

NEGATIVE ION MASS SPECTRA OF $\text{Os}_3(\text{CO})_{12}\text{X}_2$ AND $\text{Os}_3(\text{CO})_{10}\text{X}_2$ COMPLEXES (X = Br, I)

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(Received October 17th, 1978)

Summary

The negative-ion mass spectra at 70 eV of the compounds $\text{Os}_3(\text{CO})_{12}\text{X}_2$ and $\text{Os}_3(\text{CO})_{10}\text{X}_2$ (X = Br, I) are reported. Negative molecular ions are absent and only Os_3 -containing fragments due to the loss of carbonyl groups are observed. $[\text{M} - \text{CO}]^-$ is the base peak in the spectrum of $\text{Os}_3(\text{CO})_{10}\text{I}_2$ and has a very high abundance in that of $\text{Os}_3(\text{CO})_{10}\text{Br}_2$, whereas it is very weak in the spectra of $\text{Os}_3(\text{CO})_{12}\text{X}_2$, where $[\text{M} - 3\text{CO}]^-$ is the base peak. This change in the ionic intensities is related to the closed and open structure of the Os_3 unit in $\text{Os}_3(\text{CO})_{10}\text{X}_2$ and $\text{Os}_3(\text{CO})_{12}\text{X}_2$ respectively.

Introduction

The application of the negative-ion mass spectrometry is attracting increasing attention both as a valuable analytical tool and as a technique which gives information complementary to the positive-ion mass spectrometry for several classes of organic compounds [1–3]. In some cases, moreover, the negative-ion mass spectra, obtained by electron impact at 70 eV, show abundant molecular ions, which are not detectable in the corresponding positive-ion mass spectra [4,5].

The relatively few papers dealing with the study of coordination and organometallic compounds by negative-ion mass spectrometry so far published [1,6–19] were mainly concerned with investigating the electron capture processes with these compounds and correlating the negative- with the positive-ion mass spectra.

In a recent paper on trinuclear carbonyl clusters it was suggested that the comparison between the positive- and negative-ion mass spectra of these compounds can give valuable information on the structure of the ions which are formed in the ionisation chamber [19]. The results reported below on the nega-

tive-ion mass spectra of $\text{Os}_3(\text{CO})_{12}\text{X}_2$ and $\text{Os}_3(\text{CO})_{10}\text{X}_2$ ($\text{X} = \text{Br}, \text{I}$) support this suggestion.

Results and discussion

As usually observed in the negative-ion mass spectra at 70 eV of metal carbonyls which have the rare gas configuration, the negative molecular ion is absent and $[\text{M} - \text{CO}]^-$ is the highest ion in the spectrum [1].

In agreement with the behaviour shown by $\text{M}_3(\text{CO})_{12}$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) [19], the complexes $\text{Os}_3(\text{CO})_{12}\text{X}_2$ and $\text{Os}_3(\text{CO})_{10}\text{X}_2$ ($\text{X} = \text{Br}, \text{I}$) give a small number of negative ions compared with the ions present in the positive-ion spectra [20, 21], and show peaks in the low energy region for negative fragments which are indicative of dissociative electron-capture processes. Moreover the capture maxima occur at increasing energy as more carbonyls are lost. This indicates that the loss of CO groups occurs in successive steps, as is usually the case in the positive- and negative-ion fragmentation patterns of these compounds.

The most interesting feature of these spectra is the variation of the ion abundances, shown in Table 1. $[\text{M} - \text{CO}]^-$ is very weak in the spectra of $\text{Os}_3(\text{CO})_{12}\text{X}_2$, which display $[\text{M} - 3\text{CO}]^-$ as base peak, whereas $[\text{M} - \text{CO}]^-$ is the base peak in the spectrum of $\text{Os}_3(\text{CO})_{10}\text{I}_2$ and shows a very high abundance in that of $\text{Os}_3(\text{CO})_{10}\text{Br}_2$. The $\text{Os}_3(\text{CO})_{12}\text{X}_2$ compounds contain a linear arrangement of the metal atoms [20,22] and exhibit tri- bi- and mono-metal ions in their positive ion mass spectra, whereas only trimetal ions are present in the positive-ion mass spectra of $\text{Os}_3(\text{CO})_{10}\text{X}_2$, which contain the Os_3 cluster [21]. These positive-ion fragmentation patterns indicate that in the ion source the trimetal ions from $\text{Os}_3(\text{CO})_{12}\text{X}_2$ and $\text{Os}_3(\text{CO})_{10}\text{X}_2$ are likely to have the same structure as the neutral compounds. Thus one can suggest that the negative ions from these compounds also preserve the original structures and that the pattern of the ion abundances observed in the negative-ion mass spectra are strictly related to the ion structures. The presence of the Os_3 cluster in $\text{Os}_3(\text{CO})_{10}\text{X}_2$ enhances the delocalisation of the single electron and stabilises $[\text{M} - \text{CO}]^-$. In contrast, the delocalisation of the negative charge in $\text{Os}_3(\text{CO})_{12}\text{X}_2$ is made less favourable by

TABLE 1

NEGATIVE ION MASS SPECTRA (PERCENTAGE ABUNDANCES) OF $\text{Os}_3(\text{CO})_{12}\text{X}_2$ AND $\text{Os}_3(\text{CO})_{10}\text{X}_2$ ($\text{X} = \text{Br}, \text{I}$) AT 70 eV

Ion	$\text{Os}_3(\text{CO})_{12}\text{Br}_2$	$\text{Os}_3(\text{CO})_{12}\text{I}_2$	$\text{Os}_3(\text{CO})_{10}\text{Br}_2$	$\text{Os}_3(\text{CO})_{10}\text{I}_2$
$[\text{M} - \text{CO}]^-$	10	5	90	100
$[\text{M} - 2\text{CO}]^-$	30	70	100	85
$[\text{M} - 3\text{CO}]^-$	100	100	75	90
$[\text{M} - 4\text{CO}]^-$	25	35	60	85
$[\text{M} - 5\text{CO}]^-$	40	45	25	25
$[\text{M} - 6\text{CO}]^-$	65	85	10	5
$[\text{M} - 7\text{CO}]^-$	15	40	5	
$[\text{M} - 8\text{CO}]^-$	3	15		45
$[\text{M} - 9\text{CO}]^-$				30
$[\text{M} - 10\text{CO}]^-$				35

the linear arrangement of the metal atoms, and loss of two more carbonyl groups is required to give the base peak.

It can be concluded that these results confirm the hypothesis, suggested for the spectra of trinuclear carbonyl clusters [19], that the change of the negative ion abundances can give information on the structure of the ionic species.

Experimental

All the compounds were prepared as previously described [20,21].

The mass spectra were recorded on a single-focusing Hitachi RMU 6H mass spectrometer, with a trap current of 20 μ A when the ionising energy was 70 eV. The samples were introduced into the ion source through a direct inlet system. Perfluorokerosene was used as mass reference standard.

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