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Synthesis, characterization and bonding of fulvalene dimolybdenum(III) and ditungsten(III) cations with one thiolate bridging ligand.

Crystal structure

of $[\text{Mo}_2(\mu\text{-}\eta^5\text{:}\eta^5\text{-C}_{10}\text{H}_8)(\mu\text{-SC}_6\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)_2][\text{Re}_2(\mu\text{-SC}_6\text{H}_5)_3(\text{CO})_6]$

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Abstract

New bridged fulvalene ($\text{Fv} = \mu\text{-}\eta^5\text{:}\eta^5\text{-C}_{10}\text{H}_8$) binuclear molybdenum(III) and tungsten(III) compounds were obtained from the reaction of $[\text{M}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SC}_6\text{H}_5)_2]$ ($\text{M} = \text{Mo}$ or W) with dirhenium decacarbonyl. The complex $[\text{Mo}_2\text{Fv}(\mu\text{-SC}_6\text{H}_5)\text{Cp}_2][\text{Re}_2(\mu\text{-SPh})_3(\text{CO})_6]$ was characterized by single crystal X-ray diffraction. The cation $[\text{Mo}_2\text{Fv}(\mu\text{-SC}_6\text{H}_5)\text{Cp}_2]^+$ showed a relatively rigid $[\text{Mo}_2\text{FvCp}_2]$ unit with an Mo–S–Mo angle of $83.88(7)^\circ$, M–S distances 2.442(2) and 2.450(2) Å and a Mo···Mo distance of 3.256(1) Å. In the $[\text{Re}_2(\mu\text{-SPh})_3(\text{CO})_6]^-$ anion, each metal atom has an octahedral environment (three carbonyl and three thiolate groups) with the two octahedra sharing the face containing the sulphur donor atoms (Re–S–Re angles from $86.63(8)$ to $86.83(8)^\circ$). The Re···Re distance of 3.457(1) Å is long. Extended Hückel molecular orbital calculations were done in order to understand the nature of the metal–metal interaction in the cation and some related complexes. Although the Mo···Mo distance is relatively long, there is a strong interaction between the two d^3 metal atoms, assigned to a σ bond, which leads to diamagnetic behaviour (the anion with two d^6 Re^I centres is also diamagnetic).

1. Introduction

Several heterobimetallic systems based on the metallaligands $[\text{MCp}_2(\text{SR})_2]$ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$, $\text{M} = \text{Mo}^{\text{IV}}$, W^{IV} or Ti^{IV} , $\text{R} = \text{alkyl}$ or aryl) and containing a late transition metal have been reported [1–8]. Previous electrochemical studies of the molybdenum and tungsten thiolate precursors [9] revealed that some of their chemistry could be related to their redox properties. For instance, $[\text{Fe}(\text{Cp}_2)][\text{PF}_6]$ can be used as an oxidizing agent to prepare a wide range of $[\text{MCp}_2(\text{SR})\text{L}]^+$ cations ($\text{L} = \text{PPh}_3$, $\text{P}(\text{OPh})_3$, CO , NH_3 , NCCH_3 , dppe [10] and several *p*-benzonitrile derivatives) [11].

As part of our continuing interest in developing molybdenum and tungsten thiolate chemistry, we have

undertaken the study of thermal reactions with dirhenium decacarbonyl and found that new bridging fulvalene ($\text{Fv} = \mu\text{-}\eta^5\text{:}\eta^5\text{-C}_{10}\text{H}_8$) binuclear molybdenum(III) and tungsten(III) derivatives were formed, probably following reductive coupling of the cyclopentadienyl rings.

Similar fulvalene complexes have been known for a number of years and the structures of a significant number have been determined [12]. In all of them, the fulvalene is twisted around the C–C bond joining the two $\eta^5\text{-C}_5\text{H}_4$ rings, allowing a shortening of the distance between the two metal atoms. A single crystal X-ray structure determination of $[\text{Mo}_2\text{Fv}(\mu\text{-SC}_6\text{H}_5)\text{Cp}_2][\text{Re}_2(\mu\text{-SPh})_3(\text{CO})_6]$ was performed to obtain structural data of this complex. Extended Hückel molecular orbital calculations [13] were done to assess the degree of metal–metal interaction, both in the cation and in the anion.

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2. Results and discussion

2.1. Chemical studies

Reaction of the complexes [MCp₂(SC₆H₅)₂] (M = Mo or W) and [Re₂(CO)₁₀] in the stoichiometric ratio 2:1, in *p*-xylene at reflux temperature for several hours led to the formation of several products. A new compound was isolated in low yield and an X-ray analysis showed the presence of the novel cationic species [Mo₂Fv(μ-SC₆H₅)Cp₂]⁺ (**1**). A homologous tungsten cation, [W₂Fv(μ-SC₆H₅)Cp₂]⁺ (**2**) was identified by comparison with the molybdenum one. The counter ion was, in both cases, the binuclear thiolate triply-bridged dirhenate(I) complex [Re₂(μ-SC₆H₅)₃(CO)₆]⁻ (**3**), also identified by the structural analysis. Other organorhenium products were present in the mixture of products, and the X-ray analysis of one of the crystals isolated revealed a new member of the family of tetranuclear cubane M₄S₄ compounds, namely [Re₄(μ-SC₆H₅)₄(CO)₁₂] [14].

The relatively low yield (~50%) of the reaction product can be explained by the presence of thiolate decomposition products produced by the relatively high temperature (~139°C) at which the reactions took place. Both new molybdenum and tungsten compounds, isolated in the solid state as yellow-brownish crystals, are soluble in dichloromethane and acetonitrile and are moderately stable under air and moisture. The reactions were monitored by IR spectroscopy, following the evolution of the carbonyl stretching vibration pattern (2100–1800 cm⁻¹) on liquid samples taken at regular intervals from the reaction mixture. The IR spectrum of the tungsten compound (KBr pellets) showed two very strong peaks centred at 2000 (sharp) and 1890 (broad) cm⁻¹, while in the case of the Mo^{III} compound three peaks, at 2000, 1910 and 1870 cm⁻¹, were observed. In addition, the spectra contain the characteristic peaks of cyclopentadienyl groups. The diamagnetic behaviour observed in the ¹H NMR spectra is consistent with the presence of a formal M^{II}–M^{III} bond in the d³–d³ cation, as well as with the formulation proposed for the dirhenate anion, as discussed later.

Many fulvalene complexes have been found as products of attempted syntheses of low-oxidation state early-transition metal metallocenes [15] and the formation of the bridging fulvalene ligand is thought to involve reductive coupling of two bridging η¹:η⁵-C₅H₄ rings [12b,16]. In fact, the dimer [Mo₂(μ-η¹:η⁵-C₅H₄)(η⁵-C₅H₅)₃H]⁺, characterized by X-ray diffraction, is a precursor of several binuclear molybdenum derivatives, including the neutral fulvalene-bridged dimolybdenum(III) [Mo₂(Fv)(Cp)₂(H)₂] [17].

Assuming the reaction to occur in a similar way, the first step should include oxidative addition of one C–H bond from the Cp ring to the metal, forming a metal–hydride bond and a sigma-bound η¹:η⁵-C₅H₄ ligand. However, no hydride ligand was observed in the cationic complexes studied in this work. The structure of cation **1** (see below) showed only one bridging thiolate and a Mo–Mo distance in the accepted range for a metal–metal bond. The lack of any evidence for a molybdenum hydride in the IR and ¹H NMR spectra, and in the X-ray crystallographic study, led us to attribute a formal oxidation state of III to both metal atoms, resulting in a formal 18 electron count around each.

The formation of the dinuclear complex [Re₂(μ-SC₆H₅)₃(CO)₆]⁻ as a counter ion suggests that [Re(CO)₅SR] may be an intermediate after the cleavage of the metal–metal bond in [Re₂(CO)₁₀]. Although [Re₂(CO)₁₀] can lose irreversibly one electron from the σ_b orbital to form the radical cation [Re₂(CO)₁₀]^{·+}, which will then form the intermediate mentioned above [18], electrochemical studies (see below) show that this does not happen. The high temperature at which the reaction takes place favours thermally activated Re–Re bond cleavage.

The only rhenium thiolate-bridged anionic analogues known previous to this work were Et₃N[Re₂(μ-SR)₃(CO)₆] (R = Me, ^tBu, SPh or C₆F₅) [19], obtained from the reaction of [Re₂(μ-Br)₃(CO)₆] with ⁿBu₃SnSR in refluxing methanol for 2 h, and the related [Re₂(μ-mtb)₃(CO)₆]⁻, which was obtained by reaction of potassium or caesium monothiobenzoate with rhenium pentacarbonyl bromide at 85°C in ethanol [20].

2.2. Electrochemical studies

Cyclic voltammetric studies of [Mo₂Fv(μ-SC₆H₅)Cp₂][Re₂(μ-SC₆H₅)₃(CO)₆] in acetonitrile solution, in the range +1.8 to -1.6 V showed only a very irreversible wave at a relatively high potential, E_{pa} = 1.7 V, which can be associated either with the cation complex or with the anion counterpart.

In order to see whether the [Re₂(CO)₁₀]^{·+} radical cation electrochemically generated (in our experimental conditions, oxidation of [Re₂(CO)₁₀] occurred at E_{pa} = 1.3 V) could initiate the reaction, the equivalent amount of [MoCp₂(SC₆H₅)₂] was introduced into the voltammetric cell. No peak associated with our fulvalene compound (E_{pa} = 1.7 V) was observed, even after stopping the cycle for a short time at E_{pa} = 1.35 V (small amount of electrolysis).

2.3. X-Ray structure of [Mo₂Fv(μ-SC₆H₅)Cp₂][Re₂(μ-SC₆H₅)₃(CO)₆]

The X-ray study has shown that the structure is formed by [Mo₂Fv(μ-SC₆H₅)Cp₂]⁺ complex cations

TABLE 1. Selected bond lengths (Å) and angles (°) for [Mo₂(η⁵-C₅H₅)₂(η⁵:η⁵-C₁₀H₈)(μ-SPh)]⁺

Bond lengths			
S(4)–C(81)	1.791(5)		
C(61)–C(71)	1.436(9)		
C(61)–C(62)	1.440(8)	C(71)–C(72)	1.423(8)
C(62)–C(63)	1.379(10)	C(72)–C(73)	1.378(11)
C(63)–C(64)	1.422(8)	C(73)–C(74)	1.422(9)
C(64)–C(65)	1.404(10)	C(74)–C(75)	1.395(11)
C(61)–C(65)	1.449(8)	C(71)–C(75)	1.431(8)
Cp rings		Phenyl rings	
C–C range	1.375(9)	C–C range	1.375(8)
	1.426(8)		1.391(9)
Bond angles			
Mo(1)–S(4)–Mo(2)	83.88(8)		
Mo(1)–S(4)–C(81)	121.1(2)	Mo(2)–S(4)–C(81)	123.8(2)
C(61)–C(62)–C(63)	108.9(6)	C(71)–C(72)–C(73)	108.3(6)
C(62)–C(61)–C(65)	106.5(5)	C(72)–C(71)–C(75)	108.1(6)
C(62)–C(63)–C(64)	108.3(6)	C(72)–C(73)–C(74)	107.7(6)
C(63)–C(64)–C(65)	109.1(6)	C(73)–C(74)–C(75)	109.6(7)
C(61)–C(65)–C(64)	107.0(6)	C(71)–C(75)–C(74)	106.2(6)
C(62)–C(61)–C(71)	125.7(5)	C(65)–C(61)–C(71)	126.8(5)
S(4)–C(81)–C(82)	120.1(4)	S(4)–C(81)–C(86)	118.6(4)
Cp rings		Phenyl rings	
C–C–C range	105.5(9)	C–C–C range	119.6(6)
	110.2(7)		121.0(6)

and [Re₂(μ-SC₆H₅)₃(CO)₆]⁻ complex anions. Selected bond lengths and bond angles are given in Tables 1 and 2. Molecular diagrams are shown for the cationic complex in Fig. 1 and for the anionic complex in Fig. 2.

2.3.1. Molecular structure of [Mo₂Fv(μ-SC₆H₅)-Cp₂]⁺

Each Mo atom in the cation is coordinated to one Cp ring, to one η⁵-C₅H₄ ring of the bridging fulvalene to the S atom of the bridging thiophenyl and to the other Mo atom. Each of the four rings is nearly planar, with a maximum deviation of 0.022(7) Å at C(74), one of the carbon atoms of the fulvalene.

The mean distance of the Mo atoms to the Cp rings is 1.970(1) Å, to the rings of the fulvalene, 1.946(3) Å, and the mean angle between the ring normals to one Cp and to one η⁵-C₅H₄ ring is 136.8(4)°. These values fit well into the range usually reported for biscyclopentadienyl complexes [21]. Generally the planes defined by the ring normals and the equatorial plane in this family of complexes are nearly orthogonal. However, in the binuclear complex cation now reported, the relative positions of those planes for each molybdenum (where the equatorial plane means the Mo,Mo,S plane) are far from orthogonality, with deviations of 26.33(10) and 26.39(9)°, respectively.

The S atom of the thiolato bridges between the two Mo atoms, with Mo–S distances of 2.422(2) and 2.450(2)

TABLE 2. Bond lengths (Å) and angles (°) for [Re₂(μ-SPh)₃(CO)₆]⁻

Bond lengths			
Re(1)–S(1)	2.545(2)	Re(2)–S(1)	2.531(2)
Re(1)–S(2)	2.510(1)	Re(2)–S(2)	2.529(2)
Re(1)–S(3)	2.508(2)	Re(2)–S(3)	2.522(1)
Re(1)–C(4)	1.916(6)	Re(2)–C(1)	1.923(7)
Re(1)–C(5)	1.896(6)	Re(2)–C(2)	1.916(5)
Re(1)–C(6)	1.912(5)	Re(2)–C(3)	1.910(6)
S(1)–C(21)	1.796(5)	S(2)–C(11)	1.783(5)
S(3)–C(31)	1.790(6)		
Phenyl rings		C–O range	
C–C range	1.359(16)	C–O range	1.136(9)
	1.394(10)		1.153(7)
Bond angles			
Re(1)–S(1)–Re(2)	85.86(7)		
Re(1)–S(2)–Re(2)	86.63(8)	Re(1)–S(3)–Re(2)	86.83(8)
S(1)–Re(1)–S(2)	76.11(7)	S(1)–Re(2)–S(2)	76.04(7)
S(1)–Re(1)–S(3)	80.70(7)	S(1)–Re(2)–S(3)	80.71(7)
S(2)–Re(1)–S(3)	78.16(8)	S(2)–Re(2)–S(3)	77.57(7)
S(1)–Re(1)–C(4)	93.4(2)	S(1)–Re(2)–C(1)	92.0(2)
S(2)–Re(1)–C(5)	96.7(7)	S(2)–Re(2)–C(3)	100.9(2)
S(2)–Re(1)–C(4)	96.3(2)	S(2)–Re(2)–C(2)	96.7(2)
S(3)–Re(1)–C(6)	93.3(2)	S(3)–Re(2)–C(3)	91.1(2)
S(3)–Re(1)–C(5)	92.9(2)	S(3)–Re(2)–C(1)	98.9(2)
C(5)–Re(1)–C(6)	87.8(3)	C(2)–Re(2)–C(3)	88.1(3)
C(4)–Re(1)–C(6)	91.9(3)	C(1)–Re(2)–C(3)	90.7(3)
C(4)–Re(1)–C(5)	92.5(3)	C(1)–Re(2)–C(2)	87.1(3)
S(3)–Re(1)–C(4)	172.7(2)	S(3)–Re(2)–C(2)	173.9(2)
S(2)–Re(1)–C(6)	170.5(2)	S(2)–Re(2)–C(1)	176.9(2)
S(1)–Re(1)–C(5)	171.2(2)	S(1)–Re(2)–C(3)	171.7(2)
Re(1)–S(3)–C(31)	106.3(2)	Re(2)–S(3)–C(31)	118.7(2)
Re(1)–S(1)–C(21)	105.7(2)	Re(2)–S(1)–C(21)	115.8(2)
Re(1)–S(2)–C(11)	111.3(2)	Re(2)–S(2)–C(11)	121.1(2)
Re–C–O range	174.6(5)	Re–S–C range	105.7(2)
	177.7(5)		121.1(2)
S–C–C range	117.2(5)	Phenyl rings	
	124.6(5)	C–C–C range	118.3(8)
			122.1(9)

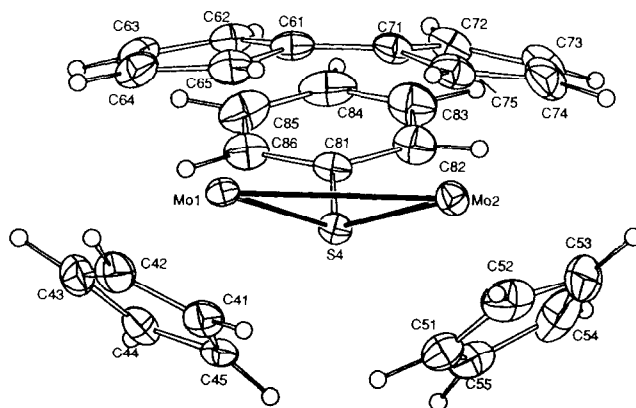


Fig. 1. Molecular diagram of complex cation [Mo₂Fv(μ-SC₆H₅)Cp₂]⁺ showing the atom labelling scheme with 30% thermal ellipsoids.

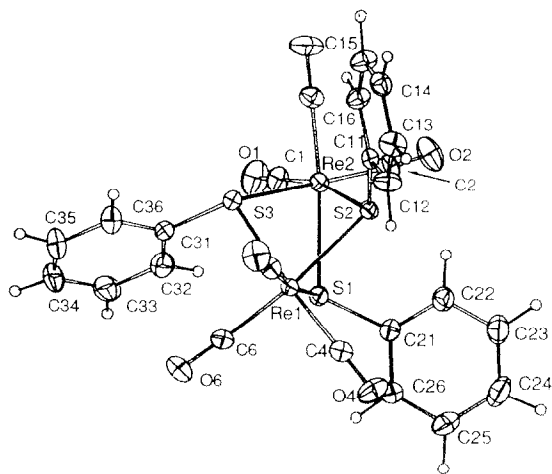
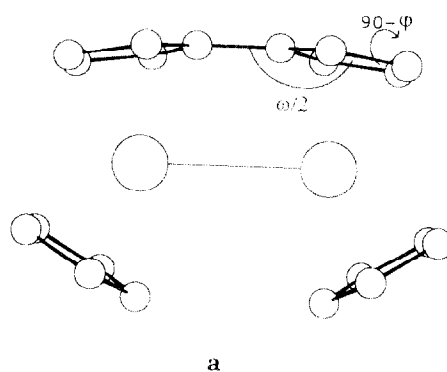


Fig. 2. Molecular diagram of complex anion $[\text{Re}_2(\mu\text{-SC}_6\text{H}_5)_3(\text{CO})_6]^-$ showing the atom labelling scheme with 30% thermal ellipsoids.

Å and an angle Mo–S–Mo of $83.88(7)^\circ$. There are many examples of binuclear complexes with thiolato bridges [22]. The geometry of the M,S,M triangle depends on the existence of an $\text{M} \cdots \text{M}$ interaction, on the number of such triangles, *i.e.* the number of thiolato bridges, and on the steric constraints imposed by nearby bulky ligands. That triangle in the complex $[\text{Mo}_2(\text{CO})_4(\mu\text{-S}(\text{CH}_2)_6)\text{Cp}_2]$ [23] ($\text{Mo} \cdots \text{Mo} = 3.212$ Å, $\text{Mo-S} = 2.531$ Å and Mo-S-M angle 86.2°) is similar to that of the title complex. If, however, the $\text{M} \cdots \text{M}$ interaction is stronger, then this distance is shorter and the Mo-S-M angles are more acute, whereas the Mo-S bonds do not change significantly. Complex $[\text{Mo}_2(\text{CO})_2(\mu\text{-SMe})_3\text{Cp}_2]^+$ [22b], with three thiolato bridges, is an example of this situation, with values of $2.785(2)$ Å and $69.1(2)^\circ$, respectively. The opposite situation is observed in $[\text{Mo}_2(\text{CO})_4(\mu\text{-SPh})_2\text{Cp}_2]$ [24], with two thiolato bridges and no interaction between the two Mo atoms and where those values are $3.940(2)$ Å and $101.62(8)^\circ$, respectively.

A comparison of relevant bond distances and angles for complexes with two Mo atoms bridged by a fulvalene ligand is presented in Table 3.

A comparable bending of this ligand, as measured by the dihedral angle formed by the planes of the C_5H_4 rings, ω , is observed in all these complexes. Another parameter that indicates distortion on the fulvalene ligand is the displacement from perpendicularity between each of the ($\eta^5\text{-C}_5\text{H}_4$) rings and the plane containing both the Mo–Mo bond and the σ C–C bond, φ . The definition of these angles is shown in a.



This last angle is quite small in $[\text{Mo}_2\text{Fv}(\mu\text{-SC}_6\text{H}_5)\text{Cp}_2]^+$ ($0.4(1)^\circ$) and all the other complexes containing both fulvalene and two Cp rings, but significant in the other type of complex. $[\text{MoFv}(\text{CO})_6]$ [12a] and $[\text{MoFv}(\text{CO})_4\{\text{P}(\text{CH}_3)_3\}_2]$ [25c] have angles of 21.1 and 24.2° , respectively.

A π -electron delocalization in the fulvalene ligand is apparent from the observed range, $1.378(11)$ – $1.449(8)$ Å, of the C–C bond lengths in both $\eta^5\text{-C}_5\text{H}_4$ rings, and in the C–C bond length between the rings, $1.436(9)$ Å. This has been observed in many other complexes [12c,26], where the fulvalene ligand is generally bent from planarity to allow a metal–metal interaction. Drage and Volhardt [12a] suggested that the fulvalene

TABLE 3. Structural parameters for dinuclear complexes of molybdenum with bridging fulvalene

Complex	Mo–Mo (Å)	Mo–Cp (Å) ^a	Mo–($\eta^5\text{-C}_5\text{H}_4$) (Å) ^b	α (°) ^b	ω (°) ^c	Ref.
$[\text{Mo}_2\text{Fv}(\mu\text{-SPh})\text{Cp}_2]^+$	3.256(1)	1.970(1)	1.946(3)	136.8(4)	15.7(3)	This work
$[\text{Mo}_2\text{Fv}(\mu\text{-OH})(\mu\text{-H})\text{Cp}_2]^{2+}$	3.053(2)	1.964	1.979	134.8	18.1	25a
$[\text{Mo}_2\text{Fv}(\text{CO})_6]$	3.371(1)		1.991(1)		15.3	12a
$[\text{Mo}_2(\text{MeFv})(\text{H}_2)(\text{MeCp})_2]$	3.2623(5)	1.957	1.927	146.5	20.2	25b
$[\text{Mo}_2\text{Fv}(\text{CO})_4(\text{PMe}_3)_2]$	3.220(1)		2.002(1)		27.0	25c
$[\text{Mo}_2\text{Fv}(\text{H}_3)\text{Cp}_2]^+$	3.227	1.957	1.94	140.4	17.5	17
$[\text{Mo}_2\text{Fv}(\mu\text{-OMoO}_3)\text{Cp}_2]$	3.076	1.994	1.947	130.6	19.3	30

^a These distances were calculated using normals to the C_5 rings. ^b α is the angle ($\eta^5\text{-C}_5\text{H}_5$)–Mo–($\eta^5\text{-C}_5\text{H}_4$). ^c ω is the dihedral angle between the planes of the rings in the fulvalene ligand.

is an electronic bridge between the two metals, even where no bond exists between them.

As mentioned earlier, the formal count of 18 electrons around each Mo atom, the absence of any electron density peak assignable to hydrides, the spectroscopic evidence, and the M–M distance of 3.256(1) Å in the title cation, are consistent with the formation of a Mo–Mo single bond.

2.3.2. Molecular structure of [Re₂(μ-SC₆H₅)₃(CO)₆][−]

In the dinuclear anion, each rhenium atom is coordinated to three sulphur atoms of the thiophenyl bridges and to three carbon atoms of the terminal carbonyls in a distorted octahedral arrangement. The two octahedra share the face defined by three S atoms of the bridging ligands.

The Re–S bonding distances range from 2.508(2) to 2.545(2) Å, the Re–C distances from 1.896(6) to 1.916(6) Å, and the Re–S–Re bonding angles range from 86.63(8) to 86.83(8)°. [Re₂(μ-mtb)₃(CO)₆][−] is another binuclear anionic complex which differs from the anion described only in the bridging ligands, which are thiobenzyl groups instead of thiophenyl groups [20]. In this latter complex, there are two sets of Re–S distances; one, shorter, and with a mean value of 2.540(5) Å, is assumed to contain some π character, resulting from electron delocalization from the thiocarbonyl of the μ-mtb group. The other set, with a mean value of 2.545(6) Å is comparable with the mean value 2.524(1) Å determined in the present anion. The mean angle at the bridging sulphur atom, 84.8(2)° is also similar to the equivalent value of 86.5(1)° in the title anion.

Cotton and Ucko [27] quantified the distortion from an ideal bioctahedron. When the terminal ligands differ from the bridging ligands, some of the parameters derived can be correlated with M···M distances. The difference between β, the M–L–M angle (M = metal centre, L = bridging ligand) and the ideal value of 70.53° for two octahedra should be zero for ideal octahedra, but greater than zero for complexes with non-interacting metal centres and long separations, and less than zero for complexes with attractive interactions between the metal centres. In complex [Re₂(μ-SC₆H₅)₃(CO)₆][−], this parameter has the values 15.10(8), 16.30(8) and 16.33(7)°, and the Re···Re distance is 3.457(1) Å; in complex [Re₂(μ-mtb)₃(CO)₆][−], the equivalent value is 14.27(2)° and the Re···Re distance is 3.404(2) Å. In another example with a bioctahedron as a central core, [Mo₂(NNPh)₄(μ-SC₆H₅)₅][−] [28], a similar situation is observed, with values of β – 70.53° of 14.4(1), 16.2(1) and 17.9(1)° for the Mo···Mo distance of 3.528(1) Å. This analysis is

TABLE 4. Metal–metal distances (Å) and overlap populations in [Mo₂FvCp₂] derivatives

Complex	Mo–Mo distance	Mo–Mo O.P.	Ref.
[Mo ₂ Fv(μ-SC ₆ H ₅)Cp ₂] ⁺ ^a	3.256	0.16	This work
[Mo ₂ Fv(μ-II)(μ-OH)Cp ₂] ²⁺	3.053	0.06	25a
[Mo ₂ Fv(H) ₂ Cp ₂] ⁺	3.362	0.20	25b
[Mo ₂ Fv(μ-H)(H) ₂ Cp ₂] ⁺	3.227	0.05	17
[Mo ₂ Fv(μ-OMoO ₃)Cp ₂]	3.076	0.18	30

^a SH was used in the calculations.

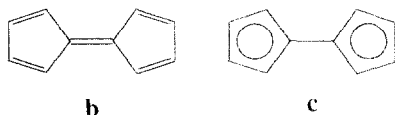
consistent with the absence of an interaction between the metal centres on these complexes, and a formal 18-electron count in each rhenium for the first two cases. However, there are many binuclear complexes with distorted bioctahedron central cores, but with short metal–metal distances, in the range 2.628–2.919 Å, considered to be bonding interactions. The angles at the sulphur bridging ligands are all acute in these cases and consequently the β–70.53° values are negative or close to zero. An example of this type of complex is [Re₂(μ-SC₆H₅)₇(NNPh)₂][−] with an Re···Re distance of 2.744(2) Å and β–70.53° values of –4.8(1), 0.3(1) and 0.3(1)° [28].

2.4. Molecular orbital calculations

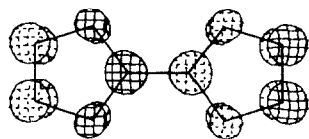
The structure of the dimolybdenum complex was discussed earlier and briefly compared with that of other fulvalene dimolybdenum complexes. One of the most interesting aspects in this small series of compounds is existence of a metal–metal bond. The Mo–Mo distance in the five compounds having both a fulvalene and two Cp rings (Table 4) spans a range from around 3.0 Å to 3.3 Å, the shortest one being observed in a formally Mo^{IV}–Mo^{IV} d²–d² complex, [Mo₂Fv(μ-H)(μ-OH)Cp₂]²⁺, in which no metal–metal bond is expected to occur: both molybdenum atoms have an 18-electron count. In the remaining complexes there are formally Mo^{III}–Mo^{III} d³–d³ species, with different types and numbers of other ligands attached to the main [Mo₂FvCp₂] frame and the presence of Mo–Mo bonds has been postulated in some of them. In this class of complex, diamagnetic behaviour is not always associated with the presence of a metal–metal bond. In some cases, coupling through the fulvalene ligand was postulated to account for the magnetic properties [26,29]. Extended Hückel molecular orbital calculations [13] were done in order to understand the bonding in these complexes. A related problem that is also addressed concerns the aromaticity or amount of π-delocalization in the fulvalene rings.

In order to simplify the interpretation, the geometry of the [Mo₂FvCp₂] frame was idealized to C_{2v} symmetry. This forces a zero torsion of the fulvalene and an eclipsed conformation for the two five-membered rings coordinated to the same Mo atom. Although the calculations show this torsion to be favoured (the optimized geometry of the [Mo₂Fv(μ-SH)Cp₂]⁺ model is very close to that of the [Mo₂Fv(μ-SC₆H₅)Cp₂]⁺ cation described above), as it is accompanied by a small lowering of energy, the qualitative nature of the results is not changed. Ligands can then be added to this skeleton to build up the five complexes, together with the appropriate charge. We show in Table 4 the metal–metal overlap populations, as a measure of the bond strengths, and the corresponding bond lengths. A positive value is found for all the complexes, although it is very small for the two Mo^{IV} compounds, [Mo₂Fv(μ-H)(μ-OH)Cp₂]²⁺ and [Mo₂Fv(μ-H)(H)₂Cp₂]⁺.

Let us start by considering only the [Mo₂FvCp₂] fragment. Neutral fulvalene is aromatic (10 π-electrons), while the dianion has 12 π-electrons. They can be represented approximately as in **b** and **c**.



The neutral species looks like two butadiene units joined by an ethylene molecule and the X-ray structure of a bulky substituted stable fulvalene shows that there is indeed such an alternation of double and single bonds [31]. However, the dianion can be described as two cyclopentadienyl anions joined by a longer C–C bond. The calculated overlap populations (using only one C–C distance in the model) reflect these trends. Populating the LUMO of the neutral species **d** does indeed lead to a longer central C–C bond (antibonding character). This orbital can also be looked upon as the HOMO of a Cp anion.

**d**

The bonding of fulvalene to the two metals resembles the bonding of a cyclopentadienyl anion to a metal (twice), with three components involving donation of electrons from filled levels of the ligand into empty orbitals of the metal fragment. Back donation is negligible. This loss of electrons from a formal dianion leaves the fulvalene ligand in an intermediate situation between **b** and **c**, above. It is expected that there will

be less alternation of C–C bond distances inside the rings than in free substituted fulvalene, but some should still occur. The same reasoning leads us to expect the inter-ring C–C bond to be longer in the complex. This model is consistent with the small fold observed, which implies only a small displacement from planarity, without much influence on the electronic structure. On the other hand, the fact that coordinated fulvalene behaves as two Cp rings is reflected in the reactivity of some complexes. For instance, it is possible to transform reversibly *cis*-fulvalene (as seen in all the previous compounds) into *trans*-fulvalene complexes with minimal changes in the environment of the two metals, implying an easy rotation around the central C–C bond [29d]. A similar analysis has been applied to the related complexes *cis*- and *trans*-[Rh₂Fv(CO)₂(PPh₃)₂] [32], and the results are comparable.

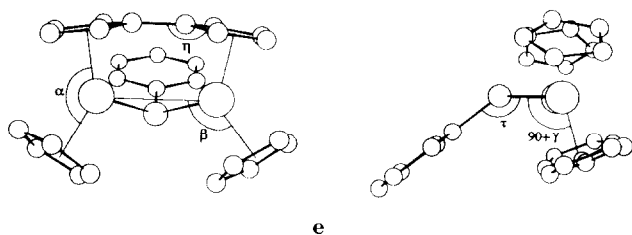
Let us now analyse the metal–metal bond in the model fragment [Mo₂FvCp₂]²⁺, which will be decomposed in two Mo(η⁵-C₅H₄)Cp⁺ units. The frontier orbitals are similar to the three frontier orbitals of the MCp₂ fragment, 1a₁, b₂, 2a₁ [33]. They will each be occupied by three electrons. The interaction between the antisymmetric π orbitals results in one bonding and one antibonding orbital, while the other four, all symmetric, give rise to four orbitals. The one with lowest energy has bonding character, while the next is approximately non-bonding. These interactions are sketched in a simplified form in Fig. 3 and the three lower levels are also shown.

The six electrons will then occupy two bonding levels (one σ, one π) and one non-bonding level. The metal–metal bond can be described as a double bond.

The situation changes when ligands are added to this basic fragment. In [Mo₂Fv(μ-SH)Cp₂]⁺ (the C_s symmetry was kept in all calculations involving a bridging LH, L being an oxygen or sulphur atom). The SH interacts with the two molybdenum atoms, donating electrons to the two LUMOs of the dimetal fragment. The two HOMOs mix and only the bonding orbital (a₁ in Fig. 3) is left relatively unchanged. Two new S–Mo bonds are formed and the Mo–Mo bond remains. This is schematically shown in Fig. 4.

The situation will be very similar for the μ-OMoO₃ derivative (see Table 4). In the dihydride complex, the two hydrides are not bridging. Their bonding to the metal does not affect the Mo–Mo bond significantly. The two remaining complexes in Table 4 still possess some metal–metal bond character in our calculations, in spite of the molybdenum atoms having more ligands around them. The bonding molecular orbital (a₁ in Fig. 3) is involved in the metal–ligand bond formation, but still retains some of its initial metal–metal bonding character.

A complete optimization of the angles in the model complex (**e**) was attempted and the geometry corresponding to the lowest energy species was very close to the experimental one. The optimized structure has the following parameters (defined in **e**, experimental values in parentheses): $\gamma = 22.5(22)$, $\beta = 121(118)$, $\alpha = 135.5(138)$, $\tau = 150(140)$, $\eta = 8(8)^\circ$.



In $[\text{Re}_2(\mu\text{-SC}_6\text{H}_5)_3(\text{CO})_6]^-$, the metals are formally Re^I , d^6 , and for this electron count an octahedral environment around each metal is strongly favoured. The observed biotetrahedral geometry is thus the expected one, as found for the whole family. No metal orbitals are available for metal–metal bonds.

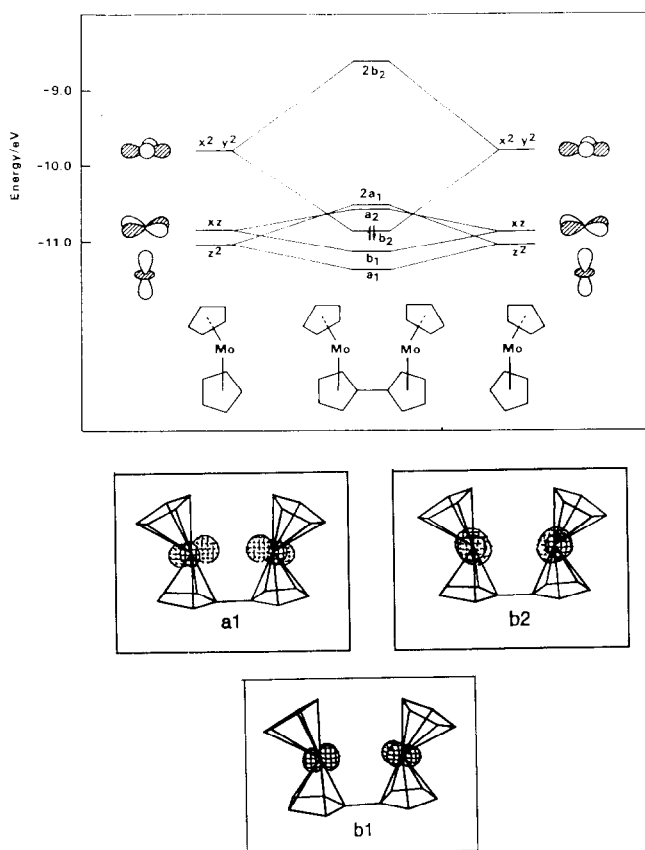


Fig. 3. Interaction diagram between the two molybdenum atoms in $[\text{Mo}_2\text{FvCp}_2]^{2+}$ and representation of the three HOMOs.

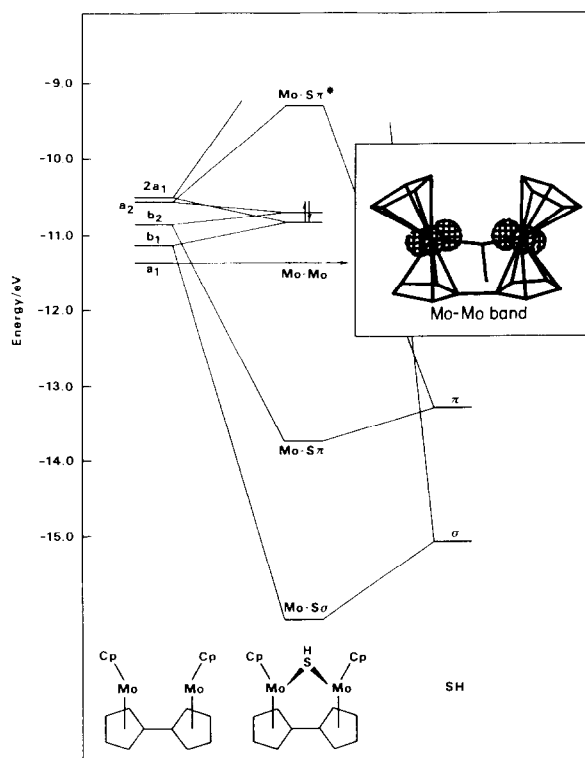


Fig. 4. Interaction diagram between $[\text{Mo}_2\text{FvCp}_2]^{2+}$ and SC_6H_5^- showing the Mo–Mo bonding orbital.

3. Conclusions

The study of the cation in the new compound $[\text{Mo}_2\text{Fv}(\mu\text{-SC}_6\text{H}_5)\text{Cp}_2][\text{Re}_2(\mu\text{-SPh})_3(\text{CO})_6]$ and its comparison with some analogues suggest that the basic $[\text{Mo}_2\text{FvCp}_2]$ unit is relatively rigid. A Mo–Mo bond length of 4 Å was proposed in an early paper as the best for the bis(fulvalene)dimolybdenum derivatives [34]. However, it seems from the larger number of structures now available, those described and others involving other metals such as titanium, niobium, zirconium [12b, c, 26, 29a–d, 35], that the preferred M–M distance in fulvalene–biscyclopentadienyl dimetal complexes is shorter. Values range from 2.8 Å to 3.6 Å, and there is no difficulty for the fulvalene to accommodate a small bending. As seen above in Table 4, the shortest distances may be found in complexes not supposed to have a metal–metal bond [25a], even though in those cases a weak metal–metal interaction was found in our calculations, while a bond between the two metals can be present when the distance is relatively long. A weak interaction between metal atoms may eventually also occur for other systems based on the same basic geometry and contribute to the diamagnetic behaviour exhibited in some cases.

4. Experimental details

All experiments were carried out under N₂ by standard Schlenk-tube techniques. IR spectra were measured on a Perkin-Elmer 457 spectrophotometer with KBr pellets or in solution using 0.1 mm NaCl spaced cells. ¹H NMR spectra were recorded on a Bruker CXP 300 spectrometer.

The solvents acetonitrile and dichloromethane were reagent grade materials, were dried over CaH₂ (acetonitrile also over P₂O₅) and distilled before use under dinitrogen. Diethyl ether was refluxed over sodium wire and distilled before use. Starting materials [MCp₂H₂] (M = Mo^{IV} or W^{IV}) were prepared as described previously [36]. Dirhenium decacarbonyl was purchased from Aldrich and used without further purification.

4.1. Preparation of [Mo₂Fv(μ-SC₆H₅)Cp₂][Re₂(μ-SC₆H₅)₃(CO)₆]

A suspension of 445 mg (~1 mmol) of [MoCp₂(SPh)₂] and 325 mg (~0.5 mmol) of Re₂(CO)₁₀ in 30 ml of *p*-xylene (b.p. ~139°C) was heated under reflux for 12 h. After cooling to room temperature, the mixture was filtered and the solvent removed under vacuum. The brown solid residue was extracted with CH₂Cl₂ and recrystallized from diethyl ether.

IR spectrum: ν(C≡O) 2000, 1910, 1870 cm⁻¹. ¹H NMR (CDCl₃): δ 5.33 (s, C₅H₅, 10 H); 5.65–6.10 (m, Fv, 8H); 7.32 (m) and 8.23 (m) (μ-SC₆H₅, 20 H).

4.2. Preparation of [W₂Fv(μ-SC₆H₅)Cp₂][Re₂(μ-SC₆H₅)₃(CO)₆]

The procedure described before was used, with 16 h of reflux time. IR: ν(C≡O) 2000, 1900 (broad) cm⁻¹. ¹H NMR: (CDCl₃): δ 5.65 (s, C₅H₅, 10 H); 5.69–6.07 (m, Fv, 8H); 7.58 (m) and 8.08 (m) (μ-SC₆H₅, 20H).

4.3. Electrochemical apparatus

The electrochemistry instrumentation consisted of a Princeton Applied Research model 173 potentiometer, model 175 voltage programmer, model 179 digital coulometer and an Omnigraphic 2000 X–Y recorder of Houston Instruments. Potentials were referred to a calomel electrode (SCE) containing a saturated solution of potassium chloride checked relative to a 0.10 M LiClO₄ solution, for which the ferricinium/ferrocene potential was in agreement with the literature [37].

The working electrode was a 2-mm piece of Pt wire. The secondary electrode was a Pt wire coil. The experiments were performed in a PAR polarographic cell at room temperature with solutions 1 mM in solute and 0.1 M in the supporting electrolyte, tetrabutylammonium hexafluorophosphate. Solutions were degassed

with dry dinitrogen before each experiment and a dinitrogen atmosphere was always maintained over the solution.

4.4. Crystal data

C₅₀H₃₈O₆Mo₂Re₂S₄, *M* = 1427.4, triclinic, *P* $\bar{1}$, *a* = 11.555(4), *b* = 14.274(4), *c* = 14.808(5) Å, α = 93.37(2), β = 106.90(2), γ = 98.09(2)°, *V* = 2301(1) Å³, *Z* = 2, *D*_c = 2.06 g cm⁻³, μ = (MoKα) 60.61 cm⁻¹, *F*(000) = 1368.

4.5. Data collection

X-Ray measurements were made on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71069 Å). Unit cell and orientation matrix were obtained by least squares refinement from 25 centred reflections with 13.0 ≤ θ ≤ 18.5°, 11472 integrated intensities were collected using a ω–2θ scan, with 1.5 ≤ θ ≤ 28°, for one unique volume of reciprocal space (range *hkl*: *h* –15 to 15, *k* 0 to 18 and *l* –19 to 19). Three standard reflections were monitored after every 3600 s and their intensities showed no significant decay throughout data collection. The data were corrected for Lorentz, polarization and absorption effects (transmission factor between 0.5231 and 0.9995) with CAD-4 software.

4.6. Structure solution and refinement

Diffraction data were consistent with space groups *P*1 and *P* $\bar{1}$. The space group *P* $\bar{1}$ was assumed with base on a centrosymmetric statistical distribution of intensities. This choice was confirmed by subsequent solution and refinement of the structure. The Re and Mo positions were located by three-dimensional Patterson synthesis. The positions of S, C and O atoms were found from subsequent difference Fourier syntheses. The hydrogen atoms in both complexes were located from difference maps and were introduced into the refinement with C–H distances constrained to 1.00 Å and refined isotropically with global temperature factors. The weighting scheme *w* = 1/[σ²(*F*_o) + (0.02 *F*_o)²] gave acceptable agreement analyses. Final refinement of 839 parameters converged at *R* = 0.030 and *R*_w = 0.032 and *S* = 1.0138 for 8553 reflections with *F*_o ≥ 2σ*F*_o. Final atomic positions and equivalent isotropic temperature factors for non-hydrogen atoms are listed in Table 5. In the final difference Fourier map, no peaks were found that could be attributed to H atoms at 1.5–1.7 Å from the Mo atom.

Statistical tests and Patterson function were calculated with SHELXSS6 [38]. Fourier syntheses and least squares refinements were done with SHELX76 [39]. The final refinement including the hydrogen atoms was made with UPALIS [40]. The illustrations were drawn

TABLE 5. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) for $[\text{Mo}_2\text{Fv}(\mu\text{-SPh})\text{Cp}_2][\text{Re}_2(\mu\text{-SPh})_3(\text{CO})_6]$

Atom	x	y	z	U_{eq}
Re(1)	825.5(2)	4204.2(1)	3203.0(1)	30.4(1)
Re(2)	430.5(2)	1971.6(1)	2009.2(1)	32.0(1)
S(1)	319(1)	3610(1)	1456(1)	34.6(4)
S(2)	-726(1)	2724(1)	2989(1)	31.9(4)
S(3)	2139(1)	2930(1)	3351(1)	35.0(4)
C(1)	1368(5)	1664(4)	1185(4)	46(2)
O(1)	1886(4)	1480(4)	671(4)	76(2)
C(2)	-976(5)	1251(4)	1075(4)	43(2)
O(2)	-1776(4)	758(4)	533(3)	69(2)
C(3)	673(5)	829(4)	2596(4)	43(2)
O(3)	830(5)	143(3)	2948(4)	72(2)
C(4)	-328(5)	5071(4)	2959(4)	43(2)
O(4)	-1032(4)	5580(3)	2780(4)	67(2)
C(5)	1175(5)	4446(4)	4536(4)	42(2)
O(5)	1436(4)	4585(4)	5350(3)	66(2)
C(6)	2161(5)	5197(4)	3288(4)	42(2)
O(6)	2997(4)	5776(3)	3382(4)	71(2)
C(11)	-755(4)	2329(3)	4104(3)	31(2)
C(12)	-1191(6)	2894(4)	4679(5)	50(2)
C(13)	-1311(6)	2612(5)	5524(5)	54(3)
C(14)	-995(5)	1768(4)	5818(4)	45(2)
C(15)	-558(6)	1206(4)	5259(4)	50(2)
C(16)	-436(5)	1476(4)	4400(4)	44(2)
C(21)	-1202(5)	3839(4)	903(4)	38(2)
C(22)	-2267(5)	3230(5)	851(4)	49(2)
C(23)	-3397(6)	3482(6)	443(5)	65(3)
C(24)	-3478(6)	4341(6)	78(6)	71(3)
C(25)	-2438(6)	4953(5)	114(5)	66(3)
C(26)	-1298(5)	4698(4)	518(5)	49(2)
C(31)	3515(4)	3443(4)	3120(4)	40(2)
C(32)	3567(6)	3663(5)	2234(5)	56(3)
C(33)	4671(7)	4093(5)	2124(6)	68(3)
C(34)	5716(6)	4297(5)	2882(7)	77(4)
C(35)	5647(6)	4075(6)	3747(8)	87(4)
C(36)	4564(5)	3644(5)	3878(5)	60(3)
Mo(1)	4854.5(5)	-245.5(3)	7408.8(3)	31.2(1)
Mo(2)	3874.9(4)	1787.6(3)	7282.8(3)	38.9(2)
S(4)	5754(1)	1309(1)	8266(1)	34.9(4)
C(41)	3380(5)	-976(4)	7998(5)	49(2)
C(42)	3903(6)	-1698(4)	7672(5)	56(3)
C(43)	5159(6)	-1592(4)	8207(5)	56(3)
C(44)	5436(5)	-810(4)	8882(5)	50(2)
C(45)	4336(5)	-420(4)	8759(4)	41(2)
C(51)	2678(6)	1273(5)	8264(5)	58(3)
C(52)	1971(6)	1652(7)	7514(6)	74(4)
C(53)	2497(10)	2634(8)	7609(8)	97(5)
C(54)	3566(9)	2809(6)	8398(8)	87(4)
C(55)	3639(6)	1957(6)	8785(5)	62(3)
C(61)	4744(5)	382(4)	6005(4)	44(2)
C(62)	5992(5)	241(5)	6413(4)	46(2)
C(63)	6008(6)	-718(5)	6478(5)	52(2)
C(64)	4784(6)	-1212(5)	6101(5)	55(3)
C(65)	3990(5)	-550(5)	5835(4)	49(2)
C(71)	4326(5)	1284(4)	5953(4)	42(2)
C(72)	5082(6)	2183(5)	6306(4)	53(2)
C(73)	4335(7)	2859(5)	6283(5)	63(3)
C(74)	3100(6)	2396(6)	5881(5)	66(3)
C(75)	3073(5)	1421(5)	5705(4)	54(2)

TABLE 5 (continued)

Atom	x	y	z	U_{eq}
C(81)	7266(4)	1856(4)	8312(4)	39(2)
C(82)	7525(5)	2823(4)	8289(5)	51(2)
C(83)	8721(7)	3251(5)	8409(5)	66(3)
C(84)	9646(6)	2712(6)	8567(5)	68(3)
C(85)	9382(6)	1740(6)	8588(5)	63(3)
C(86)	8183(5)	1304(5)	8463(4)	50(2)

with ORTEP-II [41]. The atomic scattering factors and anomalous scattering terms were taken from *International Tables* [42]. Lists of observed and calculated structure factors, tables of anisotropic thermal parameters and tables of hydrogen atomic coordinates are available from the authors.

4.7. Molecular orbital calculations

All the calculations were of the extended Hückel type [13] with modified H_{ij} 's [43]. The basis set for the metal atom consisted of ns , np , and $(n-1)d$ orbitals. The s and p orbitals were described by single Slater-type wave functions, and the d orbitals were taken as contracted linear combinations of two Slater-type wave functions.

The geometry of $[\text{Mo}_2\text{Fv}(\mu\text{-LH})\text{Cp}_2]$ ($L = \text{S}$ or O) species was modelled with C_s symmetry. The L and the two Mo atoms lie in the xz plane, the Mo-Mo axis being the xx direction. All the five-membered rings were considered regular pentagons ($\text{C-C} = 140$ pm) lying 198 and 195 pm from the Mo atoms, respectively for Cp and Fv . The remaining distances (pm) and angles (deg) were as follows: $\sigma\text{-C-C} = 144.4$, $\text{C-H} = 108$, $\text{Mo-Mo} = 326$, $\text{Mo-L} = 243.5$, $\text{L-H} = 135$, $\text{S-C} = 181$, $\text{Cp-Mo-Fv} = 141$. All the other parameters were described as needed.

Standard parameters were used for C , O , S , H , while those for Mo were as follows ($-H_{ii}/\text{eV}$, ζ): $5s$ 8.77, 1.96; $5p$ 5.60, 1.90; $4d$ 11.06, 4.54, 0.5899 (C_1), 1.90 (ζ_2), 0.5899 (C_2). The three-dimensional molecular orbital drawings were made using the program CACAO [44].

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