Ion chemistry of a series of cluster compounds with Mo_3Q_4 and $Mo_3M'Q_4$ (Q = S, Se; M′ = Cu, Co, Ni) cores containing 1,2 diphosphanes as ancillary ligands: New insights on the gas-phase stability from electrospray tandem mass spectrometry

Eva Guillamón [a], Rosa Llusar [a,*], Oscar Pozo [b], Cristian Vicent [c,**]

[a] *Department Ciències Experimentals, Universitat Jaume I, Avda. Sos Baynat s/n, E-12080 Castelló, Spain*
[b] *Research Institute for Pesticides and Water, Universitat Jaume I, Avda. Sos Baynat s/n, E-12080 Castelló, Spain*
[c] *Serveis Centrals d'Instrumentació Científica, Universitat Jaume I, Avda. Sos Baynat s/n, E-12080 Castelló, Spain*

Abstract

Electrospray ionization (ESI) and tandem mass spectrometry for the family of trinuclear $[Mo_3Q_4(dmpe)_3Cl_3]^+$ and tetranuclear $[Mo_3(M'L)Q_4(dmpe)_3Cl_3]^{0,+}$ (dmpe = 1,2-bis(dimethylphosphanyl)ethane); (Q = S, Se; M′ = Cu, Co, Ni; L = Cl, CO) complexes have been investigated. Release of two diphosphane molecules appears to be a common fragmentation channel for the trinuclear compounds while fragmentation paths in the tetranuclear complexes are mainly determined by the nature of the ligand coordinated to the heterometal M′, namely CO, Cl. Tetranuclear complexes with M′CO start evolving the CO ligand followed by two diphosphane molecules. For compounds incorporating the M′Cl fragment, the losses of the diphosphane ligands comes together with the breaking of the cuboidal $Mo_3M'Q_4$ unit to afford trinuclear Mo_3Q_4 species. In the latter case, neutral losses corresponding to M′Cl and M′Cl$_2$ fragments are observed for M′ = Cu and Co, respectively, whereas both neutral fragments are simultaneously released for M′ = Ni. Energy-dependent collision induced dissociation (CID) experiments have been used to extract information about the relative stability of these cuboidal compounds in the gas-phase. On the basis of the relative intensities of the molecular precursor ions and the fragmentations peaks, a qualitative analysis of the M′–CO, Mo-diphosphane and Mo_3–M′ bond energetics is discussed.
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Keywords: Molybdenum sulfide clusters; Diphosphane; Cuboidal complexes; ESI-MS; CID

1. Introduction

Molecular metal clusters play a crucial role in several scientific areas of current interest such as solid-state physics [1], biochemistry [2], catalysis [3] and material science [4]. A well-known class of such compounds are the cubane-type transition metal clusters chalcogenides. This category of coordination compounds includes those complexes derived from the incomplete-cuboidal M_3Q_4 unit (M = Mo, W; Q = S, Se) from which a large number of heterodimetallic $M_3M'Q_4$

cubane type clusters have been obtained by incorporation of a second transition or post transition element [5–8]. The chemistry of cubane-type M_3Q_4 and $M_3M'Q_4$ cluster complexes has been mainly developed in aqueous media where some difficulties regarding their characterisation arise due to the limited stability of these complexes, restricted to strong acid media [6]. Substitution of water molecules by several organic ligands, such as cyclopentadienyls, diphosphanes, dithiophosphates or dithiocarbamates, results in air-stable complexes, soluble in organic solvents which allows the study of their physico-chemical properties in this media [8].

While routine spectroscopic techniques such as ^{31}P, ^{13}C and ^{1}H NMR provides information on the ligands, structural information concerning the metal M_3Q_4 and $M_3M'Q_4$ cores is generally limited to X-ray diffraction methods. Some exception are the X-ray photoelectron spectroscopy studies on the M_3FeQ_4 and

* Corresponding author. Tel.: +34 964387344; fax: +34 964387309.
** Corresponding author.
E-mail addresses: llusar@exp.uji.es (R. Llusar), barrera@sg.uji.es (C. Vicent).

M_3NiQ_4 complexes [9] and the Mössbauer spectroscopy investigations on the analogous tin and iron derivatives [9–11]. Mass spectrometry using a suitable ionization source can provide a rapid and sensitive alternative of characterisation in coordination chemistry. In the past decade, Hegetschweiler et al. have showed that fast atom bombardment (FAB) mass spectrometry is a convenient tool for the identification of molybdenum–sulfur clusters with a Mo_3S_7 core bearing a wide variety of ligands [12,13]. In this context, electrospray ionization mass spectrometry (ESI-MS) and its tandem version ESI-MS/MS are rapidly becoming the technique of choice for solution mechanistic studies in chemistry and biochemistry and for high-throughput screening of homogeneous catalysis reactions since this technique allows preexisting molecules in solution to be transferred to the gas-phase with minimal fragmentation [14–20]. Applications to a large number of inorganic clusters and organometallic systems have demonstrated the versatility of the technique [21–28].

In this work we report the use of ESI-MS to investigate the family of tri- and tetranuclear cuboidal complexes of general formula $[Mo_3Q_4(dmpe)_3Cl_3]^+$ and $[Mo_3(M'L)Q_4(dmpe)_3Cl_3]^{0,+}$ (Q = S, Se; M' = Cu, Co, Ni; L = Cl, CO), respectively. The trinuclear cluster core in Mo_3Q_4 is formed by three molybdenum atoms defining an equilateral triangle, one capping chalcogenide atom and three bridging chalcogenide ligands (see Plate 1). Topologically, such triangular arrangement can be regarded as an incomplete-cuboidal structure where each Mo occupy alternating vertexes of an imaginary cube leaving a vacant site. This vacant position can be occupied by a second metal leading to a cubane-type $Mo_3M'Q_4$ arrangement in which the four chalcogen atoms are capping each face of the tetrahedra defined by the Mo_3M' core. A schematic representation of the molecular structure of the compounds studied in this work is given in Plate 1. The environment of each molybdenum atom is filled by a diphosphane molecule and one chlorine atom. For clarity, only the environment around one molybdenum atom is shown.

All complexes displayed in Plate 1 show the corresponding positively single-charged ion as base peak in their ESI-MS spectra. Furthermore, their fragmentation patterns have been determined by means of tandem MS/MS experiments. Tri- and tetranuclear clusters of formula $[Mo_3Q_4(dmpe)_3Cl_3]^+$ and $[Mo_3(M'CO)Q_4(dmpe)_3Cl_3]^+$ preserve their nuclearity up to collision energy, $E_{lab} = 70\,eV$ with evolution of two diphosphane

molecules and neutral CO in the case of the tetrametallic cluster. On the other hand $[Mo_3(M'Cl)Q_4(dmpe)_3Cl_3]^+$ clusters show in addition to the two diphosphane molecules dissociation, the fragmentation of the cuboidal unit to give trinuclear species at collision energies ranging from E_{lab} 20 to 70 eV. A qualitative analysis of the Mo–diphosphane and M'–CO energetics and the gas-phase stability of the tetranuclear $Mo_3M'Q_4$ unit with regard to the metal cluster dissociation is discussed on the basis of energy-dependent collision induced dissociation (CID) experiments.

2. Experimental

Compounds **1** (PF_6), **1a** (PF_6), **2** (PF_6), **2a** (PF_6), **3** (PF_6), **3**, **4**, **5** (PF_6) and **6** were prepared according to literature procedures [29–33]. A Quattro LC (QhQ quadrupole–hexapole–quadrupole) mass spectrometer with an orthogonal Z-spray-electrospray interface (Micromass, Manchester, UK) was used. Sample solutions (approx. $1 \times 10^{-4}\,M$) in acetonitrile:dichloromethane (1:1) were introduced through a fused-silica capillary to the ESI source via syringe pump at a flow rate of $10\,\mu L/min$. The drying gas as well as nebulizing gas was nitrogen at a flow of 300 and 50 L/h, respectively. The temperature of the source block was set to 80 °C and the interface to 120 °C. A detailed description of this spectrometer can be found elsewhere [34]. For each ion of interest, the instrument parameters were optimized for maximum ion abundances. The capillary voltage was set at 3.5 kV in the positive scan mode and the cone voltage was adjusted (typically U_c 25–35 V) to control the extent of fragmentation in the source region. The extractor cone and the radio-frequency lens voltage were kept at 3 and 0.2 V, respectively. The chemical composition of each peak obtained in the full scan mode was assigned by comparison of the isotope experimental and theoretical patterns using the MassLynx 4.0 program. Collision induced dissociation (CID) experiments were performed with argon at various collision energies, ranging from $E_{lab} = 0$–70 eV. The collision gas pressure was maintained at approximately $1.3 \times 10^{-3}\,mbar$. The most intense precursor peak of interest was mass-selected with Q1, interacted with argon in the hexapole cell while scanning Q2 to monitor the ionic fragments. The resolution setting in Q1 (isolation width 3 u) and Q2 was low, in order to obtain a good signal-to-noise ratio. For a qualitative analysis of the energy-dependent CID experiments, the laboratory
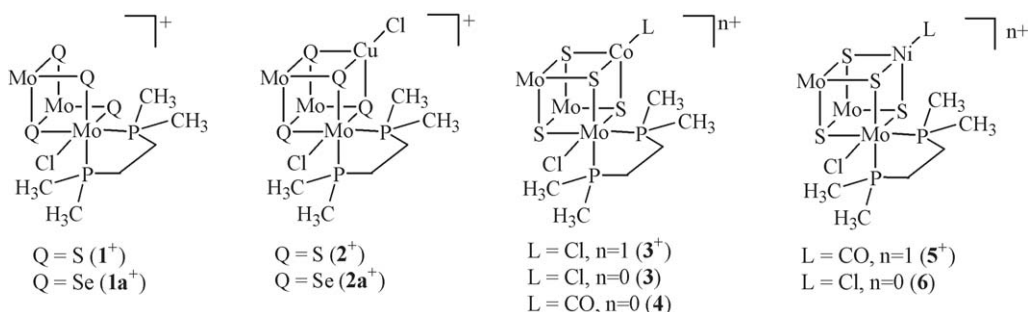

Plate 1.

Table 1
List of the molecular peaks observed at 30 V and collision energy referred to the center of mass for the dissociation of the M′–CO, Mo–(dmpe) bonds and the fragmentation of the tetranuclear ions[a]

Compound	Ion/metal electron counting	$E_{CM50\%}$ for M′–CO, Mo–(dmpe)
$[Mo_3S_4(dmpe)_3Cl_3](PF_6)$ (**1** (PF$_6$))	**1**$^+$/6	1.41 **1**$^+ \to$ [**1**–dmpe]$^+$
$[Mo_3Se_4(dmpe)_3Cl_3](PF_6)$ (**1a** (PF$_6$))	**1a**$^+$/6	1.30 **1a**$^+ \to$ [**1a**–dmpe]$^+$
$[Mo_3(CuCl)S_4(dmpe)_3Cl_3](PF_6)$ (**2** (PF$_6$))	**2**$^+$/16	1.38 **2**$^+ \to$ [**2**–CuCl–dmpe]$^+$
$[Mo_3(CuCl)Se_4(dmpe)_3Cl_3](PF_6)$ (**2a** (PF$_6$))	**2a**$^+$/16	1.31 **2a**$^+ \to$ [**2a**–CuCl–dmpe]$^+$
$[Mo_3(CoCl)S_4(dmpe)_3Cl_3](PF_6)$ (**3** (PF$_6$))·	**3**$^+$/14	1.37 **3**$^+ \to$ [**3**–dmpe]$^+$ 2.27 [**3**–dmpe]$^+ \to$ [**3**–dmpe–CoCl$_2$]$^+$
$[Mo_3(CoCO)S_4(dmpe)_3Cl_3]$ (**4**)	**4**$^+$/15	0.45 **4**$^+ \to$ [**4**–CO]$^+$ 1.40 [**4**–CO]$^+ \to$ [**4**–CO–dmpe]$^+$
$[Mo_3(NiCO)S_4(dmpe)_3Cl_3](PF_6)$ (**5** (PF$_6$))	**5**$^+$/16	0.66 **5**$^+ \to$ [**5**–CO]$^+$ 1.40 [**5**–CO]$^+ \to$ [**5**–CO–dmpe]$^+$
$[Mo_3(NiCl)S_4(dmpe)_3Cl_3]$ (**6**)	**6**$^+$/15	1.43 **6**$^+ \to$ [**6**–dmpe]$^+$ 1.82 [**6**–dmpe]$^+ \to$ [**6**–dmpe–NiCl$_2$]$^+$ + [**6**–dmpe–NiCl]$^+$

[a] Compound **3** is not included since it gives cation **3**$^+$ in the gas-phase.

collision energies were converted to the center-of-mass frame, $E_{CM} = m/(m + M)E_{lab}$, where m and M stand for the masses of the collision gas and the ionic species, respectively. For the breakdown profiles representations, signal intensities were obtained from the average of 20 scans and measuring the area of the fragmentation peaks. These graphs were represented taking into account the relative abundance of the precursor and product peaks of each compound ($I_{precursor\ ion}$ or $I_{product\ ion}/I_{precursor\ ion} + \sum I_{product\ ion}$) against E_{CM}. We selected the value of the collision energy required for 50% reduction of the precursor ion ($E_{CM50\%}$) as a qualitative measure of the single-step M′–CO and Mo–diphosphane dissociations within the series **1**$^+$–**6**$^+$. Fragmentation of the cuboidal unit was typically observed at higher collision energies to yield trinuclear species. The E_{CM} at which the presence of the trinuclear fragmentation ion predominates was chosen to compare the stability of the cuboidal clusters. The values of $E_{CM50\%}$ reported in Table 1 are averages of three independent measurements. Our experiments show that values obtained for $E_{CM50\%}$ varied less than 7% for the cationic cluster complexes **1**$^+$–**6**$^+$.

3. Results and discussion

3.1. ESI mass spectra of $[Mo_3Q_4(dmpe)_3Cl_3]^+$ (Q = S, Se) and $[Mo_3(M'L)Q_4(dmpe)_3Cl_3]^{+,0}$ (M' = Cu, Co, Ni; Q = S, Se; L = CO, Cl) complexes

The incomplete-cuboidal $[Mo_3Q_4(dmpe)_3Cl_3]^+$ clusters are electron precise with six metal electrons and a formal +4 oxidation state for the molybdenum atoms. The number of metal electrons in the cubane-type compounds $[Mo_3(M'L)Q_4(dmpe)_3Cl_3]^+$ studied here ranges from 14 to 16, depending on the heterometal incorporated and the net charge in the cluster. Table 1 list the species present under ESI conditions together with their metal electron count.

The ESI-MS spectra of the cationic trinuclear **1** (PF$_6$) and **1a** (PF$_6$) and the tetranuclear **2** (PF$_6$), **2a** (PF$_6$), **3** (PF$_6$) and **5** (PF$_6$) compounds obtained under gentle conditions, that means at low cone voltage ($U_c = 30$ V), give the expected molecular ion M$^+$ as base peak. Neutral complexes incorporating cobalt $[Mo_3(CoL)Q_4(dmpe)_3Cl_3]$ (L = Cl, CO) (**3** and **4**) and nickel $[Mo_3(NiCl)S_4(dmpe)_3Cl_3]$ (**6**) also show the single-charged

cation M$^+$ as base peak which results from the one-electron oxidation taking place in the electrospray emitter. This type of reactions are frequently observed due to the inherent electrolytic nature of the electrospray ionization technique [35]. Henderson et al. have reported a complete ESI-MS study of a series of neutral halide complexes, i.e., $[PtCl_2(dppe)]$, $[Pd_2Cl_2(\mu\text{-dppm})_2]$ [36] where the dominant ionization process corresponds to the loss of a halide ligand although aggregation with cationic species has also been detected in some cases. For the neutral compounds studied in this work, the electron detachment mechanism is clearly favoured in front of other ionization processes. This observation agrees with the electrochemical properties of these complexes in solution. In particular, cyclic voltammetry experiments for neutral clusters **3** and **4** show quasi-reversible oxidation waves at easily accessible potentials, near 0 V versus Ag/AgCl. In the case of complex **3**, the corresponding oxidation product, namely **3**$^+$ has been isolated [32]. For the nickel containing compound **6**, one oxidation process is also observed at more anodic potentials ca. 0.8 V (versus Ag/AgCl), although in this case the oxidation product **6**$^+$ has not been isolated [33].

All ions generated by ESI-MS, **1**$^+$–**6**$^+$ display a distinctive isotopic pattern due to the relative abundances of naturally occurring isotopes (Mo, Se, Cl, Cu, Ni) which actually facilitates ion stoichiometry assignment via comparison of their experimental and theoretical isotopic patterns. Two representative ESI mass spectra for the trinuclear **1a**$^+$ and the tetranuclear **3**$^+$ clusters are showed in Fig. 1, where the excellent agreement between the experimental and calculated isotopic distribution is clearly seen.

These preliminary single-stage ESI-MS experiments clearly indicate that cluster species generated in the electrospray chamber may have different metal electron counts in the gas-phase and in solution. For example, the isoelectronic nickel-containing **5** (PF$_6$) and **6** complexes posses 16 metal electrons in solution while after being electrosprayed they produce **5**$^+$ and **6**$^+$ cations in the gas-phase with 16 and 15 metal electrons, respectively. This fact allows to undertake a comparative study of the ion chemistry of these compounds in various charge states. It is also worth noting that the nature of the bridging-chalcogen does not affect the identity of the species present in the gas-phase after the ionization process.
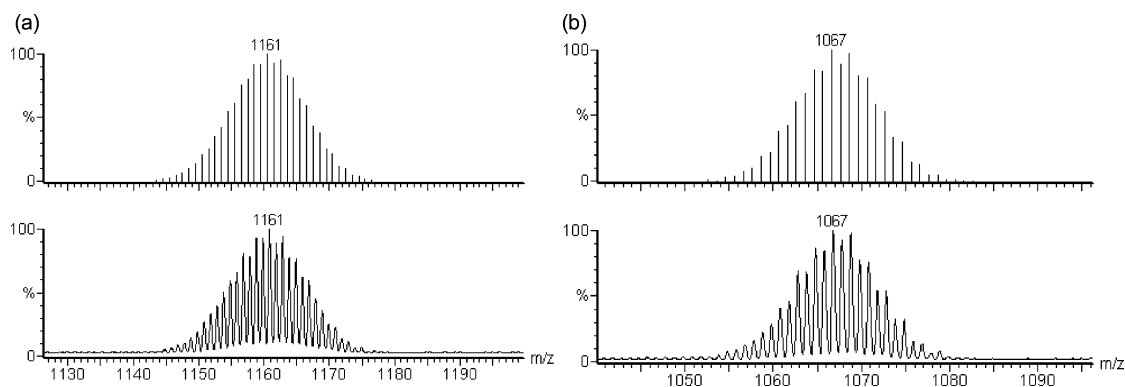
Fig. 1. Comparison of experimental (bottom) and theoretical (top) isotope patterns for the cationic complexes: (a) $[Mo_3Se_4(dmpe)_3Cl_3](PF_6)$ (**1a** (PF_6)) and (b) $[Mo_3(CoCl)S_4(dmpe)_3Cl_3](PF_6)$ (**3** (PF_6)).

3.2. Fragmentation patterns of tri- and tetranuclear $[Mo_3Q_4(dmpe)_3Cl_3]^+$ $[Mo_3(M'L)Q_4(dmpe)_3Cl_3]^+$ (M' = Cu, Co, Ni; Q = S, Se; L = CO, Cl) ions

Tandem mass spectrometry provide relevant information regarding reactivity, structural elucidation and thermochemistry of a certain ionized molecule through its fragmentation paths observed under energy-variable CID conditions [37–39]. In order to explore the fragmentation of ionized 1^+–6^+ species, we have recorded the CID spectra at increasing collision energies from $E_{lab} = 0$ to 70 eV. In these experiments, the singly positively charged cluster ions were separated by their mass to charge ratio and accelerated into the collision cell of the mass spectrometer. Fig. 2 shows four illustrative CID spectra recorded at $E_{lab} = 20$,

40 and 60 eV for mass selected ions 1^+, $2a^+$, 3^+ and 5^+. Fragmentation pathways observed for the series 1^+–6^+ are schematised in Fig. 3. Complexes have been grouped based on their fragmentation similarities in order to facilitate the following discussion.

3.2.1. Trinuclear $[Mo_3Q_4(dmpe)_3Cl_3]^+$ and tetranuclear $[Mo_3(M'CO)Q_4(dmpe)_3Cl_3]^+$ ions

The fragmentation pattern observed for the trinuclear 1^+ and $1a^+$ complexes consists in the neutral loss of one coordinated diphosphane at collision energies up to $E_{lab} = 40$ eV to yield the $[Mo_3Q_4(dmpe)_2Cl_3]^+$ species and a partial loss of a second chelating ligand that gives the $[Mo_3Q_4(dmpe)Cl_3]^+$ cation. A gradual increase of the collision energy up to $E_{lab} = 60$ eV results in an enhanced fragmentation of the second diphosphane.

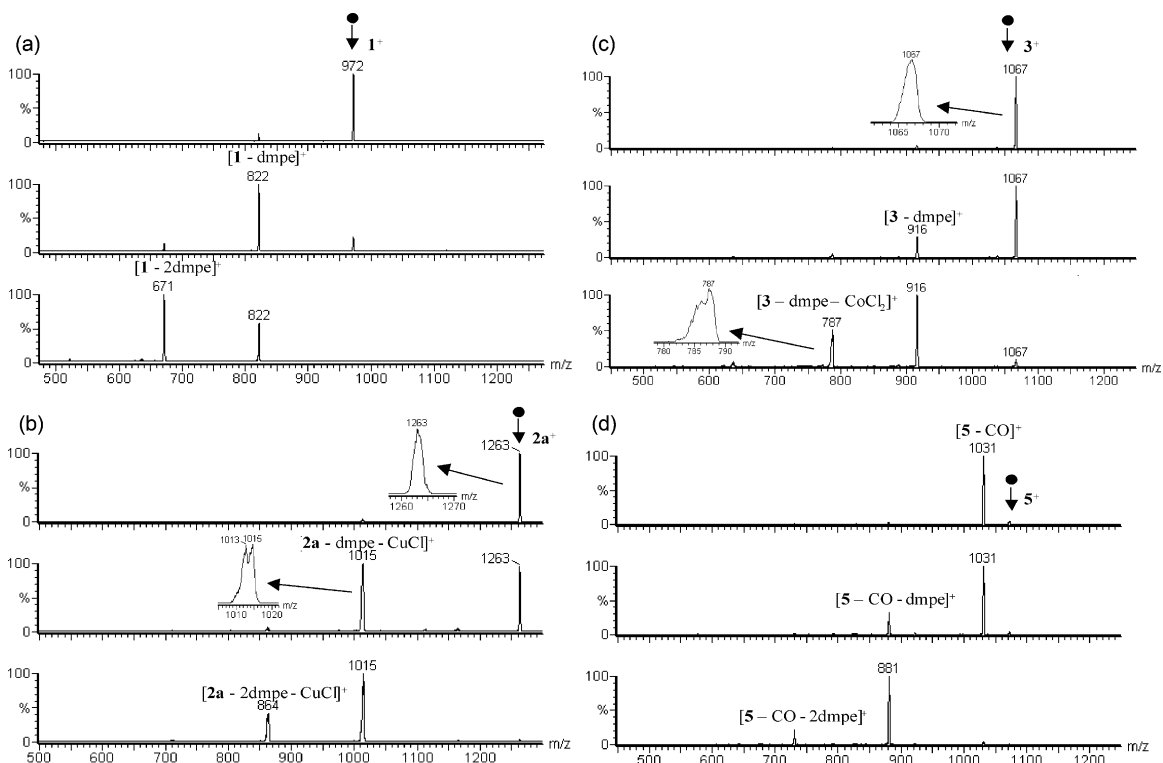Fig. 2. Representative spectrum of mass selected cations: (a) $[Mo_3S_4(dmpe)_3Cl_3]^+$ (**1**$^+$), (b) $[Mo_3(CuCl)Se_4(dmpe)_3Cl_3]^+$ (**2a**$^+$), (c) $[Mo_3(CoCl)S_4(dmpe)_3Cl_3]^+$ (**3**$^+$) and (d) $[Mo_3(NiCO)S_4(dmpe)_3Cl_3]^+$ (**5**$^+$) recorded at 20 eV (top), 40 eV (medium) and 60 eV (bottom).

(a)   Q = S, Se;   M′ = Co, Ni   (b)   Q = S, Se   M′ = Co, Ni

1⁺, 1a⁺   **4⁺, 5⁺**   **2⁺, 2a⁺**   **3⁺, 6⁺**

$[Mo_3Q_4(dmpe)_3Cl_3]^+$ $[Mo_3S_4(M'CO)(dmpe)_3Cl_3]^+$ $[Mo_3Q_4(CuCl)(dmpe)_3Cl_3]^+$ $[Mo_3S_4(M'Cl)(dmpe)_3Cl_3]^+$

$\downarrow$ - dmpe $\downarrow$ - CO $\downarrow$ - dmpe

$[Mo_3Q_4(dmpe)_2Cl_3]^+$ $[Mo_3S_4(M')(dmpe)_3Cl_3]^+$ - CuCl - dmpe $[Mo_3S_4(M'Cl)(dmpe)_2Cl_3]^+$

$\downarrow$ - dmpe $\downarrow$ - dmpe   - NiCl $\downarrow$ - M′Cl$_2$ (M′=Co, Ni)

$[Mo_3Q_4(dmpe)Cl_3]^+$ $[Mo_3S_4(M')(dmpe)_2Cl_3]^+$ $[Mo_3Q_4(dmpe)_2Cl_3]^+$ $[Mo_3S_4(dmpe)_2Cl_2]^+$

          $\downarrow$ - dmpe $\downarrow$ - dmpe $\downarrow$ - dmpe

$[Mo_3S_4(M')(dmpe)Cl_3]^+$ $[Mo_3Q_4(dmpe)Cl_3]^+$ $[Mo_3S_4(dmpe)Cl_2]^+$
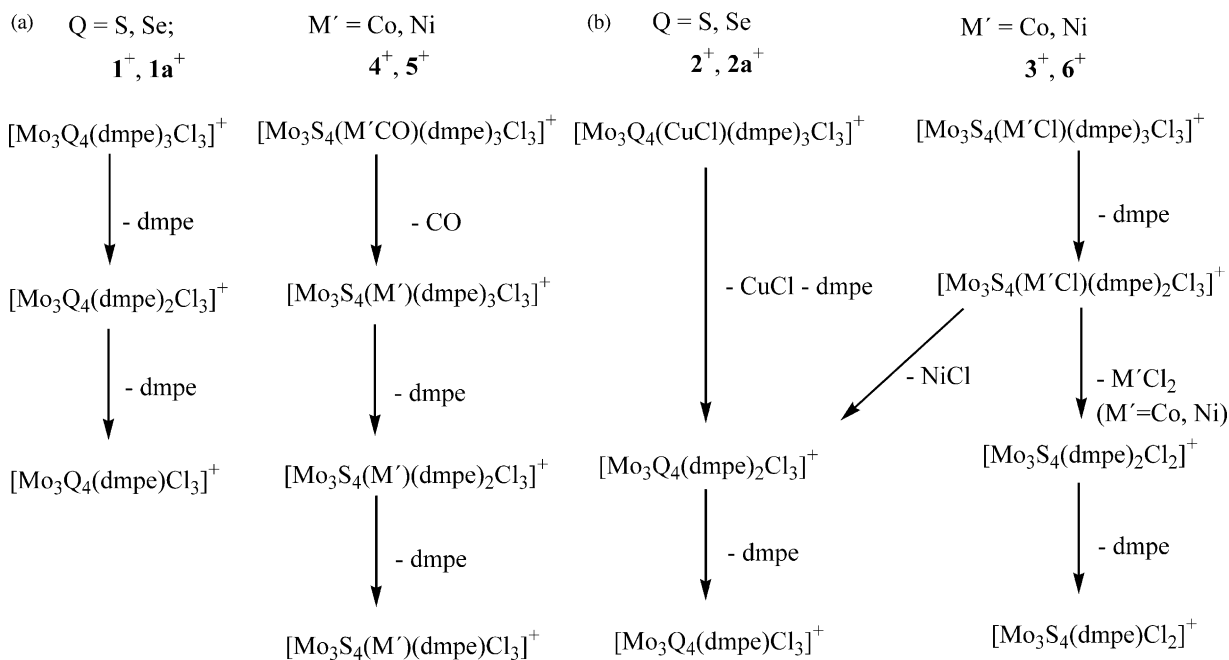
Fig. 3. Schematic representation of the fragmentation pathways observed for the series 1^+–6^+: (a) trinuclear $[Mo_3Q_4(dmpe)_3Cl_3]^+$ and tetranuclear $[Mo_3(M'CO)Q_4(dmpe)_3Cl_3]^+$ ions and (b) tetranuclear $[Mo_3(M'Cl)Q_4(dmpe)_3Cl_3]^+$ ions.

Remarkably, no fragmentation of the trinuclear Mo_3Q_4 core is detected, revealing a high robustness of this trinuclear cluster unit. Tetranuclear compounds that incorporate the heterometallic M′CO (M′ = Co, **4**; M′ = Ni, **5⁺**) fragment first evolve the CO ligand at low collision energies (typically below $E_{lab} = 20$ eV) to give species of general formula $[Mo_3(M')S_4(dmpe)_3Cl_3]^+$. When the collision energy is increased up to $E_{lab} = 60$ eV, a fragmentation pathway analogous to that of its trinuclear precursor 1^+ is observed, in which two diphosphane molecules are sequentially ejected to afford $[Mo_3(M')S_4(dmpe)_2Cl_3]^+$ and $[Mo_3(M')S_4(dmpe)Cl_3]^+$, respectively.

Releasing of either CO or diphosphane is a common fragmentation channel found in the vast majority of mono- or polynuclear complexes containing this sort of ligands [25,27,40,41]. In general, this characteristic dissociation pattern directly reflects its molecular organisation and can be used as an alternative means of structural elucidation on related cluster complexes. In addition, fragmentation peaks in 1^+, $1a^+$, 4^+ and 5^+ cations always appear due to losses of neutral molecules, where not only the cluster nuclearity is retained with regard to that of the precursor ions but also the metal electron count: 6 for the trinuclear cations and 15 and 16 for the cobalt and nickel tetranuclear cationic clusters, respectively.

3.2.2. Tetranuclear $[Mo_3(M'Cl)Q_4(dmpe)_3Cl_3]^+$ ions

Heterodimetallic clusters where the heterometal, Co, Ni or Cu, is coordinated to a halide ligand, present a different fragmentation mechanism. For the copper-containing ions 2^+ and $2a^+$, evolution of one diphosphane ligand is accompanied by the loss of a "CuCl" fragment to give $[Mo_3Q_4(dmpe)_2Cl_3]^+$ ions at collision energies below 40 eV. All attempts to adjust the collision energy aimed to detect $[2–dmpe]^+$, $[2a–dmpe]^+$ or $[2–CuCl]^+$, $[2a–CuCl]^+$ species were unsuccessful. This behaviour can be

interpreted as a simultaneous ejection of the dmpe and "CuCl" fragments although a mechanism involving migration of one dmpe to the copper site liberating the Cu(dmpe)Cl fragment can not be definitively ruled out. When the collision energy is raised to 60 eV, cationic $[Mo_3Q_4(dmpe)_2Cl_3]^+$ (Q = S, Se) species generated from ions 2^+ and $2a^+$ behave as their trinuclear precursors 1^+ or $1a^+$, that is, loosing a second diphospane molecule. Incidentally, the fragmentation in the gas-phase for the $[Mo_3CuClQ_4(dmpe)_3Cl_3]^+$ cluster core corresponds to the reverse step of the procedure used for the condensed-phase synthesis of these complexes starting from preassembled trinuclear 1^+ or $1a^+$ clusters and neutral CuCl [30,31].

Unlike the copper-containing complexes, cuboidal compounds that incorporate cobalt, 3^+ or nickel 6^+, start their fragmentation ejecting one diphosphane ligand at low collision energies (typically $E_{lab} = 20$–40 eV) with retention of the tetranuclear cuboidal core unit. A further increase of E_{lab} up to 60 eV, results in neutral fragments losses of $\Delta m = 130$ u for the $[Mo_3(CoCl)S_4(dmpe)_2Cl_3]^+$ cobalt containing specie and $\Delta m = 94$ and 129 u for the $[Mo_3(NiCl)S_4(dmpe)_2Cl_3]^+$ nickel cation. On the basis of mass differences alone, the neutral fragments may be tentatively identified as "CoCl$_2$" ($\Delta m = 130$ u), "NiCl$_2$" ($\Delta m = 129$ u) and "NiCl" ($\Delta m = 94$ u) that produces $[Mo_3S_4(dmpe)_2Cl_2]^+$ for both cobalt and nickel complexes and also $[Mo_3S_4(dmpe)_2Cl_3]^+$ for the nickel system. Additional information about the nature of the fragments evolved can be obtained through the width peak analysis of the parent ions as described in the following paragraph.

Under the conditions employed in the CID experiments, that is, an isolation width of 3 u, numerous isotopomers are present in the collision cell which contain various isobaric combinations i.e., $^{96}Mo^{65}Cu^{35}Cl$ and $^{98}Mo^{63}Cu^{35}Cl$ fragments are present in the $[Mo_3(CuCl)Se_4(dmpe)_3Cl_3]^+$ ($2a^+$) cation. In this case, a

wider isotopic pattern is expected for the product ions which result from the loss of the CuCl fragment than from those resulting from losses of the diphosphane ligands. This is due to the possibility of evolving either $^{63}Cu^{35}Cl$ or $^{65}Cu^{35}Cl$ and our point is clearly illustrated in Fig. 2 where the width peak of the product ions that results from losses of diphosphane neutral molecules clearly matches that of its precursor ion. The wider isotopic patterns observed for the product ion in comparison with that of their precursor ions when metal fragments, such as M′Cl (M = Cu, Co and Ni) and M′Cl$_2$ (M = Co and Ni), are evolved (see Fig. 2b and c) clearly supports the fragmentation pathways schematized in Fig. 3b. It has to be pointed out that copper-containing clusters invariably release CuCl or Cu(dmpe)Cl fragments, while cobalt and nickel derivatives lose CoCl$_2$ and NiCl or NiCl$_2$ fragments, respectively. The expulsion of M′Cl$_2$ fragments involves chlorine migration from one molybdenum atom to the heterometal prior to dissociation and these processes are observed at collision energies E_{lab} within the 50–60 eV range. Because at these collision energies the copper containing ions are present as trinuclear species, this mechanism will not be operative for the copper species and the expulsion of CuCl$_2$ fragments has not been detected experimentally.

The trinuclear product ions generated from **3⁺** or **6⁺**, namely [Mo$_3$S$_4$(dmpe)$_2$Cl$_2$]⁺ [Mo$_3$S$_4$(dmpe)$_2$Cl$_3$]⁺, differ in their number of metal electrons, seven and six, respectively. In all other cases the precursor or product trinuclear species in the gas-phase posses a general formula of [Mo$_3$Q$_4$(dmpe)$_x$Cl$_3$]⁺ with x = 1, 2 or 3 and 6 metal electrons. Trinuclear M$_3$Q$_4$ cluster complexes with seven metal electrons are very unstable in solution and only one example of this type of complexes has been fully characterised [42]. With the aim to compare the stability of these trinuclear species in condensed and gas-phase, the seven [Mo$_3$S$_4$(dmpe)$_2$Cl$_2$]⁺ and six [Mo$_3$S$_4$(dmpe)$_2$Cl$_3$]⁺ metal electron ions were mass-selected and subjected to CID experiments covering a collision energy range, E_{lab} up to 120 eV. These ions can be easily generated in the gas-phase by "in-source" fragmentation starting from **3⁺** and **6⁺** (cone voltage U_c = 150 V). Examination of the CID spectra shows that the only product ions detected are those resulting from losses of one diphosphane molecule to afford [Mo$_3$S$_4$(dmpe)Cl$_2$]⁺ and [Mo$_3$S$_4$(dmpe)Cl$_3$]⁺. These results indicate that the robustness of the trinuclear unit remains unaffected by the metal electron population. Such parallelism is not found in condensed-phase, where the seven-metal electrons trinuclear clusters are very unstable and we believe that they are highly reactive in the presence of moisture or air which explains their instability in the condensed-phase.

Incidentally, only the most electron deficient precursor ions [Mo$_3$(CoCl)S$_4$(dmpe)$_3$]⁺ (14 metal electrons) and [Mo$_3$(NiCl)S$_4$(dmpe)$_3$]⁺ (15 metal electrons) give rise to 7-metal electron fragmentation ions through losses of M′Cl$_2$ neutral fragments. Both Co(II) and Ni(II) form stable complexes that occur in a great variety of structural environments. In contrast the cobalt and nickel carbonyl complexes [Mo$_3$(CoCO)S$_4$(dmpe)$_3$]⁺ (15 metal electrons) and [Mo$_3$(NiCO)S$_4$(dmpe)$_3$]⁺ (16 metal electrons) do not produce Mo$_3$Q$_4$ trinuclear fragments. In consequence no definite conclu-

sion can be drawn regarding the key factors governing a certain fragmentation mechanism where both the nature or the fragment incorporated, metal halide or metal carbonyl, and the number of metal electrons 14, 15 or 16 e⁻, seem to contribute to favour a certain mechanism.

3.3. Mo–diphosphane and M′–CO energetics and stability of the Mo$_3$M′Q$_4$ core

Diphosphane and carbonyl ligands are ubiquitous in transition metal chemistry and afford extremely reactive and versatile homogeneous catalyst. Metal–phosphane and metal–CO dissociations are critical to many organometallic reaction sequences, being the M–P or M–CO bond strength a useful parameter in the evaluation of possible reaction mechanisms, particularly in catalysis. Recently, Westmore and Rosenberg et al. have proved that coupling of electrospray ionization with a Fourier transform ion cyclotron resonance analyzer can be used to quantitatively determine Ru–PPh$_2$H bond dissociation energies [40]. Chen et al. have also shown that modified commercial spectrometers can be used to obtain accurate thermochemical data of rhodium–phosphaethyne bond energies [43]. On the other hand, several studies dealing with the estimation of metal–carbonyl dissociation energies have been published [44–46].

We are aware that commercial triple quadrupole (QhQ) mass spectrometers do not allow to directly extract quantitative threshold information from CID experiments [47,48]. Particularly, although electrospray ionization is able to control the internal energy deposited on the ionic species [49–51], there is not guarantee that a suitable kinetic energy distribution for quantitative work can be achieved precluding a reliable quantitative analysis of the threshold CID experiments. In the present case, other factors such as multiple collision conditions in the hexapole or differences in rates of unimolecular dissociation experimented by the large cluster ions **1⁺–6⁺** are also overestimated. Nevertheless similarities in size among all cluster investigated in this work, and identical instrumental settings allow us to extract reliable comparative data. The utility of variable energy CID data to qualitatively estimate bonding parameters or relative stabilities of the electrosprayed species is well-documented [52,53] especially when ions with identical size, molecular structure and charge are compared under equivalent experimental conditions [54–57]. Therefore, the ions series **1⁺–6⁺** investigated in this work provides a unique opportunity to study the influence that the bridging chalcogenide, S or Se, the heterometal M′ = Cu, Co, Ni or the ligand L (L = Co, Cl) coordinated to M', have on the gas-phase cluster stability for this isostructural series.

In order to explore the consecutive fragmentation behaviour of ionized **1⁺–6⁺** species in more detail, mass selected **1⁺–6⁺** cations were subjected to CID experiments covering the E_{lab} = 0–70 eV range at intervals of 3 eV to promote ligand dissociation and obtain their breakdown profiles. Because a rigorous quantitative threshold analysis of the CID data is limited in the present study, crude estimates for the decaying energy of the ionic precursor ions were derived as described above (see Section 2). Table 1 list the $E_{CM50\%}$ values obtained for the low energy M′–CO and Mo–diphosphane fragmentation channels
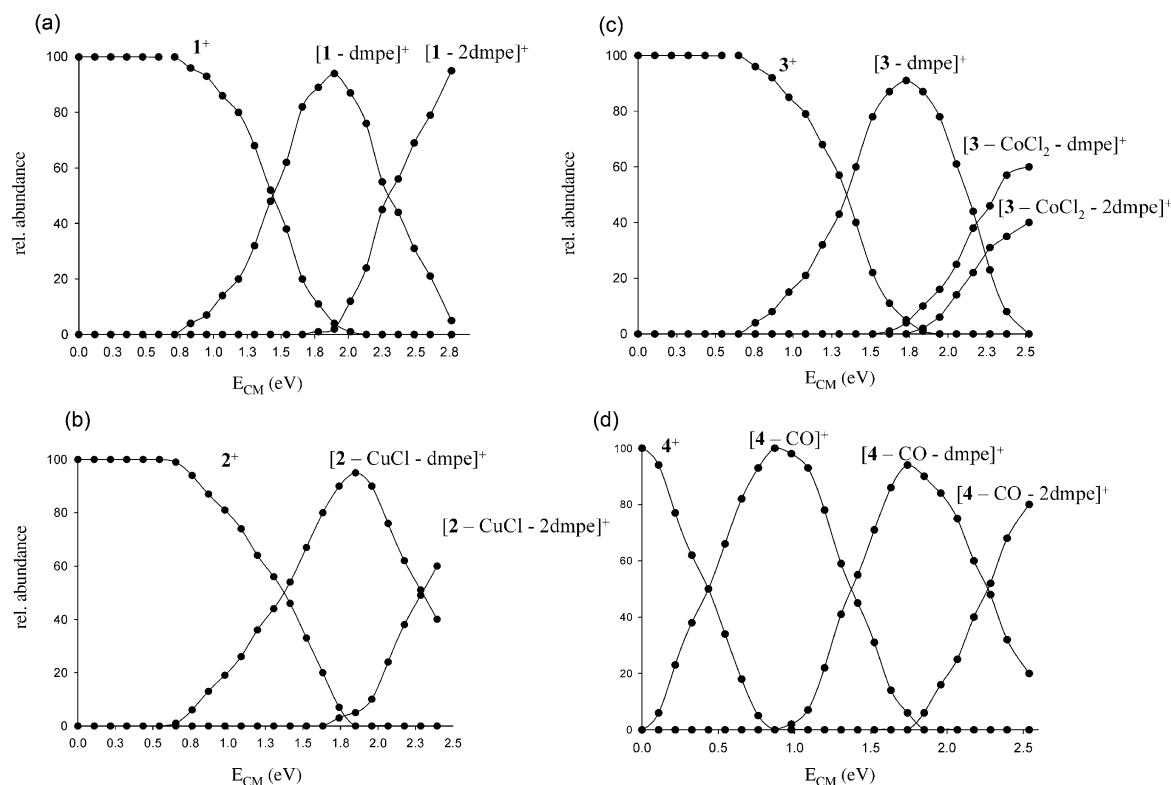
Fig. 4. Representative breakdown profiles of precursor ions: (a) $[Mo_3S_4(dmpe)_3Cl_3]^+$ (1^+), (b) $[Mo_3(CuCl)S_4(dmpe)_3Cl_3]^+$ (2^+), (c) $[Mo_3(CoCl)S_4(dmpe)_3Cl_3]^+$ (3^+) and $[Mo_3(CoCO)S_4(dmpe)_3Cl_3]^+$ (4^+).

and for the tetranuclear cluster unit breaking. Breakdown curves for the trinuclear cluster 1^+ and for the tetranuclear 2^+, 3^+ and 4^+ are presented in Fig. 4 in order to exemplify the different fragmentation behaviours.

3.3.1. Trinuclear [Mo₃Q₄(dmpe)₃Cl₃]⁺ and tetranuclear [Mo₃(M′CO)S₄(dmpe)₃Cl₃]⁺ ions

A feature of the fragmentation in these trinuclear complexes is the sequential loss of diphosphane ligands in two single-step processes where the precursor ion is first quantitatively converted to the $[1–diphosphane]^+$ cation. The $E_{CM50\%}$ values for the loss of the first diphosphane are 0.1 eV lower for the $1a^+$ selenide that for the 1^+ sulfide indicating a higher stability for the Mo–P bond in the Mo_3S_4 complexes.

The tetranuclear $[Mo_3(M′CO)S_4(dmpe)_3Cl_3]^+$ (M′ = Co, Ni) carbonyl ions always start their fragmentation with the loss of a neutral CO ligand where the $E_{CM50\%}$ value for the cobalt-containing complexes is clearly lower than that of the nickel cluster. In consequence the Ni–CO bond energy is higher than that of the Co–CO bond. The ν_{CO} frequency for the nickel carbonyl cluster equals $2038\,cm^{-1}$ suggesting a limited back donation for the Ni–CO bond which has basically a σ donor character. Energy differences between the heterometal "d" orbitals and the carbonyl lone pair are expected to be lower for nickel than for cobalt ($E_{Ni} < E_{Co}$) which would explain the higher stability of the nickel–carbon bond. No carbonyl frequencies are available for the cobalt 4^+ complex because this cation has been generated in the electrospray chamber. Data on the sequential M′–CO bond dissociation energy for the $[Co(CO)_x]^+$ (x = 1–5) and $[Ni(CO)_x]^+$

(x = 1–4) cations have been determined by Armentrout et al. by threshold collision induced dissociation experiments [58,59]. It is illustrative to compare the bond dissociation energy for the sequences $[M(CO)_x]^+ \rightarrow [M(CO)_{x-1}]^+$–CO (x = 1–4) (M = Co, Ni) where M–CO bond energies are found to be slightly lower for the cobalt series, as found in our cobalt 4^+ and nickel 5^+ carbonyl cations.

The product $[Mo_3M′S_4(dmpe)_3Cl_3]^+$ cations undergo two consecutive diphosphane losses in a similar way to that seen for its trinuclear precursor 1^+. The $E_{CM50\%}$ values observed for cobalt and nickel are identical and very similar to those found for the trinuclear 1^+ and $1a^+$ complexes. These results suggest a prominent dative character for the molybdenum–diphosphane bond as predicted by the theoretical calculations on the model $[Mo_3(M′L)S_4(PH_3)_6Cl_3]^+$ compound [60]. In contrast we have previously found for the $[Mo_3(M′PPh_3)Q_4(CH_3OH)_6Cl_3]^+$ (Q = S, Se; M′ = Ni, Pd) series that the energy of the Mo–CH₃OH bond depends on the nature of the heterometal incorporated as well as on the nature of the bridging chalcogen [61]. For the diphosphino clusters investigated in this work only the chalcogen, sulfur or selenium, seems to affect the energetics of the terminal metal–ligand bond.

3.3.2. Tetranuclear [Mo₃(M′Cl)Q₄(dmpe)₃Cl₃]⁺ ions

For the copper complexes, the diphosphane and CuCl fragments are lost simultaneously with $E_{50\%CM}$ values similar to those found for their trinuclear precursors. Again a slight decrease of $E_{50\%CM}$ is observed on going from the sulfur to the selenium derivatives. It is interesting to note that for the

copper containing clusters, the lost of the heterometal occurs at $E_{CM50\%}$ close to 1.4 eV while for the nickel and cobalt containing clusters, the lost of the heterometal occurs at higher energies, 1.8 eV for nickel and 2.3 eV for cobalt. Based on this, the stability of the tetrametallic $M_3M'S_4$ unit follows the order $Mo_3CuS_4 < Mo_3NiS_4 < Mo_3CoS_4$. Harris and coworkers have calculated the net metal–metal bonding interaction to increase in the order $Ni < Co$ in good agreement with our experimental results [62]. This unit became more robust upon carbonyl coordination to the heterometal where the $Mo_3M'S_4$ tetrametallic cluster unit is retained up to $E_{CM} = 2.5$ eV. For the Mo_3CuS_4 clusters, there is not evidence that the carbonyl ligand could be coordinated to copper. For the nickel and cobalt complexes, it has been reported that coordination of a carbonyl group to the heterometal in the aquo $[Mo_3(M'CO)(H_2O)_9]^{4,5+}$ complexes produces an enhancement in the solution stability towards decomposition [5]. Qualitative information on this relative stability is easily obtained through an analysis of the ESI fragmentation paths observed under energy-variable CID conditions.

4. Conclusions

The electrospray ionization source is very useful for the MS analysis of cationic and neutral Mo_3Q_4 and $Mo_3M'LQ_4$ (Q = S, Se; M' = Cu, Co, Ni; L = Co, Cl) cluster complexes with diphosphanes as outer ligands. Differences in the fragmentation pathways have been found, on one side the trinuclear $[Mo_3Q_4(dmpe)_3Cl_3]^+$ and tetranuclear $[Mo_3(M'CO)Q_4(dmpe)_3Cl_3]^+$ complexes lose two diphosphane and one carbon monoxide molecules in sequential single-steps retaining their nuclearity. On the other side, the copper, nickel and cobalt chlorine clusters $[Mo_3(M'Cl)Q_4(dmpe)_3Cl_3]^+$ do not preserve their central tetrametallic unit. It has been shown that beyond the classical criterion of identification, tandem mass spectrometry provides direct evidences of the relative stability of the analyzed clusters in the gas-phase, i.e., the $Mo_3M'S_4$ cluster core stability increases in the order $Mo_3CuS_4 < Mo_3NiS_4 < Mo_3CoS_4$. The heterometal does not affect the energy of the terminal Mo–P bond while this bond is more stable for the sulfide than for the selenide clusters.

References

[1] L.J. de Jongh, Physics and Chemistry of Metal Cluster Compounds: Model Systems for Small Metal Particles, Kluwer Academic Publishers, Dordrecht, 1994.
[2] J.B. Howard, Chem. Rev. 96 (1996) 2965.
[3] P. Braunstein, L.A. Oro, P.R. Raithby, in: P. Braunstein, L.A. Oro (Eds.), Metal Clusters in Chemistry, vol. II, Wiley-VCH, Weinheim, 1999.
[4] S. Shi, in: D.M. Roundhil, J.P. Fackler Jr. (Eds.), Optoelectronic Properties of Inorganic Compounds, Plenum, New York, 1999.
[5] R. Hernández-Molina, A.G. Sykes, Coord. Chem. Rev. 187 (1999) 291.
[6] R. Hernández-Molina, M.N. Sokolov, A.G. Sykes, Acc. Chem. Res. 34 (2001) 223.
[7] M. Hidai, S. Kuwata, Y. Mizobe, Acc. Chem. Res. 33 (2000) 46.
[8] R. Llusar, S. Uriel, Eur. J. Inorg. Chem. (2003) 1271.
[9] T. Shibahara, G. Sakane, Y. Naruse, K. Taya, H. Akashi, A. Ichimura, H. Adachi, Bull. Chem. Soc. Jpn. 68 (1995) 2769.
[10] A. Müller, V.P. Fedin, E. Diemann, H. Bogge, E. Krickemeyer, D. Solter, A.M. Giuliani, R. Barbieri, P. Adler, Inorg. Chem. 33 (1994) 2243.
[11] P.W. Dimmock, D.P.E. Dickson, A.G. Sykes, Inorg. Chem. 29 (1990) 5120.
[12] K. Hegetschweiler, T. Keller, W. Amrein, W. Schneider, Inorg. Chem. 30 (1991) 873.
[13] K. Hegetschweiler, P. Caravatti, V.P. Fedin, M.N. Sokolov, Helv. Chim. Acta 75 (1992) 1659.
[14] R.G. Cooks, D.X. Zhang, K.J. Koch, F.C. Gozzo, M.N. Eberlin, Anal. Chem. 73 (2001) 3646.
[15] M.A.O.V. Volland, C. Adlhart, C.A. Kiener, P. Chen, P. Hofmann, Chem. Eur. J. 7 (2001) 4621.
[16] Z. Takats, S.C. Nanita, R.G. Cooks, Angew. Chem. Int. Ed. Engl. 115 (2003) 3645.
[17] A.A. Sabino, A.H.L. Machado, C.R.D. Correia, M.N. Eberlin, Angew. Chem. Int. Ed. Engl. 43 (2004) 2514.
[18] P. Chen, Angew. Chem. Int. Ed. Engl. 42 (2003) 2832.
[19] M.A. Otfried-Volland, C. Adlhart, C.A. Kiener, P. Chen, P. Hofmann, Chem. Eur. J. 7 (2003) 4621.
[20] C. Adlhart, C. Hinderling, H. Baumann, P. Chen, J. Am. Chem. Soc. 122 (2000) 8204.
[21] W. Henderson, J. Fawcett, R.D.W. Kemmit, D.R. Rusell, J. Chem. Soc., Dalton Trans. (1995) 3007.
[22] X. Yang, X.-B. Wang, L.-S. Wang, Int. J. Mass Spectrom. 228 (2003) 797.
[23] S.H. Toma, S. Nikolau, D.M. Tomazela, M.N. Eberlin, H.E. Toma, Inorg. Chim. Acta 357 (2004) 2253.
[24] D. Plattner, Int. J. Mass Spectrom. 207 (2001) 125.
[25] C.P.G. Butcher, P.J. Dyson, B.F.G. Johnson, T. Khimyak, J. Scott McIndoe, Chem. Eur. J. 9 (2003) 944.
[26] G.A. Khitrov, G.F. Strouse, J.J. Gaumet, J. Am. Soc. Mass Spectrom. 15 (2004) 260.
[27] D. Rondeau, S. Perruchas, N. Avarvari, P. Batail, K. Vékey, J. Mass Spectrom. 40 (2005) 60.
[28] J.J. Gaumet, G.F. Strouse, J. Am. Soc. Mass Spectrom. 11 (2000) 338.
[29] F. Estevan, M. Feliz, R. Llusar, J.A. Mata, S. Uriel, Polyhedron 20 (2001) 527.
[30] M. Feliz, J.M. Garriga, R. Llusar, S. Uriel, M.G. Humphrey, N.T. Lucas, M. Samoc, B. Luther-Davies, Inorg. Chem. 40 (2001) 6132.
[31] R. Llusar, S. Uriel, C. Vicent, J. Chem. Soc., Dalton Trans. (2001) 2813.
[32] M. Feliz, R. Llusar, S. Uriel, C. Vicent, E. Coronado, C.J. Gomez-Garcia, Chem. Eur. J. 10 (2004) 4308.
[33] M. Feliz, R. Llusar, S. Uriel, C. Vicent, M. Brorson, K. Herbst, Polyhedron 24 (2005) 1212.
[34] C. Hao, R.E. March, T.R. Croley, J.C. Smith, S.P. Rafferty, J. Mass Spectrom. 36 (2001) 79.
[35] G.J. Van Berkel, in: R.B. Cole (Ed.), Electrospray Ionization Mass Spectrometry, Fundamentals Instrumentation and Applications, The Electrolytic Nature of Electrospray, John Wiley and Sons, New York, 1997, p. 65.
[36] W. Henderson, C. Evans, Inorg. Chim. Acta 294 (1999) 183.
[37] G.N. Khairallah, R.A.J. O'Hair, Dalton Trans. (2005) 2702.
[38] R. Llusar, S. Triguero, C. Vicent, M.N. Sokolov, D. Domercq, M. Fourmigue, Inorg. Chem. 44 (2005) 8937.
[39] M.T. Rodgers, P.B. Armentrout, Mass Spectrom. Rev. 19 (2000) 215, and references therein.
[40] J.B. Westmore, L. Rosenberg, T. Hooper, G.D. Willet, K.J. Fisher, Organometallics 21 (2002) 5688.
[41] C. Adlhart, P. Chen, Helv. Chim. Acta 86 (2003) 941.

[42] R.E. Cramer, K. Yamada, H. Kawaguchi, K. Tatsumi, Inorg. Chem. 35 (1996) 1743.
[43] Y.-M. Kim, P. Chen, Int. J. Mass Spectrom. 202 (2000).
[44] L.S. Sunderlin, R.R. Squires, Int. J. Mass Spectrom. 182 (1999) 149.
[45] F. Muntean, P.B. Armentrout, J. Chem. Phys. 115 (2001) 1213.
[46] L.A. Hammad, G. Gerdes, P. Chen, Organometallics 24 (2005) 1907.
[47] V.J. Nesatyy, J. Laskin, Int. J. Mass Spectrom. 221 (2002) 245.
[48] D. Schröeder, T. Weiske, H. Schwarz, Int. J. Mass Spectrom. 219 (2002) 729.
[49] C. Collette, L. Drahos, E. De Pauw, K. Vékey, Rapid Commun. Mass Spectrom. 12 (1998) 1673.
[50] C. Collette, E. De Pauw, Rapid Commun. Mass Spectrom. 12 (1998) 165.
[51] L. Drahos, R.M. Hereen, C. Collette, E. De Pauw, K. Vékey, J. Mass Spectrom. 34 (1999) 1373.
[52] K.J. Hart, S.A. McLuckey, J. Am. Soc. Mass Spectrom. 5 (1994) 250.
[53] A. Colorado, J. Brodbelt, J. Am. Soc. Mass Spectrom. 7 (1996) 1116.
[54] M. Satterfield, J.S. Brodbelt, Inorg. Chem. 40 (2001) 5393.
[55] N. Vinokur, V. Ryzhov, J. Mass Spectrom. 39 (2004) 1268.
[56] M.L. Reyzer, J.S. Brodbelt, S.M. Kerwin, D. Dumar, Nucl. Acid Res. 29 (2001) E103.
[57] C.L. Hunter, A.G. Mauk, D.J. Douglas, Biochemistry 36 (1997) 1018.
[58] S. Goebel, C.L. Haynes, F.A. Khan, P.B. Armentrout, J. Am. Chem. Soc. 117 (1995) 6994.
[59] F.A. Khan, D.L. Steele, P.B. Armentrout, J. Phys. Chem. 99 (1995) 7819.
[60] J. Andres, S. Berski, M. Feliz, R. Llusar, F. Sensato, B. Silvi, C.R. Chimie 8 (2005) 1400.
[61] M.N. Sokolov, E.V. Chubarova, R. Hernández-Molina, M. Clausen, D.Y. Naumov, C. Vicent, R. Llusar, V.P. Fedin, Eur. J. Inorg. Chem. (2005) 2139.
[62] C.S. Bahn, A. Tan, S. Harris, Inorg. Chem. 37 (1998) 2770.