexes Cr<sub>2</sub>(mhp)<sub>4</sub> and Mo<sub>2</sub>(mhp)<sub>4</sub>, values which are very close to  $\bar{D}(\text{Co}-\text{N}) = 142\text{--}159$  kJ mol<sup>-1</sup>, in the substituted pyridine complexes M(3Brpy)<sub>2</sub>Cl<sub>2</sub>, where M is Co, Ni or Cu.

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

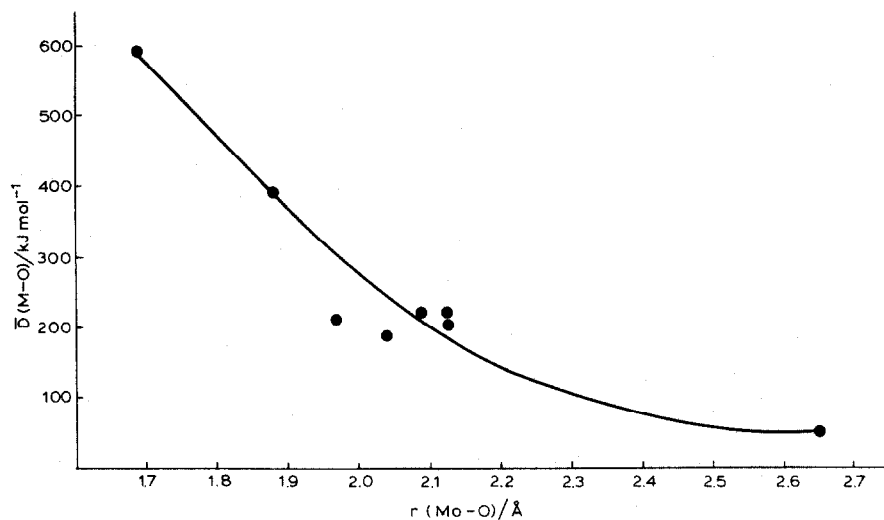


Fig. 11. Bond energy plot for Mo–O bonds.

points are included by the authors of the paper from which this figure is taken [64];  $\overline{D}(\text{Mo-O}) = 589 \pm 7 \text{ kJ mol}^{-1}$ ,  $r(\text{Mo-O}) = 1.69 \text{ \AA}$  in  $\text{MoO}_3$  and  $\overline{D}(\text{Mo-O}) = 50 \text{ kJ mol}^{-1}$ ,  $r(\text{Mo-O}) = 2.64 \text{ \AA}$ , which is a measure of the intermolecular Mo-O contracts in  $\text{Mo}_2(\text{O}_2\text{CMe})_4$ , 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 ( $\text{kJ mol}^{-1}$ )

Compound	Enthalpy of formation	Ref.
H(g)	218.00 $\pm$ 0.01	50
Cl(g)	121.302 $\pm$ 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 <sub>2</sub> O(l)	–(285.83 $\pm$ 0.01)	66
NH <sub>3</sub> (g)	–(46.11 $\pm$ 0.001)	50
NH <sub>4</sub> Cl(c)	–(314.43 $\pm$ 0.05)	50
N <sub>2</sub> H <sub>4</sub> (l)	50.63 $\pm$ 0.05	50
[HCl, in 4.40 H <sub>2</sub> O](l)	–(154.106 $\pm$ 0.004)	67
[HCl, in 5.55 H <sub>2</sub> O](l)	–(156.824 $\pm$ 0.004)	67
[HCl, in 7.97 H <sub>2</sub> O](l)	–(159.971 $\pm$ 0.001)	67
[HCl, in 11.60 H <sub>2</sub> O](l)	–(161.920 $\pm$ 0.001)	67
[HCl, in 51.3 H <sub>2</sub> O](l)	–(165.295 $\pm$ 0.001)	67
[HCl, in $\infty$ H <sub>2</sub> O](l)	–(167.059 $\pm$ 0.001)	67
[H <sub>2</sub> SO <sub>4</sub> , in 53.54 H <sub>2</sub> O](l)	–(886.87 $\pm$ 0.01)	50
[H <sub>2</sub> SO <sub>4</sub> , in 108 H <sub>2</sub> O](l)	–(887.74 $\pm$ 0.01)	50
[HClO <sub>4</sub> , in 3.03 H <sub>2</sub> O](l)	–(119.1 $\pm$ 0.4)	67
TiCl <sub>4</sub> (l)	–(804.6 $\pm$ 2.0)	95
VCl <sub>4</sub> (l)	–(569.9 $\pm$ 1.6)	96
CrCl <sub>3</sub> ·6 H <sub>2</sub> O(c)	–(2452.7 $\pm$ 0.8)	50
MnCl <sub>2</sub> (c)	–(481.3 $\pm$ 0.5)	50
MnCl <sub>2</sub> ·4 H <sub>2</sub> O(c)	–(1687.4 $\pm$ 0.5)	50
FeCl <sub>2</sub> (c)	–(341.8 $\pm$ 0.5)	50
FeCl <sub>3</sub> (c)	–(399.5 $\pm$ 0.5)	50
CoCl <sub>2</sub> (c)	–(312.5 $\pm$ 0.5)	50

## APPENDIX 1 (continued)

Compound	Enthalpy of formation	Ref.
$\text{CoCl}_2 \cdot 6 \text{H}_2\text{O}(\text{c})$	$-(2115.4 \pm 0.5)$	50
$\text{CoSO}_4 \cdot 6 \text{H}_2\text{O}(\text{c})$	$-(2683.6 \pm 0.5)$	50
$\text{NiCl}_2(\text{c})$	$-(305.3 \pm 0.1)$	50
$\text{NiCl}_2 \cdot 6 \text{H}_2\text{O}(\text{c})$	$-(2103.2 \pm 0.5)$	50
$\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}(\text{c})$	$-(2682.8 \pm 0.5)$	50
$\text{Ni}(\text{ClO}_4)_2 \cdot 6 \text{H}_2\text{O}(\text{c})$	$-(2035.9 \pm 0.5)$	50
$\text{CuCl}_2(\text{c})$	$-(220.1 \pm 0.5)$	50
$\text{CuCl}_2 \cdot 2 \text{H}_2\text{O}(\text{c})$	$-(821.3 \pm 0.5)$	50
$\text{CuBr}_2(\text{c})$	$-(141.8 \pm 0.5)$	50
$\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}(\text{c})$	$-(2279.6 \pm 0.5)$	50
$\text{ZnCl}_2(\text{c})$	$-(415.1 \pm 0.5)$	50
$\text{ZnBr}_2(\text{c})$	$-(328.7 \pm 0.5)$	50
$\text{ZnI}_2(\text{c})$	$-(208.0 \pm 0.5)$	50
$\text{CdCl}_2(\text{c})$	$-(391.5 \pm 0.5)$	50
$\text{CdBr}_2(\text{c})$	$-(316.2 \pm 0.5)$	50
$\text{CdI}_2(\text{c})$	$-(203.2 \pm 0.5)$	50
$\text{HgCl}_2(\text{c})$	$-(224.3 \pm 0.5)$	50
$\text{HgBr}_2(\text{c})$	$-(170.9 \pm 0.5)$	50
$\text{PdCl}_2(\text{c})$	$-(163.2 \pm 10)$	87
$\text{NaCl}(\text{c})$	$-(411.0 \pm 0.01)$	50
$\text{Na}_2\text{SO}_4(\text{c})$	$-(1387.9 \pm 0.9)$	96
$\text{Na}_2(\text{CrO}_4)(\text{c})$	$-(1344.0 \pm 2.1)$	68
$\text{Na}_2(\text{MoO}_4)(\text{c})$	$-(1467.6 \pm 3.3)$	68
$\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2(\text{c})$	$-(383.2 \pm 7.5)$	69
$\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2(\text{c})$	$-(95.8 \pm 2.5)$	69
$\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2(\text{c})$	$-(71.1 \pm 2.5)$	69
$(\text{NH}_4)_2\text{PdCl}_2(\text{c})$	$-(841.0 \pm 1.7)$	83
$(\text{CH}_3)_2\text{NH}(\text{l})$	$-(43.9 \pm 0.4)$	74
$(\text{C}_2\text{H}_5)_2\text{NH}(\text{l})$	$-(103.8 \pm 1.1)$	74
$(\text{n-C}_3\text{H}_7)_2\text{NH}(\text{l})$	$-(156.1 \pm 1.0)$	74
$(\text{n-C}_4\text{H}_9)_2\text{NH}(\text{l})$	$-(206.0 \pm 0.9)$	74
$\text{C}_2\text{H}_5\text{OH}(\text{l})$	$-(277.1 \pm 0.2)$	74
$\text{i-C}_3\text{H}_7\text{OH}(\text{l})$	$-(317.9 \pm 0.4)$	74
$\text{t-C}_4\text{H}_9\text{OH}(\text{l})$	$-(359.2 \pm 1.4)$	74
$\text{n-C}_3\text{H}_7\text{SH}(\text{l})$	$-(99.9 \pm 0.6)$	74
$\text{i-C}_3\text{H}_7\text{SH}(\text{l})$	$-(105.8 \pm 0.6)$	74
$\text{n-C}_4\text{H}_9\text{SH}(\text{l})$	$-(124.7 \pm 1.2)$	74
$\text{t-C}_4\text{H}_9\text{SH}(\text{l})$	$-(140.5 \pm 0.8)$	74
$\text{CH}_3\text{COOH}(\text{l})$	$-(484.3 \pm 0.2)$	74
$\text{CF}_3\text{COOH}(\text{l})$	$-(1069.2 \pm 1.1)$	74
$\text{C}_6\text{H}_5\text{COOH}(\text{c})$	$-(384.9 \pm 0.6)$	74
$[(\text{C}_2\text{H}_5)_2\text{NH}_2][\text{S}_2\text{CN}(\text{C}_2\text{H}_5)_2](\text{c})$ (diethylammonium diethyldithiocarbamate)	$-(198.8 \pm 4.1)$	82
$\text{CH}_2(\text{NH}_2)\text{COOH}(\text{c})$ (glycine)	$-(530.3 \pm 3.5)$	74
$(\text{C}_2\text{H}_5)_2\text{S}(\text{l})$	$-(119.4 \pm 0.8)$	74

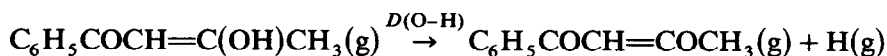
## APPENDIX 1 (continued)

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
$(C_5H_5N)NHCOCH_3(c)$ ( <i>N</i> -(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

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



$$D(O-H) = 352 \pm 6 \text{ kJ mol}^{-1} \text{ as calculated for phenol [46,49].}$$

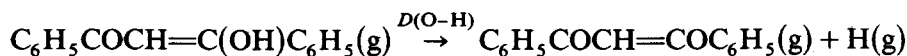
$$\Delta H_f^0(C_6H_5COCH_2COCH_3, c) = -(335.1 \pm 2.8) \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{sub}}(C_6H_5COCH_2COCH_3, c) = 83.8 \pm 0.4 \text{ kJ mol}^{-1} \text{ (ref. 76).}$$

$$\Delta H_f^0(C_6H_5COCH=C(OH)CH_3, g) = -(251.3 \pm 3.2) \text{ kJ mol}^{-1}$$

Hpbd(g) is assumed to be entirely in the enolic form.

$$\Delta H_f^0(C_6H_5COCH=CO^cH_5, g) = \Delta H_f^0(dppd, g) = -(5.3 \pm 13) \text{ kJ mol}^{-1}$$



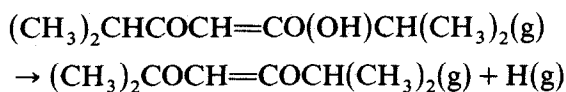
$$D(O-H) = 352 \pm 6 \text{ kJ mol}^{-1} \text{ as calculated for phenol.}$$

$$\Delta H_f^0(C_6H_5COCH_2COC_6H_5, c) = -(224.3 \pm 1.5) \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{sub}}(C_6H_5COCH_2COC_6H_5) = (85 \pm 5) \text{ kJ mol}^{-1} \text{ (estimated).}$$

$\Delta H_f^0(\text{C}_6\text{H}_5\text{COCH}=\text{C}(\text{OH})\text{C}_6\text{H}_5, \text{g}) = -(139.3 \pm 6.5) \text{ kJ mol}^{-1}$   
 Hdppd(g) is assumed to be entirely in the enolic form.

$\Delta H_f^0((\text{CH}_3)_3\text{CCOCH}=\text{COC}(\text{CH}_3)_3, \text{g}) = \Delta H_f^0(\text{tmhd}, \text{g}) = -381.4 \pm 12 \text{ kJ mol}^{-1}$



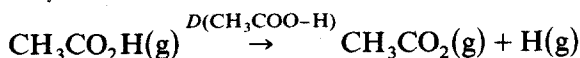
$D(\text{O}-\text{H}) = 365 \pm 6 \text{ kJ mol}^{-1}$  as assumed in the enolic form of pentane-2,4-dione.

$\Delta H_f^0((\text{CH}_3)_2\text{CHCOCH}_2\text{COCH}(\text{CH}_3)_2, \text{c}) = -(587.7 \pm 3.8) \text{ kJ mol}^{-1}$

$\Delta H_{\text{sub}}(\text{CH}_3)_2\text{CHCOCH}_2\text{COCH}(\text{CH}_3)_2 = 59.3 \pm 2 \text{ kJ mol}^{-1}$  (ref. 75) to 100% enol form.

$\Delta H_f^0((\text{CH}_3)_2\text{CHCOCH}=\text{C}(\text{OH})\text{CH}(\text{CH}_3)_2, \text{g}) = -(528.4 \pm 6) \text{ kJ mol}^{-1}$

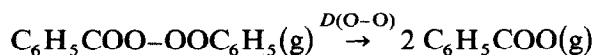
$\Delta H_f^0(\text{CH}_3\text{COO}, \text{g}) = -(217 \pm 10) \text{ kJ mol}^{-1}$



$D(\text{CH}_3\text{COO}-\text{H}) = 433 \pm 10 \text{ kJ mol}^{-1}$  (ref. 55).

$\Delta H_f^0(\text{CH}_3\text{CO}_2\text{H}, \text{g}) = -(432.1 \pm 0.4) \text{ kJ mol}^{-1}$  (ref. 74).

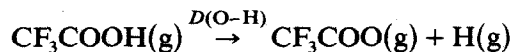
$\Delta H_f^0(\text{C}_6\text{H}_5\text{COO}, \text{g}) = -(76.3 \pm 3.0) \text{ kJ mol}^{-1}$



$D(\text{O}-\text{O}) = 125.5 \pm 4.2 \text{ kJ mol}^{-1}$  (ref. 77).

$\Delta H_f^0([\text{C}_6\text{H}_5\text{COO}]_2, \text{g}) = -(278.2 \pm 4.2) \text{ kJ mol}^{-1}$  (ref. 74).

$\Delta H_f^0(\text{CF}_3\text{COO}, \text{g}) = -(815.7 \pm 10) \text{ kJ mol}^{-1}$  (based on  $D(\text{O}-\text{H}) = 433 \pm 10$ ).  
 $-(788.7 \pm 17) \text{ kJ mol}^{-1}$  (based on  $D(\text{O}-\text{H}) = 460 \pm 17$ ).



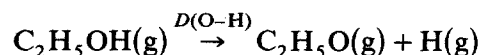
$D(\text{O}-\text{H})$  assumed to be equal to  $D(\text{CH}_3\text{COO}-\text{H}) = 433 \pm 10 \text{ kJ mol}^{-1}$  (ref. 55).

$D(\text{RCOO}-\text{H})$  in carboxylic acids ca.  $460 \pm 17 \text{ kJ mol}^{-1}$  (ref. 78).

$\Delta H_f^0(\text{CF}_3\text{COOH}, \text{g}) = -(1030.7 \pm 1.4) \text{ kJ mol}^{-1}$  (ref. 74).

$\Delta H_f^0(\text{H}, \text{g}) = 218.00 \pm 0.01 \text{ kJ mol}^{-1}$  (ref. 50).

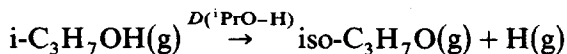
$\Delta H_f^0(\text{C}_2\text{H}_5\text{O}, \text{g}) = -(26 \pm 10) \text{ kJ mol}^{-1}$



$$D(\text{O}-\text{H}) = 427 \text{ kJ mol}^{-1} \text{ (ref. 47).}$$

$$\Delta H_f^0(\text{C}_2\text{H}_5\text{OH}, \text{g}) = -(234.8 \pm 0.2) \text{ kJ mol}^{-1} \text{ (ref. 74).}$$

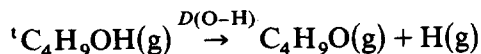
$$\Delta H_f^0(\text{i-C}_3\text{H}_7\text{O}, \text{g}) = -(27 \pm 10) \text{ kJ mol}^{-1}$$



$$D(\text{i-PrO}-\text{H}) = 464 \text{ kJ mol}^{-1} \text{ (ref. 100).}$$

$$\Delta H_f^0(\text{i-C}_3\text{H}_7\text{OH}, \text{g}) = -(272.5 \pm 0.4) \text{ kJ mol}^{-1} \text{ (ref. 74).}$$

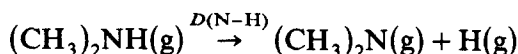
$$\Delta H_f^0(\text{'C}_4\text{H}_9\text{O}, \text{g}) = -(67 \pm 10) \text{ kJ mol}^{-1}$$



$$D(\text{O}-\text{H}) = 464 \text{ kJ mol}^{-1} \text{ (ref. 100).}$$

$$\Delta H_f^0(\text{t-C}_4\text{H}_9\text{OH}, \text{g}) = -(312.4 \pm 2.8) \text{ kJ mol}^{-1} \text{ (ref. 74).}$$

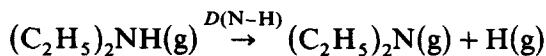
$$\Delta H_f^0((\text{CH}_3)_2\text{N}, \text{g}) = 123.4 \pm 4 \text{ kJ mol}^{-1}$$



$$D(\text{N}-\text{H}) = 360 \text{ kJ mol}^{-1} \text{ (ref. 97).}$$

$$\Delta H_f^0((\text{CH}_3)_2\text{NH}, \text{g}) = -(18.5 \pm 0.4) \text{ (ref. 74).}$$

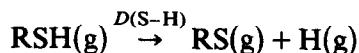
$$\Delta H_f^0((\text{C}_2\text{H}_5)_2\text{N}, \text{g}) = 69 \pm 5 \text{ kJ mol}^{-1}$$



$$D(\text{N}-\text{H}) = \text{ca. } 360 \text{ kJ mol}^{-1} \text{ (assumed same as } D(\text{Me}_2\text{N}-\text{H})).$$

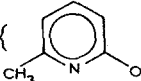
$$\Delta H_f^0((\text{C}_2\text{H}_5)_2\text{NH}, \text{g}) = -(72.6 \pm 1.9) \text{ kJ mol}^{-1} \text{ (ref. 74).}$$

$$\Delta H_f^0(\text{RS}, \text{g})$$



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

	n-C <sub>3</sub> H <sub>7</sub>	i-C <sub>3</sub> H <sub>7</sub>	n-C <sub>4</sub> H <sub>9</sub>	t-C <sub>4</sub> H <sub>9</sub>
$\Delta H_f^0(\text{RSH}, \text{g})$ (kJ mol <sup>-1</sup> )	-(67.9 ± 0.6)	-(76.2 ± 0.6)	-(88.1 ± 1.2)	-(109 ± 0.8)
$\Delta H_f^0(\text{RS}, \text{g})$ (kJ mol <sup>-1</sup> )	99.0 ± 9	90.7 ± 9	78.8 ± 10	57.3 ± 9

$$\Delta H_f^0(\text{mhp}, \text{g}) = \Delta H_f^0(\text{mhp}, \text{g}) = 23 \pm 13 \text{ kJ mol}^{-1}$$




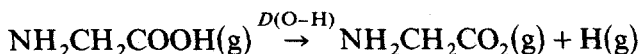
$$D(\text{O-H}) = 362 \pm 10 \text{ kJ mol}^{-1}$$

$$\Delta H_f^0(\text{Hmhp}, \text{c}) = -(213.05 \pm 2.3) \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{sub}}(\text{Hmhp}) = (92 \pm 1.5) \text{ kJ mol}^{-1} \text{ (estimated).}$$

$$\Delta H_f^0(\text{Hmhp}, \text{g}) = -(121.0 \pm 3.0) \text{ kJ mol}^{-1}$$

$$\Delta H_f^0(\text{NH}_2\text{CH}_2\text{COO}, \text{g}) = -(178.9 \pm 13.5)$$



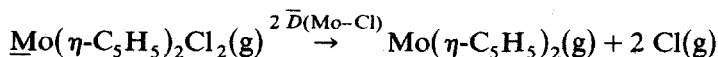
$$D(\text{O-H}) = 433 \pm 10 \text{ kJ mol}^{-1} \text{ as in } \text{CH}_3\text{COOH} \text{ (ref. 55).}$$

$$\Delta H_f^0(\text{NH}_2\text{CH}_2\text{COOH}, \text{c}) = -(530.3 \pm 3.5) \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{sub}}(\text{NH}_2\text{CH}_2\text{COOH}) = 136.5 \text{ (419 K) (ref. 81).}$$

$$\Delta H_f^0(\text{NH}_2\text{CH}_2\text{COOH}, \text{g}) = -(393.8 \pm 3.5) \text{ kJ mol}^{-1}$$

$$\Delta H_f^0[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2, \text{g}] = 369.6 \pm 7 \text{ kJ mol}^{-1}$$



$$\bar{D}(\text{Mo-Cl}) \text{ assumed to be equal to the mean bond dissociation energy.}$$

$$\bar{D}(\text{Mo-Cl}) = 303.8 \text{ kJ mol}^{-1} \text{ in } \text{MoCl}_6.$$

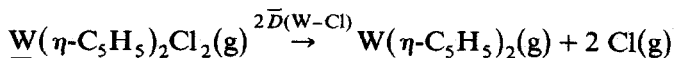
$$\Delta H_f^0[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2, \text{c}] = -(95.8 \pm 2.5) \text{ kJ mol}^{-1} \text{ (ref. 69).}$$

$$\Delta H_{\text{sub}}[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2] = (100.4 \pm 4.1) \text{ kJ mol}^{-1} \text{ (estimated).}$$

$$\Delta H_f^0[\text{Mo}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2, \text{g}] = 4.6 \pm 6.6 \text{ kJ mol}^{-1}$$

$$\Delta H_f^0(\text{Cl}, \text{g}) = 121.302 \pm 0.008 \text{ kJ mol}^{-1}$$

$$\Delta H_f^0[\text{W}(\eta\text{-C}_5\text{H}_5)_2, \text{g}] = 484.5 \pm 7 \text{ kJ mol}^{-1}$$



$$\bar{D}(\text{W-Cl}) \text{ assumed to be equal to mean bond dissociation energy.}$$

$$\bar{D}(\text{W-Cl}) = 347.3 \text{ kJ mol}^{-1} \text{ in } \text{WCl}_6.$$

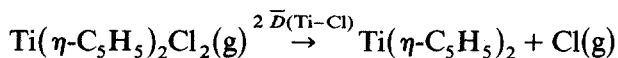
$$\Delta H_f^0[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2, \text{c}] = -(71.1 \pm 2.5) \text{ kJ mol}^{-1} \text{ (ref. 69).}$$

$$\Delta H_{\text{sub}}[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2] = 104.6 \pm 4.1 \text{ kJ mol}^{-1} \text{ (ref. 69).}$$

$$\Delta H_f^0[\text{W}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2, \text{g}] = 33.5 \pm 6.6 \text{ kJ mol}^{-1}$$

$$\Delta H_f^0(\text{Cl}, \text{g}) = 121.302 \pm 0.08 \text{ kJ mol}^{-1}$$

$$\Delta H_f^0[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2, \text{g}] = +352.4 \pm 10 \text{ kJ mol}^{-1}$$





$\overline{D}(\text{Ti}-\text{Cl})$  assumed to be equal to mean bond dissociation energy.

$\overline{D}(\text{Ti}-\text{Cl}) = 430.5 \text{ kJ mol}^{-1}$  in  $\text{TiCl}_4$ .

$\Delta H_f^0[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2, \text{c}] = -(383.2 \pm 7.5) \text{ kJ mol}^{-1}$  (ref. 69).

$\Delta H_{\text{sub}}[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2] = 117.2 \pm 2.0 \text{ kJ mol}^{-1}$  (ref. 69).

$\Delta H_f^0[\text{Ti}(\eta\text{-C}_5\text{H}_5)_2\text{Cl}_2, \text{g}] = -(266.0 \pm 9.5) \text{ kJ mol}^{-1}$

$\Delta H_f^0(\text{Cl}, \text{g}) = 121.302 \pm 0.008 \text{ kJ mol}^{-1}$

### APPENDIX 3

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

	$\Delta H_{\text{sub}}$	Ref.
$\text{MnCl}_2$	$217.6 \pm 2$	50
$\text{FeCl}_2$	$193.3 \pm 2$	50
$\text{CoCl}_2$	$234 \pm 1.7$	88
$\text{CoBr}_2$	$222 \pm 2$	89
$\text{CoI}_2$	$209 \pm 2$	89
$\text{NiCl}_2$	$246 \pm 2$	89
$\text{NiI}_2$	$214 \pm 2$	90
$\text{CuCl}_2$	$194 \pm 2$	91
$\text{CuBr}_2$	$188 \pm 2$	89
$\text{ZnCl}_2$	$149.0 \pm 2$	50
$\text{ZnBr}_2$	$131 \pm 2$	92
$\text{ZnI}_2$	$120 \pm 2$	92
$\text{CdCl}_2$	$181.2 \pm 2$	93
$\text{CdBr}_2$	$151.5 \pm 2$	92
$\text{CdI}_2$	$137.7 \pm 2$	92
$\text{HgCl}_2$	$82.8 \pm 2$	94
$\text{HgBr}_2$	$84.1 \pm 2$	94
$\text{HgI}_2(\text{yellow})$	$85.8 \pm 2$	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



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  $\Delta H_{\text{vap}}^T$  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  $\Delta H_{\text{vap}}^T$  to  $\Delta H_{\text{vap}}^{298\text{K}}$  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  $\Delta C_p$  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  $\Delta C_p$  correction to their data and make the assumption that  $\Delta H_{\text{vap}}^T \approx \Delta H_{\text{vap}}^{298\text{K}}$  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.

## REFERENCES

- 1 S.J. Ashcroft and C.T. Mortimer, *Thermochemistry of Transition Metal Complexes*, Academic Press, London, 1970.
- 2 J.J. Christensen, D.J. Eatough and R.M. Izatt, *Handbook of Metal Ligand Heats*, 2nd edn., Dekker, New York, 1975.
- 3 G. Beech, C.T. Mortimer and E.G. Tyler, *J. Chem. Soc. A*, (1967) 925.
- 4 C.T. Mortimer and J.L. McNaughton, *Thermochim. Acta*, 10 (1974) 125.
- 5 C.T. Mortimer and J.L. McNaughton, *Thermochim. Acta*, 10 (1974) 207.
- 6 C.T. Mortimer and J.L. McNaughton, *Thermochim. Acta*, 6 (1973) 269.
- 7 C.T. Mortimer and J.L. McNaughton, *Thermochim. Acta*, 8 (1974) 265.
- 8 C.T. Mortimer, in R. Barbucci, (Ed.), *Calorimetry*, Edizioni Scuola Universitaria, Firenze, Italy, 1979, p. 167.
- 9 G. Beech, C.T. Mortimer and E.G. Tyler, *J. Chem. Soc. A*, (1967) 1111.
- 10 M.A.V. Ribeiro da Silva, Faculdade de Ciencias do Porto, personal communication.
- 11 G. Beech, S.J. Ashcroft and C.T. Mortimer, *J. Chem. Soc. A*, (1967) 929.
- 12 E. Tomus and E. Segal, *An. Univ. Bucuresti*, 12 (1963) 103.
- 13 S.J. Ashcroft, *J. Chem. Soc. A*, (1970) 1020.
- 14 M.S. Barvinok and L.G. Lukina, *Zh. Neorg. Khim.*, 26 (1981) 253.
- 15 K.F. Purcell and J.C. Kotz, *Inorganic Chemistry*, Saunders, London, 1977, p. 543.
- 16 C. Airoidi and A.P. Chagas, *Thermochim. Acta*, 33 (1979) 371.
- 17 J.C. de Queiroz, C. Airoidi and A.P. Chagas, *J. Chem. Soc. Dalton Trans.*, (1978) 1102.
- 18 J.C. de Queiroz, C. Airoidi and A.P. Chagas, *J. Inorg. Nucl. Chem.*, 43 (1981) 1207.
- 19 C. Airoidi, A.P. Chagas and M.N. Filho, *J. Inorg. Nucl. Chem.*, 43 (1981) 89.
- 20 C. Airoidi, A.P. Chagas and F.A. Assunção, *J. Chem. Soc. Dalton Trans.*, (1980) 1823.
- 21 K.F. Purcell and J.C. Kotz, *Inorganic Chemistry*, Saunders, London, 1977, p. 541.
- 22 S.O. Adeosun and V.O. Nwanze, *J. Inorg. Nucl. Chem.*, 37 (1975) 2091.
- 23 A. Evans and C.T. Mortimer, *J. Chem. Thermodyn.*, 7 (1975) 363; and unpublished results.
- 24 R.J. Irving and M.A.V. Ribeiro da Silva, *J. Chem. Soc. Dalton Trans.*, (1981) 99.
- 25 R.J. Irving and M.A.V. Ribeiro da Silva, *J. Chem. Soc. Dalton Trans.*, (1978) 399.
- 26 M.A.V. Ribeiro da Silva and A.M.M.V. Reis, *Bull. Chem. Soc. Jpn.*, 52 (1979) 3080.
- 27 J.O. Hill and K.J. Irving, *J. Chem. Soc. A*, (1967) 1413.
- 28 J.O. Hill and K.J. Irving, *J. Chem. Soc. A*, (1968) 3116.
- 29 J.O. Hill and K.J. Irving, *J. Chem. Soc. A*, (1968) 1052.

- 30 G. Pilcher, K.J. Cavell, C.D. Garner and S. Parkes, *J. Chem. Soc. Dalton Trans.*, (1978) 1311.
- 31 W. Kałolowicz and E. Geira, *Proc. 4ème Conf. Int. de Thermodyn. Chem.*, (1975) 1/11.
- 32 W. Kałolowicz and E. Geira, *Thermochim. Acta*, 32 (1979) 19.
- 33 E.W. Berg and J.T. Truemper, *Anal. Chim. Acta*, 32 (1965) 245.
- 34 S.J. Ashcroft, *Thermochim. Acta*, 2 (1971) 512.
- 35 R.J. Irving, R.A. Shultz and H. Naghibi, quoted in ref. 24.
- 36 P. Burkinshaw and C.T. Mortimer, unpublished results.
- 37 R. Teghil, D. Ferro, L. Bencivenni and M. Pelmo, *Thermochim. Acta*, 44 (1981) 213.
- 38 G. Beech and R.M. Lintonbon, *Thermochim. Acta*, 3 (1971) 97.
- 39 M.M. Jones and J.L. Wood, *Inorg. Chem.*, 3 (1964) 1553.
- 40 R.J. Irving and T.N. Lockyer, *J. Chem. Soc. A*, (1976) 2140.
- 41 K.J. Cavell and G. Pilcher, *J. Chem. Soc. Faraday Trans. I*, (1977) 1590.
- 42 G.R. Nicholson, *J. Chem. Soc.*, (1957) 2431.
- 43 L.W. Reeves, *Can. J. Chem.*, 35 (1957) 1351.
- 44 H.J. Bernstein and J. Powling, *J. Am. Chem. Soc.*, 73 (1951) 4353.
- 45 R.J. Irving and I. Wadsö, *Acta Chem. Scand.*, 24 (1970) 589.
- 46 J.D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London and New York, 1970.
- 47 J.A. Kerr, *Chem. Rev.*, 66 (1966) 465.
- 48 J.O. Hill and R.J. Irving, *J. Chem. Soc. A*, (1966) 971.
- 49 P. Natalis and J.L. Franklin, *J. Phys. Chem.*, 69 (1965) 2943.
- 50 Tech. Note 270-3 (1968), 270-4 (1969), *Nat. Bur. Stand.*, Washington, DC.
- 51 K.J. Cavell, J.O. Hill and R.J. Magee, *J. Chem. Soc. Dalton Trans.*, (1980) 763, 1638.
- 52 K.J. Cavell, J.O. Hill and R.J. Magee, *Thermochim. Acta*, 34 (1979) 155.
- 53 G. D'Ascenzo and W.W. Wendlandt, *J. Therm. Anal.*, 1 (1969) 423.
- 54 T.L. Allen, *J. Chem. Phys.*, 31 (1959) 1039.
- 55 K.D. Cook and J.W. Taylor, *Int. J. Mass Spectrom. Ion Phys.*, 30 (1979) 93.
- 56 M.A. Bernard, N. Bois and M. Daireaux, *Thermochim. Acta*, 16 (1976) 283.
- 57 Circ. 500, (1952) *Nat. Bur. Stand.*, Washington D.C.
- 58 I. Igumenov, N.E. Fedotova and S.V. Lemskov, *Koord. Khim.*, 6 (1980) 903.
- 59 J.C.G. Calado, A.R. Dias, M.S. Salema and J.A. Martinho-Simões, *J. Chem. Soc. Dalton Trans.*, (1981) 1174.
- 60 A.R. Dias, J.A. Martinho-Simões and C. Teixeira, *J. Chem. Soc. Dalton Trans.*, (1980) 1178.
- 61 D.C. Bradley and M.J. Hillyer, *Trans. Faraday Soc.*, 62 (1966) 2367, 2374, 2382.
- 62 K.J. Cavell, C.D. Garner, J.A. Martinho-Simões, G. Pilcher, H.A. Skinner, G. Al-Takhin, I.B. Walton and M.T. Zarfarani-Moattar, *J. Chem. Soc. Faraday Trans. I*, 77 (1981) 2927.
- 63 K.J. Cavell, C.D. Garner, G. Pilcher and S. Parks, *J. Chem. Soc. Dalton Trans.*, (1979) 174.
- 64 K.H. Cavell, J.A. Connor, G. Pilcher, M.A.V. Ribeiro da Silva, M.D.M.C. Ribeiro da Silva, H.A. Skinner, Y. Virmani and M.T. Zafarani-Moattar, *J. Chem. Soc. Faraday Trans. I*, 77 (1981) 1585.
- 65 F.A. Adedeji, K.J. Cavell, S. Cavell, J.A. Connor, G. Pilcher, H.A. Skinner and M.T. Zarfarani-Moattar, *J. Chem. Soc. Faraday Trans. I*, 75 (1979) 603.
- 66 CODATA, *J. Chem. Thermodyn.*, 3 (1971) 1.
- 67 J.D. Cox, in J.B. Pedley (Ed.), *CATCH Tables, Halogen Compounds*, Univ. Sussex, 1972.

- 68 D.S. Barnes, in J.B. Pedley (Ed.), *CATCH Tables, Cr, Mo and W Compounds*, Univ. Sussex, 1974.
- 69 V.I. Tel'noi and I.B. Rabinovich, *Usp. Khim.*, 46 (1977) 1336.
- 70 A. Lüttringhaus and H.W. Dirksen, *Angew. Chem. Int. Ed. Engl.*, 3 (1964) 260.
- 71 A.S. Gonçalves, A.P. Chagas and C. Airoidi, *J. Chem. Soc. Dalton Trans.*, (1979) 159.
- 72 I. Wadsö, *Acta Chem. Scand.*, 19 (1965) 1079.
- 73 A.F. Bedford and C.T. Mortimer, *J. Chem. Soc.*, (1960) 1622.
- 74 J.B. Pedley and J. Rylance, *NPL Computer Analysed Thermochemical Data, Organic and Organometallic Compounds*, Univ. Sussex, 1977.
- 75 M.L.C.C.H. Ferrão, M.A.V. Ribeiro da Silva, S. Suradi, G. Pilcher and H.A. Skinner, *J. Chem. Thermodyn.*, 13 (1981) 567.
- 76 A. Aihara, *Bull. Chem. Soc. Jpn.*, 32 (1959) 1243.
- 77 C.E.H. Baum and S.F. Mellish, *Trans. Faraday Soc.*, 47 (1951) 1216.
- 78 R. Yamdagni and P. Kebarle, *J. Am. Chem. Soc.*, 95 (1973) 4050, 6833.
- 79 CODATA, *J. Chem. Thermodyn.*, 10 (1978) 903.
- 80 S.W. Benson, *Chem. Rev.*, 78 (1978) 23.
- 81 C.G. de Kruif, J. Voogd and J.C.A. Offringa, *J. Chem. Thermodyn.*, 11 (1979) 651.
- 82 K.J. Cavell, J.O. Hill and R.J. Magee, *Thermochim. Acta*, 33 (1979) 377.
- 83 A. Evans and C.T. Mortimer, *J. Chem. Thermodyn.*, 8 (1976) 499.
- 84 V.G. Tsvetkov and B.I. Kozyrkin, *Thermodyn. Org., Soedin.*, 7 (1978) 73.
- 85 D.W. Scott et al., *J. Am. Chem. Soc.*, 74 (1952) 4656.
- 86 H.A. Skinner, *Adv. Organomet. Chem.*, 2, (1964) 49.
- 87 R.N. Goldberg and L.G. Hepler, *Chem. Rev.*, 68 (1968) 229.
- 88 M.P. Kularni and V.V. Dadape, *High Temp. Sci.*, 3 (1979) 277.
- 89 L. Brewer, G.R. Somayajulu and E. Brackett, *Chem. Rev.*, 63 (1963) 111.
- 90 Von H. Opperman and A. Tosher, *Z. Anorg. Chem.*, 463 (1980) 45.
- 91 R.R. Hammer and N.W. Gregory, *J. Phys. Chem.*, 68 (1964) 3229.
- 92 O. Kubachewski, E.L. Evans, and C.B. Alcock, *Metallurgical Thermochemistry*, Int. Ser. Monographs Metal Phys. Phys. Met., 4th edn., Vol. 1, Pergamon Press, London, 1967.
- 93 F.J. Kenesha and D. Cubbiciotti, *J. Chem. Phys.*, 40 (1964) 1778.
- 94 L.G. Hepler and G. Olofsson, *Chem. Rev.*, 75 (1975) 588.
- 95 W.H. Johnson, R.A. Nelson and E.J. Prosen, *J. Res. Nat. Bur. Stand.*, 62 (1959) 49.
- 96 P. Gross and C. Hayman, *Trans. Faraday Soc.*, 60 (1964) 45.
- 97 J.A. Kerr, R.C. Sekkar and A.F. Trotman-Dickenson, *J. Chem. Soc.*, (1963) 3217.
- 98 D.R. Stull (Director), *JANAF Thermochem. Tables PB 168 370-2*, Aug. 1967.
- 99 G. Pilcher, 1981, personal communication.
- 100 L.V. Gurvich, G.C. Karachevtsev, V.N. Kondratiev, Yu.A. Lebedev, V.A. Medvedev, V.K. Potapov and Yu.S. Hodnev, *Energies of Dissociation of Chemical Bonds*, Akad. Nauk U.S.S.R., Moscow, 1974.
- 101 D.R. Stull and H. Prophet, *JANAF Thermochem. Tables and Addenda I-III*, Dow Chemical Corp., Midland, Michigan, 1965-68.
- 102 (a) J.L. Margrave, *The Characterisation of High-Temperature Vapours*, Wiley, New York, 1967.
- (b) H.A. Skinner, *M.T.P. Int. Rev. of Sci., Phys. Chem. Ser. 1*, Vol. 10, *Thermochem. Thermodyn.*, Butterworths, London, 1972.
- 103 (a) C.G. de Kruif, T. Kuipers, J.C. van Miltenburg, R.C.F. Schaake, and G. Stevens, *J. Chem. Thermodyn.*, 13 (1981) 1081.
- (b) G.O. Twu and S. Blairs, *J. Chem. Thermodyn.*, 2 (1970) 275.
- 104 O. Kaposi, A. Popovi and J. Mansel, *J. Inorg. Nucl. Chem.*, 39 (1977) 1809, and refs. therein.

- 105 See, for example, ref. 101.
- 106 C.G. de Kruif and C.H.D. van Ginkel, *J. Chem. Thermodyn.*, 9 (1977) 725.
- 107 T.P. Melia and R. Merrifield, *J. Inorg. Nucl. Chem.*, 32 (1970) 1489.
- 108 (a) E.W. Berg and J.W. Truemper, *J. Phys. Chem.*, 64 (1960) 487.  
(b) J.L. Wood and M.M. Jones, *Inorg. Chem.*, 3 (1964) 1553.
- 109 J. Sachinidis and J.O. Hill, *Thermochim. Acta*, 35 (1980) 59.
- 110 G. Beech and R.M. Lintonbon, *Thermochim. Acta*, 3 (1971) 97.