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Energetics of transition-metal-sulfur and -oxygen bonds in M(.eta.5-C5H5)2L2 complexes (M = Ti, Mo, W). Molecular structure of Mo(.eta.5-C5H5)2(SO4)

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in which the intact ligand skeleton has been broken down.[23] For the transformation of carbodiimides RN=C=NR into isonitrile and dehydroguanidinium complexes ligand dimerization has been found to be the key step, thus excluding the existence of a free nitrene intermediate.[24] Relatedly it is of interest that the stabilization of an imido ligand has been achieved in II. The simultaneous presence of the imido and the isocyanide ligand may be indicative of the elusive carbodiimide-bridged molybdenum dimer, which appears to be too labile under these stereochemical constraints. This point will be the subject of further investigations.

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Supplementary Material Available: Tables of full bond lengths and bond angles, least-squares planes and dihedral angles (Table VII), and structure factors for II and a stereoscopic view (Figure 2) of the unit cell packing (22 pages). Ordering information is given on any current masthead page.

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Energetics of Transition-Metal–Sulfur and –Oxygen Bonds in $M(\eta^5\text{-}C_5H_5)_2L_2$ Complexes (M = Ti, Mo, W). Molecular Structure of $Mo(\eta^5\text{-}C_5H_5)_2(SO_4)$

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The energetics of transition-metal–sulfur bonds in bis(η^5-cyclopentadienyl)bis(thiolato)metal complexes, $M(\eta^5\text{-}C_5H_5)_2(SR)_2$ (M = Mo, W, Ti), has been reinvestigated and compared with reevaluated metal–oxygen data on the same type of molecules. Bond enthalpy terms, E(Mo–SR) (R = $n\text{-}C_3H_7$, $i\text{-}C_3H_7$, $n\text{-}C_4H_9$, $t\text{-}C_4H_9$, and $n\text{-}C_{10}H_{21}$), which were obtained by using calorimetric values for the standard enthalpies of formation of the complexes, confirm a strong steric effect in the case of $t\text{-}C_4H_9S$ and indicate an increase in metal–sulfur bond strength with the length of the n-alkyl chain, $E(\text{Mo–SC}_{10}H_{21}\text{-}n) \gtrsim E(\text{Mo–SC}_4H_9\text{-}n) \gtrsim E(\text{Mo–SC}_3H_7\text{-}n)$. The thermochemistry of the complex $Mo(\eta^5\text{-}C_5H_5)_2(SO_4)$ was also studied, leading to $E(\text{Mo–O}) \approx 338 \pm 13$ kJ mol^{-1}. This value excludes noticeable strain on the metallacycle, since it compares with other molybdenum–oxygen bond enthalpy terms. The molecular structure of the sulfate complex, which was also determined in the present study, is compatible with the Mo–O bond enthalpy. The structural data were obtained by X-ray diffraction and show bidentate coordination of the sulfate ligand, with O–Mo–O = 66.1 (2)° and Mo–O = 211.3 (3) pm. The angle O–S–O = 98.3 (2)° (coordinated oxygen) shows a small distortion of this moiety, and extended Hückel calculations show that the rigidity of the SO_4 geometry is responsible for the small O–Mo–O angle. The sulfate complex crystallizes in the orthorhombic space group *Cmcm* with four molecules per unit cell; the lattice constants are a = 935.6 (5) pm, b = 854.7 (2) pm, and c = 1297.9 (4) pm.

Introduction

Early studies on the chemistry of transition-metal molecules containing metal–sulfur bonds were fostered by the growing interest in heterogeneous catalytic problems. This can be illustrated by studies involving metal sulfides, which are used as catalysts in many industrial processes.[1] Among these, sulfur removal from petroleum-based feedstocks through hydrodesulfurization (HDS) reactions[2] is of particular importance, not only to minimize environmental problems but also because sulfur inhibits the activity of many catalysts.[3-5] This led to detailed investigations about the HDS reactions mechanisms, which often include the formation or the cleavage of transition-metal–sulfur bonds,[2,6-9] and also to the study of "poisoning" processes, usually associated with the formation of sulfur products at the catalyst surface.[4,5,10]

Several recent studies on transition-metal complexes containing metal–sulfur bonds explore the general advantages[11] of homogeneous over heterogeneous catalysis.

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For example, it has been shown that homogeneous catalysts are less susceptible to poisoning caused either by sulfur compounds or by other chemicals.[12]

The thermodynamics of the relevant elementary steps of both heterogeneous and homogeneous pathways are crucial for their understanding.[13] Despite being virtually impossible to obtain experimental values of enthalpy changes for most of them, these data can be estimated if one has suitable information on the nature and energetics of metal–sulfur bonds.

Thermochemical studies on $M(Cp)_2L_2$ complexes (M = transition metal; Cp = η^5-C_5H_5; L = H, CH_3, C_6H_5, OR, SR, etc.) have provided useful data to discuss *general* trends of the energetics of transition-metal–ligand bonds.[14,15] Despite the fair amount of metal–ligand bond enthalpies presently available, involving either coordinately saturated complexes or organometallic fragments and ions,[15] there are still many gaps before we reach a satisfactory knowledge in this area.

The well-known difficulties of thermochemical studies aiming to derive metal–ligand bond enthalpies[15] often imply the acceptance of data whose accuracy is not comparable with that usually obtained for organic substances, but which are satisfactory as first approximations. Only from evaluations of new values, providing comparisons and yielding trends, can one ascertain the reliability of those data.

When the systematics of Mo–SR bond enthalpies in $Mo(Cp)_2(SR)_2$ complexes (R = n-C_3H_7, i-C_3H_7, n-C_4H_9, t-C_4H_9) were discussed in a previous paper,[14e] a point was raised about the possibility that the obtained values for E(Mo–SC_3H_7-i), E(Mo–SC_4H_9-n), and E(Mo–SC_4H_9-t) were too low compared with E(Mo–SC_3H_7-n), even when considering the existence of strong steric factors, particularly in the cases of i-C_3H_7S and t-C_4H_9S. This led us to reinvestigate the thermochemistry of these complexes and also to study a few other selected systems in order to improve the present scanty information about the energetics of this type of bond.[16,17] A structural study of the complex $Mo(Cp)_2(SO_4)$, which provides complementary data for discussion of the thermochemical values, is also reported in this paper.

Experimental Section

Calorimetry. The reaction and solution enthalpies were measured in the reaction–solution calorimeter previously described.[18] There was no need to make the measurements under nitrogen since all the complexes involved are fairly air-stable.

Table I. Composition of the Reaction Solutions

reactn	ligand	$HCl(aq)^a$/ mol dm^{-3} $H_2SO_4(aq)$/ mol dm^{-3}	$v/v^{b,c}$	designatn
1	i-C_3H_7SH	8.3	1:3	A
1	t-C_4H_9SH	8.3	1:3	A
1	t-C_4H_9SH	8.3	1:1	B
2	t-$C_4H_9SH^d$	*6.43*	*1:3*	C
1	n-C_4H_9SH	10.0	1:4	D
1	n-$C_{10}H_{21}SH^d$	8.3		E
2	n-$C_{10}H_{21}SH^d$	*6.43*		F
3	C_6H_5COOH	*6.43*	*1:3*	C

[a] Values in italics refer to H_2SO_4 solutions. [b] Volumetric ratio [HCl(aq)/acetone]. [c] Volumetric ratio [H_2SO_4(aq)/Me_2SO] in italics. [d] The thiol is insoluble in the reaction medium.

Table II. Crystallographic Data and Enraf-Nonius CAD-4 Data Collection Parameters

formula	$C_{40}H_{40}O_{16}S_4Mo_4$
crystallographic system	orthorhombic
space group	*Cmcm*
M_r	322.19
a, pm	935.6 (5)
b, pm	854.7 (2)
c, pm	1297.9 (4)
V, pm^3	1037.9×10^6
Z	4
d_{calcd}, g/cm^3	2.06
radiatn	Mo Kα (λ = 71.07 pm)
μ(Mo Kα), cm^{-1}	13.13
scan type	ω–2θ
scan width ($\Delta\omega$), deg	$0.85 + 0.35 \tan \theta$
max counting time, s	60
collectn range	$\pm h, +k, +l$; $3.0 < 2\theta < 50.0$
no. of data collected	1030
no. of unique data	513
no. of data $F > 3\sigma(F)$	473
decay during collectn	None
no. of variables	75
largest shift/error value on final cycle	0.45
largest peak in final difference Fourier, e/pm^3	0.5×10^{-6}
R^a	0.0251
$R_w{}^b$	0.0356

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

Compounds. The complexes were prepared and purified as described in the literature.[19] The reaction solutions were prepared from B.D.H. AnalaR or Merck p.a. hydrochloric acid, Merck p.a. sulfuric acid, Merck p.a. dimethyl sulfoxide, and Merck p.a. acetone, which were used without further treatment. B.D.H. AnalaR benzoic acid was resublimed before use. Compounds RSH(Fluka) were dried over calcium oxide (R = n-C_4H_9 and t-C_4H_9) or over calcium dichloride (R = i-C_3H_7 and n-$C_{10}H_{21}$) and distilled under dry nitrogen.

Reactions. Thermochemical measurements on reaction 1, 2, or 3 (see also Table I) were used to derive the standard enthalpies of formation of the complexes studied. The reaction media were

$$Mo(Cp)_2(SR)_2(c) + 2HCl(soln) \rightarrow Mo(Cp)_2Cl_2(soln) + 2RSH(soln) \quad (1)$$

$$Mo(Cp)_2(SR)_2(c) + H_2SO_4(soln) \rightarrow Mo(Cp)_2(SO_4)(soln) + 2RSH(soln) \quad (2)$$

$$Mo(Cp)_2(O_2CC_6H_5)_2(c) + H_2SO_4(soln) \rightarrow Mo(Cp)_2(SO_4)(soln) + 2C_6H_5COOH(soln) \quad (3)$$

selected so that a rapid and complete reaction for each complex together with a maximum solubilization of the respective thiol could be achieved. The errors caused by an incomplete solubi-

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Table III. Thermochemical Results (kJ mol^{-1})

complex	reactn mixture	ΔH_r	ΔH_{d1}	ΔH_{d2}	ΔH_{d3}	ΔH_{d4}
$Mo(Cp)_2(SC_3H_7\text{-}i)_2$	A	47.7 ± 2.0	1.1 ± 3.3	3.3 ± 1.1	−17.56 ± 0.27	−2.17 ± 0.06
$Mo(Cp)_2(SC_4H_9\text{-}t)_2$	A	25.7 ± 4.4	1.1 ± 3.3	5.60 ± 0.29	−17.56 ± 0.27	−2.17 ± 0.06
$Mo(Cp)_2(SC_4H_9\text{-}t)_2$	B	30.1 ± 2.6	2.2 ± 1.1[a]	11.6 ± 2.0	−5.65 ± 0.28[a]	−1.31 ± 0.03
$Mo(Cp)_2(SC_4H_9\text{-}t)_2$	C	35.2 ± 3.0	5.4 ± 1.6	8.4 ± 1.7	−43.71 ± 0.85	−3.94 ± 0.05
$Mo(Cp)_2(SC_4H_9\text{-}n)_2$	D	10.3 ± 3.0	−16.1 ± 1.7	−18.68 ± 0.91	−18.48 ± 0.51[a]	−3.66 ± 0.15
$Mo(Cp)_2(SC_{10}H_{21}\text{-}n)_2$	E	15.40 ± 0.60	12.9 ± 1.1[b]	−1 ± 1		−1.93 ± 0.04
$Mo(Cp)_2(SC_{10}H_{21}\text{-}n)_2$	F	17.7 ± 3.1	1.6 ± 2.6	−0.80 ± 0.57		−2.45 ± 0.03
$Mo(Cp)_2(O_2CC_6H_5)_2$	C	7.7 ± 1.2	5.4 ± 1.6	13.75 ± 0.21	−43.71 ± 0.85	−3.94 ± 0.05

[a] From ref 20. [b] Calado, J. C. G.; Dias, A. R.; Martinho Simões, J. A.; Ribeiro da Silva, M. A. V. *J. Chem. Soc., Chem. Commun.* **1978**, 737.

lization of the thiols are discussed in the Results. The disadvantages of using mixtures of hydrochloric acid and acetone have been reported elsewhere.[20] The products of reactions 1, 2, and 3 were confirmed by IR spectroscopic analysis. All reaction and solution enthalpies presented are mean values of five independent experiments at 298 K. The uncertainties are twice the standard deviation of the mean in each case.

Auxiliary Data. Standard enthalpies of formation, vaporization and sublimation at 298 K, which were used in evaluating the thermochemical results, were quoted from data compilations or from previous papers[20-26] and are collected in Table X. Auxiliary data for recalculating early thermochemical values for sulfur complexes are listed elsewhere.[14e]

X-ray Data Collection, Structure Determination, and Refinement. Green crystals of $Mo(Cp)_2(SO_4)$ were obtained through the method described by Green, Lynch, and Swanwick[19] with slight modifications.[27] Cell dimensions were obtained by least-squares refinement of setting angles for 25 automatically centered reflections. Intensity data were collected at room temperature on an Enraf-Nonius CAD-4 automated diffractometer (with graphite-monochromatized molybdenum radiation) to $2\theta = 50°$ by using the ω–2θ method and corrected for absorption empirically[28] (minimum and maximum transmission factors of 0.828 and 0.999, respectively). The pertinent crystallographic parameters are listed in Table II. All calculations were done by using the SHELX system of programs,[29] and, for the drawing of illustrations, the program SNOOPI[30] was used. Atomic scattering factors and anomalous scattering terms were taken from the literature.[31]

The structure was solved by a combination of Patterson and Fourier methods and refined by least-squares. The systematic absences observed in the complete set of data were consistent with the space groups *Cmcm*, *Cmc*2$_1$, and *Ama*2. The calculated density indicated a Z value of 4, which in all three possibilities requires a molecule with internal symmetry. Initially, attempts were made to refine the structure in space groups *Cmc*2$_1$ and *Ama*2. For the former, in which the mirror plane coincides with the Mo, S, and terminal O atoms, the best solution ($R = 0.0320$) was obtained with a mutually staggered arrangement of the two Cp units, each of which were bisected by the *m* plane. For the *Ama*2 solution, in which the mirror plane coincides with the Mo, S, and Mo-bonded O atoms, the best solution ($R = 0.0322$) was obtained with mutually eclipsed Cp groups, related by the mirror plane. In each case, however, the expected symmetry for the SO_4 group in which the $Mo–O_{bridge}$, $O_{bridge}–S$, and $So–O_{terminal}$ bond lengths were internally equivalent was not found. Accordingly, we examined the structure in the space group *Cmcm*, in which the MoO_2SO_2 unit has *mm* symmetry and the Cp sites were represented by 50% occupation of the two orientations, these being a composite of the indications given by the two previous refinements, and at the refinement level equivalent to those quoted above, R was 0.029. Accordingly, we felt that the best model for this structure is the last one, although examination of the U_{ij} parameters thus obtained indicates that the disorder may be slightly more complicated than this model assumes. For the final stages of refinement in *Cmcm*, it was found more convenient to refine with the Cp C–C distances constrained to be equivalent, at 139.0 pm. No hydrogen atoms were included in the final model, and a weighting scheme of $w = 1.4044/[\sigma^2|F_o| + 0.000615F_o^2]$ was found to give acceptable agreement analysis. The reflection 002, which was thought to be suffering from extinction, was removed from the data.

Results

Thermochemistry. The thermochemical results are summarized in Table III. ΔH_r represents the enthalpy of reaction 1, 2, or 3; ΔH_{d1} refers to the enthalpy of solution of the dichloride complex in solution A, B, D, or E or to the enthalpy of solution of the sulfate complex in solution C or F (small residues of the dichloride or the sulfate complex were observed when measuring ΔH_{d1} but the resulting errors must be within the uncertainty intervals); ΔH_{d2} represents the enthalpy of solution of the ligand in solutions containing a stoichiometric amount of the dichloride or sulfate complex; ΔH_{d3} was obtained by breaking ampules containing a stoichiometric amount of aqueous hydrochloric or sulfuric acid solutions in the respective reaction medium (solutions A-D); finally, ΔH_{d4}, which gives the enthalpy change associated with the dilution of the acid solution, was determined by breaking ampules of stoichiometric amounts of distilled water in solutions A–F. ΔH_{d3} values were used to estimate[20] the enthalpies of formation of hydrochloric acid in solutions A, B, and D and of sulfuric acid in solution C. For solutions B and D the values are listed in Table X and $\Delta H_f°(\text{HCl, soln A}) = -174.38 \pm 0.27$ kJ mol^{-1} and $\Delta H_f°(\text{H}_2\text{SO}_4\text{, soln C}) = -917.0 \pm 0.9$ kJ mol^{-1}.

The standard enthalpies of formation of the crystalline and gaseous complexes are collected in Table IV together with the estimated enthalpies of sublimation at 298 K. Table IV also includes values corrected for acid dilution (ΔH_{d4}) for similar complexes which have been reported

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Table IV. Enthalpies of Formation, $\Delta H_f°(c)$ and $\Delta H_f°(g)$ (kJ mol^{-1})

complex	$\Delta H_f°$(c)	$\Delta H_s°$ [a]	$\Delta H_f°$(g)
$Mo(Cp)_2(SC_3H_7\text{-}i)_2$	-22.7 ± 5.3	(90 ± 10)	67.3 ± 11.3
$Mo(Cp)_2(SC_3H_7\text{-}n)_2$	-10.7 ± 5.3	(90 ± 10)	79.3 ± 11.3
$Mo(Cp)_2(SC_4H_9\text{-}t)_2$	-68.3 ± 4.3	(92 ± 10)	23.7 ± 10.9
$Mo(Cp)_2(SC_4H_9\text{-}n)_2$	-96.0 ± 5.5	(92 ± 10)	-4.0 ± 11.4
$Mo(Cp)_2(SC_{10}H_{21}\text{-}n)_2$	-361.5 ± 4.3	(105 ± 10)	-256.5 ± 10.9
$Mo(Cp)_2(SC_6H_5)_2$	282.0 ± 4.8	(95 ± 10)	377.0 ± 11.1
$Mo(Cp)_2(SO_4)$	-650.4 ± 3.4	(72 ± 10)	-578.4 ± 10.6
$W(Cp)_2(SC_3H_7\text{-}n)_2$	9.0 ± 5.6	(94 ± 10)	103.0 ± 11.4
$Ti(Cp)_2(SC_3H_7\text{-}n)_2$	-267.5 ± 9.7	(108 ± 8)	-159.5 ± 12.5
$Ti(Cp)_2(SC_6H_5)_2$	34.0 ± 7.9	(113 ± 10)	147.0 ± 12.7
$Ti(Cp)_2(S_2C_6H_3CH_3)$	-30.3 ± 9.5	(110 ± 10)	79.7 ± 13.8

[a] Estimated values.

Table V. Final Fractional Atomic Coordinates (×10^4) for $Mo(\eta^5\text{-}C_5H_5)_2(SO_4)$

	x	*y*	*z*
Mo	0	7883 (1)	2500
S	0	4644 (2)	2500
O(3)	1233 (3)	5811 (4)	2500
O(1)	0	3730 (4)	3433 (4)
C(11)	0	9884 (21)	3655 (16)
C(12)	1268 (13)	9063 (13)	3795 (13)
C(13)	765 (12)	7679 (11)	4225 (8)
C(111)	0	7669 (15)	4186 (12)
C(121)	1213 (10)	8542 (11)	3959 (10)
C(131)	751 (15)	9944 (11)	3531 (9)

[a] All carbon atom sites are half-occupied.

earlier. For complexes $M(Cp)_2(SC_6H_5)_2$ (M = Mo, Ti)[14e] $\Delta H_{d4} = -3.12 \pm 0.04$ [HCl(aq) (10.0 mol dm^{-3})] or -3.8 ± 0.1 kJ mol^{-1} [HCl(aq) (10.4 mol dm^{-3})/acetone (1:4)], respectively. The value for $\Delta H_f°[Mo(Cp)_2(SC_4H_9\text{-}t)_2(c)]$ in Table IV is the average between the results obtained with reaction media A (-65.5 ± 6.3 kJ mol^{-1}) and B (-71.1 ± 5.8 kJ mol^{-1}). As expected (see Introduction) these values differ from the ones reported in a previous work.[14a] This may be due to the small solubility of $t\text{-}C_4H_9SH$ in a neat aqueous hydrochloric acid solution. When this happens, the reliability of ΔH_r and ΔH_{d2} will depend on the diffusion rate of the thiol through the solution. If the process is too fast (as it is for $n\text{-}C_4H_9SH$, $t\text{-}C_4H_9SH$, and $i\text{-}C_3H_7SH$ in the absence of a suitable organic solvent), the thiol rapidly reaches the surface of the reaction medium and may evaporate and interact with the brass lid of the calorimeter, undergoing side reactions. However, if the process is slow (cases of $n\text{-}C_{10}H_{21}SH$ and C_6H_5SH), the thiol will remain dispersed in the medium and no side effects are likely to occur. The results obtained for the *tert*-butyl complex in solutions A and B support the above discussion and led us to repeat the experiments with $Mo(Cp)_2(SR)_2$ (R = $i\text{-}C_3H_7$, $n\text{-}C_4H_9$) by using a mixture of aqueous hydrochloric acid and acetone (Tables I and III). The enthalpy of formation of $Mo(Cp)_2(SO_4)$ quoted in Table IV is the average between the values obtained from reaction 2 with R = $n\text{-}C_{10}H_{21}$ (-649.9 ± 5.5 kJ mol^{-1}) and reaction 3 (-650.9 ± 3.9 kJ mol^{-1}). The agreement between these two independent results also supports the previous discussion.

Structural Results. Final atomic positional parameters are listed in Table V. Tables of anisotropic thermal parameters and structure factors are given in the supplementary material.

Molecules of $Mo(Cp)_2(SO_4)$ have the bent metallocene structure in which the molybdenum atom is attached to two oxygen atoms of the sulfate ligand and to two Cp groups in a distorted tetrahedral coordination (Figure 1). The choice of space group discussed above gives the molecule *mm* (C_{2v}) symmetry with one unique distance for each $Mo\text{-}O_{bridging}$, $O_{bridging}\text{-}S$, and $S\text{-}O_{terminal}$ distance. Interatomic distances and angles are given in Table VI.

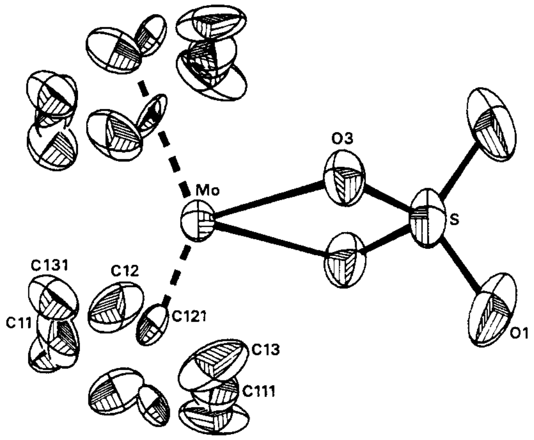

Figure 1. Molecular structure of $Mo(Cp)_2(SO_4)$ with 30% probability thermal elipsoids with *mm* symmetry. For sake of clarity the bonds in the two half occupied descriptions of the Cp rings have been omitted.

Table VI. Interatomic Distances (pm) and Angles (deg)

	Bond Distances		
Mo-O(3)	211.3 (3)	S-O(3)	152.5 (3)
		S-O(1)	144.1 (5)
Mo-C(11)	227.4 (20)	Mo-C(111)	219.6 (15)
Mo-C(12)	229.1 (17)	Mo-C(121)	227.8 (14)
Mo-C(13)	235.7 (10)	Mo-C(131)	232.1 (12)
mean Mo-C	228.6		
	Bond Angles		
O(3)-Mo-O(3)[a]	66.1 (2)	O(3)-S-O(3)[a]	98.3 (2)
Mo-O(3)-S	97.8 (2)	O(3)-S-O(1)	110.8 (1)
		O(1)-S-O(1)[b]	114.4 (2)

[a] This atom is at $-x, y, z$ relative to O(3). [b] This atom is at $x, y, 0.5 - z$ relative to O(1).

Discussion

Molecular Structure and Calculations. The sulfate ligand is coordinated in a bidentate manner to the Mo atom. Not unexpectedly the $O_{bridging}\text{-}S$ distance of 152.5 (3) pm is longer than the $S\text{-}O_{terminal}$ distance of 144.1 (5) pm. The sulfate ligand has a distorted tetrahedron geometry with O-S-O bond angles of 98.3 (2)° between the bridging oxygens, 114.4 (2)° between the terminal oxygens, and 110.8 (1)° at the other four positions.

As a consequence of the bidentate coordination of the sulfate ligand, the O-Mo-O angle [66.1 (2)°] is the smallest observed for a complex of this type. An example of a complex that presents a similar geometry around the Mo atom is $[(Cp)_2MoO_2PO_2Mo(Cp)_2](PF_6)$[32] with a mean

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[32] Prout, C. K.; Couldwell, M. C.; Forder, R. A. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1977, *B33*, 218.

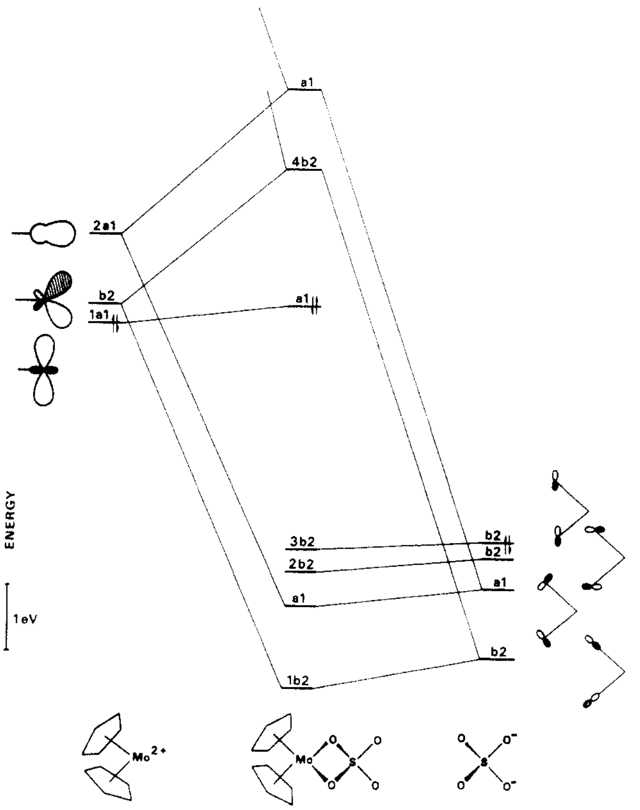


Figure 2. Molecular orbital diagram for the $Mo(Cp)_2(SO_4)$ molecule.

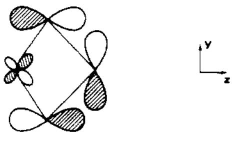
Mo–O bond length of 212.6 (3) pm and a mean O–Mo–O bond angle of 68.7 (1)°. However, this is a binuclear compound with a bridging phosphate ligand, whereas $Mo(Cp)_2(SO_4)$ is mononuclear. Further comparisons are provided by other bidentate ligand molecules such as $Mo(Cp)_2(S_2O_3)$,[33] $[Mo(Cp)_2(N_2C_3H_3C(CH_3)_2O)](PF_6)$,[34] and also some amino acid molybdenum bis(cyclopentadienyl) complexes.[35,36] In the first two cases the angles L–Mo–L′ are 72.3 (1)° and 75.4 (1)°, respectively, and in the amino acid molecules the angles ranges from 73.4 (6)° (sarcosine) to 76.2 (3)° (leucine). In the two-ligand complex $Mo(Cp)_2(O_2CC_6H_5)_2$ the O–Mo–O angle is 72.3 (2)°.[37]

The Mo–O bond length is comparable to the lengths observed in other $Mo(Cp)_2LL'$ complexes. Typical values are 202.6 (2) pm in $[Mo(Cp)_2(N_2C_3H_3C(CH_3)_2O)](PF_6)$, 210 (2) pm in the glycine and sarcosine amino acid complexes, 210.8 (4) pm in the proline complex,[36] 213.4 (4) pm in the thiosulfate complex,[33] and 210.2 (4) pm in the benzoate complex.[37]

The least-squares planes of the two disordered Cp rings are not quite coincident, but we consider this to be an artifact of the refinement process rather than a structurally significant result. Accordingly we use parameters for the average ring position in the following discussion. The molybdenum lies at 196.4 pm from the best plane of the cyclopentadienyl ring, and the angle between the ring normals is 134.1 (4)°.

An interesting feature of the structure of the sulfate complex is the relation of the O–S–O angle in the sulfate moiety with the O–Mo–O angle. In order to investigate this point we have made some theoretical calculations by using the extended Hückel method. The SO_4^{2-} ion interacts with the $Mo(Cp)_2^{2+}$ fragment frontier orbitals ($1a_1$, b_2, $2a_1$)[38] through a_1 and b_2 combinations of oxygen s and p orbitals as shown in the molecular orbital diagram (Figure 2). The $1a_1$ orbital remains approximately nonbonding.

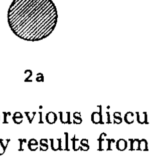
In the equilibrium geometry (see below) there is a net overlap population of 0.347 between SO_4^{2-} and $Mo(Cp)_2^{2+}$ fragments. However, a strong repulsion between the molybdenum atom and sulfur (−0.114) is also predicted. The origin of this electronic effect lies in orbitals such as $1b_2$, which is bonding either between Mo and oxygens or between oxygens and sulfur. On the other hand, there is an antibonding π-type interaction between Mo and S, as shown in **1** (cyclopentadienyl rings are not represented). An increase in the Mo···S distance may decrease this repulsive interaction, making this molecular orbital more stable.



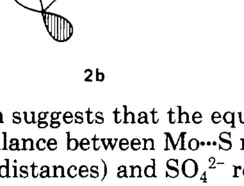
1

The previous point was explored by increasing the Mo···S distance from 276.8 pm (value in the complex) to 300 pm. The Mo–O and O–S bond lengths were kept fixed, implying limiting values of 56° and 80° for O–Mo–O and O–S–O angles, respectively. The total energy of the complex increased by 0.78 eV, the Mo–O overlap population became 0.276 (as compared with 0.255 in the initial configuration), and the Mo···S repulsive interaction decreased (overlap population −0.102). Therefore, despite a more favorable electronic interaction between SO_4^{2-} and $Mo(Cp)_2^{2+}$ fragments, this geometry has a much higher energy. If the SO_4^{2-} ion is considered separately and its geometry is changed as before, the energy increases by 1.30 eV. This indicates that the opposition of the SO_4^{2-} fragment to distortion (namely decreasing the O–S–O angle) is the controlling factor of the final geometry in the sulfate complex.

When the O–S–O angle is changed, the two oxygen atoms approach each other and begin to interact. The SO_4^{2-} molecular orbitals that could be considered nonbonding will become bonding or antibonding according to their symmetry with respect to the *xz* plane, the antibonding interaction being predominant. For instance, in the molecular orbital **2a** the energy changes by +0.85 eV when the angle goes from 98 to 80°, whereas **2b** becomes more stable by 0.38 eV. The O···O overlap population is "raised" from −0.033 to −0.101.



2a



2b

The previous discussion suggests that the equilibrium geometry results from a balance between Mo···S repulsion (which favors long Mo···S distances) and SO_4^{2-} resistance to distortion. However, one could also imagine that the Mo···S repulsion might equally well be minimized by de-

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[33] Kubas, G. J.; Ryan, R. R. *Inorg. Chem.* **1984**, *23*, 3181.

[34] Carrondo, M. A. A. F. de C. T.; Domingos, A. M. T. S. *J. Organomet. Chem.* **1983**, *253*, 53.

[35] Prout, C. K.; Critchley, S. R.; Cannillo, E.; Tazzoli, V. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *B33*, 456.

[36] Prout, C. K.; Allison, G. B.; Delbaere, L. T. J.; Gore, E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 3043.

[37] Carrondo, M. A. A. F. de C. T.; Hursthouse, M. B.; Dawes, H. M., to be submitted for publication.

[38] Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

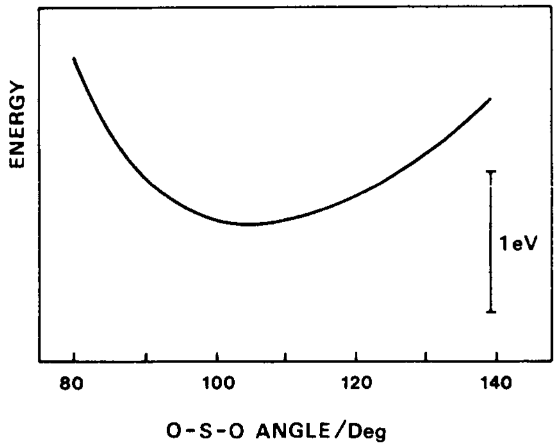

Figure 3. Energy change for the sulfate ions as a function of the $^-$O–S–O$^-$ angle.

Table VII. Energetics of Metal-Sulfur Bonds (kJ mol^{-1})

complex	E(M–S)	$\bar{D}$(M–S)
$Mo(Cp)_2(SC_3H_7\text{-}i)_2$	217 ± 12	233 ± 13
$Mo(Cp)_2(SC_3H_7\text{-}n)_2$	220 ± 12	235 ± 13
$Mo(Cp)_2(SC_4H_9\text{-}t)_2$	206 ± 9	221 ± 9
$Mo(Cp)_2(SC_4H_9\text{-}n)_2$	241 ± 12	256 ± 12
$Mo(Cp)_2(SC_{10}H_{21}\text{-}n)_2$	243 ± 12	259 ± 12
$Mo(Cp)_2(SC_6H_5)_2$	251 ± 12	237 ± 12
$W(Cp)_2(SC_3H_7\text{-}n)_2$	266 ± 10	281 ± 10
$Ti(Cp)_2(SC_3H_7\text{-}n)_2$	331 ± 10	347 ± 10
$Ti(Cp)_2(SC_6H_5)_2$	358 ± 10	344 ± 10
$Ti(Cp)_2(S_2C_6H_3CH_3)$	333 ± 10	

creasing the distance while opening the O–Mo–O and O–S–O angles. Keeping the Mo–O and O–S distances, for Mo···S = 230 pm those angles are 81 and 123°, respectively. With this geometry the Mo···S overlap population drops to −0.063 but the same happens to the Mo–O overlap population (0.179). The energy increases by ca. 1.0 eV (with a contribution of 0.12 eV from the SO_4^{2-} fragment).

In summary, the observed structure for the sulfate complex has the preferred geometry around the sulfur atom. The potential energy has a smooth variation with O–Mo–O angle, whereas the same curve for O–S–O in the fragment SO_4^{2-} (Figure 3) presents a distinct minimum at O–S–O ≈ 103°.

Thermochemistry. Bond enthalpy terms E(M–S) and E(M–O) and mean bond dissociation enthalpies $\bar{D}$(M–S) and $\bar{D}$(M–O) in cyclopentadienyl complexes are presented in Tables VII and VIII. Typical equations used for calculating these values and which may be applied to any $M(Cp)_2L_n$ complex are presented below (eq 4 and 5).[39] Here an asterisk indicates a nonreorganized fragment and ER_1 and ER_3 represent the reorganization enthalpies of the moieties $M(Cp)_2$ from the complex $M(Cp)_2L_n$ and from the "reference" molecule $M(Cp)_2Cl_2$, respectively.[14b,15,40] n = 1 or 2 for bidentate or monodentate ligands, respectively.

$$E(\text{M–L}) = E(\text{M–Cl}) + \frac{n}{2}\Delta H_f^\circ[\text{L*(g)}] - \Delta H_f^\circ[\text{Cl(g)}] - \{\Delta H_f^\circ[\text{M(Cp)}_2\text{L}_n\text{(g)}] - \Delta H_f^\circ[\text{M(Cp)}_2\text{Cl}_2\text{(g)}]\}/2 + (ER_3 - ER_1)/2 \quad (4)$$

$$\bar{D}(\text{M–L}) = E(\text{M–Cl}) + \frac{n}{2}\Delta H_f^\circ[\text{L(g)}] - \Delta H_f^\circ[\text{Cl(g)}] - \{\Delta H_f^\circ[\text{M(Cp)}_2\text{L}_n\text{(g)}] - \Delta H_f^\circ[\text{M(Cp)}_2\text{Cl}_2\text{(g)}]\}/2 + ER_3/2 \quad (5)$$

Table VIII. Energetics of Metal-Oxygen Bonds (kJ mol^{-1})

complex	E(M–O)	$\bar{D}$(M–O)
$Mo(Cp)_2(O_2CC_6H_5)_2$	327 ± 12	312 ± 10
$Mo(Cp)_2(O_2CCF_3)_2$	334 ± 12	316 ± 14
$Mo(Cp)_2(SO_4)$	338 ± 9	
$W(Cp)_2(O_2CC_6H_5)_2$	365 ± 10	349 ± 7
$W(Cp)_2(O_2CCF_3)_2$	365 ± 10	347 ± 11
$Ti(Cp)_2(OC_6H_5)_2$	462 ± 9	373 ± 11
$Ti(Cp)_2(2\text{-}CH_3C_6H_4O)_2$	454 ± 9	365 ± 11
$Ti(Cp)_2(3\text{-}CH_3C_6H_4O)_2$	430 ± 9	341 ± 11
$Ti(Cp)_2(4\text{-}CH_3C_6H_4O)_2$	457 ± 9	368 ± 11
$Ti(Cp)_2(2\text{-}ClC_6H_4O)_2$	440 ± 10	351 ± 12
$Ti(Cp)_2(O_2CC_6H_5)_2$	455 ± 9	440 ± 6
$Ti(Cp)_2(O_2CCCl_3)_2$	464 ± 9	446 ± 11
$Ti(Cp)_2(O_2CCF_3)_2$	451 ± 9	433 ± 11

E(M–Cl) are the bond enthalpy terms in the dichloride complexes and were taken as 303.8 ± 7.1 (M = Mo), 347.3 ± 0.8 (M = W), and 430.5 ± 1.3 kJ mol^{-1} (M = Ti).[15,24] These are actually the bond enthalpy terms for the metal chlorides $MoCl_6$, WCl_6, and $TiCl_4$ which are therefore transferred to the complexes. Although there is some evidence that this assumption is reasonable,[41] particularly in the case of titanium where the formal oxidation state of the metal is maintained, one must use some caution when discussing *absolute* magnitudes of the data in Tables VII and VIII.

The enthalpies of formation of the nonreorganized fragments (L*) were evaluated by the usual method, i.e., assuming that the molecular structures of L are identical in the molecules LH and $M(Cp)_2L_n$ and using the Laidler terms E(L–H).[14b,40] This procedure has been discussed,[15] the main conclusion being that it has at least the merit of providing a set of internally consistent data. Theoretical calculations yielding direct values for the relaxation energies, from which one can derive more meaningful results for ΔH_f°[L*(g)] are in progress. The metal–sulfur bond enthalpy terms in Table VII rely on E(S–H) = 360.3 ± 8 kJ mol^{-1}, and the metal–oxygen values (Table VIII) were obtained from E(O–H) = 451.2 ± 8 kJ mol^{-1}.[42] Except for the sulfate complex, the thermochemistry of all the complexes involving metal–oxygen bonds was described in early studies.[43] The values quoted in Table VIII differ slightly from those originally reported due to the correction for the acid dilution (ΔH_{34}). The respective enthalpies of formation are collected in Table XII.

When the geometries of the fragment L in the complex $M(Cp)_2L_n$ and the parent molecule LH are known, it is possible to correct the ΔH_f°[L*(g)] values as determined above. Extended Hückel calculations suggest, however, that these corrections are usually small.[44] For L = SO_4 the results indicate that the energy of this fragment in the metal complex is very close to its energy in sulfuric acid.

Estimates of ER_1 and ER_3 are also possible by using extended Hückel calculations.[14e] The energy of fragments $M(Cp)_2$ is mainly a function of Cp–M–Cp angles, and curves relating these two parameters are available.[15] Most $M(Cp)_2L_n$ complexes have identical centroid angles, and therefore the differences $ER_3 - ER_1$ are negligible.[14e] This can be illustrated with the sulfate complex whose ring normal angle is 3.6° wider than the one in the dichloride complex, yielding $(ER_3 - ER_1)/2 \approx -14$ kJ mol^{-1}. The

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[39] These equations were not actually used to obtain E and $\bar{D}$ values since they overestimate the uncertainty intervals (see, e.g., ref 14b). However, they may be applied in the absence of direct experimental data.

[40] Dias, A. R.; Martinho Simões, J. A. *Rev. Port. Quim.* **1982**, *24*, 191.

[41] See, e.g.: ref 15 and also the continuing discussion.

[42] Cox, J. D.; Pilcher, G. "Thermochemistry of Organic and Organometallic Compounds"; Academic Press: London, New York, 1970.

[43] See: ref 14b and references therein.

[44] An exception is provided by L = N_3. See: Calhorda, M. J.; Gomes da Costa, R.; Dias, A. R.; Martinho Simões, J. A. *J. Chem. Soc., Dalton Trans.* **1982**, *2327*.

[45] See ref 14e and references cited therein.

Table IX. Energetics of Titanium–Oxygen Bonds in $Ti(OR)_4$ Compounds (kJ mol^{-1})[a]

R	*E*(Ti–OR)	R	*E*(Ti–OR)
C_2H_5	456 ± 8	*sec*-C_4H_9	458 ± 8
n-C_3H_7	469 ± 8	*t*-C_4H_9	453 ± 9
i-C_3H_7	469 ± 8	*n*-C_5H_{11}	472 ± 9
n-C_4H_9	470 ± 8	*t*-C_5H_{11}	476 ± 14
i-C_4H_9	469 ± 8		

[a] Data from ref 47 and 48.

remaining complexes in Tables VII and VIII have (or are expected to have) ring normal angles closer to those in the respective $M(Cp)_2Cl_2$ complexes, implying adjustments of *E*(M–S) and *E*(M–O) in the range of ca. +1 to −5 kJ mol^{-1}.

The enthalpies of formation of SR radicals were obtained from *D*(RS–H) = 375.7 ± 8.4 kJ mol^{-1} (R = alkyl) and from *D*(C_6H_5S–H) = 345.8 ± 8.4 kJ mol^{-1}.[14e] The enthalpies of formation of oxygen radicals were calculated as described elsewhere.[14b,20] These values allowed the evaluation of metal–sulfur and –oxygen mean bond dissociation enthalpies presented in Tables VII and VIII. It is worth mentioning that $\bar{D}$(M–S) and $\bar{D}$(M–O) results were not corrected for the term $ER_3/2$. Extended Hückel calculations suggest that this correction is very small for d^2 metals (ca. −5 kJ mol^{-1}) and quite significant in the case of d^4 metals (−40 kJ mol^{-1} for Mo and −50 kJ mol^{-1} for W).[14e,15] (The number of metal d electrons refers to $M(Cp)_2$ fragments.)

The new results for the $Mo(Cp)_2(SR)_2$ complexes (R = *i*-C_3H_7, *t*-C_4H_9, and *n*-C_4H_9) are in agreement with our previous general conclusions about the influence of the bulkiness of the alkyl groups on Mo–SR bond enthalpy terms.[14e] The large difference between *E*(Mo–SC_4H_9-*n*) and *E*(Mo–SC_4H_9-*t*), ca. 35 kJ mol^{-1}, reflects considerable steric effects in the *tert*-butyl complex. Interestingly, these effects are not observed in the isopropyl complex, as indicated by the small difference between *E*(Mo–SC_3H_7-*n*) − *E*(Mo–SC_3H_7-*i*). Another feature emerging from data in Table VII for molybdenum complexes is that the metal–sulfur bond strength increases with the length of the *n*-alkyl chain, i.e., *E*(Mo–SC_3H_7-*n*) < *E*(Mo–SC_4H_9-*n*) $\lesssim$ *E*(Mo–S$C_{10}H_{21}$-*n*). This is not confirmed by extended Hückel calculations, which indicate that the nature of the molybdenum–sulfur bond is almost independent of the alkyl chain. For example, it was found that the SR ligands interact with $M(Cp)_2$ in the same way for R = CH_3 and C_6H_5, the frontier orbitals being mostly located in the sulfur atom.[46]

There are not many studies involving the determination of metal–ligand bond energies from which one can try to correlate these data with the size and the bulkiness of the ligands. A series of values which has strong similarities with *E*(Mo–SR) is provided by titanium–alkoxyde bond enthalpy terms (Table IX). The thermochemistry of compounds $Ti(OR)_4$ has been studied by Bradley and Hillyer,[47] and it is possible to recalculate *E*(Ti–OR) values from the reported standard enthalpies of formation of those molecules in the gas phase and from the Laidler term *E*(O–H) mentioned above.[48] As observed for *E*(Mo–SR), the difference between *E*(Ti–OC_4H_9-*n*) and *E*(Ti–OC_4H_9-*t*) is large whereas *E*(Ti–OC_3H_7-*n*) − *E*(Ti–OC_3H_7-*i*) ≈ 0. Moreover, the titanium–oxygen bond enthalpy terms also increase with the size of the *n*-alkyl chain.

Table X. Auxiliary Thermochemical Data (kJ mol^{-1})

molecule	$\Delta H_f°$	$\Delta H_{s/v}°$ [a]
HCl(aq) (8.3 mol dm^{-3})	−156.824 ± 0.004[b]	
HCl(soln B)	−162.47 ± 0.28[c]	
HCl(soln D)	−172.59 ± 0.51[c]	
H_2SO_4(aq) (6.43 mol dm^{-3})	−873.3 ± 0.4[d]	
H_2SO_4(g)	−737 ± 8[e]	
$Mo(Cp)_2Cl_2$(c)	−95.8 ± 2.5[f]	(100.4 ± 4.2)
i-C_3H_7SH(l)	−105.8 ± 0.6[g]	29.6 ± 0.1[g]
t-C_4H_9SH(l)	−140.5 ± 0.8[g]	30.9 ± 0.2[g]
n-C_4H_9SH(l)	−124.7 ± 1.2[g]	36.6 ± 0.1[g]
n-$C_{10}H_{21}$SH(l)	−276.7 ± 1.3[g]	64.5 ± 0.4[g]
C_6H_5COOH(c)	−384.9 ± 0.6[g]	90.8 ± 1.5[g]
Cl(g)	121.302 ± 0.008[h]	
H(g)	217.997 ± 0.006[h]	

[a] Standard enthalpy of sublimation or vaporization. Values in parentheses are estimates. [b] Reference 21. [c] Reference 20. [d] Reference 22. [e] Average between the values presented in ref 23a and 23b. [f] Reference 24. [g] Reference 25. [h] Reference 26.

The values in Table IX allow another useful comparison. It may be noticed that *E*(Ti–OR) are in the same range as the titanium–oxygen bond enthalpy terms in Table VIII. This point has been made previously,[14b] but the agreement between the two series of data has improved with the correction for the acid dilution. It also suggests that an average *E*(Ti–O) can be calculated and transferred to other molecules, and it supports the assumption that *E*(Ti–Cl) is similar in $TiCl_4$ and $Ti(Cp)_2Cl_2$.

The relatively narrow range of values for *E*(M–O) for each metal is perhaps surprising. Particularly in the case of $Mo(Cp)_2(SO_4)$, one could expect that the four-membered metallacycle would imply some degree of strain, causing a decrease in the molybdenum–oxygen bond strength. The bond enthalpy data do not confirm this, since *E*(Mo–O) is close to *E*(Mo–$O_2CC_6H_5$) and *E*(Mo–O_2CCF_3), and they are supported by the structural results for the sulfate and the benzoate complexes (e.g., similar Mo–O bond lengths). Calculated Mo–O overlap populations in $Mo(Cp)_2(SO_4)$ and $Mo(Cp)_2(O_2CCF_3)_2$ are in the same range: 0.26 for the sulfate complex and 0.29 for the trifluoroacetate complex.

The bond enthalpy data in Tables VII and VIII rely on estimated values of sublimation enthalpies. This matter has been analyzed in detail, and it was concluded that the assumptions will not significantly affect the relative order of those values.[15] In the case of the sulfate complex, an increase of 20 kJ mol^{-1} in $\Delta H_s°$ will imply a decrease of 10 kJ mol^{-1} in *E*(Mo–O).

Conclusions

The usefulness of the bond enthalpy term concept, which has been demonstrated for a variety of ligands,[15] is evidenced once again from the above discussion. *E*(M–L) data enable the estimation of new mean bond dissociation enthalpies by using a consistent set of numbers for the reorganization enthalpies of the ligands. They also allow the extraction of energetic information in cases where the enthalpy of formation of the L radical is not available, as, for example, for SO_4. Future developments should include the calculation of more realistic values for the reorganization enthalpies of L* as well as attempts to estimate "partial" (and not "mean") bond dissociation enthalpies, which are the desirable parameters to define energy diagrams of chemical reactions.

Metal–sulfur bond enthalpies are 100–120 kJ mol^{-1} weaker than metal–oxygen bond enthalpies. The obtained *E*(Mo–SR) data reflects strong steric effects for R = *t*-C_4H_9 and indicates an increase of metal–sulfur bond strength with the size of the *n*-alkyl chain. This point will be

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Table XI. Orbital Exponents and Parameters Used for the Extended Hückel Molecular Orbital Calculations

orbital	Slater exponent	$-H_{ii}{}^{a}$/eV
H 1s	1.300	13.60[b]
C 2s	1.625	21.40[b]
C 2p	1.625	11.40[b]
O 2s	2.275	32.30[b]
O 2p	2.275	14.80[b]
S 3s	1.817	20.0[c]
S 3p	1.817	13.30[c]
Mo 5s	1.96	8.77[d]
Mo 5p	1.90	5.60[d]
Mo 4d	*e*	11.60[d,f]

[a] 1 eV = 96.4845 kJ mol^{-1}. [b] Reference 49. [c] Chen, M. M.-L.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1647. [d] Kamata, M.; Hirotsu, K.; Higuchi, T.; Tatsumi, K.; Hoffmann, R.; Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 5772. [e] $\xi_1 = 4.54$, $\xi_2 = 1.90$, $C_1 = 0.5899$, and $C_2 = 0.5899$. [f] Richardson, J. W.; Nieuwpoort, W. C.; Powell, R. R.; Edgell, W. E. *J. Chem. Phys.* **1962**, *36*, 1057.

Table XII. Standard Enthalpies of Formation of Oxygen Complexes (kJ mol^{-1})[a]

complex	$\Delta H_f°$(c)	$\Delta H_s°$[b]	$\Delta H_f°$(g)
$Mo(Cp)_2(O_2CC_6H_5)_2$	−500.7 ± 3.4	94 ± 10	−406.7 ± 10.6
$Mo(Cp)_2(O_2CCF_3)_2$	−1984.2 ± 4.2	90 ± 10	−1894.2 ± 10.8
$W(Cp)_2(O_2CC_6H_5)_2$	−463.4 ± 3.7	98 ± 10	−365.4 ± 10.7
$W(Cp)_2(O_2CCF_3)_2$	−1933.2 ± 3.8	94 ± 10	−1839.2 ± 10.7
$Ti(Cp)_2(OC_6H_5)_2$	−393.7 ± 8.0	97 ± 8	−296.7 ± 11.3
$Ti(Cp)_2(2\text{-}CH_3C_6H_4O)_2$	−448.9 ± 8.2	104 ± 8	−344.9 ± 11.5
$Ti(Cp)_2(3\text{-}CH_3C_6H_4O)_2$	−408.1 ± 8.1	104 ± 8	−304.1 ± 11.4
$Ti(Cp)_2(4\text{-}CH_3C_6H_4O)_2$	−448.7 ± 7.9	104 ± 8	−344.7 ± 11.3
$Ti(Cp)_2(2\text{-}ClC_6H_4O)_2$	−439.8 ± 22	90 ± 10	−349.8 ± 24
$Ti(Cp)_2(O_2CC_6H_5)_2$	−789.7 ± 8.1	112 ± 8	−677.7 ± 11.4
$Ti(Cp)_2(O_2CCCl_3)_2$	−1095.0 ± 19	130 ± 8	−965.0 ± 20
$Ti(Cp)_2(O_2CCF_3)_2$	−2251.2 ± 8.2	108 ± 8	−2143.2 ± 11.4

[a] Data from ref 14b and from Dias, A. R.; Salema, M. S.; Martinho Simões, J. A. *Rev. Port. Quim.* **1984**, *26*, 227. [b] Estimated values.

further explored by studying the energetics of the M–SC_2H_5 bond.

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Appendix. Molecular Orbital Calculations

The extended Hückel molecular orbital calculations were made by using the ICON8 program with the modified Wolfsberg–Helmholtz method.[49–51] The basis set for the molybdenum atom consisted of 4d, 5s, and 5p orbitals. Only 3s and 3p orbitals were considered for the sulfur atom. The s and p orbitals were described by single Slater-type wave functions and the d orbitals as contracted linear combinations of two Slater-type wave functions. The orbital exponents and the parameters for the extended Hückel calculations are collected in Table XI.

The $Mo(Cp)_2(SO_4)$ molecule was considered as having C_{2v} symmetry. The bond lengths and angles used were Mo–C_5H_5 = 196, C–C = 140, C–H = 108, Mo–O = 206, O–S = 143.8 and 152.6, and Mo···S 276.6 pm and the ring normal angle = 134.8° and O–Mo–O = 65.9°. The complex $Mo(Cp)_2(O_2CCF_3)_2$ was modeled according to the structure of $Mo(Cp)_2(O_2CC_6H_5)_2$.[37] The following distances and angles were used: O—C = 129.0, C=O = 120.9, C—C = 150.5, and C—F = 136.0 pm; Mo–O–C = 130° and O–Mo–O = 72.3°.

Registry No. $Mo(Cp)_2(SC_3H_7\text{-}i)_2$, 78305-75-6; $Mo(Cp)_2(SC_4H_9\text{-}t)_2$, 78305-76-7; $Mo(Cp)_2(SC_4H_9\text{-}n)_2$, 11082-51-2; $Mo(Cp)_2(SC_{10}H_{21}\text{-}n)_2$, 100350-30-9; $Mo(Cp)_2(O_2CC_6H_5)_2$, 58802-60-1; $Mo(Cp)_2(SC_3H_7\text{-}n)_2$, 78305-74-5; $Mo(Cp)_2(SC_6H_5)_2$, 12246-18-3; $Mo(Cp)_2(SO_4)$, 37298-38-7; $W(Cp)_2(SC_3H_7\text{-}n)_2$, 79453-19-3; $Ti(Cp)_2(SC_3H_7\text{-}n)_2$, 1292-07-5; $Ti(Cp)_2(SC_6H_5)_2$, 1292-47-3; $Ti(Cp)_2(S_2C_6H_3CH_3)$, 100350-31-0; $Mo(Cp)_2(O_2CCF_3)_2$, 58802-59-8; $W(Cp)_2(O_2CC_6H_5)_2$, 58802-64-5; $W(Cp)_2(OC_6H_5)_2$, 12246-19-4; $Ti(Cp)_2(2\text{-}CH_3C_6H_4O)_2$, 12309-37-4; $Ti(Cp)_2(3\text{-}CH_3C_6H_4O)_2$, 80592-40-1; $Ti(Cp)_2(4\text{-}CH_3C_6H_4O)_2$, 12309-38-5; $Ti(Cp)_2(2\text{-}ClC_6H_4O)_2$, 12309-06-7; $Ti(Cp)_2(O_2CC_6H_5)_2$, 12156-48-8; $Ti(Cp)_2(O_2CCCl_3)_2$, 12212-37-2; $Ti(Cp)_2(O_2CCF_3)_2$, 1282-45-7.

Supplementary Material Available: Tables of anisotropic thermal parameters and structure factors (3 pages). Ordering information is given on any current masthead page.

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