Enthalpies of Formation of Complexes $[M(\eta\text{-}C_5H_5)_2(SR)_2]$ (M = Mo, W, or Ti; R = C_3H_7, C_4H_9, or C_6H_5); Metal–Sulphur Bond Enthalpies

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Standard enthalpies of formation (kJ mol^{-1}) at 298.15 K were determined by reaction-solution calorimetry: $\Delta H_f^\circ\{[Mo(\eta\text{-}C_5H_5)_2(SC_6H_5)_2],c\} = 309.4 \pm 4.8$; $\Delta H_f^\circ\{[W(\eta\text{-}C_5H_5)_2\{SC_3H_7\text{-}n)_2],c\} = 23.5 \pm 5.6$; $\Delta H_f^\circ\{[Ti(\eta\text{-}C_5H_5)_2(SC_3H_7\text{-}n)_2],c\} = -253.0 \pm 9.7$; $\Delta H_f^\circ\{[Ti(\eta\text{-}C_5H_5)_2(SC_6H_5)_2],c\} = 65.8 \pm 7.9$; and $\Delta H_f^\circ\{[Ti(\eta\text{-}C_5H_5)_2(S_2C_6H_3CH_3)]\} = 1.9 \pm 9.4$. From these data the metal–sulphur mean bond-dissociation enthalpies ($\bar{D}$) and bond-enthalpy terms (E) have been derived, using extended-Hückel molecular-orbital calculations to take account of changes in structure upon dissociation.

Despite the increasing interest in transition metal–sulphur organometallic complexes,[1] thermodynamic data for this type of compounds are still very scarce.[2] As a result, the energetics of metal–sulphur bonding are poorly known compared, for example, with metal–oxygen bonding.

In a previous paper[3] we reported metal–sulphur bond-enthalpy values for several $[Mo(\eta\text{-}C_5H_5)_2(SR)_2]$ complexes, where R = n-C_3H_7, i-C_3H_7, n-C_4H_9, or t-C_4H_9. The evaluation of other metal–sulphur bond enthalpies for the same type of molecules but involving different metals and/or ligands was an obvious extension of that work. Thus, such data for bis(η-cyclopentadienyl) complexes should not only confirm the reliability of the earlier results but would also improve our understanding of the energetics of those bonds.

The aim of the present paper is therefore to report new thermochemical data for metal–sulphur bond enthalpies and also to discuss the available set of values in terms of the molecular structures of the complexes.

Experimental

Calorimetry.—The reaction and solution enthalpies were measured in the calorimeter previously described.[4] There was no need to make the measurements under nitrogen because all the compounds involved are fairly air-stable. The enthalpy of melting of toluene-3,4-dithiol was determined in a Perkin-Elmer DSC 1B differential scanning calorimeter, using indium as a calibrant.

Compounds.—The complexes $[M(\eta\text{-}C_5H_5)_2(SR)_2]$ [M = Mo or Ti, R = C_6H_5; M = Ti or W, R = n-C_3H_7; M = Ti, $(SR)_2$ = toluene-3,4-dithiolate] were prepared and purified as described in the literature.[5-10] The reaction solutions were prepared from B.D.H. Analar or Merck p.a. hydrochloric acid and Merck p.a. acetone, which were used without further treatment. Propanethiol (Fluka) was dried over $CaCl_2$ and distilled under dry nitrogen. Benzenethiol (Fluka) was purified as described in the literature.[11] Merck 99% p.a. toluene-3,4-dithiol, a very hygroscopic compound, was handled in a dry nitrogen atmosphere and was purified by sublimation and drying in vacuum for several hours before use.

Reactions.—Thermochemical measurements on reactions (1) (M = Mo or Ti, R = C_6H_5; M = Ti or W, R = n-C_3H_7) and (2) were used to derive the standard enthalpies of formation of the complexes studied. The composition of the medium was chosen so as to ensure a rapid and complete reaction for each complex (Table 1). Possible errors inherent in the use of these mixtures and in the oxidation of $[M(\eta\text{-}C_5H_5)_2Cl_2]$ in acid solutions were discussed previously.[12] The products of reactions (1) and (2) were confirmed by i.r. spectroscopic analysis.

Table 1. Composition of the reaction mixtures

Reaction	M	Ligand	HCl(aq)/ mol dm^{-3}	HCl(aq): acetone (v/v)	Designation
(1)	Mo	C_6H_5SH	10.0	—	A
(1)	Ti	C_6H_5SH	10.4	1 : 4	B
(1)	Ti	n-C_3H_7SH	8.3	1 : 1	C
(1)	W	n-C_3H_7SH	8.3	1 : 1	C
(2)	Ti	$CH_3C_6H_3(SH)_2$	10.0	1 : 4	D

$$[M(\eta\text{-}C_5H_5)_2(SR)_2](c) + 2HCl(soln) \longrightarrow [M(\eta\text{-}C_5H_5)_2Cl_2](soln) + 2RSH(soln) \quad (1)$$

$$[Ti(\eta\text{-}C_5H_5)_2(S_2C_6H_3CH_3)](c) + 2HCl(soln) \longrightarrow [Ti(\eta\text{-}C_5H_5)_2Cl_2](soln) + CH_3C_6H_3(SH)_2(soln) \quad (2)$$

All reaction and solution enthalpies presented are mean values from at least five independent experiments and refer to 298 K. The uncertainties are twice the standard deviation of the mean in each case.

Auxiliary Data.—The following standard enthalpies of formation, vaporization, and sublimation at 298.15 K were used in evaluating the thermochemical results (values in kJ mol^{-1}): $\Delta H_f^\ominus[HCl, aq\ (10.0\ mol\ dm^{-3})] = -154.106 \pm 0.004$;[13] $\Delta H_f^\ominus(HCl, soln.\ B) = -171.86 \pm 0.34$;[14] $\Delta H_f^\ominus(HCl, soln.\ C) = -162.47 \pm 0.28$;[12] $\Delta H_f^\ominus(HCl, soln.\ D) = -172.59 \pm 0.51$;[12] $\Delta H_f^\ominus\{[Mo(\eta\text{-}C_5H_5)_2Cl_2],c\} = -95.8 \pm 2.5$;[15] $\Delta H_f^\ominus\{[W(\eta\text{-}C_5H_5)_2Cl_2],c\} = -71.1 \pm 2.5$;[15] $\Delta H_f^\ominus[\{Ti(\eta\text{-}C_5H_5)_2Cl_2],c\} = -383.2 \pm 7.5$;[15] $\Delta H_f^\ominus(C_6H_5SH,l) = 63.7 \pm 0.7$;[16] $\Delta H_f^\ominus(n\text{-}C_3H_7SH,l) = -99.9 \pm 0.6$;[16] $\Delta H_v^\ominus(C_6H_5SH) = 48.7 \pm 0.2$;[16] $\Delta H_v^\ominus(n\text{-}C_3H_7SH) = 32.0 \pm 0.1$;[16] $\Delta H_f^\ominus(Cl, g) = 121.302 \pm 0.008$;[17] $\Delta H_f^\ominus(H,g) = 217.997 \pm 0.006$;[17] $\Delta H_s^\ominus\{[Mo(\eta\text{-}C_5H_5)_2Cl_2]\} = 100.4 \pm 4.2$;[15] $\Delta H_s^\ominus\{[W(\eta\text{-}C_5H_5)_2Cl_2]\} = 104.6 \pm 4.2$;[15] and $\Delta H_s^\ominus\{[Ti(\eta\text{-}C_5H_5)_2Cl_2]\} = 118.8 \pm 2.1$.[15]

The standard enthalpy of formation of toluene-3,4-dithiol is not available in the literature. By using both Laidler and Benson schemes,[18] we obtained the average value $\Delta H_f^\ominus[CH_3C_6H_3(SH)_2,g] = 108 \pm 2$ kJ mol^{-1}. The estimation of the enthalpy of vaporization of this substance was made by using Wadsö's equation for slightly or non-associated liquids[18] and also by comparison with other similar organic compounds. The obtained value, *ca.* 64 ± 4 kJ mol^{-1}, together with $\Delta H_m^\ominus[CH_3C_6H_3(SH)_2]$ = 16.5 ± 0.7 kJ mol^{-1}, determined with the d.s.c. apparatus, led to $\Delta H_f^\ominus[CH_3C_6H_3(SH)_2,c]$ = 28 ± 5 kJ mol^{-1} and $\Delta H_s^\ominus[CH_3C_6H_3(SH)_2]$ = 80 ± 4 kJ mol^{-1}.

The following standard enthalpies of formation and vaporization at 298.15 K were used in recalculating the thermochemical results derived earlier[3] (values in kJ mol^{-1}):[16] $\Delta H_f^\ominus$(i-C_3H_7SH,l) = −105.8 ± 0.6; $\Delta H_f^\ominus$(n-C_4H_9SH,l) = −124.7 ± 1.2; $\Delta H_f^\ominus$(t-C_4H_9SH,l) = −140.5 ± 0.8; $\Delta H_v^\ominus$(i-C_3H_7SH) = 29.6 ± 0.1; $\Delta H_v^\ominus$(n-C_4H_9SH) = 36.6 ± 0.1; and $\Delta H_v^\ominus$(t-C_4H_9SH) = 30.9 ± 0.2.

Calculations.—The extended-Hückel molecular-orbital calculations were made by using the ICON8 program, developed by Hoffmann and co-workers.[19,20] The basis set for the molybdenum (tungsten) atom consisted of 4*d*(5*d*), 5*s*(6*s*), and 5*p*(6*p*) orbitals. The *s* and *p* orbitals were described by single Slater-type wavefunctions and the *d* orbitals as contracted linear combinations of two Slater-type wavefunctions.

Table 2. Orbital exponents and parameters used for the extended-Hückel molecular-orbital calculations

Orbital	Slater exponent	$-H_{ii}$/eV[a]
H_{1s}	1.300	13.60[b]
C_{2s}	1.625	21.40[b]
C_{2p}	1.625	11.40[b]
Mo_{5s}	1.96	8.77[c]
Mo_{5p}	1.90	5.60[c]
Mo_{4d}	*d*	11.60[c,e]
W_{6s}	2.341	8.26[f]
W_{6p}	2.309	5.17[f]
W_{5d}	*g*	10.37[e,f]

[a] eV = 96.4845 kJ mol^{-1}. [b] Ref. 19. [c] M. Kamata, K. Hirotsu, T. Higuchi, K. Tatsumi, R. Hoffmann, T. Yoshida, and S. Otsuka, *J. Am. Chem. Soc.*, 1981, **103**, 5772. [d] ξ_1 = 4.54, ξ_2 = 1.90, C_1 = 0.5899, and C_2 = 0.5899. [e] J. W. Richardson, W. C. Nieuwpoort, R. R. Powell, and W. E. Edgell, *J. Chem. Phys.*, 1962, **36**, 1057. [f] P. Kubacek and R. Hoffmann, *J. Am. Chem. Soc.*, 1981, **103**, 4332. [g] ξ_1 = 4.982, ξ_2 = 2.068, C_1 = 0.6685, and C_2 = 0.5424.

The orbital exponents and the parameters for the extended-Hückel calculations are collected in Table 2.

All calculations were performed by using the modified Wolfsberg–Helmholz method.[21] The model fragments M(η-$C_5H_5)_2$ (M = Mo or W) were considered as having C_{2v} symmetry. The bond lengths Mo–C 232.8, W–C 232.8, C–C 140, and C–H 109 pm were taken from *X*-ray-determined structures of several M(η-$C_5H_5)_2$ derivatives.[22]

Results

The thermochemical results are summarized in Table 3: ΔH_r represents the enthalpy of reactions (1) and (2), ΔH_{d1} refers to the enthalpy of solution of the respective dichloride complex, and ΔH_{d2} represents the enthalpy of solution of the liquid thiol.

It must be mentioned that a small residue of the dichloride complexes was always observed in each reaction. The resulting error however will lie within the uncertainty interval assigned to ΔH_{d1}. On the other hand, ΔH_{d2} for toluene-3,4-dithiol was measured after melting the sample inside the bulb, and therefore refers to the thiol in the liquid state. This procedure had to be used since the initially solid substance partially melted inside the calorimeter, yielding irreproducible results for ΔH_{d2}.

The standard enthalpies of formation of crystalline and gaseous complexes are collected in Table 4, together with the estimated enthalpies of sublimation at 298.15 K. Also included are the values obtained previously for the same type of complexes, which were recalculated by using the auxiliary data given above.

Discussion

The metal–sulphur bond-enthalpy terms (*E*) and mean bond-dissociation enthalpies ($\bar{D}$), presented in Table 7, were calculated through equations equivalent to (3) and (4), respectively,[23,24] by using the experimental results of Table 2 and the auxiliary data given above. The equations also apply to the case of [Ti(η-$C_5H_5)_2(S_2C_6H_3CH_3)$] if $\Delta H_f^\ominus$(SR*,g) and

Table 3. Thermochemical results (kJ mol^{-1})

Complex	Reaction mixture	ΔH_r	ΔH_{d1}	ΔH_{d2}
[Mo(η-$C_5H_5)_2(SC_6H_5)_2$]	A	35.3 ± 1.6	4.9 ± 2.8[a]	(0 ± 1)[b]
[Ti(η-$C_5H_5)_2(SC_6H_5)_2$]	B	39.04 ± 0.75	15.9 ± 1.5[c]	0.49 ± 0.27[d]
[Ti(η-$C_5H_5)_2(SC_3H_7$-n$)_2$]	C	−19.9 ± 3.0	5.2 ± 1.8[e]	−10.0 ± 2.4[d]
[W(η-$C_5H_5)_2(SC_3H_7$-n$)_2$]	C	24.8 ± 1.8	12.1 ± 3.3	−8.9 ± 1.5[d]
[Ti(η-$C_5H_5)_2(S_2C_6H_3CH_3)$]	D	27.6 ± 1.5	22.2 ± 2.0[a]	1.33 ± 0.56

[a] ΔH_{d1} obtained by dissolving the dichloride complex in a solution containing a stoicheiometric amount of the thiol. [b] Estimated. [c] From ref. 14. [d] ΔH_{d2} obtained by dissolving the thiol in a solution containing a stoicheiometric amount of the dichloride complex. [e] From ref. 12.

Table 4. Enthalpies of formation; $\Delta H_f^\ominus$(c) and $\Delta H_f^\ominus$(g), in kJ mol^{-1}

Complex	$\Delta H_f^\ominus$(c)	$\Delta H_s^\ominus$ *	$\Delta H_f^\ominus$(g)
[Mo(η-$C_5H_5)_2(SC_3H_7$-n$)_2$]	3.8 ± 5.3	(90 ± 10)	93.8 ± 11.3
[Mo(η-$C_5H_5)_2(SC_3H_7$-i$)_2$]	56.5 ± 5.7	(90 ± 10)	146.5 ± 11.5
[Mo(η-$C_5H_5)_2(SC_4H_9$-n$)_2$]	13.3 ± 5.7	(92 ± 10)	105.3 ± 11.5
[Mo(η-$C_5H_5)_2(SC_4H_9$-t$)_2$]	6.3 ± 4.4	(92 ± 10)	98.3 ± 10.9
[Mo(η-$C_5H_5)_2(SC_6H_5)_2$]	309.4 ± 4.8	(95 ± 10)	404.4 ± 11.1
[W(η-$C_5H_5)_2(SC_3H_7$-n$)_2$]	23.5 ± 5.6	(94 ± 10)	117.5 ± 11.5
[Ti(η-$C_5H_5)_2(SC_3H_7$-n$)_2$]	−253.0 ± 9.7	(108 ± 8)	−145.0 ± 12.6
[Ti(η-$C_5H_5)_2(SC_6H_5)_2$]	65.8 ± 7.9	(113 ± 10)	178.8 ± 12.7
[Ti(η-$C_5H_5)_2(S_2C_6H_3CH_3)$]	1.9 ± 9.4	(110 ± 10)	111.9 ± 13.7

* Estimated values.

Table 5. Reorganization enthalpies (kJ mol^{-1}) of $M(\eta-C_5H_5)_2$ fragments

Parent compound	θ[a]/°	$-E_R$	$E_{R_3} - E_{R_1}$
$[Mo(\eta-C_5H_5)_2Cl_2]$	130.5[b]	82[c]	—
$[Mo(\eta-C_5H_5)_2(SC_3H_7-n)_2]$	(131)	78[d]	−4
$[Mo(\eta-C_5H_5)_2(SC_3H_7-i)_2]$	(131)	78[d]	−4
$[Mo(\eta-C_5H_5)_2(SC_4H_9-n)_2]$	(131)	78[d]	−4
$[Mo(\eta-C_5H_5)_2(SC_4H_9-t)_2]$	130.4[e]	83[d]	1
$[Mo(\eta-C_5H_5)_2(SC_6H_5)_2]$	(131)	78[d]	−4
$[W(\eta-C_5H_5)_2Cl_2]$	(130)	107[c]	—
$[W(\eta-C_5H_5)_2(SC_3H_7-n)_2]$	(131)	98[d]	−9
$[Ti(\eta-C_5H_5)_2Cl_2]$	130.97[f]	10[c]	—
$[Ti(\eta-C_5H_5)_2(SC_3H_7-n)_2]$	132.1[g]	7[d]	−3
$[Ti(\eta-C_5H_5)_2(SC_6H_5)_2]$	132.4[h]	6[d]	−4
$[Ti(\eta-C_5H_5)_2(S_2C_6H_3CH_3)]$	(133)	5[d]	−5

[a] Estimated values in parentheses. [b] K. Prout, T. S. Cameron, R. A. Forder, S. R. Critchley, B. Denton, and G. V. Rees, *Acta Crystallogr., Sect. B*, 1974, **30**, 2290. [c] E_{R_3} value. [d] E_{R_1} value. [e] M. A. A. F. C. T. Carrondo, P. M. Matias, and G. A. Jeffrey, *Acta Crystallogr., Sect. C*, 1984, **40**, 932. [f] A. Clearfield, D. K. Warner, C. H. Saldarriaga-Molina, R. Ropal, and I. Bernal, *Can. J. Chem.*, 1975, **53**, 1622. [g] C. Lauricci, J. R. Lechat, and R. A. Santos, unpublished work. [h] E. G. Muller, S. F. Watkins, and L. F. Dahl, *J. Organomet. Chem.*, 1976, **111**, 73.

Table 6. Structural data for $[M(\eta-C_5H_5)_2L_2]$ complexes; bond lengths in pm, bond angles in °

Molecule	θ	$M-\eta-C_5H_5$	M−L	L−M−L
$[Mo(\eta-C_5H_5)_2Cl_2]$[a]	130.5[b]	198[c]	247	82.0
$[Mo(\eta-C_5H_5)_2(SC_4H_9-t)_2]$[d]	130.4[b]	201[c]	249.6	71.1
$[Mo(\eta-C_5H_5)_2S_4]$[e]	134.2[b]	200.0[c]	245.3	88.2
$[Mo(\eta-C_5H_5)_2(S_2C_6H_3CH_3)]$[f]	132.5[b]	199.6[c]	243.3	82.4
$[Mo(\eta-C_5H_5)_2(S_2C_6H_4)]$[g]	138.0[b]	202[c]	243.7	81.9
$[W(\eta-C_5H_5)_2S_4]$[h]	133.3[i]	201[j]	241.9	89.1
$[W(\eta-C_5H_5)_2(S_2C_6H_4)]$[k]	137[b]	200.4[c]	242.1	82.3
$[Ti(\eta-C_5H_5)_2Cl_2]$[l]	130.97[i]	205.9[j]	236.4	94.53
$[Ti(\eta-C_5H_5)_2(SCH_3)_2]$[m]	130.0[b,n]	207.0[c,n]	240.3	93.6
$[Ti(\eta-C_5H_5)_2(SC_3H_7-n)_2]$[o]	132.1[i]	207.9[j]	239.8	93.8
$[Ti(\eta-C_5H_5)_2(SC_6H_5)_2]$[p]	132.4[i]	207[j]	241	99.3
$[Ti(\eta-C_5H_5)_2S_4]$[q]	133.7[b]	206.8[c]	243.5	94.6
$[Ti(\eta-C_5H_5)_2(S_2C_6H_4)]$[r]	129.9[b]	206[c]	241.6	82.2
$[Ti(\eta-C_5H_5)_2\{S_2C_2(CN)_2\}]$[s]	130.7[b]	205.1[c]	244.7	81.9
$[Ti(\eta-C_5H_5)_2\{S_2(CH)_2\}]$[t]	130.9[b]	206.0[c]	241.7	83.2
$[Ti(\eta-C_5H_5)_2(O_2CC_6H_5)]$[u]	131.7[i]	206[j]	192.6	91.4

[a] See footnote *b* of Table 5. [b] Ring normal angle. [c] Ring normal distance. [d] See footnote *e* of Table 5. [e] H. D. Block and R. Allmann, *Cryst. Struct. Commun.*, 1975, **4**, 189. [f] J. R. Knox and C. K. Prout, *Acta Crystallogr., Sect. B*, 1969, **25**, 2013. [g] A. Kutoglu and H. Köpf, *J. Organomet. Chem.*, 1970, **25**, 455. [h] B. R. Davies and I. Bernal, *J. Cryst. Mol. Struct.*, 1972, **2**, 135. [i] Centroid angle. [j] Centroid distance. [k] T. Debaerdemaeker and A. Kutoglu, *Acta Crystallogr., Sect. B*, 1973, **29**, 2664. [l] See footnote *f* of Table 5. [m] M. A. A. F. C. T. Carrondo and G. A. Jeffrey, *Acta Crystallogr., Sect. C*, 1983, **39**, 42. [n] The ring centroid angle is 131.4° and the titanium–ring centroid distance is 206.9 pm. [o] See footnote *g* of Table 5. [p] See footnote *h* of Table 5. [q] E. F. Epstein, I. Bernal, and H. Köpf, *J. Organomet. Chem.*, 1971, **26**, 229. [r] A. Kutoglu, *Z. Anorg. Allg. Chem.*, 1972, **390**, 195. [s] A. C. Villa, A. G. Manfredotti, and C. Guastini, *Acta Crystallogr., Sect. B*, 1976, **32**, 909. [t] A. Kutoglu, *Acta Crystallogr., Sect. B*, 1973, **29**, 2891. [u] D. H. Hoffmann, N. D. Chester, and R. C. Fay, *Organometallics*, 1983, **2**, 48.

$$E(M-S) = E(M-Cl) + \Delta H_f^{\circ}(SR^*,g) - \Delta H_f^{\circ}(Cl,g) - (\Delta H_f^{\circ}\{[M(\eta-C_5H_5)_2(SR)_2],g\} - \Delta H_f^{\circ}\{[M(\eta-C_5H_5)_2Cl_2],g\})/2 + (E_{R_3} - E_{R_1})/2 \quad (3)$$

$$\bar{D}(M-S) = E(M-Cl) + \Delta H_f^{\circ}(SR,g) - \Delta H_f^{\circ}(Cl,g) - (\Delta H_f^{\circ}\{[M(\eta-C_5H_5)_2(SR)_2],g\} - \Delta H_f^{\circ}\{[M(\eta-C_5H_5)_2Cl_2],g\})/2 + E_{R_3}/2 \quad (4)$$

$\Delta H_f^{\circ}(SR,g)$ are replaced by $\Delta H_f^{\circ}(S_2C_6H_3CH_3^*,g)/2$ and $\Delta H_f^{\circ}(S_2C_6H_3CH_3,g)/2$ respectively. Here $E(M-Cl)$ is the bond-enthalpy term in the dichloride complex, taken as 303.8 ± 7.1 (M = Mo), 347.3 ± 0.8 (M = W), and 430.5 ± 1.3 kJ mol^{-1} (M = Ti).[15,23] The superscript star indicates a non-reorganized fragment, and E_{R_1} and E_{R_3} represent the reorganization enthalpies of the moieties $M(\eta-C_5H_5)_2$ from the complexes $[M(\eta-C_5H_5)_2(SR)_2]$ and $[M(\eta-C_5H_5)_2Cl_2]$, respectively.

The molecular structures of the thiols involved in the present study are not available. Therefore the enthalpies of formation of SR* cannot be computed.[25] However, if it is assumed that these fragments have identical structures in RSH and in $[M(\eta-C_5H_5)(SR)_2]$, $\Delta H_f^{\circ}(SR^*)$ can be obtained[23,24] by taking the Laidler term $E(S-H) \approx 360.3 \pm 8$ kJ mol^{-1}.[18] This assumption was also applied in the case of $S_2C_6H_3CH_3^*$. It may be noted that in several similar complexes containing a benzene ring (see Table 6 and also ref. 26) the carbon–carbon distances in the ring are quite constant and close to the same values in the benzene molecule.[27] Carbon–sulphur bond lengths are also approximately constant in those complexes. All this suggests that the error induced by the previous assumption will not have a dramatic effect on the value of E(Ti–S), the same being probably true in the case of the remaining thiolato-complexes. It is clear, however, that a more detailed analysis, based on molecular-orbital calculations, will be possible only when the molecular structures of the complexes and ligands in this study become available.

The reorganization enthalpies E_{R_1} and E_{R_3} can be evaluated if the structure of the complexes and, in particular, the values of the angles $\eta-C_5H_5-M-\eta-C_5H_5$ are known. Extended-Hückel molecular-orbital calculations yield curves which represent the change in total energy of the fragments $M(\eta-C_5H_5)_2$ (M = Mo or W) as a function of those angles (θ).† An equivalent curve for $Ti(\eta-C_5H_5)_2$ is reported elsewhere.[25] As mentioned before, the most stable geometry is achieved with θ = 140° for a metal having two d electrons (Ti) and with θ = 180° for metals with four d electrons (Mo or W).‡ This behaviour has been discussed by Lauher and Hoffmann.[22]

The angle θ and the metal–ring bond distances are fairly constant for each metal and so the term $E_{R_3} - E_{R_1}$ is usually very small, as evidenced in Table 5. Also included are θ values which were estimated by analysing the structural data for similar complexes (Table 6).

Although the reorganization enthalpies in equation (3) represent a minor correction for metal–sulphur bond-enthalpy terms, that is not so for mean bond-dissociation enthalpies, obtained through equation (4). The contribution of $E_{R_3}/2$ to the values of $\bar{D}$ is significant, particularly for the molybdenum and tungsten complexes (Table 5). This correction is, however, less reliable than that for bond-enthalpy terms since it involves an absolute value of a reorganization enthalpy.

The enthalpies of formation of SR radicals were calculated from $D(RS-H) = 375.7 \pm 8.4$ kJ mol^{-1} (R = alkyl)[29,30] and

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† The energy of the fragments $M(\eta-C_5H_5)_2$ depends mainly on the angle θ and less on the $M-\eta-C_5H_5$ distances. Besides, for each metal, these distances are fairly constant (see Table 6).

‡ There is recent experimental evidence for this conclusion in the case of $Mo(\eta-C_5H_5)_2$.[28]

Table 7. Metal–sulphur bond-enthalpy values (kJ mol^{-1})

Complex	E(M–S) [a]	$\bar{D}$(M–S) [b]
$[Mo(\eta\text{-}C_5H_5)_2(SC_3H_7\text{-}n)_2]$	212 ± 12	228 ± 13
	210	189
$[Mo(\eta\text{-}C_5H_5)_2(SC_3H_7\text{-}i)_2]$	178 ± 12	193 ± 13
	176	154
$[Mo(\eta\text{-}C_5H_5)_2(SC_4H_9\text{-}n)_2]$	186 ± 12	202 ± 13
	184	163
$[Mo(\eta\text{-}C_5H_5)_2(SC_4H_9\text{-}t)_2]$	168 ± 12	184 ± 12
	169	143
$[Mo(\eta\text{-}C_5H_5)_2(SC_6H_5)_2]$	237 ± 12	223 ± 12
	235	184
$[W(\eta\text{-}C_5H_5)_2(SC_3H_7\text{-}n)_2]$	258 ± 10	274 ± 10
	253	225
$[Ti(\eta\text{-}C_5H_5)_2(SC_3H_7\text{-}n)_2]$	324 ± 10	339 ± 10
	323	335
$[Ti(\eta\text{-}C_5H_5)_2(SC_6H_5)_2]$	342 ± 10	328 ± 10
	340	325
$[Ti(\eta\text{-}C_5H_5)_2(S_2C_6H_3CH_3)]$	317 ± 10	
	315	

[a] Values in the second row for each complex include $(E_{R_3} - E_{R_1})/2$.
[b] Values in the second row for each complex include $E_{R_3}/2$.

from $D(C_6H_5S\text{–}H) = 345.8 \pm 8.4$ kJ mol^{-1}.[30,31] Each of these values represents the average of two slightly different bond-dissociation enthalpies reported in the literature. For toluene-3,4-dithiol we did not try to estimate $D[CH_3C_6H_3(SH)S\text{–}H)] + D[CH_3C_6H_3(S)S\text{–}H]$ and so no value for $\bar{D}$(Ti–S) in the respective complex is included in Table 7.

It is possible to draw several conclusions from the data in Table 7. In S-alkyl molybdenum complexes the bond-enthalpy terms decrease with increasing bulkiness of the ligands,[3] this being particularly noticeable for the t-butyl complex. In this case the S–Mo–S angle (Table 6) is markedly below the range observed for similar molecules. This may be due to repulsions between the cyclopentadienyl rings and the $S(t\text{-}C_4H_9)$ ligands, while the bulky t-butyl groups pull the sulphur atom away from the metal, resulting in a longer Mo–S bond length and a lower E(Mo–S). However, it is also possible that the value quoted in Table 7 represents a low limit since the difference $E(Mo\text{–}SC_3H_7\text{-}n) - E(Mo\text{–}SC_4H_9\text{-}t) \approx 44$ kJ mol^{-1} seems too high to account for those steric factors. A reinvestigation of the thermochemistry of the complexes $[Mo(\eta\text{-}C_5H_5)_2(SR)_2]$ ($R = i\text{-}C_4H_9$, $n\text{-}C_4H_9$, or $t\text{-}C_4H_9$) is presently being done.

Although the differences $E(Mo\text{–}SC_6H_5) - E(Mo\text{–}SC_3H_7\text{-}n) \sim 25$ kJ mol^{-1} and $E(Ti\text{–}SC_6H_5) - E(Ti\text{–}SC_3H_7\text{-}n) \sim 17$ kJ mol^{-1} are similar, which is a usual feature when bond enthalpies involving different metals and the same ligands are compared[32,33] (see also Figure), the fact is that $E(M\text{–}SC_6H_5) > E(M\text{–}SC_3H_7\text{-}n)$ is not in agreement with the corresponding bond lengths (see Table 6 for M = Ti). Assuming that the thermochemical and the structural data are correct, steric and electronic effects due to the presence of the phenyl rings may be the origin of this contradiction. It is also interesting that a similar pattern emerges from the bond-enthalpy data for $[Ti(\eta\text{-}C_5H_5)_2(OR)_2]$ complexes ($OR = O_2CC_6H_5, O_2CCF_3, O_2CCl_3$, or OC_6H_5): the phenoxy-complex also shows the largest E(Ti–O).[12,23]

The low value of E(Ti–S) in the toluene-3,4-dithiolate complex is consistent with the structural data in Table 6 for five-membered chelate molecules. In these cases the S–Ti–S angle falls in the same range (78—83°) found for d^2 systems with unidentate ligands, indicating that for these compounds the angle S–M–S is independent of the electron occupancy. The slightly longer titanium–sulphur bond length should therefore indicate, as it does, a decrease in E(Ti–S).

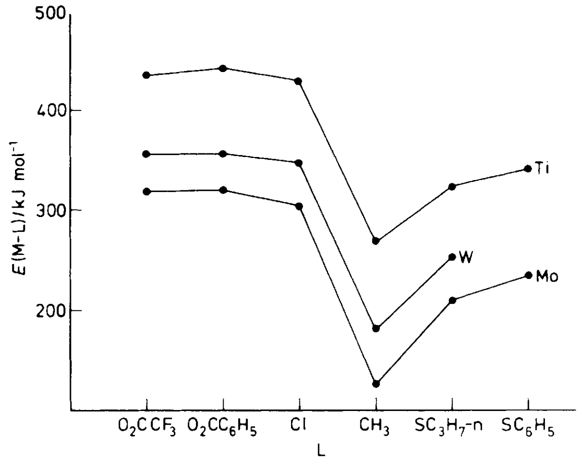

Figure. Variation of E(M–L) (M = Mo, W, or Ti) as a function of L

The set of bond-enthalpy values in Table 7 looks, in general, fairly consistent, particularly for those used in the Figure, where E(M–S) values are compared with other bond-enthalpy terms previously determined.[23,34]

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References

1 C. G. Kuehen and S. S. Isied, *Prog. Inorg. Chem.*, 1980, **27**, 153.
3 P. M. Burkinshaw and C. T. Mortimer, *Coord. Chem. Rev.*, 1983, **48**, 101.
3 A. R. Dias, J. A. Martinho Simões, and C. Teixeira, *J. Chem. Soc., Dalton Trans.*, 1981, 1178.
4 J. C. G. Calado, A. R. Dias, J. A. Martinho Simões, and M. A. V. Ribeiro da Silva, *Rev. Port. Quim.*, 1979, **21**, 129.
5 M. L. H. Green and W. E. Lindsell, *J. Chem. Soc. A*, 1967, 1455.
6 S. A. Giddings, *Inorg. Chem.*, 1967, **6**, 849.
7 . H. Köpf and M. Schmidt, *Z. Anorg. Allg. Chem.*, 1965, **340**, 139.
8 A. R. Dias and M. H. Garcia, *Rev. Port. Quim.*, 1979, **21**, 145.
9 M. G. Harris, M. L. H. Green, and W. E. Lindsell, *J. Chem. Soc., A*, 1969, 1453.
10 H. Köpf and M. Schmidt, *J. Organomet. Chem.*, 1965, **4**, 426.
11 D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, 'Purification of Laboratory Chemicals,' 2nd edn., Pergamon Press, Oxford, 1980.
12 J. C. G. Calado, A. R. Dias, M. S. Salema, and J. A. Martinho Simões, *J. Chem. Soc., Dalton Trans.*, 1981, 1174.
13 J. D. Cox, CATCH Tables, Halogen Compounds, School of Molecular Sciences, University of Sussex, Brighton, 1972.
14 R. Gomes da Costa, A. R. Dias, and J. A. Martinho Simões, unpublished work.
15 V. I. Tel'noi and I. B. Rabinovich, *Usp. Khim.*, 1977, **46**, 1337.
16 J. B. Pedley and J. Rylance, 'Sussex-N.P.L. Computer Analysed Thermochemical Data: Organic and Organometallic Compounds,' University of Sussex, Brighton, 1977.
17 CODATA, Recommended Key Values for Thermodynamics; *J. Chem. Thermodyn.*, 1978, **10**, 903.
18 J. D. Cox and G. Pilcher, 'Thermochemistry of Organic and Organometallic Compounds,' Academic Press, London and New York, 1970.
19 R. Hoffmann, *J. Chem. Phys.*, 1963, **39**, 1397.
20 R. Hoffmann and W. N. Lipscomb, *J. Chem. Phys.*, 1962, **36**, 2179.
21 J. H. Ammeter, H-B. Bürgi, J. C. Thibeault, and R. Hoffmann, *J. Am. Chem. Soc.*, 1978, **100**, 3686.

22 J. W. Lauher and R. Hoffmann, *J. Am. Chem. Soc.*, 1976, **98**, 1729.
23 A. R. Dias, M. S. Salema, and J. A. Martinho Simões, *J. Organomet. Chem.*, 1981, **222**, 69.
24 A. R. Dias and J. A. Martinho Simões, *Rev. Port. Quim.*, 1982, **24**, 191.
25 M. J. Calhorda, R. Gomes da Costa, A. R. Dias, and J. A. Martinho Simões, *J. Chem. Soc., Dalton Trans.*, 1982, 2327.
26 K. Prout and G. V. Rees, *Acta Crystallogr., Sect. B*, 1974, **30**, 2717.
27 L. E. Sutton (ed.), Tables of Interatomic Distances and Configuration in Molecules and Ions, *Special Publ.*, The Chemical Society, London, 1965, no. 18.
28 J. Chetwind-Talbot, P. Grebenik, and R. N. Perutz, *Inorg. Chem.*, 1982, **21**, 3647.
29 B. K. Janousek, K. J. Reed, and J. I. Brauman, *J. Am. Chem. Soc.*, 1980, **102**, 3125.
30 D. F. McMillen and D. M. Golden, *Annu. Rev. Phys. Chem.*, 1982, **33**, 493.
31 S. W. Benson, *Chem. Rev.*, 1978, **78**, 23.
32 J. A. Connor, *Top. Curr. Chem.*, 1977, **71**, 71.
33 G. Pilcher and H. A. Skinner, 'The Chemistry of the Metal–Carbon Bond,' eds. F. R. Hartley and S. Patai, Wiley, New York, 1982.
34 M. S. Salema, Tese de Doutoramento, Instituto Superior Técnico, Lisbon, 1984.

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