



# ELECTRON IMPACT MASS SPECTRA OF BIS-THIOLATO COMPLEXES OF MOLYBDENUM(IV) AND TUNGSTEN(IV)

*The mass spectra of the following compounds,  $(\pi-C_5H_5)_2M(SR)_2$  with  $M=Mo(IV)$ ,  $W(IV)$ ,  $R=alkyl$ , have been obtained and are discussed in detail. All four compounds exhibit unimolecular metastable transitions which were used to support fragmentation pathways. The molecular ion is significant for all the compounds and the structure of the alkyl groups strongly determines the fragmentation pattern for this type of complexes. Further, the results suggest that the stability of the metal-cyclopentadienyl bond is higher than that of the metal-sulphur bond.*

## 1 — INTRODUCTION

The electron impact mass spectra of organometallic compounds show a great variety of peaks due to the presence of numerous ions containing at least one polyelectronic element. This is particularly the case with complexes of the type bithiolato in which not only a metal but also sulphur is present. For this reason it is sometimes rather easy, using the isotopic distribution of the peaks, to deduce the probable composition of a particular ion. Moreover the structure of the ion can be determined and is supported in many cases by observed metastable transitions.

Following this approach the electron impact mass spectra of complexes of the type  $(\pi-C_5H_5)_2M(SR)_2$  with  $M=Mo(IV)$ ,  $W(IV)$ ,  $R=alkyl$ , have been studied and are discussed in detail. This paper reports the results obtained with the organometallic compounds of  $Mo(IV)$  and  $W(IV)$ : bis-*n*-hexanethiolato (bis- $\pi$ -cyclopentadienyl) tungsten(IV), bis-*n*-heptanethiolato (bis- $\pi$ -cyclopentadienyl) tungsten(IV), bis-methanethiolato (bis- $\pi$ -cyclopentadienyl) molybdenum(IV) and bis-*t*-butanethiolato (bis- $\pi$ -cyclopentadienyl) molybdenum(IV), which were prepared according to established methods in the literature [1,2].

## 2 — EXPERIMENTAL

The mass spectra were recorded with a AEI MS9 mass spectrometer using the direct insertion probe technique under the following conditions: accelerating voltage 8 kV, electron beam energy 70 eV, current emission 100  $\mu A$ . The source temperature varying between 190 and 260°C was chosen for each compound to ensure that decomposition previous to ionisation did not occur.

## 3 — RESULTS AND DISCUSSION

3.1 — *Bis-n-hexanethiolato (bis- $\pi$ -cyclopentadienyl) tungsten(IV):  $(\pi-C_5H_5)_2W(S n-C_6H_{13})_2(I)$ ; bis-n-heptanethiolato (bis- $\pi$ -cyclopentadienyl) tungsten(IV):  $(\pi-C_5H_5)_2W(S n-C_7H_{15})_2(II)$ .*

The relative abundances of the most important ions in the mass spectra of these compounds are shown in Table 1 and 2 and their fragmentation patterns in figs. 1 and 2.

Table 1  
Relative abundance of ions of the mass  
spectrum of  
( $\pi$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>W(S n-C<sub>6</sub>H<sub>13</sub>)<sub>2</sub> (I)

Ion m/z	Intensity as percentage of base peak
65	3.1
311	13.6
312	27.9
313	66.7
314	65.1
315	57.6
316	57.6
317	50.0
344	24.2
345	90.9
346	69.7
347	100.0
348	33.3
349	81.8
378	6.1
429	65.2
430	53.0
431	84.8
432	24.2
433	72.7
434	18.2
463	4.8
546	24.0
547	20.0
548	35.0
549	14.0
550	10.0

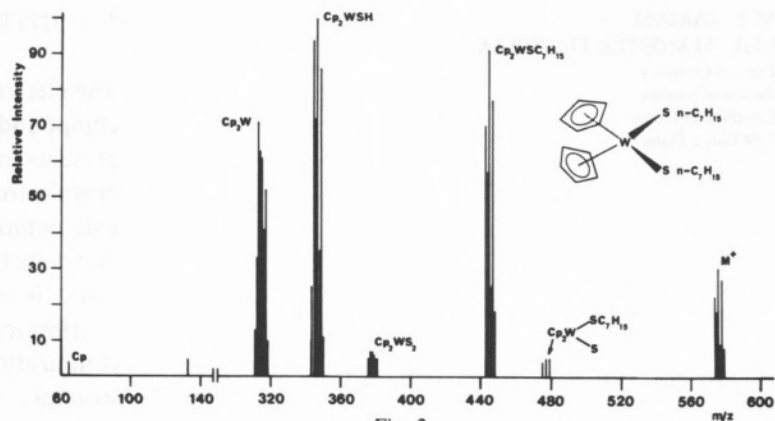


Fig. 2  
Mass spectrum of bis-n-heptanethiolato(bis- $\pi$ -cyclopentadienyl)  
tungsten(IV)

Table 2  
Relative abundance of ions of the mass  
spectrum of  
( $\pi$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>W(S n-C<sub>7</sub>H<sub>15</sub>)<sub>2</sub> (II)

Ion m/z	Intensity as percentage of base peak
65	4.0
132	5.0
311	13.0
312	36.0
313	72.0
314	63.0
315	61.0
316	41.0
317	52.0
318	10.0
343	10.0
344	25.0
345	94.0
346	72.0
347	100.0
348	35.0
349	86.0
350	11.0
376	5.0
377	7.0
378	7.0
379	6.0
380	5.0
443	70.0
444	57.0
445	91.0
446	25.0
447	77.0
448	18.0
475	4.0
476	3.0
477	5.0
479	4.8
574	22.0
575	18.0
576	30.0
577	9.0
578	27.0
579	8.0

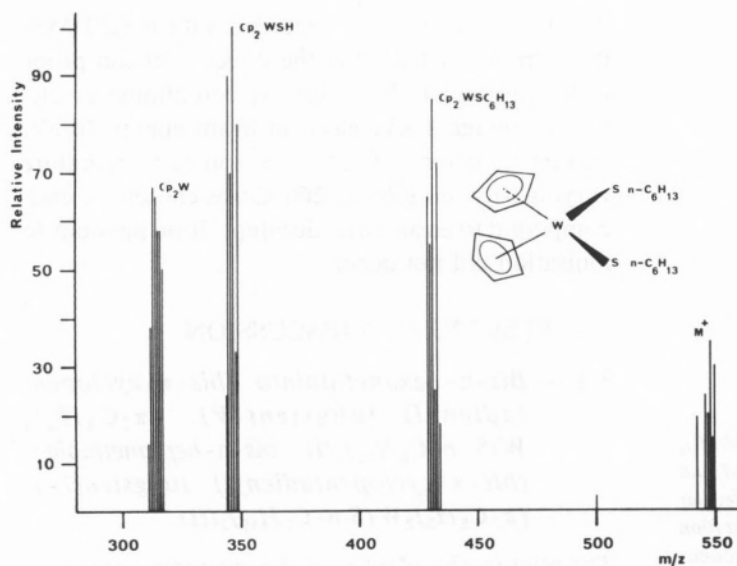
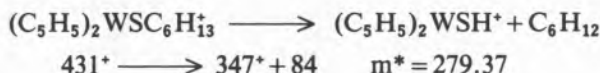


Fig. 1  
Mass spectrum of bis-n-hexanethiolato(bis- $\pi$ -cyclopentadienyl)  
tungsten(IV)

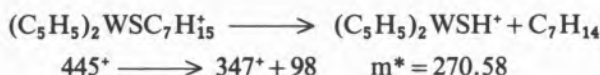
Both spectra are very similar presenting the following common features. The molecular ion is one of the most intense peaks and the most abundant fragment ions always contain the two cyclopentadienyl groups attached to tungsten either with or without the sulphur containing moieties. This seems to lead to the conclusion that cleavage of metal-cyclopentadienyl bond is more difficult than cleavage of metal-sulphur bond.

Elimination of a neutral alkene leads to mass 347 (base peak) in an important fragmentation in which the intact alkyl group is lost by  $(C_5H_5)_2WSC_6H_{13}$  with transfer of a hydrogen atom back to a sulphur atom of the ionic moiety. The existence of a hydride species in the mass spectra of organometallic compounds has already been mentioned [3]. On the other hand this type of mechanism is common when the compound contains an heteroatom with an alkyl group attached to it [4].

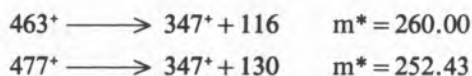
For compound I this is supported by the observed metastable transition:



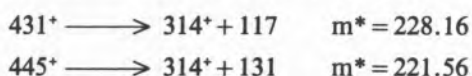
A similar situation is observed for compound II the corresponding metastable transition being:



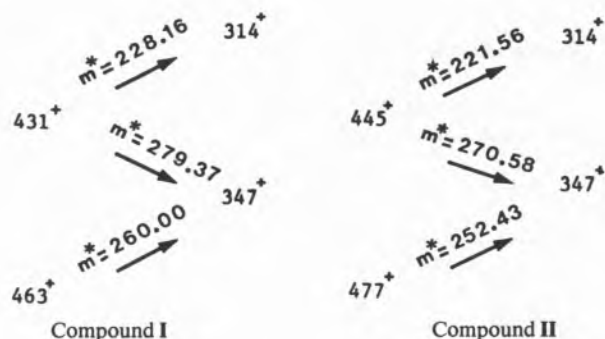
However the peak of mass 347 can also be formed from ion of mass 463 in compound I and from ion of mass 477 in compound II, through a similar mechanism accompanied by the loss of the second sulphur atom. In support of this the following metastable transitions were observed:



Two other metastable transitions corresponding to the formation of peak of mass 314 to which can be assigned the structure  $(C_5H_5)_2W$ , were observed respectively in compound I and compound II:



The similar origin for ions of mass 314 and 347 found in both spectra and metastable supported can be summarised according to the following scheme:



### 3.2 — Bis-*n*-methanethiolato (bis- $\pi$ -cyclopentadienyl) molybdenum(IV): $(\pi-C_5H_5)_2Mo(SCH_3)_2$ (III); bis-*t*-butanethiolato (bis- $\pi$ -cyclopentadienyl) molybdenum(IV): $(\pi-C_5H_5)_2Mo(S t-C_4H_9)_2$ (IV).

The relative abundances of the most important ions of the mass spectra of these compounds are shown in Tables 3 and 4 and their fragmentation patterns in figs. 3 and 4.

In both spectra the molecular ions exist being an abundant ion in the methyl derivative but of low abundance in the complex containing the *t*-butyl groups.

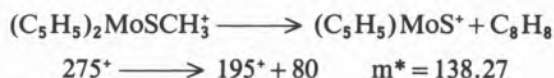
As it was observed in the two complexes of tungsten the cleavage of metal-cyclopentadienyl bond is also more difficult than the cleavage of the metal-sulphur bond.

Comparison of the intensities of the ions with the same structure originated from compounds III and IV show several differences in the respective abundance:

i — ion of mass 292,  $(C_5H_5)_2MoS_2^+$ , is the most intense peak in compound IV but negligible in compound III.

ii — ion of mass 260,  $(C_5H_5)_2MoS^+$ , is less abundant in compound III than in compound IV.

iii — ion of mass 195,  $CpMoS^+$  shows lower yield in compound III than in compound IV. For the methyl complex the following metastable transition accounts for its origin:



This fragmentation path can be explained by the loss of one alkyl group accompanied by the cleavage of one cyclopentadienyl-metal bond. Coupling of both radicals thus obtained, favoured by the exis-

Table 3  
Relative abundance of ions of the mass  
spectrum of  
( $\pi$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mo(SCH<sub>3</sub>)<sub>2</sub> (III)

Ion m/z	Intensity as percentage of base peak
65	2.0
130	8.4
195	12.2
222	48.9
223	28.9
224	33.3
225	68.9
226	84.4
227	64.4
228	100.0
229	46.7
230	35.5
231	18.9
254	7.8
255	5.6
256	10.0
257	20.0
258	14.4
259	20.0
260	21.1
261	15.6
262	13.3
263	13.3
269	13.3
270	8.0
271	8.9
272	16.7
273	17.8
274	13.3
275	24.4
277	8.9
292	2.7
310	3.4
316	15.6
318	11.1
319	17.8
320	20.0
321	13.3
322	27.8
324	13.3

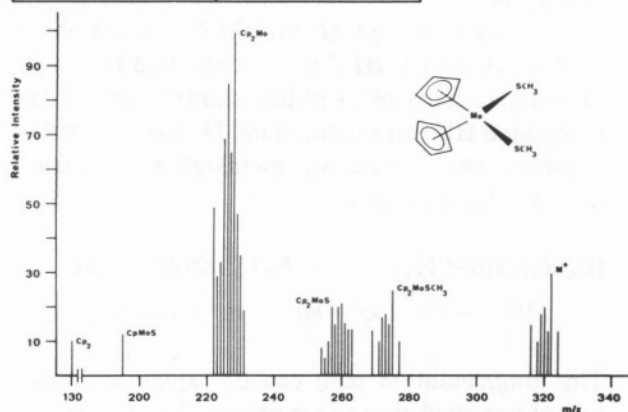


Fig. 3

Mass spectrum of bis-methane-thiolato(bis- $\pi$ -cyclopentadienyl)  
molybdenum(IV)

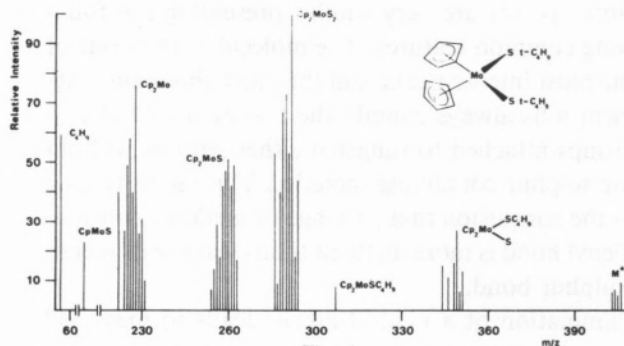


Fig. 4

Mass spectrum of bis-t-butanethiolato(bis- $\pi$ -cyclopentadienyl)  
molybdenum(IV)

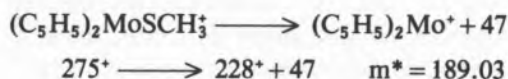
Table 4  
Relative abundance of ions of the mass  
spectrum of  
( $\pi$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Mo(S t-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub> (IV)

Ion m/z	Intensity as percentage of base peak
57	60.0
195	22.6
222	40.0
224	26.7
225	48.9
226	57.8
227	40.0
228	75.6
229	25.6
230	31.1
231	9.6
232	4.9
254	7.3
255	14.2
256	28.9
257	17.8
258	42.2
259	46.7
260	51.1
261	42.2
262	48.9
263	16.9
286	53.3
287	9.3
288	40.0
289	66.7
290	73.3
291	53.3
292	100.0
293	17.8
294	44.4
317	7.6
344	15.3
346	11.3
348	15.6
349	26.7
350	6.0
351	12.9
403	6.0
404	7.0
405	5.0
406	8.9

tence of  $\pi$  electrons in the cyclopentadienyl ring which are easily shared after ionisation and cleavage, most probably accounts for the formation of the neutral molecule cyclohexadiene 1-3.

However the corresponding metastable transition for the *t*-butyl complex could not be detected.

iv — ion of mass 228,  $(C_5H_5)_2Mo^+$ , the most intense peak in the spectrum of compound **III** arises from ion of mass 275 and the corresponding metastable transition was observed.



In compound **IV** mass 228 also gives a rather intense peak but no metastable transition was observed which could indicate a similar origin.

A peak at  $m/z = 402$  observed in the mass spectrum of compound **III** occurs at a mass greater than the molecular ion. It is unlikely that it arises from a dimeric species since no other ions consistent with such possibility were found. A more likely explanation is that the peak can be assigned to a rearrangement ion due to an ion molecule reaction although ion-molecule reactions are rather unusual under normal operating pressures.

Finally it is of interest to note that the compounds studied show some similar behaviour under electron impact although enough particular details can be detected that allow for their characterization. The mass spectra of the two tungsten complexes present the same fragmentation features. This should be expected considering that the only difference in their structure consists of the length of the normal chain of the alkyl groups. The molecular ion is present in the spectra of all four compounds but its abundance is very low in the molybdenum complex with the tertiary alkyl group. On the contrary, the peaks corresponding to all fragment ions with the same structure arising in the four compounds studied, are much less intense for the tertiary alkyl molybdenum complex than for the other three. This is probably due to the more bulky structure of tertiary alkyl when compared with the structure of the normal chain of the alkyl groups present in the other complexes. The results obtained show that the structure of the alkyl groups strongly determines the fragmentation pathways for this type of compounds. It can also be inferred that the cyclopenta-

dienyl ring is not easily lost. This is the usual behaviour for transition metal complexes when the metal is to the left of the Co-Rh-Ir triad [6]. This fact accounts for a higher stability of the metal-cyclopentadienyl bond than that of the metal-sulphur bond.

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## RESUMO

**Espectros de massa por impacto electrónico de complexos bis-tiolato de molibdénio(IV) e de tungsténio(IV).**

Os espectros de massa de compostos do tipo  $(\pi-C_5H_5)_2M(SR)_2$ , em que  $M = Mo(IV)$ ,  $W(IV)$  e  $R =$  alquilo, são discutidos em pormenor e comparados.

Os compostos estudados apresentam transições metastáveis às quais se recorreu para interpretar os processos de fragmentação envolvidos em cada caso. Todos os compostos originam um ião molecular importante e verifica-se que neste tipo de complexos os grupos alquilo presentes determinam, de maneira decisiva, o mecanismo de fragmentação. Além disso os resultados permitem inferir que a estabilidade da ligação metal-ciclopentadienilo é maior que a da ligação metal-enxofre.