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Doubly charged ions in the mass spectra of mono- and binuclear metal carbonyl derivatives

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Abstract

Doubly charged ions produced in the mass spectra of mono- and bimetallic carbonyl compounds at 40, 70 and 100 eV electron beam energies are reported. $Fe_2(CO)_9$ and $Mn_2(CO)_{10}$ give very weak doubly charged ions, whilst a strong increase of the relative abundances of these species is observed in the mass spectra of $Re_2(CO)_{10}$. The presence of the halogeno ligands in $Mn(CO)_5X$ and $Re(CO)_5X$ (X=Cl, Br, I) produces a stabilizing effect on the doubly charged ions. A higher ion current is transported by doubly charged fragments of $Mn(CO)_5X$ with respect to $Mn_2(CO)_{10}$, while $[M]^{2+}$ accompanied by doubly charged high mass fragments are originated by $Re(CO)_5X$. The strong increase of the relative abundances of doubly charged ions observed in the mass spectra of $Fe_2(CO)_6C_4(C_2H_5)_4$ and $Os_2(CO)_6C_4(C_2H_5)_4$ suggests a significant effect of the unsaturated organic ligands, which adds to that of the nature of the metal atom on the stabilization of multiply charged ions.

Introduction

Recently, a strong interest has arisen for multiply charged ions since the electrospray ionization method has given the opportunity of studying high molecular weight compounds through highly charged ions [1].

In the mass spectra of carbonyl transition metal compounds, obtained by electron beams at 70 eV, doubly charged ions are frequently observed [2–4]. We have previously investigated the factors affecting the stability and abundance of doubly charged ions in the mass spectra of trinuclear carbonyl metal compounds [4] and in this paper we report the formation of doubly charged ions at different electron energies from mono- and binuclear metal compounds and the factors affecting their abundances. Data on doubly charged ions produced at 70 eV from some of the compounds here studied have been reported previously [5].

Experimental

$Mn_2(CO)_{10}$, $Re_2(CO)_{10}$ and $Fe_2(CO)_9$ were purchased from Fluka. The other compounds were prepared according to the literature: $Mn(CO)_5X$ (X=Cl, Br, I), $Re(CO)_5X$ (X=Cl, Br, I) [6, 7]; $Fe_2(CO)_6S_2$ [8]; $Fe_2(CO)_6C_4(C_2H_5)_4$ [9, 10]; $Os_2(CO)_6C_4(C_2H_5)_4$ [11].

The mass spectra were run on a double-focusing Kratos MS 80 with emission current of 100 μA, accelerating voltage of 2.7 kV, resolution 1000 (10% valley definition) and scan rate of 10 s/dec.

The samples were introduced into the ion source at the most convenient distance from the electron beam to obtain the strongest intensities of the peaks in the high mass region. A glass rod inserted on a probe was used, on which a little amount of each sample has been deposited. The source was maintained at room temperature [12].

Results and discussion

In the mass spectrum of $Mn_2(CO)_{10}$ at 100 eV the base peak is $[M-10CO]^+$, relative abundance (r.a.) 100, and a percentage abundance higher than 0.5 is shown only by two doubly charged bimetallic ions, $[M-8CO]^{2+}$ (r.a. 2) and $[M-7CO]^{2+}$ (r.a. 1.5). Also $[Mn(CO)_3]^{2+}$, $[Mn(CO)_2]^{2+}$ and $[MnCO]^{2+}$ are observed. The total charge transported by doubly charged ions is 3.5%, when the energy

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of the electron beam is 100 eV and decreases to 1% at 70 eV. The doubly charged ions show a relative abundance lower than 0.1% with ionizing electrons of 40 eV.

Rather abundant doubly charged ions are present in the mass spectra of $Re_2(CO)_{10}$ at 100, 70 and 40 eV (Table 1). They show a trend analogous to that observed in the mass spectra of trinuclear carbonyl metal compounds, such as $Os_3(CO)_{12}$ and $RuOs_2(CO)_{12}$ [4]. The fragmentation of the singly charged ions is not substantially affected when the electron beam energy is decreased from 100 to 40 eV, whilst the fragmentation of the doubly charged ions is strongly reduced. This behaviour of the doubly charged species can be ascribed to the higher reduction of the metal–CO bond order. In fact, a decreased backdonation to the CO ligands is induced by the double positive charge mainly localized on the metal atoms. Moreover, the relative abundances of the ions containing few CO groups strongly decrease with decreasing energy of the ionizing electrons and at the same time those containing more CO groups increase. Differently from $Os_3(CO)_{12}$, $RuOs_2(CO)_{12}$ and $Ru_2Os(CO)_{12}$ [4], $Re_2(CO)_{10}$ does not give either $[M]^{2+}$ or doubly charged ions with more than six carbonyl groups under the conditions investigated.

A comparison between the mass spectra of isostructural $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ indicates a strong effect of the nature of the metal atom on the stability of doubly charged species in the gas phase, which increases by descending from the first to the third transition series.

The data of Tables 2 and 3 show that the presence of the ligand X (X = Cl, Br, I) in $Mn(CO)_5X$ and $Re(CO)_5X$ complexes increases the stabilization of doubly charged ions, which is higher for the rhenium compounds. The nature of X does not affect the behaviour in this respect in a definite way.

The $Re(CO)_5X$ compounds give $[M]^{2+}$ and all the doubly charged fragments due to the stepwise loss of the CO groups and of X (Table 3). Their relative abundances follow the same trends described above for $Re_2(CO)_{10}$. Moreover, the charge transported by $[M]^{2+}$ at 100 eV increases with the decreasing beam energy from about 5% of the sum of all the doubly charged ions to about 10% at 40 eV for $Re(CO)_5Cl$.

From the data of Table 2 it can be seen that also the doubly charged ions originated by $Mn(CO)_5X$ compounds are more stable than those displayed by $Mn_2(CO)_{10}$. However, $[M]^{2+}$ is not present in their mass spectra and the total charges transported by doubly charged fragments are significantly lower than those produced by the corresponding rhenium complexes.

A comparison of the percentage of the total charge transported by the doubly charged ions originated by $Mn(CO)_5X$ and by $Mn_2(CO)_{10}$ shows values remarkably higher for the halogenopentacarbonyl complexes. This can be ascribed to the presence of the

TABLE 1. Percentage abundances of bimetallic singly (S) and doubly (D) charged ions[a] in the mass spectra of $Re_2(CO)_{10}$ at different electron beam energies (eV)

Ions	100 eV		70 eV		40 eV	
	S	D	S	D	S	D
$[M]^{n+}$	52		56		58	
$[M-CO]^{n+}$	3		3		4	
$[M-2CO]^{n+}$	9		8		12	
$[M-3CO]^{n+}$	100		100		100	
$[M-4CO]^{n+}$	38		37		34	
$[M-5CO]^{n+}$	34	3	31	3	32	1.5
$[M-5CO-O]^{n+}$	1	1	1	1	1.5	
$[M-6CO]^{n+}$	39	26	32	19	42	9
$[M-6CO-O]^{n+}$	1	1	1	0.7	2	
$[M-7CO]^{n+}$	29	25	26	18	21	7
$[M-7CO-O]^{n+}$	1.5	1.5	2	1	2	
$[M-8CO]^{n+}$	26	35	31	29	27	8
$[M-8CO-O]^{n+}$	2	5	2	3	3	
$[M-9CO]^{n+}$	20	25	21	20	18	2
$[M-9CO-O]^{n+}$	7	14	10	6	11	
$[M-10CO]^{n+}$	35	21	38	15	22	1
Total charge (%)	71.6	28.4	77.5	22.5	93.2	6.8

$n=1$ for S and $n=2$ for D.

TABLE 2. Percentage abundances of bimetallic singly (S) and doubly (D) charged ions[a] in the mass spectra of $Mn(CO)_5X$ (X = Cl, Br, I) compounds at different electron beam energies (eV)

Ions	$Mn(CO)_5Cl$						$Mn(CO)_5Br$						$Mn(CO)_5I$					
	100 eV		70 eV		40 eV		100 eV		70 eV		40 eV		100 eV		70 eV		40 eV	
	S	D	S	D	S	D	S	D	S	D	S	D	S	D	S	D	S	D
$[M]^{n+}$	82		70		100		82		97		100		100		100		100	
$[M-\mathrm{CO}]^{n+}$	1	1	1	2	2		0.1	0.1	0.1	0.1	0.1	0.1	2	1	2	2	2	0.5
$[M-\mathrm{X}]^{n+}$	61	0.5	33		46		5	0.1	12	0.1	8	0.1	6		6		6	
$[M-\mathrm{CO}-\mathrm{X}]^{n+}$	21	3	6	3	11	1.5	1	1.5	6	1	5	0.7	3	0.2	4	0.2	3	0.1
$[M-2\mathrm{CO}]^{n+}$	29	3	28	3	28	1	15	3	32	5	15	2	52	5	37	3	38	1.5
$[M-2\mathrm{CO}-\mathrm{X}]^{n+}$	32	7	19	6	17	1.5	7	4	13	4	9	1.5	4	1.5	3	1	3	0.2
$[M-3\mathrm{CO}]^{n+}$	100	2	100	2	92	0.7	55	7	100	8	55	3	44	10	32	5	31	0.1
$[M-3\mathrm{CO}-\mathrm{X}]^{n+}$	55	21	47	14	30	3	30	11	47	9	27	4	19	4	8	2	7	0.5
$[M-4\mathrm{CO}]^{n+}$	53	3	55	3	42		21	10	38	11	23	4	31	12	22	4	22	2
$[M-4\mathrm{CO}-\mathrm{X}]^{n+}$	85	25	63	10	37	2	49	6	70	2	48	2	42	4	22	2	14	0.1
$[M-4\mathrm{CO}-\mathrm{X}-\mathrm{O}]^{n+}$	2	1	2	0.5	2		5		7		6							
$[M-5\mathrm{CO}]^{n+}$	90	1	96		78		47	2	84	1	56	1.5	95	2	68	1	56	0.2
$[M-5\mathrm{CO}-\mathrm{X}]^{n+}$	95	0.5	98		95		100	0.1	87	0.1	95		97		71		32	
Total charge (%)	91.2	8.8	93.4	6.6	98.3	1.7	90.5	9.5	93.5	6.5	95.9	4.1	92.6	7.4	94.9	5.1	98.4	1.6

[a] $n=1$ for S and $n=2$ for D.

TABLE 3. Percentage abundances of bimetallic singly (S) and doubly (D) charged ions[a] in the mass spectra of $Re(CO)_5X$ (X = Cl, Br, I) compounds at different electron beam energies (eV)

Ions	$Re(CO)_5Cl$						$Re(CO)_5Br$						$Re(CO)_5I$					
	100 eV		70 eV		40 eV		100 eV		70 eV		40 eV		100 eV		70 eV		40 eV	
	S	D	S	D	S	D	S	D	S	D	S	D	S	D	S	D	S	D
$[M]^{n+}$	88	5	88	3	100	4	97	7	91	8	79	1	100	8	100	8	100	4
$[M-\mathrm{CO}]^{n+}$	87	8	82	4	94	7	85	10	76	8	66	4	53	13	54	10	56	6
$[M-\mathrm{X}]^{n+}$	6	1	6	0.5	8	0.5	1	1	1	0.5	1	0.5	1	0.4	1	0.4	0.7	
$[M-\mathrm{CO}-\mathrm{X}]^{n+}$	7	3	8	3	7	0.5	10	2	12	1	12	1	4	0.5	6	0.5	6	0.2
$[M-2\mathrm{CO}]^{n+}$	50	10	54	6	51	6	52	17	39	15	47	7	34	11	35	10	32	5
$[M-2\mathrm{CO}-\mathrm{X}]^{n+}$	25	5	30	4	26	2	35	3	37	1	35	1	21	1	25	1	19	0.4
$[M-3\mathrm{CO}]^{n+}$	100	25	100	16	95	12	100	32	100	27	94	10	75	20	80	21	70	7
$[M-3\mathrm{CO}-\mathrm{X}]^{n+}$	17	10	15	8	22	2	19	6	24	7	24	3	6	2	8	2	8	0.5
$[M-3\mathrm{CO}-\mathrm{X}-\mathrm{O}]^{n+}$	2	2	2	2	2		2	2.5	3	2	1	0.2	1	0.5	1	0.7	1	
$[M-4\mathrm{CO}]^{n+}$	48	20	59	15	56	5	60	35	70	31	72	8	41	19	50	20	48	4
$[M-4\mathrm{CO}-\mathrm{X}]^{n+}$	10	9	18	7	18	1	14	10	19	9	21	2	4	2	7	2	4	0.5
$[M-4\mathrm{CO}-\mathrm{X}-\mathrm{O}]^{n+}$	18	0.5	21		13		29	0.5	38	0.2	29		13	0.2	22	0.2	10	
$[M-5\mathrm{CO}]^{n+}$	44	3	62	3	51	2	72	14	95	10	100	2	52	8	68	9	64	1
$[M-5\mathrm{CO}-\mathrm{X}]^{n+}$	45	0.5	65	0.5	40		68	0.5	96	0.5	89		33	0.2	48	0.2	32	
Total charge (%)	84.3	15.7	89.4	10.6	93.3	6.7	82.1	17.9	85.3	14.7	94.4	5.6	83.7	16.3	85.5	14.5	94.1	5.9

[a] $n=1$ for S and $n=2$ for D.

TABLE 4. Percentage abundances of bimetallic singly (S) and doubly (D) charged ions[a] in the mass spectra of $Fe_2(CO)_6C_4(C_2H_5)_4$ and $Os_2(CO)_6C_4(C_2H_5)_4$ compounds at different electron beam energies (eV)

Ions	$Fe_2(CO)_6C_4(C_2H_5)_4$						$Os_2(CO)_6C_4(C_2H_5)_4$					
	100 eV		70 eV		40 eV		100 eV		70 eV		40 eV	
	S	D	S	D	S	D	S	D	S	D	S	D
$[M]^{n+}$	34		40		45		100		100		100	
$[M-CO]^{n+}$	20	2	17	2	27	1.5	18	14	17	20	17	7
$[M-CO-H_2]^{n+}$							3	2	4		3	
$[M-2CO]^{n+}$	32	5	20	4	40	4	21	13	19	11	16	8
$[M-2CO-H_2]^{n+}$							47	3	45	2	32	1
$[M-2CO-2H_2]^{n+}$							18		12		10	
$[M-3CO]^{n+}$	31	7	37	5	38	4	21	14	19	13	18	7
$[M-3CO-H_2]^{n+}$							65	9	70	4	62	3
$[M-3CO-2H_2]^{n+}$							12	6	11	3	12	3
$[M-4CO]^{n+}$	100	12	100	8	100	7	6	17	4	14	4	6
$[M-4CO-H_2]^{n+}$	1	3	1	2	1	1	13	10	13	6	14	4
$[M-4CO-2H_2]^{n+}$							15	2	19	2	16	1
$[M-5CO]^{n+}$	65	22	64	15	64	10	3	27	4	20	3	10
$[M-5CO-H_2]^{n+}$	1	7	1	3	1	2	7	4	6	5	7	2
$[M-5CO-2H_2]^{n+}$							16	9	20	3	20	2
$[M-5CO-3H_2]^{n+}$							8		3		2	
$[M-6CO]^{n+}$	52	30	52	28	47	13	4	24	4	19	4	6
$[M-6CO-H_2]^{n+}$	36	11	23	9	35	4	8	22	6	20	7	7
$[M-6CO-2H_2]^{n+}$	16	1	10		18		18	30	20	25	22	5
$[M-6CO-3H_2]^{n+}$							21	25	15	22	20	
$[M-6CO-4H_2]^{n+}$							6		6		4	
Σ[b]	50		57		69		38	15	35	19	20	
Total charge (%)	81.4	18.6	84.7	15.3	91.2	8.8	65.5	34.5	70.6	29.4	85.2	14.8

[a] $n = 1$ for S and $n = 2$ for D. [b] Sum of abundances of bimetallic ions originated from $[M-6CO]^{n+}$ ions following the loss of one or more organic units heavier than H_2.

TABLE 5. Percentage abundances of bimetallic singly (S) and doubly (D) charged ions[a] in the mass spectra of $Fe_2(CO)_6S_2$ at different electron beam energies (eV)

Ions	100 eV		70 eV		40 eV	
	S	D	S	D	S	D
$[M]^{n+}$	29		37		35	
$[M-CO]^{n+}$	8	1	11	1	10	1
$[M-2CO]^{n+}$	5	6	9	5	8	3
$[M-3CO]^{n+}$	7	7	11	4	10	4
$[M-4CO]^{n+}$	30	18	31	9	26	5
$[M-5CO]^{n+}$	97	10	96	8	100	1
$[M-6CO]^{n+}$	100	5	100	1	92	
$[M-6CO-S]^{n+}$	40	2	42	2	45	
$[M-6CO-2S]^{n+}$	23	2	28	1	26	
Total charge (%)	86.2	13.8	92.2	7.8	96.2	3.8

[a] $n=1$ for S and $n=2$ for D.

halogeno ligand, which is an electron rich species and, therefore, fit for stabilizing the double charge of the ions. This stabilizing effect of the halogeno ligand on the charge is also observed in the mass spectra of $Re(CO)_5X$ complexes, which show $[M]^{2+}$ ions. The occurrence of the doubly charged molecular ion is also favoured by the reduced fragmentation which is related to the higher average Re–CO bond dissociation energies of $Re(CO)_5X$ [13] with respect to $Re_2(CO)_{10}$ [14].

In the mass spectrum of $Fe_2(CO)_9$ at 100 eV about 1% of the total charge is transported by bimetallic doubly charged ions, $[M-7CO]^{2+}$ and $[M-4CO]^{2+}$ being the only species observed. $[Fe(CO)_m]^{2+}$ ($m=4$–2) ionic species are also present in the spectrum with relative abundances 4, 8 and 5, respectively compared with the base peak $[Fe(CO)]^+$. The presence of ligands, such as sulfur atoms, in the binuclear $Fe_2(CO)_6S_2$ complex, provides an increase of the stabilization already observed in the trinuclear $Fe_3(CO)_9S_2$ complex [4]. Table 5 reports the percentage abundances of singly and doubly charged species at 100, 70 and 40 eV electron beam energies.

A further improvement in the stabilization of doubly charged ions is displayed in the mass spectra of the binuclear complexes containing organic ligands (Table 4). $Fe_2(CO)_6C_4(C_2H_5)_4$ and $Os_2(CO)_6C_4(C_2H_5)_4$, prepared from 3-hexyne and dodecacarbonyltriiron and -triosmium, respectively, show a structure in which a metal-cyclopentadiene ring is coordinated by a tricarbonylmetal unit with a π bond [15]. The unsaturated moiety provides a significant enhancement of the charge delocalization and consequent rather strong relative abundances of doubly charged ions (Table 4) in agreement with the data reported for the analogous trinuclear complexes [4]. A higher stabilization of multiply charged species has been previously observed in the mass spectrum at 70 eV, of $Os_2(CO)_6C_4(C_6H_5)_4$, which is isostructural with $Os_2(CO)_6C_4(C_2H_5)_4$ and differs only for the presence of the four phenyl substituents on the metal-cyclopentadiene ring, which replace the ethyl substituents. $Os_2(CO)_6C_4(C_6H_6)_4$ gives triply charged ions, such as $[Os_2C_4(C_6H_5)_4]^{3+}$ and $[Os_2C_4(C_6H_5)_{4-n}H_2]^{3+}$ ($n=1$–4), which transport about 1% of the total charge [16].

From the data above reported it can be concluded that also for mono- and binuclear carbonyl metal complexes the relative abundances of multiply charged ions are mainly affected by: (i) the nature of the metal related to the different stability of its high oxidation states; (ii) the presence of ligands which produces variations of the excitation energy of the ionic species by affecting the ionization and the metal–CO bond dissociation energies and modifies to a greater extent the fragmentation of multiply charged ions.

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