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Energetics of Metal–Sulfur Bonds in the Complexes $M(\eta^5\text{-}C_5H_5)_2(SC_2H_5)_2$ (M = Ti, W) and $W(\eta^5\text{-}C_5H_5)_2(SC_6H_5)_2$. Molecular Structure of $Ti(\eta^5\text{-}C_5H_5)_2(SC_2H_5)_2$

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Reaction–solution calorimetric studies of the title complexes led to Ti–SC_2H_5, W–SC_2H_5, and W–SC_6H_5 bond enthalpies. The results support a previous view that M–SR bond strengths increase with the size of the *n*-alkyl chain and that M–SC_6H_5 bond enthalpies are higher than M–S(alkyl) bond enthalpies. The molecular structure of $Ti(\eta^5\text{-}C_5H_5)_2(SC_2H_5)_2$, determined by X-ray diffraction, shows a distorted tetrahedron geometry around the Ti central atom, with S–Ti–S and centroid–Ti–centroid angles of 93.8 (1) and 131.8 (4)°, respectively, and a mean Ti–S bond length of 239.3 (3) pm. Extended Hückel molecular orbital calculations show that an exo conformation of the thiolate ligands is preferred for molybdenum complexes, while an endo geometry is favored by the titanium analogues. The conformation of cyclopentadienyl rings is also discussed by using the same theoretical method. Potential energy calculations indicate that the complex $Mo(\eta^5\text{-}C_5H_5)_2(SC_4H_9\text{-}t)_2$ is destabilized by steric effects, these being negligible in the case of $Ti(\eta^5\text{-}C_5H_5)_2(SC_6H_5)_2$.

Introduction

The energetics of transition-metal–sulfur and –oxygen bonds in several bis(cyclopentadienyl) complexes of titanium, molybdenum, and tungsten has been addressed in a recent publication.[1] One of the main conclusions of this work was that metal–sulfur bond enthalpies in $Mo(Cp)_2(SR)_2$ complexes (Cp = η^5-C_5H_5; R = C_3, C_4, and C_{10} *n*-alkyls) increase with the length of the *n*-alkyl chain but are lower than Mo–SC_6H_5 bond enthalpy. Since it has also been shown that variations of metal–ligand bond enthalpies follow identical patterns for different metals,[2] a similar behavior for the analogous titanium and tungsten molecules may be expected. In order to further substantiate these points, thermochemical results for the complexes $M(Cp)_2(SC_2H_5)_2$ (M = Ti, W) and $W(Cp)_2(SC_6H_5)_2$ are presented here. The X-ray diffraction study of $Ti(Cp)_2(SC_2H_5)_2$ is also reported and, together with early data for some related bis(cyclopentadienyl) compounds, allows a more detailed analysis of the energetics of metal–sulfur bonds. Extended Hückel molecular orbital calculations and steric energy calculations are also used to discuss the molecular structure, particularly the orientations of the Cp rings and the thiolate ligands.

Experimental Section

Calorimetry. The reaction and solution enthalpies at 298 K were measured in the isoperibol calorimeter previously described.[3] There was no need to perform the experiments under nitrogen, since all the complexes are fairly air stable.

Compounds. The complexes were prepared and purified as described in the literature.[4] The reaction solutions were prepared from BDH AnalaR or Merck p.a. hydrochloric acid and Merck p.a. acetone, which were used without further treatment. Ethanethiol (Fluka) was dried for several hours over $CaCl_2$ and distilled under dry nitrogen. The purification of benzenethiol (Fluka) followed the method recommended in the literature.[5]

Reactions. Thermochemical measurements on reaction 1 were used to derive the standard enthalpies of formation of the complexes. The

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

reaction media were selected so as to ensure a rapid and complete reaction for each complex and also a maximum solubilization of both the thiol and $M(Cp)_2Cl_2$. The ethanethiolate ligands are readily replaced by chlorine atoms in a 1:1 mixture of 8.3 mol dm^{-3} aqueous HCl and acetone (solution A); stronger acidic conditions, a more efficient stirring, and addition of a few drops of Teepol, were needed to achieve a fast and complete reaction for the tungsten thiophenolate complex. A 1:4 mixture of 10.4 mol dm^{-3} aqueous HCl and acetone (solution B) was chosen in this case; no signs of oxidation of the dichloride were detected.

The errors inherent to the use of aqueous HCl–acetone mixtures and to incomplete solubilization of thiols have been previously discussed.[1,6]

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

molecule	$\Delta H_f°$	$\Delta H_{s/v}°$ [a]
HCl (soln A)	−162.47 ± 0.28[b]	
HCl (soln B)	−171.86 ± 0.34[c]	
$W(Cp)_2Cl_2(c)$	−71.1 ± 2.5[d]	104.6 ± 4.2[d]
$Ti(Cp)_2Cl_2(c)$	−383.2 ± 7.5[d]	118.8 ± 2.1[d]
$C_2H_5SH(l)$	−73.6 ± 0.6[e]	27.32 ± 0.04[e]
$C_6H_5SH(l)$	63.7 ± 0.7[e]	48.7 ± 0.2[e]
Cl(g)	121.302 ± 0.008[f]	
H(g)	217.997 ± 0.006[f]	

[a] Standard enthalpy of sublimation or vaporization. [b] Reference 6. [c] Reference 7. [d] Reference 8. [e] Reference 9. [f] Reference 10.

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

formula	$C_{14}H_{20}S_2Ti$
cryst syst	monoclinic
space group	$P2_1/c$
M_r	300.34
a, pm	929.0 (4)
b, pm	2061.9 (10)
c, pm	835.4 (3)
β, deg	112.28 (3)
V, pm^3	1480.74 × 10^6
Z	4
d_{calcd}, g/cm^3	1.347
radiation	Ag K$\bar{\alpha}$ (λ = 56.09 pm)
μ(Ag Kα), cm^{-1}	5.55
scan type	ω–2θ
scan width ($\Delta\omega$), deg	0.57 + 0.45 tan θ
max counting time, s	120
collcn range	$\pm h,+k,+l$ $4.0 < 2\theta < 36.0$
no. of unique data	1583
no. of data with $F < 3\sigma(F)$	407
decay during collcn	none
no. of variables	164
largest shift/error value on final cycle	0.072
largest peak in final difference Fourier, e/Å^3	0.48
R[a]	0.0629
R_w[a]	0.0566

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

The reaction products were confirmed by IR spectroscopic analysis. All reaction and solution enthalpies presented are mean values of at least five

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

complex	$W(Cp)_2(SC_2H_5)_2$	$W(Cp)_2(SC_6H_5)_2$	$Ti(Cp)_2(SC_2H_5)_2$
soln	A	B	A
ΔH_r	19.8 ± 2.7	63.8 ± 3.5	−25.2 ± 2.1
ΔH_{d1}	12.1 ± 3.3	14.5 ± 2.8^a	5.2 ± 1.8^b
ΔH_{d2}	−10.83 ± 0.73^{c,d}	0.49 ± 0.27^{c,e}	−10.83 ± 0.73^c
ΔH_{d3}	−5.65 ± 0.28^b	−18.45 ± 0.34^f	−5.65 ± 0.28^b
ΔH_{d4}	−1.31 ± 0.03^g	−3.8 ± 0.1^g	−1.31 ± 0.03^g

[a] Containing a stoichiometric amount of C_6H_5SH. [b] Reference 6. [c] Containing a stoichiometric amount of $Ti(Cp)_2Cl_2$ (see text). [d] One experiment in the presence of a stoichiometric amount of $W(Cp)_2Cl_2$ led to $\Delta H_{d2} = -10.73$ kJ mol^{-1}. [e] Reference 2. One experiment without $Ti(Cp)_2Cl_2$ in the solution afforded $\Delta H_{d2} = 0.43$ kJ mol^{-1}. [f] Reference 7. [g] Reference 1.

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

complex	ΔH_f°(c)	$\Delta H_s^{\circ\,a}$	ΔH_f°(g)
$W(Cp)_2(SC_2H_5)_2$	62.7 ± 5.3	(92 ± 10)	154.7 ± 11.3
$W(Cp)_2(SC_6H_5)_2$	319.9 ± 5.5	(99 ± 10)	418.9 ± 11.4
$Ti(Cp)_2(SC_2H_5)_2$	−211.3 ± 8.2	(106 ± 10)	−105.3 ± 12.9

[a] Estimated values.

Table V. Positional Parameters (×10^4) for $[Ti(\eta^5\text{-}C_5H_5)_2(SC_2H_5)_2]$

	x	y	z
Ti	3324 (2)	1189 (1)	5857 (2)
S(1)	1523 (3)	514 (1)	3672 (3)
S(2)	1602 (3)	2097 (1)	5196 (3)
C(1)	953 (11)	936 (5)	1602 (11)
C(2)	−74 (11)	816 (6)	502 (13)
C(3)	−198 (11)	1881 (5)	5439 (14)
C(4)	−1503 (13)	2217 (7)	4294 (17)
C(10)	4110 (10)	1827 (5)	3907 (12)
C(11)	4942 (10)	2055 (5)	5611 (14)
C(12)	5930 (11)	1566 (5)	6550 (13)
C(13)	5710 (11)	1019 (5)	5473 (14)
C(14)	4615 (10)	1194 (6)	3824 (12)
C(20)	2045 (13)	640 (5)	7494 (11)
C(21)	2804 (13)	1182 (6)	8461 (11)
C(22)	4408 (14)	1105 (5)	8935 (11)
C(23)	4654 (14)	503 (6)	8279 (12)
C(24)	3194 (15)	224 (5)	7409 (12)

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

	Bond Distances		
Ti–S(1)	239.8 (3)	S(1)–C(1)	182.5 (9)
		C(1)–C(2)	151.1 (12)
Ti–S(2)	238.7 (3)	S(2)–C(3)	181.4 (9)
		C(3)–C(4)	140.9 (13)
Ti–C(10)	241.2 (8)	Ti–C(20)	240.7 (9)
Ti–C(11)	239.3 (9)	Ti–C(21)	240.1 (9)
Ti–C(12)	239.5 (9)	Ti–C(22)	238.6 (8)
Ti–C(13)	238.2 (9)	Ti–C(23)	239.2 (10)
Ti–C(14)	242.1 (9)	Ti–C(24)	240.3 (9)
mean Ti–C	239.9 (9)		
C(10)–C(11)	141.9 (12)	C(20)–C(21)	140.2 (13)
C(11)–C(12)	138.9 (12)	C(21)–C(22)	139.9 (13)
C(12)–C(13)	140.7 (12)	C(22)–C(23)	140.8 (13)
C(13)–C(14)	141.4 (12)	C(23)–C(24)	139.7 (13)
C(14)–C(10)	139.7 (12)	C(24)–C(20)	139.2 (13)
mean C–C	140.2 (12)		
	Bond Angles		
S(1)–Ti–S(2)	93.8 (1)		
C(1)–S(1)–Ti	108.2 (3)	C(3)–S(2)–Ti	110.3 (4)
C(2)–C(1)–S(1)	111.1 (7)	C(4)–C(3)–S(2)	113.3 (8)
C(10)–C(11)–C(12)	108.5 (9)	C(20)–C(21)–C(22)	108.7 (1.0)
C(11)–C(12)–C(13)	108.4 (9)	C(21)–C(22)–C(23)	107.6 (1.0)
C(12)–C(13)–C(14)	107.2 (9)	C(22)–C(23)–C(24)	107.3 (1.1)
C(13)–C(14)–C(10)	108.7 (9)	C(23)–C(24)–C(20)	109.3 (1.0)
C(14)–C(10)–C(11)	107.1 (9)	C(24)–C(20)–C(21)	107.0 (1.0)
mean C–C–C	108.0		

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 298.15 K, used in evaluating the thermochemical results, were taken from data compilations or from previous papers[6-10] and are collected in Table I.

X-ray Data Collection, Structure Determination, and Refinement. Crystals of $Ti(Cp)_2(SC_2H_5)_2$ suitable for diffraction measurements were prepared as described in the literature.[4a] Preliminary cell dimensions and space group were determined from Weissenberg and precession photographs. Data were measured on a Enraf-Nonius CAD-4 automated diffractometer with graphite-monochromatized Ag $K\bar{\alpha}$ radiation. The pertinent crystallographic parameters are listed in Table II. Data were corrected for Lorenz and polarization effects and merged to a unique set of reflections. All calculations required to solve and refine the structure were done by using SHELX76[11] and the drawing was done with ORTEP.[12] Atomic scattering factors and anomalous scattering terms were taken from the literature.[13]

The Ti position was obtained from a sharpened Patterson synthesis and the S and C positions from a subsequent difference Fourier synthesis. Full-matrix least-squares refinement with isotropic temperature factors gave $R = 0.097$. Refinement was then continued with anisotropic thermal parameters. The hydrogen atoms were introduced at their calculated positions with a fixed C–H distance of 108 pm. The weighting scheme $w = 1.356/[\sigma^2|F_o| + 0.0003F_o^2]$ was found to give an acceptable agreement analysis. No absorption correction was applied ($\mu = 5.55$ cm^{-1}). The final refinement converged at $R = 0.063$ and $R_w = 0.057$.

Results

Thermochemistry. The thermochemical results are summarized in Table III. ΔH_r represents the enthalpy of reaction 1 and ΔH_{d1} refers to the enthalpy of solution of the dichloride complex in solutions A or B (small residues of both tungsten and titanium dichlorides were observed, but the resulting error must be within the uncertainty interval assigned to ΔH_{d1}). ΔH_{d2}, the enthalpy of solution of the thiol in the reaction mixture, should be determined in the presence of stoichiometric amounts of $M(Cp)_2Cl_2$. However, previous results[2,14] have shown that these quantities are fairly independent of the nature of the dichloride (M = Ti, Mo, W) present in the solution. Therefore, the ΔH_{d2} values measured for the titanium systems were used for the tungsten analogues (see also footnotes *d* and *e* of Table III). Due to the volatility of C_2H_5SH, a precision 100-μL Hamilton syringe (and not a glass ampule) was used to add the required amount of that substance to the calorimetric solution. ΔH_{d3} was obtained by breaking ampules containing a stoichiometric amount of aqueous hydrochloric acid in the reaction media; these results, together with the standard enthalpies of formation of the aqueous acids, led to the values of ΔH_f°(HCl,soln) listed in Table I, according to a pro-

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(4) $Ti(Cp)_2(SC_2H_5)_2$: (a) Köpf, K.; Schmidt, M. *Z. Anorg. Allg. Chem.* **1965**, *340*, 139. $W(Cp)_2(SC_6H_5)_2$: (b) Green, M. L. H.; Lindsell, W. E. *J. Chem. Soc. A* **1967**, 1455. $W(Cp)_2(SC_2H_5)_2$: (c) Dias, A. R.; Green, M. L. H. *J. Chem. Soc. A* **1971**, 2807. (d) Dias, A. R.; Garcia, M. H. *Rev. Port. Quím.* **1979**, *21*, 145. (e) Harris, M. G.; Green, M. L. H.; Lindsell, W. E. *J. Chem. Soc. A* **1969**, 1453.

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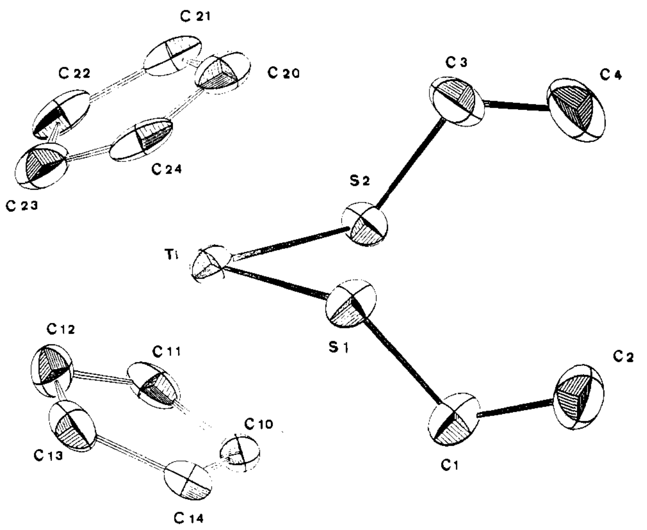


Figure 1. Molecular structure of $Ti(Cp)_2(SC_2H_5)_2$ with 30% probability thermal ellipsoids.

cedure described elsewhere.[6] Finally, ΔH_{d4}, which gives the enthalpy change associated with the acid dilution, was previously determined by breaking ampules containing stoichiometric amounts of distilled water in solutions A or B.

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.

Structural Results. Final atomic positional and thermal parameters are listed in Table V. Selected interatomic distances and angles are listed in Table VI. Tables of anisotropic thermal parameters and structure factors are given as supplementary material. The crystal structure of $Ti(Cp)_2(SC_2H_5)_2$ is composed of discrete molecules with the configuration shown in Figure 1. The metal atom is π-bonded to two cyclopentadienyl ligands and σ-bonded to two ethanethiolate ligands.

Discussion

Molecular Structure and Calculations. The coordination geometry about the Ti atom, defined by the Cp ring centroids and the S atoms, is a distorted tetrahedron. A projection onto the Ti, S(1), S(2) plane shows that the cyclopentadienyl rings have a staggered conformation.

The average Ti–S distance of 239.3 (3) pm and the S(1)–Ti–S(2) bond angle of 93.8 (1)° are comparable with the corresponding values of 240.3 (1) pm and 93.6 (1)° observed in $Ti(Cp)_2(SCH_3)_2$.[15] In the $Ti(Cp)_2(SC_6H_5)_2$ complex the Ti–S average distance is of the same order of magnitude, but the angle at the metal atom, 99.3°, is larger than the equivalent value in the two previous examples.[16]

The geometry of $M(Cp)_2$ fragments are variously described in terms of *either* $M(Cp\ centroid)_2$ or $M(Cp\ ring\ normal)_2$ values, significant differences arising if the Cp rings are "tilted". In the present complex there is very little ring tilt. The metal-to-ring centroid distances are equivalent to the metal-to-ring normal distances, 208.6 (9) and 208.7 (9) pm, and the corresponding centroid–Ti–centroid angle of 131.8 (4)° is similar to the ring normal–Ti–ring normal angle of 130.5 (4)°. The Ti–C distances are in the usual range, 238.2–242.1 pm, with a mean value of 239.9 pm. The cyclopentadienyl carbon atoms are coplanar with a maximum deviation from the best least-squares planes of 1.5 and 0.7 pm on each ring, respectively.

The conformational preferences of complexes $M(Cp)_2(SR)_2$ have been briefly discussed by Lauher and Hoffmann in their study of $M(Cp)_2$ derivatives, namely $M(Cp)_2LL'$, where L and L′ are π-donor ligands.[17] Structures of several bis(thiolate) complexes of molybdenum and titanium are now available, evidencing some differences that can be interpreted on the basis of electronic and steric effects. The latter cannot be neglected when the R groups are large (phenyl or *tert*-butyl, for instance).

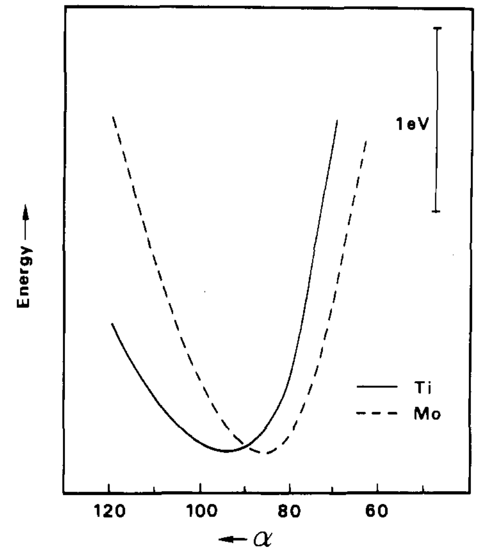
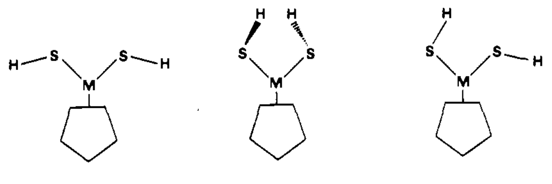


Figure 2. Calculated energy change of $M(Cp)_2(SH)_2$ (M = Ti, Mo) as a function of α (S–M–S angle).

In order to study the electronic effects, we can use SH as a model for the thiolate ligand in the extended Hückel calculations (see Appendix for further details). The energy changes associated with varying the S–M–S (α) angle are shown in Figure 2, for Ti and Mo. The S–H bonds were kept fixed in the bisector to the ring normals plane, *yz*, which may be unfavorable for large α. Indeed, for α = 120°, the energy is lowered by 0.4 eV if the torsion angles S–M–S–H are increased to approximately 100°. Although the preferred angle is smaller for Mo than for Ti, the potential barrier to change it within reasonable limits is small for both metals, thus explaining the experimental range of values observed.

After choosing the preferred α angle (95° for titanium and 85° for molybdenum), we looked at the three typical conformations: the exo structure, having the S–H bonds in *yz* (**1**); the endo structure, where the torsion S–M–S–H is 60°, to relieve the steric clash that would occur for an angle of 0° (**2**); the asymmetric structure, also having the S–H bonds in *yz* (**3**).



ΔE (eV)	Ti	+0.57	0.0	+0.63
	Mo	0.0	+0.17	+0.02
		1	**2**	**3**

The exo conformation is preferred for Mo and the endo for Ti, as shown by their relative energies. In order to understand this behavior, we can look at the simplified molecular orbital diagrams showing the interactions between $Ti(Cp)_2^{2+}$ fragments and the two SH ligands, for situations **1** and **2** (Figure 3). For the exo conformation, on the left, the main interactions involve the three $Ti(Cp)_2$ frontier orbitals, $1a_1$, b_2, and $2a_1$,[17] which are empty, and filled sulfur orbitals having a suitable symmetry.

b_2 interacts with an antisymmetric combination of sulfur p orbitals (the HOMO of the ligands) and $2a_1$ with low-energy sp hybrid orbitals of a_1 symmetry. $1a_1$ is involved in a π-interaction with a combination of sulfur lone pairs (also sp hybrids), resulting in the strong antibonding character of the LUMO ($3a_1$). The other

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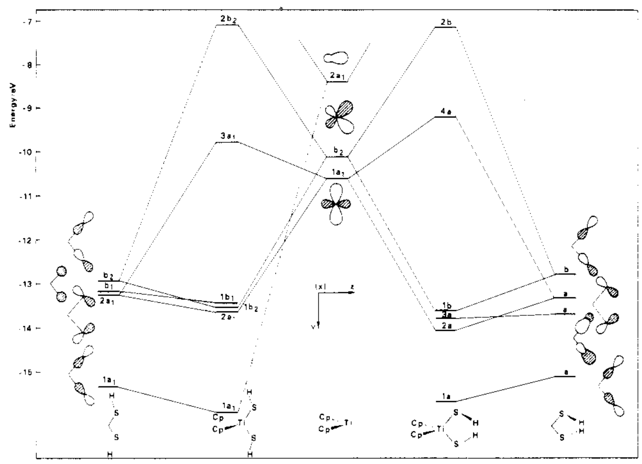
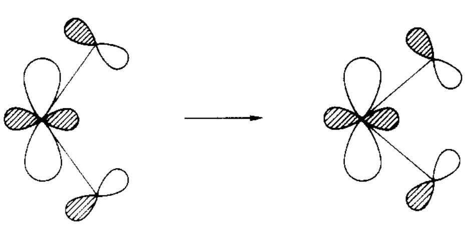


Figure 3. Molecular orbital diagram for the interaction between Ti(Cp)$_2^{2+}$ and the SH ligands for exo (left) and endo (right) conformations.

sulfur lone pairs, which are pure p, are not involved in the bonding.

Let us now look at the right side of Figure 3. The symmetry of the molecule is lowered from C_{2v} to C_2. The greatest change occurs in the π-interaction, which now becomes stronger. Since the geometry of the ligands is different, the sulfur orbitals involved are the pure p orbitals, lying at higher energy, closer to that of the 1a$_1$ orbital, resulting in a better interaction and a more destabilized LUMO (4a). The HOMOs of the complex (not shown in Figure 3) are mostly cyclopentadienyl orbitals destabilized by four-electron interactions with sulfur orbitals. Their energy is slightly lower for this conformation.

If the titanium atom is replaced by molybdenum, the two extra electrons are going to occupy the next empty orbital (3a$_1$ or 4a), which has a lower energy for the exo conformation, this being therefore the preferred geometry for molybdenum. However, that orbital is still a high-energy antibonding orbital. A smaller S–M–S angle, as shown in 4 (see Figure 2), will decrease this character by weakening the π-interaction. The a$_1$ orbitals in sulfur will be then mainly involved in interactions with 2a$_1$, which is empty, leaving 1a$_1$ almost a nonbonding orbital.



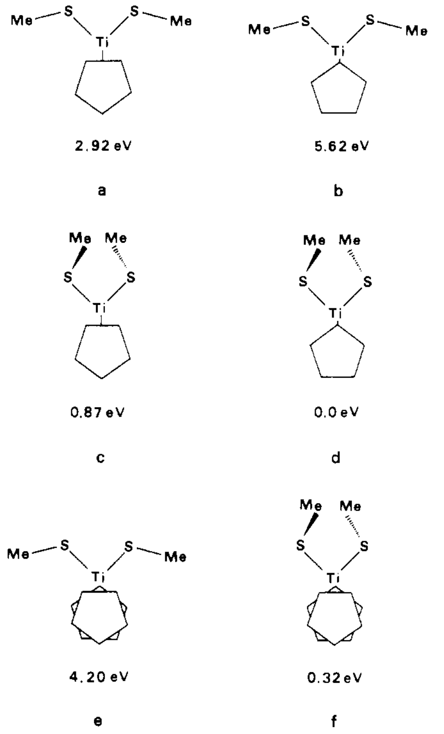
4

The asymmetric structure, **3**, is intermediate in terms of bonding, never being the preferred one, although its energy is very close to that of **1** for molybdenum.

To test the influence of steric effects, methyl groups were introduced in the model compound, Ti(Cp)$_2$(SCH$_3$)$_2$. Three ligand–ligand types of repulsion can occur: between the cyclopentadienyl rings, between the thiolate ligands, and between a thiolate and a cyclopentadienyl, their relative importance depending on the bulkiness of the R group. Three possible relative orientations for the Cp rings can be added to the limiting endo and exo conformations of the other ligands (**5**).

In **5a,c** the Cp rings are eclipsed and have a very short H···H distance; alternatively, **5b,d** have also eclipsed Cp rings with two not so short H···H distances. Other factors being absent, this conformation for the Cp rings is preferred on steric grounds. **5e,f** have staggered Cp rings, the intermediate situation. Their relative energies are shown below each diagram.

Although a full optimization was not made, some conclusions can be drawn from the previous results. The SR ligands prefer an endo geometry, to avoid Cp–thiolate repulsion (**5c,d,f** have the lower energies), these being minimized by eclipsed Cp rings with two short H···H contacts (**5d**); in these situations, as the SR ligands are placed one above and the other below the bisector plane, there is more room between the rings to accommodate them (the R groups are further away from the cyclopentadienyl hydrogens). Let us now suppose that the R groups are very bulky and the SR–SR repulsion is very strong. The preferred conformation would then be exo. But for the exo geometries (**5a,b,e**), eclipsed Cp rings with only one H···H close contact are preferred (**5a**) to minimize Cp–SR repulsion. As expected, geometries with staggered Cp rings are inbetween.



5

Having discussed the influence of electronic and steric factors in determining the conformations adopted by M(Cp)$_2$(SR)$_2$ complexes, we can look again at the experimentally determined structures, which are available for M = Ti, R = CH$_3$,[15] C$_2$H$_5$, *n*-C$_3$H$_7$,[18] and C$_6$H$_5$[16] and M = Mo, R = *t*-C$_4$H$_9$.[19]

All the structures of titanium complexes are of the endo type, as expected from electronic requirements. The methyl, ethyl, and *n*-propyl derivatives can accommodate their linear alkyl chains above and below the bisector plane. However, the S–M–S angles in these complexes are smaller than the corresponding value for the SC$_6$H$_5$ derivative. The stronger steric interactions occur between cyclopentadienyl hydrogens and alkyl hydrogens (closer contacts are 262.3 and 259.5 pm for Ti(Cp)$_2$(SCH$_3$)$_2$ and 225.4, 230.0, 220.3, and 223.1 pm for Ti(Cp)$_2$(SC$_2$H$_5$)$_2$) or between phenyl hydrogens on adjacent rings for Ti(Cp)$_2$(SC$_6$H$_5$)$_2$. The different steric interactions lead to the large value observed for this complex. The balance between electronic preferences on one side and the steric repulsions on the other is responsible for the different bond angles and lengths observed. The Cp rings adopt a conformation that is intermediate between staggered and eclipsed with two short H···H contacts (**5d,f**) for both Ti(Cp)$_2$(SCH$_3$)$_2$[15] and Ti(Cp)$_2$(SC$_2$H$_5$)$_2$ (Figure 4).

For the molybdenum complex, electronic requirements should force an exo conformation. Also, the *tert*-butyl group is very bulky, the steric effects thus helping the molecule to adopt such a geometry. The exo species are more stable when Cp rings are eclipsed with one close H···H contact (**5a**). This is indeed the geometry that was observed.[19] Unfortunately we do not know any other structure of Mo(Cp)$_2$(SR)$_2$ complexes, in order to further test these results. However, in the related monothiolate complex

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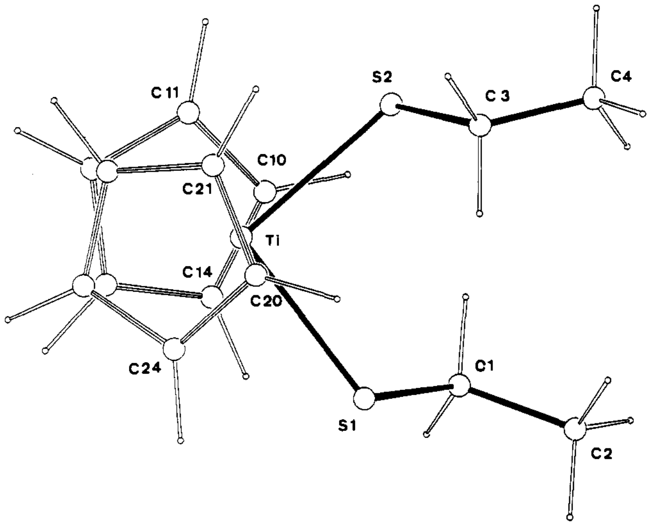

Figure 4. View of the molecule of $Ti(Cp)_2(SC_2H_5)_2$ normal to the plane defined by Ti, S1, and S2.

$[Mo(Cp)_2(NH_3)(SC_6H_5)]^+$, the SC_6H_5 ligand lies in the bisector plane, exhibiting an exo conformation as expected for molybdenum.[20]

Potential energy calculations (using the EENY2 program)[21] were made for the complexes having the larger R substituents, $Ti(Cp)_2(SC_6H_5)_2$ and $Mo(Cp)_2(SC_4H_9\text{-}t)_2$, in order to take fully into account the steric interactions. For the titanium complex, an optimization of the four torsion angles around the thiolate ligands led to minor changes in the value of the potential energy. The energy for this molecule was approximately zero, showing that in the adopted geometry no strong steric repulsions occur. On the other hand, for the molybdenum derivative no geometry similar to that of the titanium complex (endo) could be obtained except for very high energies.

Starting from the real geometry of $Mo(Cp)_2(SC_4H_9\text{-}t)_2$, we allowed the Mo–S bond lengths to decrease from 250.1 and 248.1 pm (and the torsion angles optimized) in order to be comparable with Mo–S bond lengths in other Mo(IV) derivatives. The steric energy increased by 12 kJ mol^{-1} when both Mo–S bonds were shortened by 4 pm (approximating the value obtained for $[Mo(Cp)_2(NH_3)(SC_6H_5)]^+$, 246 pm) and by 20 kJ mol^{-1} when the Mo–S bond lengths became 244.1 and 243.1 pm (a typical Mo–S bond length).[19]

Thermochemistry. All the available bond enthalpy terms, $E(M–S)$, and mean bond dissociation enthalpies, $\bar{D}(M–S)$, in bis(cyclopentadienyl) thiolate complexes are displayed in Table VII. Most of those data, as well as the method used to calculate them, have been reported previously[22] and therefore the present discussion will be limited to a few selected points. Concerning the calculation method, it is just mentioned that the evaluation of $E(M–S)$ requires similar geometries for the thiolate moiety SR in the complex and the molecule RSH, this being indeed observed for $Ti(Cp)_2(SC_2H_5)_2$ and C_2H_5SH.[23]

The new results for the ethyl thiolate complexes support the early finding that metal–sulfur bond enthalpies increase with the length of the *n*-alkyl chain. A similar trend is observed for Ti–OR bond enthalpies in $Ti(OR)_4$ compounds (R = C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, and $n\text{-}C_5H_{11}$).[22] Gas-phase ion cyclotron spectroscopy studies have also shown that the bonding between transition-metal cations like Mn^+ or $CpNi^+$ and organic bases RXH (X = sulfur or oxygen) is strengthened when the alkyl group R has an increasing number of carbon atoms.[24,25] The trend observed for

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
$W(Cp)_2(SC_2H_5)_2$	261 ± 10	277 ± 10
$W(Cp)_2(SC_3H_7\text{-}n)_2$	266 ± 10	281 ± 10
$W(Cp)_2(SC_6H_5)_2$	288 ± 10	274 ± 10
$Ti(Cp)_2(SC_2H_5)_2$	326 ± 10	341 ± 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	

$E(M–SR\text{-}n)$ may be questioned by the uncertainty intervals affecting each value. Note, however, that smaller uncertainties should be considered on a relative basis. In fact, they are mainly caused by the errors assigned to the estimated sublimation enthalpies of the complexes (see Table IV and also ref 1), and these errors are substantially decreased when differences $\Delta H_s°[M(Cp)_2(SR)_2] - \Delta H_s°[M(Cp)_2(SR')_2]$ are predicted for a given M.

As stressed before,[2] the differences $E(M–L) - E(M–L')$ are rather similar for M = Ti, Mo, and W and for a variety of ligands. On this basis, taking for example $E(Ti–SC_6H_5) - E(Ti–SC_2H_5)$ = 32 kJ mol^{-1} and $E(W–SC_2H_5)$ = 261 kJ mol^{-1}, one obtains $E(W–SC_6H_5)$ = 293 kJ mol^{-1}, which is very close to the value shown in Table VII.

Trends of metal–ligand bond lengths are frequently used to infer an inverse order of bond strengths. $E(Ti–SR)$ data in Table VII and Ti–SR bond lengths in the ethyl (239 pm), *n*-propyl (240 pm),[18] and phenyl (241 pm)[16] complexes, where no significant steric effects occur, seem to contradict that relationship. However, the small variation of Ti–S bond lengths and the uncertainty intervals associated to the bond enthalpy values do not allow us to draw a firm conclusion on this.

A more interesting feature emerges from the last value of Table VII. $E(Ti–S)$ and the Ti–S bond length (242 pm)[26] in the bidentate complex $Ti(Cp)_2(S_2C_6H_3CH_3)$ are similar to the values for the ethyl and *n*-propyl molecules, suggesting a negligible strain in the metallacycle. This contrasts with the relatively high strain energies (40–80 kJ mol^{-1}) reported for several oxygen $M(Cp)_2L$ complexes (M = Ti, L = $O_2C_{14}O_8$; M = Mo, L = $O_2C_6H_4$, $O_2C_{10}H_6$, $O_2C_{14}H_8$; M = W, L = $O_2C_6H_4$).[27] The larger size of the sulfur atom, compared with oxygen, causing a relaxation of the five-membered ring, is a possible explanation for that difference. The same pattern is observed in cyclic organic molecules $\underline{\overline{(CH_2)_{n-1}X}}$ (X = CH_2, O, NH, S), discussed by Cox and Pilcher:[28] for $n = 5$ when oxygen is replaced by sulfur, there is a decrease of ca. 15 kJ mol^{-1} in the strain energy.

Stepwise metal–sulfur bond dissociation enthalpies can be estimated from the data in Table VII by using a simple method reported elsewhere.[29] For the model compound $M(Cp)_2(SCH_3)_2$, it was predicted that the enthalpy required to break the first M–S bond was substantially lower than the second bond dissociation enthalpy ($D_2 - D_1$ = 120 or 160 kJ mol^{-1} respectively for M = Ti and Mo). Differences in the same range may be expected for the other thiolate ligands. It is worth mentioning that a recent calorimetric study of several $Ti(Cp^*)_2L_2$ and $Ti(Cp^*)_2L$ complexes ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$; L = CH_3, C_6H_5, Cl) has shown that the experimentally derived Ti–L bond dissociation enthalpies are in

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Table VIII. Exponents and Parameters for Ti and Mo

orbital	ζ_1	$-H_{ii}$/eV^a	ζ_2^b	C_1^b	C_2^b
Ti^c 4s	1.075	8.97			
Ti 4p	0.6750	5.44			
Ti^d 3d	4.55	10.81	1.40	0.4206	0.7839
Mo^e 5s	1.96	8.77			
Mo 5p	1.90	5.60			
Mo^d 4d	4.54	11.60	1.90	0.5899	0.5899

^{a} 1 eV = 96.4845 kJ mol^{-1}. ^{b} Exponents and coefficients in the double Slater-type wave functions. ^{c} Reference 17. ^{d} Richardson, J. W.; Nieuwpoort, W. C.; Powell, R. R.; Edgell, W. E. *J. Chem. Phys.* **1962**, *36*, 1057. ^{e} Kamata, M.; Hirotsu, K.; Higuchi, T.; Tatsumi, K.; Hoffmann, R.; Yoshida, T.; Otsuka, S. *J. Am. Chem. Soc.* **1981**, *103*, 5772.

good agreement with the values obtained by the above method.[30]

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Appendix

The extended Hückel molecular orbital calculations were made by using the ICON8 program[31] with the Wolfsberg–Helmholz modification.[32] Standard parameters were used for C, S, and H. Only 3s and 3p orbitals were considered for sulfur. The exponents and parameters for titanium and molybdenum are listed in Table VIII. The following distances (pm) and angles (degrees) were used: Ti–S, 240; Ti–Cp, 207; S–H, 150; C–C(Cp), 140; C–H, 108; Mo–S, 245; Mo–Cp, 200; Cp–M–Cp, 132.0; M–S–H, 110; S–Ti–S, 95; S–Mo–S, 85.

Registry No. W(Cp)$_2$(SC$_2$H$_5$)$_2$, 37328-24-8; W(Cp)$_2$(SC$_6$H$_5$)$_2$, 12246-20-7; Ti(Cp)$_2$(SC$_2$H$_5$)$_2$, 1291-79-8.

Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen atomic coordinates (2 pages); a table of structure factors (5 pages). Ordering information is given on any current masthead page.

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Reactions of Molybdate with Dithiothreitol. Structure of [TEA]$_2$[Mo$_2$O$_5$dtt]†

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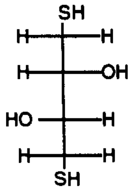
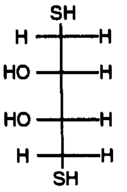
The preparation of [TEA]$_2$[Mo$_2$O$_5$(L-dithiothreitolate)] from reaction of [TEA]$_2$[MoO$_4$] and L-dithiothreitol is described. The structure of the dimer has been confirmed by X-ray crystallography. The material crystallizes in the monoclinic space group $P2_1$ with lattice parameters a = 7.402 (2) Å, b = 30.67 (2) Å, c = 18.567 (5) Å, β = 94.57 (2)°, V = 4208 (5) Å^3, and Z = 6. ^{95}Mo NMR and infrared spectral data for the dimer are given. A product having an EPR spectrum characteristic of Mo(V) is obtained when the reaction of the molybdate reagent and dithiothreitol is performed under inert-atmosphere conditions. These results are relevant to the reconstitution of molybdenum-deficient molybdenum cofactor samples using molybdate and dithiothreitol or dithioerythritol solutions.

Dithiothreitol is widely used in biological studies to maintain a reducing environment for anaerobic manipulations of proteins and enzyme cofactors. For example, in the nitrate reduction assay for the molybdenum cofactor, Mo-co, maximal activity is obtained when both additional molybdenum (as MoO$_4^{2-}$) *and* dithiothreitol or dithioerythritol are added to the reconstituting mixture. This effect suggests that isolated Mo-co samples that have partially lost molybdenum can regain the needed metal if the molybdate is added in the presence of DTT or DTE. However, the simple molybdate ion may not be the effective reconstituting form of molybdenum. Aqueous MoO$_4^{2-}$/DTT solutions used during the reconstitution become yellow on standing, indicating the presence of a new species, presumably a molybdenum–dithiothreitol complex.[1] Dithiothreitol is also a required component in the aqueous reaction of MoO$_4^{2-}$, FeCl$_2$, S$_2$O$_3^{2-}$, and the sulfur-transfer enzyme rhodanese, which forms cubane clusters that model the Fe–Mo cofactor of nitrogenase.[2]

L-DTT



DTE



These reports prompted our studies of the molybdenum/dithiothreitol system through which we seek to establish the binding of the potentially polydentate dithiothreitol ligand. The arrangement of the two thiolate and two hydroxyl groups of DTT permits at least tridentate chelation at a single metal center and perhaps coordination of the fourth donor atom if distortion from octahedral geometry is allowed. We report our studies of the molybdate/dithiothreitol system, including a single-crystal X-ray structure of a dimer having a [Mo$_2$O$_5$]$^{2+}$ core bound to a single dtt tetraanion. A reduced product having an EPR spectrum characteristic of Mo(V) has also been observed.

Experimental Section

L-DTT was used as received from Sigma Biochemicals and stored in a desiccator in a freezer. Tetraethylammonium molybdate was prepared from [TEA]$_2$[SO$_4$] and BaMoO$_4$. ^{95}Mo NMR spectra were recorded on a Bruker 400-MHz instrument observing the nucleus at 25.92 MHz. Chemical shifts are referenced to 2 N sodium molybdate in D$_2$O at apparent pH 11. Infrared spectra of samples as KBr disks were recorded on a Perkin-Elmer Model 683 instrument and referenced to 906.2-cm^{-1} absorption of polystyrene. X-Band EPR spectra were examined with a Varian E-3 spectrometer.

[TEA]$_2$[Mo$_2$O$_5$dtt] was prepared by the aerobic reaction of [TEA]$_2$[MoO$_4$] and L-DTT in methanol. [TEA]$_2$[MoO$_4$], 2 mmol, was dissolved in 60 mL of methanol. A solution of 1.5 mmol of L-DTT in

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† Dithiothreitol and dithioerythritol are abbreviated as DTT and DTE, respectively, while dtt and dte denote the tetraanionic ligand forms.

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