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Negative-Ion Mass Spectra of Tetranuclear Carbonyl Clusters

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The negative-ion mass spectra at 70 eV of the carbonyl clusters $Co_4(CO)_{12}$, $Rh_4(CO)_{12}$, $Ir_4(CO)_{12}$, $Co_3Rh(CO)_{12}$, $Co_2Rh_2(CO)_{12}$ and $CoRh_3(CO)_{12}$ are reported. Negative molecular ions are absent and only tetrametal fragments, formed by loss of carbonyl groups, are observed. $[M_4(CO)_{10}]^-$ is the base peak in the spectrum of all the compounds except $CoRh_3(CO)_{12}$, whereas $[M_4(CO)_{11}]^-$ is present only in the spectrum of $Ir_4(CO)_{12}$ with a good intensity and in that of $Co_4(CO)_{12}$ with a weak abundance. This trend is explained by the variation of the metal–metal bond strength and by the different back-donation to the carbonyl groups as measured by the ionisation potential of the metal.

Introduction

A number of papers on the negative-ion mass spectra of metal-containing compounds have recently been published [1–10]. These papers usually concern the study of the electron capture processes by these compounds and the information complementary to the positive-ion mass spectra.

As part of an investigation on the negative-ion mass spectra of organic [11, 12] and metal containing compounds [13], we discuss here the negative-ion mass spectra of the tetranuclear carbonyl clusters $M_4(CO)_{12}$ and compare the results with those observed in the spectra of trinuclear carbonyl clusters [13].

Experimental

All the compounds were prepared as described in the literature [14–17]. The mass spectra were recorded on a single focusing Hitachi RMU 6H mass spectrometer with a trap current of 20 μA, when the ionising energy was 70 eV. All the samples were introduced into the ion source through a direct inlet system. Perfluorokerosene was used as mass reference standard.

Results and Discussion

The negative-ion mass spectra at 70 eV of the $M_4(CO)_{12}$ (M = Co, Rh, Ir) compounds display the behaviour which is usually shown by the metal carbonyls with the rare gas configuration [1]. The molecular negative ions are absent and a low number of ions formed upon loss of carbonyl groups and containing the four metal atoms is present. Reso-

TABLE. Negative-Ion Mass Spectra (Percentage Abundances) of $M_4(CO)_{12}$ Compounds at 70 eV.

Species	$Co_4(CO)_{12}$	$Rh_4(CO)_{12}$	$Ir_4(CO)_{12}$	$Co_3Rh(CO)_{12}$	$Co_2Rh_2(CO)_{12}$	$CoRh_3(CO)_{12}$
$[M_4(CO)_{11}]^-$	1		18			
$[M_4(CO)_{10}]^-$	100	100	100	100	100	90
$[M_4(CO)_9]^-$	70	95	35	45	95	100
$[M_4(CO)_8]^-$	25	30	30	15	5	5
$[M_4(CO)_7]^-$	30	22	30			
$[M_4(CO)_6]^-$	20	28	25			
$[M_4(CO)_5]^-$	23	40	20			
$[M_4(CO)_4]^-$	10	10	5			
$[M_4(CO)_3]^-$	2					

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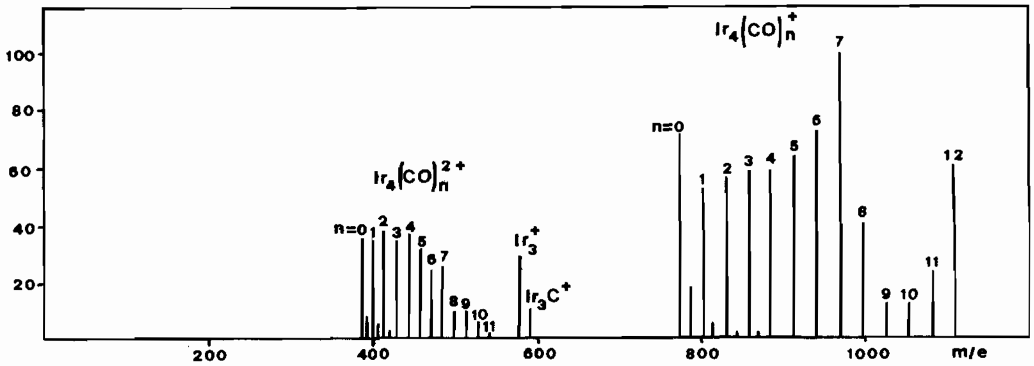

Fig. 1. Positive-ion mass spectrum of $Ir_4(CO)_{12}$ (the ions of the ^{193}Ir isotope are reported).

nance peaks, observed for the various negative ions in the low energy region, are indicative of dissociative electron-capture processes.

The spectrum of $Co_2Rh_2(CO)_{12}$ exhibits fragments originated by loss of carbonyl groups and also ions originated from $Co_3Rh(CO)_{12}$ and $CoRh_3(CO)_{12}$, which have both been reported to be formed by $Co_2Rh_2(CO)_{12}$ through a redistribution process of the neutral $Co_2Rh_2(CO)_{12}$ [17].

As shown in the table, the base peak is $[M_4(CO)_{10}]^-$ in the spectra of all the compounds examined, except $CoRh_3(CO)_{12}$. $[M_4(CO)_{11}]^-$ is observed to a good extent in the spectrum of $Ir_4(CO)_{12}$ whereas it is just detected in the spectrum of $Co_4(CO)_{12}$ and absent in that of $Rh_4(CO)_{12}$. Moreover, the spectra of the three mixed Co–Rh dodecacarbonyls show that the ion current transported by $[M_4(CO)_{10}]^-$ decreases and that transported by $[M_4(CO)_9]^-$ increases when Co is gradually substituted by Rh in the tetranuclear cluster. Thus, in this class of carbonyl clusters, Ir contributes the highest stability to $[M_4(CO)_{11}]^-$, Rh decreases the stability of the ions in the highest mass region, and Co seems to be in an intermediate position.

The trend of the ionic abundances in the negative-ion mass spectra of $M'_3(CO)_{12}$ (M' = Fe, Ru, Os) has been assumed to be related to the variation of the metal–metal bond strengths and consequently to the open or closed structures of the trimetal ions [13]. The trend described here for the tetranuclear carbonyl clusters $M_4(CO)_{12}$ appears to be significantly different, in particular for the behaviour shown by the compounds containing rhodium atoms. A reason for this may be found in the structure of these compounds, in which each metal atom is bonded to other three metal atoms, and this makes the influence of the metal–metal bond strengths less important compared with the trinuclear clusters. A remarkably different behaviour is also revealed by the positive-ion mass spectra of $M'_3(CO)_{12}$ and $M_4(CO)_{12}$. In all the $M_4(CO)_{12}$ compounds examined the positive-ion current is mainly transported by tetrametal ions [18] and in particular 74% in $Co_4(CO)_{12}$, 89% in $Rh_4(CO)_{12}$ and 97% in $Ir_4(CO)_{12}$. The positive-ion mass spectrum of $Ir_4(CO)_{12}$ is shown in the Fig. 1.

It can be suggested that the increase of the metal–metal bond strength, passing from the first to the third transition series, gives some contribution to the variation of the abundances of the negative ions of $M_4(CO)_{12}$ and, in particular, to the stability of $[Ir_4(CO)_{11}]^-$, similarly to the behaviour displayed by $Os_3(CO)_{12}$ [13]. However, other factors, in this case, must also be responsible for the fragmentation pattern and the small differences of the spectral features of $Co_4(CO)_{12}$ and $Rh_4(CO)_{12}$ can be due to the different back donation from the metals. A relative increase of stability of the ionic species containing a lower number of CO groups, occurring when Co is substituted by Rh, can be ascribed to the lowest ionisation potential of the atomic rhodium (7.46 eV) in the group. The highest back-donation to the carbonyl groups from rhodium atoms, compared with cobalt and iridium, should give the best delocalisation of the charge, after loss of two or three carbonyl groups.

We have no indications that hypothetical different arrangements of the carbonyl groups in these species can give a contribution to the fragmentation pattern.

From the observations discussed above it can be concluded that, compared to $M'_3(CO)_{12}$, less drastic differences in the negative-ion mass spectra occur upon changing the metal in $M_4(CO)_{12}$ compounds and this is in agreement with the observations made on their positive-ion mass spectra. The more complicated trend of the ion abundances of $M_4(CO)_{12}$ can be due to the effect of more than one factor on the ion stabilities.

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