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Multiply Charged Ions in the Mass Spectra of Trinuclear Carbonyl Metal Compounds and their Derivatives

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Abstract

Doubly charged ions observed in the mass spectra of trimetal carbonyl compounds of the iron group and of their derivatives at different ionizing energy are reported. In the case of $Os_3(CO)_{12}$, $Ru_3(CO)_{12}$, $RuOs_2(CO)_{12}$ and $Ru_2Os(CO)_{12}$ the abundances of the doubly charged ions decrease gradually when osmium atoms are substituted by ruthenium atoms and when ionizing electrons energy is decreased. They follow a characteristic trend in which the highest charge is transported by fragments containing a number of carbonyl groups which increases with decreasing ionizing energy. The mass spectrum of $Fe_3(CO)_{12}$ contains very weak doubly charged species. $H_2Os_3(CO)_{12}$ exhibits a behaviour similar to that of $Os_3(CO)_{12}$, while $Os_3(CO)_{10}Br_2$ and $Os_3(CO)_{12}Br_2$ show that different structures do not appreciably affect the occurrence of doubly charged ions.

The strong increase of the stabilization of doubly charged species, observed in the mass spectra of $Fe_3(CO)_8[C_2(C_6H_5)_2]_2$, $Ru_3(CO)_8[C_2(C_6H_5)_2]_2$ and $Os_3(CO)_8[C_2(C_6H_5)_2]_2$, shows a drastic influence of the organic ligands superimposed to that of the nature of metal atoms. In the mass spectrum of $Os_3(CO)_8[C_2(C_6H_5)_2]_2$ at 70 eV a rather strong $[M - 8CO]^{3+}$ is observed.

Introduction

Interaction of an electron beam at 70 eV with some polynuclear carbonyl transition metal compounds gives, in the ion source of a mass spectrometer, doubly charged ions in addition to the usual monocharged species [1–3]. In particular doubly charged ions have been reported to be abundant for $Os_3(CO)_{12}$ [2] and weak for $Ru_3(CO)_{12}$, $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ [1]. Polynuclear complexes prepared from metalcarbonyls and organic ligands usually show a more pronounced tendency to eject more than one electron, even though the occurrence of multiply charged ions is reported in only a few papers [4–12]. Usually their presence is considered, in fact, not to be important for the characterization of the complexes.

As a part of a mass spectrometric investigation on the gas phase behaviour of metal containing compounds [9, 13–22] it seems to be interesting to study the factors affecting the formation and abundances of multiply charged ions in the mass spectra of some polynuclear carbonyl metal compounds.

Experimental

$Os_3(CO)_{12}$ was purchased from Strem. The other compounds were prepared according to the literature: $Ru_3(CO)_{12}$ [23], $Fe_3(CO)_{12}$ [24], $RuOs_2(CO)_{12}$ and $Ru_2Os(CO)_{12}$ [14], $H_2Os_3(CO)_{10}$ [25], $Os_3(CO)_{12}Br_2$ [26], $Os_3(CO)_{10}Br_2$ [27], $Fe_3(CO)_9X_2$ (X = S, Se, Te) [28], $Fe_3(CO)_8[C_2(C_6H_5)_2]_2$ [29], $Ru_3(CO)_8[C_2(C_6H_5)_2]_2$ [30] and $Os_3(CO)_8C_2[(C_6H_5)_2]_2$ [31].

The mass spectra were run on the double-focusing Kratos MS 80 mass spectrometer of the Laboratory of Gas Chromatography–Mass Spectrometry, Provincia of Turin, University of Turin, with emission current of 100 μA, accelerating voltage of 2 kV, resolution 1000 (10% valley definition) and scan rate of 30 s/dec.

The samples were introduced through a direct inlet system at the minimum temperature at which the ion abundances are reproducible.

Results and Discussion

In order to investigate the effect of the nature of metal atoms on the occurrence of doubly charged ions we initially examined the trinuclear carbonyl metal compounds of the iron group, because the mass spectrum of $Os_3(CO)_{12}$ at 70 eV contains all the $[Os_3(CO)_n]^{2+}$ (n = 12–0) ions and that of $Ru_3(CO)_{12}$ contains the $[Ru_3(CO)_n]^{2+}$ (n = 2–0).

The abundances of the $[Os_3(CO)_n]^{2+}$ (n = 12–0) ions (Table I), originated at different energies of the

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TABLE I. Abundances of Trimetallic Singly (S) and Doubly (D) Charged Ions[a] in the Mass Spectra of $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ at Different Electron Beam Energies[b]

Ions	$Os_3(CO)_{12}$										$Ru_3(CO)_{12}$					
	100		70		50		40		30		100		70		50	
	S	D	S	D	S	D	S	D	S	D	S	D	S	D	S	D
$[M]^{n+}$	52	0.5	52	1	50	1	61	1	54	2	53		51		32	
$[M - CO]^{n+}$	28	8	30	7	26	5	29	7	26	4	42		43		21	
$[M - 2CO]^{n+}$	10	6	9	6	10	3	11	5	11	3	10		9		8	
$[M - 3CO]^{n+}$	31	7	41	8	27	4	35	6	34	3	21		20		13	
$[M - 4CO]^{n+}$	100	29	100	26	100	19	100	20	100	9	99		98		55	
$[M - 5CO]^{n+}$	65	27	67	24	66	15	68	14	72	5	100		100		60	
$[M - 6CO]^{n+}$	36	25	42	27	43	16	49	12	51	4	59		56		39	
$[M - 7CO]^{n+}$	43	31	55	38	50	21	61	11	61	2	62		50		46	
$[M - 8CO]^{n+}$	30	42	42	32	38	18	42	10	42	2	61		67		52	1
$[M - 9CO]^{n+}$	37	50	59	39	60	19	58	7	58		50	1	55	1	48	1
$[M - 9CO - O]^{n+}$		4		5							5		5			
$[M - 10CO]^{n+}$	38	47	48	46	50	12	45	1	39		48	5	51	4	43	3
$[M - 10CO - O]^{n+}$	7	9	6	9	4						7	2	6	2		
$[M - 11CO]^{n+}$	25	52	36	38	32	6	29		18		42	7	50	8	46	3
$[M - 11CO - O]^{n+}$	15	21	18	18	10						14	5	18	2		
$[M - 12CO]^{n+}$	26	55	38	32	37	2	20		6		83	6	95	3	100	1
% total charge	56.8	43.2	64.4	35.6	81.0	19.0	86.6	13.4	94.4	5.6	96.7	3.3	97.5	2.5	98.4	1.6

[a] $n = 1$ for S and $n = 2$ for D. [b] Energy is given in eV.

electron beam, follow a characteristic trend: at 100 eV nominal energy $[M - 12CO]^{2+}$, $[M - 11CO]^{2+}$ and $[M - 9CO]^{2+}$ display the strongest abundances, at 70 eV $[M - 10CO]^{2+}$, at 50 eV $[M - 9CO]^{2+}$ and $[M - 7CO]^{2+}$, at 40 eV $[M - 5CO]^{2+}$ and $[M - 4CO]^{2+}$, while at 30 eV only $[M - 4CO]^{2+}$ shows a rather good abundance (Fig. 1). Moreover the charge transported by $[M]^{2+}$, with respect to that of all the doubly charged ions, increases gradually from about 1% at 100 eV to about 6% at 30 eV, even though the doubly charged ions transport 45.2% of the total ionic charge at 100 eV and only 5.6% at 30 eV.

When one osmium is substituted by one ruthenium atom in the mixed carbonyl metal compound $RuOs_2(CO)_{12}$ the percentage of the total charge of the $[RuOs_2(CO)_n]^{2+}$ (n = 12–0) ions is lower than that of $[Os_3(CO)_n]^{2+}$ (n = 12–0) ions at the electron energies investigated and the most abundant doubly charged ions contain one carbonyl group at 100 eV, two, three, four and eight carbonyl groups at 70, 50, 40 and 30 eV respectively (Table II).

A further decrease of the doubly charged ions abundances is observed in the mass spectrum of $Ru_2Os(CO)_{12}$, while $Ru_3(CO)_{12}$ displays only weak $[Ru_3(CO)_n]^{2+}$ ions with n = 3–0 and $[Ru_3(CO)_nC]^{2+}$ with n = 2–0 at 70 and 100 eV. Under 50 eV electron energy no doubly charged ion is observed in the spectrum of $Ru_3(CO)_{12}$.

Also at the usual energies at which mass spectra are recorded (100–50 eV) the abundances of the doubly charged ions observed in the spectra of these compounds seem to be strongly affected by the energy of the ionizing electrons and by the consequent variation of the excitation energy of the ions, whilst the abundances of the corresponding singly charged ions are substantially unchanged. This behaviour of the doubly charged ions can be ascribed to the fact that the double positive charge, mainly localized on the metal atoms, strongly reduces the back donation to the ligands and consequently the metal–CO bond order.

The decrease of the metal–CO bond strength is important in this respect since metastable transitions support that any doubly charged ion with (n – 1) carbonyl groups is originated, at least in part, by loss of a CO molecule from the corresponding doubly charged ion with n carbonyl groups.

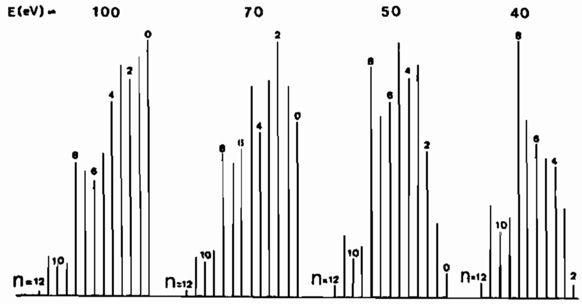

Fig. 1. Relative abundances of $[Os_3(CO)_n]^{2+}$ (n = 12–0) ions at 100, 70, 50 and 40 eV ionizing electrons energy.

TABLE II. Abundances of Trimetallic Singly (S) and Doubly (D) Charged Ions[a] in the Mass Spectra of $RuOs_2(CO)_{12}$ and $Ru_2Os(CO)_{12}$ at Different Electron Beam Energies[b]

Ions	$RuOs_2(CO)_{12}$										$Ru_2Os(CO)_{12}$					
	100		70		50		40		30		100		70		50	
	S	D	S	D	S	D	S	D	S	D	S	D	S	D	S	D
$[M]^{n+}$	31	2	38	1	30	1	37	1	47	0.8	36		35		40	
$[M-CO]^{n+}$	29	5	34	3	27	3	33	3	40	2	37		41		38	
$[M-2CO]^{n+}$	10	13	10	4	6	3	10	3.5	11	3	19		23		21	
$[M-3CO]^{n+}$	12	3	15	4	11	2	15	2	17	1	11		12		15	2
$[M-4CO]^{n+}$	100	13	100	8	100	6	100	7	100	5	61		65	2	64	6
$[M-5CO]^{n+}$	62	21	57	10	59	12	58	8	61	4	100	1.5	100	5	100	7
$[M-6CO]^{n+}$	45	28	50	8	50	9	52	6	55	3	50	3	49	2	57	2
$[M-7CO]^{n+}$	48	22	52	11	64	11	56	7	58	3	56	7	64	12	75	6
$[M-8CO]^{n+}$	36	41	36	17	46	19	39	10	49	3	48	12	56	5	60	11
$[M-9CO]^{n+}$	45	38	48	18	61	24	54	8	57	1	44	17	51	13	56	7
$[M-9CO-O]^{n+}$		3	6													
$[M-10CO]^{n+}$	42	40	41	19	60	18	42	6	45	0.5	32	14	42	16	43	18
$[M-10CO-O]^{n+}$	4	5	3	4							2	3		2	4	
$[M-11CO]^{n+}$	30	44	31	16	47	13	34	4	30	0.4	30	22	34	25	36	10
$[M-11CO-O]^{n+}$	12	16	10	5							5	5	8	6		
$[M-12CO]^{n+}$	48	29	47	12	58	7	54	1	28	0.2	51	25	65	12	45	4
% total charge	63.3	36.7	80.3	19.7	82.9	17.1	90.7	9.3	95.7	4.3	84.2	15.8	86.6	13.4	89.2	9.8

[a] $n = 1$ for S and $n = 2$ for D. [b] Energy is given in eV.

The hypothesis mentioned above explains the three main features observed in the mass spectra of the compounds considered above. When the electron beam energy and then the excitation energy deposited on the ions is gradually decreased: (i) the percentage of the charge transported by the doubly charged ions decreases, because the overall probability of metal–CO bond ruptures decreases; (ii) the fragmentation of the doubly charged ions is reduced and, therefore, the relative abundances of the ions containing few CO groups decrease and at the same time those of the ions containing more CO groups increase; (iii) the amount of the charge transported by $[M]^{2+}$ relatively increases, as the fragmentation lessens. Also the rupture of the C–O bond occurs in doubly charged ions as in singly charged ions, when most of the carbonyl groups have been lost.

In the mass spectrum of $Fe_3(CO)_{12}$ very weak trinuclear doubly charged species are observed: at 100 eV $[Fe_3]^{2+}$, relative abundance (r.a.) 1.5 with respect to $[Fe_3(CO)_7]^+$, r.a. 100, and at 70 eV $[Fe_3(CO)_2]^{2+}$ r.a. 0.5 and $[Fe_3]^{2+}$ r.a. 3. At both 100 eV and 70 eV also weak doubly charged species at m/z 70 and 56 are present.

These results, together with those reported in Tables I and II, clearly show that the nature of the metal atoms plays the main role with respect to occurrence and abundances of doubly charged ions. A strictly related behaviour with the increase of the stabilization of higher oxidation states observed in solution chemistry is operative in the gas phase.

For energies in the 100–40 eV range the abundances of the singly charged ions originated from carbonyl transition metal compounds are weakly affected by the energy of the ionizing electrons. At 30 eV, on the contrary, significant decreases of the abundances of the light singly charged fragments are observed (Tables I and II), but this does not prevent one from fully characterizing the sample. For this reason mass spectra of this type of complexes run at 30–40 eV nominal energy seem to be useful to eliminate overlapping of doubly charged ions.

In the mass spectrum of $H_2Os_3(CO)_{10}$ the $[H_2Os_3(CO)_n]^+$ (n = 10–0) singly charged ions are present with good abundance and loss of H_2 is first observed for $n = 6$ (the ratio between $[H_2Os_3(CO)_6]^+$ and $[Os_3(CO)_6]^+$ is about 1:1) and from ions containing three, two, one and no carbonyl groups. The $[H_2Os_3(CO)_n]^{2+}$ doubly charged ions were observed for n = 10–0 in the range 100–40 eV and ejection of H_2 is firstly observed from $[H_2Os_3(CO)_7]^{2+}$ and also from ions containing three, two, one and no carbonyl groups as in the case of singly charged species. At 30 eV electron energy only doubly charged ions containing at least five carbonyl groups are present.

The trend of the ionic abundances is very similar to that described above for $Os_3(CO)_{12}$ and the maximum of the charge is transported by ions containing none and one carbonyl group at 100 eV, two and three carbonyl groups at 70 eV and five carbonyl groups at 50 eV. The $[H_2Os_3(CO)_{10}]^{2+}$ molecular ion is observed in the whole 30–100 eV energy range and its relative abundance gradually increases from 0.4% at 100 eV to 8% at 30 eV of the total charge of the doubly charged ions.

Large differences are observed in the singly charged ions present in the mass spectra of $Os_3(CO)_{10}Br_2$ and $Os_3(CO)_{12}Br_2$, which were ascribed to the different structures of the two compounds. $Os_3(CO)_{10}Br_2$ is characterized by an Os_3 closed cluster and displays only trinuclear charged species [27], whilst $Os_3(CO)_{12}Br_2$, in which a linear arrangement of osmium atoms is present, shows abundant singly charged ions containing three, two or one osmium atoms [26]. Both complexes give abundant trimetallic $[Os_3(CO)_nBr_2]^{2+}$ ions, which transport at 100 eV 24% and 22% of the total charge and at 70 eV 23% and 20% for $Os_3(CO)_{10}Br_2$ and $Os_3(CO)_{12}Br_2$ respectively. In addition, $Os_3(CO)_{12}Br_2$ gives also rather weak bimetallic doubly charged species. All these data may indicate that, in complexes containing the same metal atoms and ligands, different structures and numbers of metal–metal bonds affect to little extent the stabilization of the doubly charged ions.

The trend of the abundances of the doubly charged ions in the mass spectra of $Ir_4(CO)_{12}$ and $Re_2(CO)_{10}$ [32] is rather similar to that of $Os_3(CO)_{12}$ and confirms that the number of metal–metal bonds and structural features play only a secondary effect in this respect.

A significant improvement in the stabilization of doubly charged ions is usually observed in the trimetallic complexes obtained from the metal-carbonyls of Fe, Ru and Os with ligands of a very different nature. In the mass spectra of the $Fe_3(CO)_9X_2$ (X = S, Se, Te) complexes, run in the 100–50 eV energy range, the $[Fe_3(CO)_nX_2]^{2+}$ ions transport a charge representing 25% to 10% of the total charge of the trimetallic ions. A comparison with the results reported above on $Fe_3(CO)_{12}$ shows that the presence of only two chalcogen atoms as ligands causes a substantially high increase of the stabilization of species containing two positive charges.

A much higher increase of the stabilization of multiply charged ions is exhibited in the mass spectra of complexes containing organic ligands with moieties fit for charge delocalization, such as $Fe_3(CO)_8[C_2(C_6H_5)_2]_2$ [29], $Ru_3(CO)_8[C_2(C_6H_5)_2]_2$ [30] and $Os_3(CO)_8[C_2(C_6H_5)_2]_2$ [31]. Table III reports the abundances of singly and doubly charged trimetallic ions, at 40 and 70 eV, of the three complexes.

The effect of the ligand, which in these complexes is part of a five membered metalcyclopentadiene ring, is remarkable in that $[M - 8CO]^{2+}$ is the base peak not only in the spectra of osmium and ruthenium complexes but also in that of the iron complex at 70 eV. In the mass spectrum of $Fe_3(CO)_8[C_2(C_6H_5)_2]_2$ the $[M - nCO]^{2+}$ (n = 8–0) ions are accompanied by species which are originated by elimination of H_2 molecules from $[M - 8CO]^{2+}$ and by bimetallic ions. In the spectra of $Ru_3(CO)_8[C_2(C_6H_5)_2]_2$ and $Os_3(CO)_8[C_2(C_6H_5)_2]_2$ elimination

TABLE III. Abundances of the Trimetallic Singly (S) and Doubly (D) Charged Ions[a] in the Mass Spectra of $Fe_3(CO)_8[C_2(C_6H_5)_2]_2$, $Ru_3(CO)_8[C_2(C_6H_5)_2]_2$ and $Os_3(CO)_8[C_2(C_6H_5)_2]_2$ at Different Electron Beam Energies[b]

Ions	$Fe_3(CO)_8[C_2(C_6H_5)_2]_2$				$Ru_3(CO)_8[C_2(C_6H_5)_2]_2$				$Os_3(CO)_8[C_2(C_6H_5)_2]_2$			
	70		40		70		40		70		40	
	S	D	S	D	S	D	S	D	S	D	S	D
$[M]^{n+}$	1		1		14	1	15	2	48	1	67	1.5
$[M - CO]^{n+}$	9		10		41	2	51	2	61	4	100	6
$[M - 2CO]^{n+}$	79	1	87	2	11	6	16	5	16	19	21	21
$[M - 3CO]^{n+}$	49	3	58	7	87	7	81	9	62	12	83	19
$[M - 4CO]^{n+}$	51	2	54	6	42	19	51	22	31	30	50	38
$[M - 5CO]^{n+}$	78	5	85	7	33	9	54	13	40	21	58	18
$[M - 6CO]^{n+}$	61	12	39	10	26	14	40	16	27	29	42	28
$[M - 7CO]^{n+}$	83	17	92	12	22	10	31	12	25	35	71	25
$[M - 8CO]^{n+}$	86	100	100	81	78	100	100	62	35	100	82	67
$[M - 8CO - H_2]^{n+}$	20	18	31	15	2	47	38	25	8	66	32	52
$[M - 8CO - 2H_2]^{n+}$	7	2	9	1	51	32	2	8	40	32	74	12
$[M - 8CO - 3H_2]^{n+}$					21	10	71		12	60	78	13
$[M - 8CO - 4H_2]^{n+}$					6	7			19	35	36	
Σ[c]					150	90	119	15	50	140	33	17
% Total charge	76.6	23.4	80.1	19.9	62.5	37.5	77.9	22.1	44.8	55.2	72.3	27.7

[a] n = 1 for S and n = 2 for D. [b] Energy is given in eV. [c] Sum of abundances of trimetallic ions originated from $[M - 8CO]^{n+}$ ionic species following the loss of one or more C_2H_2 and H_2 molecules.

of one or more C_2H_2 and H_2 molecules from $[M - 8CO]^{2+}$ also occurs, to give species whose abundances are reported in Table III as sum (Σ).

Superimposed on the effect of the ligand is the influence of the nature of the metal atoms: both at 70 and 40 eV electron energy the charge transported by the doubly charged ions increases passing from the iron to the ruthenium and osmium complex. The strong ability of osmium to favour the formation of multiply charged ions is confirmed by the figure (55.2%) of the charge which the doubly charged ions of $Os_3(CO)_8[C_2(C_6H_5)_2]_2$ transport at 70 eV electron energy and by the presence of $[M - 8CO]^{3+}$ with a relative abundance of 23 (r.a. 100 for $[M - 8CO]^{2+}$).

In conclusion, the nature of the metal and of the ligand plays the major role in the stabilization of the multiply charged ions present in the mass spectra of trimetallic complexes, run at the usual energy range, whilst structures and number of metal–metal bonds do not show significant effects in this respect. Regular and characteristic trends of the abundances of the doubly charged ions originated by these compounds are observed as a function of the ionizing electrons energy.

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