Liquid matrix induced processes in fast atom bombardment mass spectrometry of polyazacrown transition metal complexes

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Abstract

A FAB-MS study of several macrocyclic divalent (Ni(II), Cu(II), Ag(II)) and trivalent (Cr(III), Mn(III), Fe(III), Co(III), Ni(III), Rh(III)) transition metal (M) polyamine complexes based on 1,4,7-triazacyclononane ([9]ane-N_3) (L^1) and 1,4,8,11-tetraazacyclotetradecane ([14]ane-N_4) (L^2) has been undertaken, using glycerol, thioglycerol and *m*-nitrobenzyl alcohol (*m*-NBA) as matrices. Removal of one neutralizing anion from the complexes ([9]ane-N_3)$_2$M^{n+}nX$^-$ and [([14]ane-N_4)M^{n+}$(n-1)$X$^-$]Y$^-$ produces cations [([9]ane-N_3)$_2$M^{n+}$(n-1)$X$^-$]$^+$ and [([14]ane-N_4)M^{n+}$(n-1)$X$^-$]$^+$ that, in most of the cases, represent the highest mass ion in the spectra. Subsequent matrix assisted one-electron reduction(s) and concomitant anion loss(es) produce singly charged species [([9]ane-N_3)$_2$M$^{(n-1)+}$$(n-2)X^-$]$^+$ and [([14]ane-N_4)M$^{(n-1)+}$$(n-2)X^-$]$^+$, with the metal in a lower oxidation state, which undergo successive oxidative dehydrogenations.

Introduction

Fast atom bombardment (FAB) and liquid secondary ion mass spectrometry (LSIMS) [1] have been reported to be useful techniques for elucidating the composition and structure of organometallic compounds [2]. Recently, these techniques have also been used for studying supramolecular interactions [3] and for the characterization of cationic coordination complexes [4, 5]. FAB ionization not only allows the determination of the molecular ions but also the related observed fragmentations of the structure of organometallic compounds. Thus, the combination of FAB and MS/MS techniques was recently used for a detailed study of ruthenium(II) complexes containing multidentate polypyridine ligands [6].

We are interested in the characterization of both neutral and cationic macrocyclic transition metal complexes containing heterocyclic ligands related to azaporphyrins and phthalocyanines with properties of organic semiconductors [7]. Our former experiences in

this area using FAB ionization [8, 9] have shown that in some cases chemical processes occurring in the matrix are predominant. Among others [10], reduction, demetallation reactions and electron transfer processes in metalloporphyrins have been studied extensively by Naylor *et al.* [11].

We have now undertaken an FAB-MS study of macrocyclic transition metal polyamine complexes as model compounds for other more complex nitrogen containing macrocyclic systems. Here we report on two systems with different complexation ability towards transition metals: the dimeric 1,4,7-triazacyclononane ([9]ane-N_3) (L^1) complexes (**1**) [12] and the more stable complexes of 1,4,8,11-tetraazacyclotetradecane ([14]ane-N_4) (L^2) (**2**) [13]. The ability of these macrocyclic polyamines to form stable complexes with transition metal ions has been known for many years [14] and the X-ray structure has been described in some cases [15].

These systems can be considered to be simple models of enzymes [16] and some authors have developed related analogues based on their skeleton to afford, for example, kinetically stable radioisotope complexes

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that could be used *in vivo* for diagnostic purposes [17]. On the other hand, transition metal complexes of cyclam (L^2) are versatile catalysts for the oxidation of organic substrates [18]. Recently, an FAB-MS study on related coordination complexes of the ligands 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane was reported [19].

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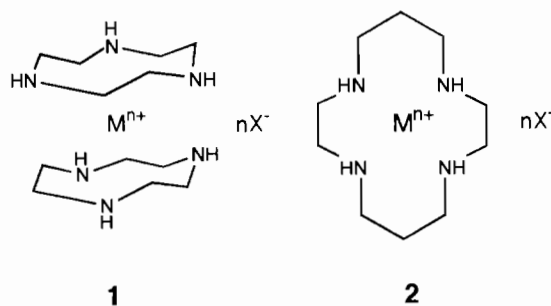
Results and discussion

([9]ane-N$_3$)$_2$MX$_2$ and ([9]ane-N$_3$)$_2$MX$_3$ complexes (1)

According to X-ray analysis and other data [15, 20], the [9]ane-N$_3$ complexes $(L^1)_2MX_2$ containing M^{2+} and M^{3+} cations of Cr, Fe, Co, Ni and Cu have a sandwich-like structure with the six saturated secondary amine nitrogen atoms of the two [9]ane-N$_3$ ligands coordinating metal centers in nearly octahedral environments [15]. Figure 1 shows the FAB spectrum of a Cu(II) complex as an example. Glycerol was usually employed as the matrix, taking into account its good miscibility with aqueous solutions of the metal complexes, but the studies

were also carried out with other matrices, such as *m*-nitrobenzyl alcohol (*m*-NBA) and thioglycerol. Tables 1 and 2 give the intensities of the relevant peaks for nine complexes with different metal ions and anions. Finally, Scheme 1 rationalizes the fragmentation behavior.

As established [2], removal of one neutralizing anion from the complexes $(L^1)_2MX_2$ produces cations $[(L^1)_2MX]^+$ which are in all cases the highest mass ion in the spectra. Subsequent matrix assisted one-electron reduction with concomitant loss of the second anion [19] produces singly charged species $[(L^1)_2M]^+$ with the metal in an oxidation state $+1$. The intensities of the peaks corresponding to the ions $[(L^1)_2MX]^+$ and $[(L^1)_2M]^+$ change into a great extent according to the matrix. Thus, for example, for the complex $(L^1)_2CuCl_2$ the relative intensity of the quasi-molecular ion $[(L^1)_2CuCl]^+$ is much higher in thioglycerol than in glycerol. This type of effect may be explained in terms of the reducing potential of the matrix: glycerol enhances the reduction of the metal ion in $[(L^1)_2CuCl]^+$ and therefore facilitates the production of ions $[(L^1)_2Cu]^+$ with the metal in a lower oxidation state. Ions $[(L^1)_2M]^+$ undergo two successive oxidative dehydrogenations to afford $[(L^1-H)_2M]^+$. Similar fragmentation behavior has been observed by Miller and co-workers in related complexes [19]. Also in our case, the ease of oxidation has shown to be metal-ion dependent. As the proposed oxidative mechanism involves higher oxidation states of the metal, it is reasonable to assume that species with metal ions in a favorable oxidation state will present more intensive peaks. This is observed indeed if one compares the intensity of the peaks $[(L^1)_2M]^+$,
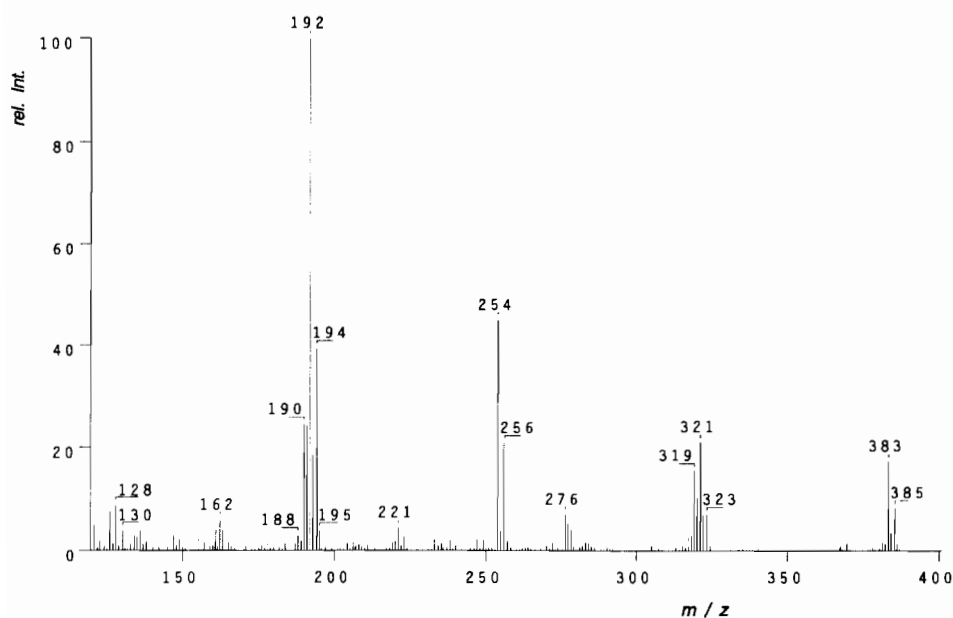

Fig. 1. FAB mass spectrum of ([9]ane-N$_3$)$_2$Cu(NO$_3$)$_2$ in glycerol.

TABLE 1. FAB-MS fragmentation of [9]ane-N_3 metal complexes $(L^1)_2MX_2$[a]

Ions	Complex				
	$(L^1)_2NiCl_2$	$(L^1)_2Ni(ClO_4)_2$	$(L^1)_2Ni(NO_3)_2$	$(L^1)_2CuCl_2$	$(L^1)_2Cu(NO_3)_2$
$[(L^1)_2MX]^+$	351 (100) [57] {90}	415 (100) [100]	378 (61) [100] {72}	356 (67) [100] {49}	383 (17)
$[(L^1)(L^1-H)MX]^+$	350 (4) [4] {3}	414 (9) [8]	377 (8) [5] {3}	355 (7) [3] {1}	382 (1)
$[(L^1-H)_2MX]^+$	349 (3) [6] {4}	413 (−) [6]	376 (5) [4] {3}	354 (3) [3] {2}	381 (2)
$[(L^1)_2M]^+$	316 (53) [12] {24}	316 (26) [10]	316 (38) [30] {23}	321 (32) [22] {27}	321 (11)
$[(L^1)(L^1-H)M]^+$	315 (97) [30] {50}	315 (41) [28]	315 (100) [83] {60}	320 (23) [7] {7}	320 (10)
$[(L^1-H)_2M]^+$	314 (38) [17] {27}	314 (9) [11]	314 (40) [35] {26}	319 (25) [15] {14}	319 (16)
$[(L^1)MX]^+$	222 (94) [100] {100}	286 (−) [42]	249 (50) [76] {100}	227 (36) [63] {41}	254 (45)
$[(L^1)M]^+$	187 (−)[b] [11] {20}	187 (−)[b] [12]	187 (−)[b] [18] {19}	192 (100) [91] {100}	192 (100)
$[(L^1-H)M]^+$	186 (−)[b] [9] {14}	186 (−)[b] [8]	186 (−)[b] [13] {12}	191 (30) [12] {16}	191 (24)
$[(L^1-2H)M]^+$	185 (−)[b] [14] {25}	185 (−)[b] [14]	185 (−)[b] [27] {25}	190 (22) [16] {20}	190 (24)

[a]Mass (m/z) of the lowest peak of the cluster (intensity, isotope corrected); matrix: ( ) glycerol; [ ] thioglycerol; { } m-NBA.
[b]Intensity not calculated because the low intensity ($<10\%$) of this peak may be part of the isotopic cluster of m/z 185 (glycerol).

$[L^1(L^1-H)_2M]^+$ and $[(L^1-H)_2M]^+$ in Table 1 for the nickel and copper complexes $(L^1)_2MX_2$, taking into account the increasing oxidation state $+1 \rightarrow +2 \rightarrow +3$ attributed to the metal in the three mentioned fragments. The use of an oxidizing matrix (such as m-NBA) or a slightly oxidizing one (such as thioglycerol), instead of glycerol, does not affect significantly the extent of the oxidative dehydrogenation as can be inferred from a comparison of the relative intensities of the peaks $[L^1(L^1-H)M]^+$ and $[(L^1-H)_2M]^+$ and their parent ion $[(L^1)_2M]^+$ in all three matrices. The production of the characteristic ions $[(L^1)_2M]^+$ and $[L^1(L^1-H)M]^+$ from $[(L^1)_2MX]^+$ could be also rationalized by a different pathway. Thus, removal of the anion from $[(L^1)_2MX]^+$ could produce highly energetic double charged ions $[(L^1)_2M]^{2+}$ as intermediates. Stabilization of these by a matrix assisted one-electron reduction [21] or by removal of a proton would lead to $[(L^1)_2M]^+$

and $[L^1(L^1-H)M]^+$, respectively. Double charged ions have been detected in the fragmentation of several metal complexes. Thus, for example, ions of this type of considerable intensity have been observed in the FAB mass spectra of ruthenium complexes containing polypyridine ligand measured in m-nitrobenzyl alcohol [6, 22]. In these cases the aromatic ligands may contribute to the stabilization of the double charge. However, in the present study double charge ions could not be detected in the measurements carried out in glycerol, m-NBA or thioglycerol. For all these reasons, in our case, a mechanism based on the intermediacy of double charge ions cannot be claimed. In most of the cases it is possible to observe also the loss of one ligand from $[(L^1)_2MX]^+$ to give $[(L^1)MX]^+$. This is chemically logical because, according to the literature, there exist stable [9]ane-N_3 metal complexes with only one ligand [23]. One-electron reduction of $[(L^1)MX]^+$

TABLE 2. FAB-MS fragmentation of [9]ane-N_3 metal complexes $(L^1)_2MX_3$[a]

Ions	Complex			
	$(L^1)_2Ni(ClO_4)_3$	$(L^1)_2FeCl_3$	$(L^1)_2CoBr_3$	$(L^1)_2CrCl_3$
$[(L^1)_2MX_2]^+$				380 (9) [8]
$[(L^1)_2MX]^+$	415 (100) [36]	349 (30)	396 (13) [16]	345 (40) [17]
$[(L^1)(L^1-H)MX]^+$	414 (17) [4]	348 (20)	395 (18) [35]	344 (75) [32]
$[(L^1-H)_2MX]^+$	413 (13) [7]	347 (11)	394 (−) [3]	343 (18) [7]
$[(L^1)_2M]^+$	316 (25) [7]	314 (25)	317 (6) [3]	310 (10) [18]
$[(L^1)(L^1-H)M]^+$	315 (78) [12]	313 (15)	316 (38) [26]	309 (50) [58]
$[(L^1-H)_2M]^+$	314 (24) [13]	312 (44)	315 (100) [100]	308 (100) [12]
$[(L^1)MX]^+$	286 (3) [100]	220 (100)	267 (12) [72]	216 (60) [20]
$[(L^1)M]^+$	187 (−)[b] [38]	185 (−)[b]	188 (20) [13]	181 (−) [100]
$[(L^1-H)M]^+$	186 (−)[b] [27]	184 (11)	187 (−)[b] [16]	180 (−) [10]
$[(L^1-2H)M]^+$	185 (−)[b] [59]	183 (25)	186 (−)[b] [32]	179 (−) [25]

[a]Mass (m/z) of the lowest peak of the cluster (intensity, isotope corrected); matrix: ( ) glycerol; [ ] thioglycerol. [b]Intensity not calculated because the window intensity (<10%) of this peak may be part of the isotopic cluster of m/z 185 (glycerol).

with loss of the second anion would lead to $[(L^1)M]^+$. On the other hand, the ratio of the intensities $[(L^1)_2M]^+/[(L^1)_2MX]^+$ should represent a measure of the facility to split an anion from the complexes with the same metal. In fact, the data from Table 1 demonstrate a series of $NO_3^- > Cl^- > ClO_4^-$ in glycerol as well as in thioglycerol as matrices, which is in good agreement with the decreasing basicity of these anions.
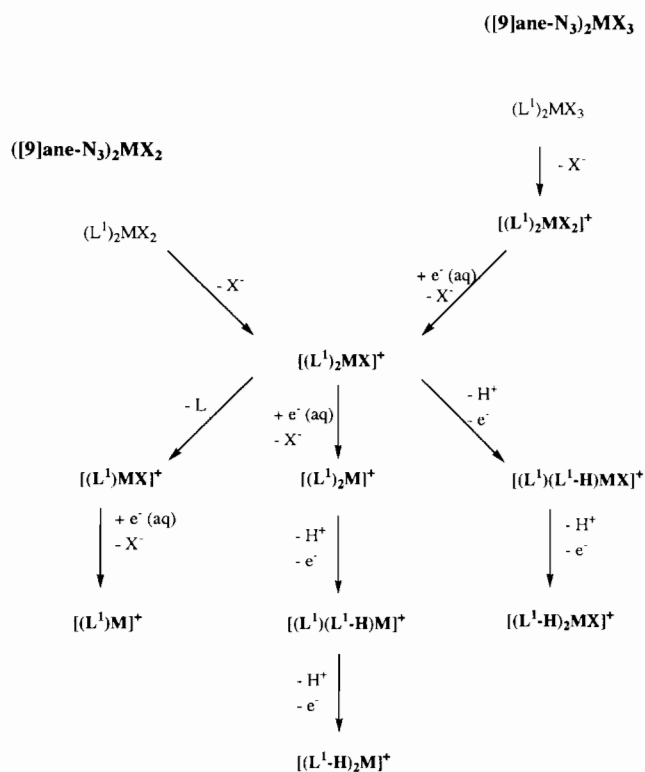
The $([9]ane-N_3)_2MX_3$ complexes show a similar fragmentation pattern. The lack of solubility of the metal complexes in m-nitrobenzyl alcohol prevented a parallel study in this matrix. It is interesting to know that in this series a high oxidation state cation $[(L^1)_2CrCl_2]^+$ could only be observed for the chromium(III) chloride complex (Table 2). The complexes of Fe(III), Co(III) and Ni(III), after removal of one neutralizing anion, would also give $[(L^1)_2MX_2]^+$ ions not visible in the spectra, which would undergo an easy one-electron reduction with loss of the second anion to afford the highest mass ion in the spectra: $[(L^1)_2MX]^+$. This is in good agreement with the high negative reduction potential of the metallotriazacyclononane Cr(III) complex (-1.4 V), in comparison with those observed for the other metal complexes, Co(III): -0.41, Fe(III):

+0.13 and Ni(III): +0.93 [20b]. On the other hand, $[(L^1)_2M]^+$ is discussed to be generated from $[(L^1)_2MX]^+$ by the same pathway proposed for the divalent complexes. In both [9]ane-N_3 series demetallation processes are not observed.

([14]ane-N_4)MX$_2$ and ([14]ane-N_4)MX$_2$Y complexes (2)

According to the X-ray analysis the [14]ane-N_4 complexes have an octahedral structure with the metal surrounded by a square planar array of nitrogen atoms and weak axial interactions with two monodentate anions. In the M^{3+} complexes this structure is neutralized by a third anion in a second coordination sphere [15, 24].

Figure 2 shows the FAB spectrum of ([14]ane-N_4)Co(III)Cl$_3$ which is, as far as the masses are concerned, identical to the spectrum of the ([14]ane-N_4)Co(III)Cl$_2$NO$_3$ complex. Tables 3 and 4 collect the characteristic fragments of twelve metal complexes in glycerol, thioglycerol and m-NBA as matrices and Scheme 2 rationalizes the fragmentation of both series of the ([14]ane-N_4)MX$_2$ and the [([14]ane-N_4)MX$_2$]Y complexes.

([9]ane-N$_3$)$_2$MX$_3$

([9]ane-N$_3$)$_2$MX$_2$

(L^1)$_2$MX$_3$

| - X$^-$

(L^1)$_2$MX$_2$ [(L^1)$_2$MX$_2$]$^+$

- X$^-$ + e$^-$ (aq)
                              - X$^-$

[(L^1)$_2$MX]$^+$

- L   + e$^-$ (aq)   - H$^+$
              - X$^-$ - e$^-$

[(L^1)MX]$^+$ [(L^1)$_2$M]$^+$ [(L^1)(L^1-H)MX]$^+$

+ e$^-$ (aq)   - H$^+$ - H$^+$
- X$^-$ - e$^-$ - e$^-$

[(L^1)M]$^+$ [(L^1)(L^1-H)M]$^+$ [(L^1-H)$_2$MX]$^+$

- H$^+$
- e$^-$

[(L^1-H)$_2$M]$^+$

Scheme 1. FAB induced fragmentation of [9]ane-N$_3$ (L^1) metal complexes. Peaks observed in the mass spectra are given in bold.

As observed in the [9]ane-N$_3$ series, splitting of one anion from the neutral complex yields cations [(L^2)MX]$^+$ and [(L^2)MX$_2$]$^+$, respectively. According to the preparation of complexes of [14]ane-N$_4$-Co(III) with different anions, the third anion (Y$^-$), more weakly bound to the metal ion, is in fact the first unit to be

eliminated. Fragmentation behavior can be rationalized in a similar way as in the [9]ane-N$_3$ complexes. The cobalt(III) complexes (L^2)CoX$_2$Y generally show quasi-molecular ions [(L^2)CoX$_2$]$^+$ which are the base peaks of the spectra. Complex (L^2)Co(N$_3$)$_2$ClO$_4$ represents an exception, showing low intensities for the ions [(L^2)Co(N$_3$)$_2$]$^+$ and [(L^2)Co(N$_3$)]$^+$ due to the characteristic easy loss of ClO$_4^-$ and N$_3^-$, in agreement with the results observed by other authors for related cobalt complexes [19]. Again no double charged ions and no metal free complexes are detected, even using m-NBA as a matrix. The loss of the four hydrogens bound to the nitrogens of the [14]ane-N$_4$ molecule by means of successive oxidative dehydrogenations seems to be characteristic as in the previous case. Also here, the use of m-NBA or thioglycerol as oxidizing matrices instead of glycerol does not seem to facilitate the dehydrogenation processes. In the case of the [14]ane-N$_4$ complexes the changes in the matrix do not affect significantly the intensities of the different fragments, as it occurred in the [9]ane-N$_3$ series, probably as a consequence of the higher chemical stability of the former complexes.

In conclusion, FAB mass spectra of complexes of [9]ane-N$_3$ and [14]ane-N$_4$ have shown different liquid matrix induced processes besides the well-known loss of neutralizing anions. Thus, matrix assisted one-electron reductions and loss of hydrogen atoms by means of oxidative dehydrogenation are characteristic processes in the fragmentation of this type of complex. The complexes studied here produce no double charged ions upon measurement in m-NBA, glycerol and thioglycerol. No ions of ligands without metal are observed.
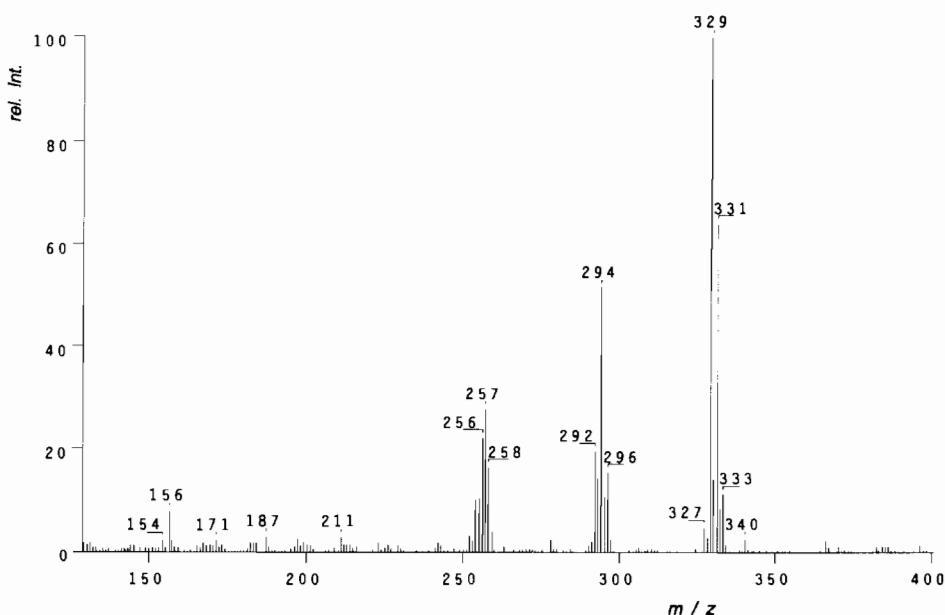
Fig. 2. FAB mass spectrum of ([14]ane-N$_4$)CoCl$_3$ in glycerol.

TABLE 3. FAB-MS fragmentation of [14]ane-N_4 metal complexes $(L^2)MX_2$[a]

Ions	Complex			
	$(L^2)NiCl_2$	$(L^2)Ni(ClO_4)_2$	$(L^2)CuCl_2$	$(L^2)Ag(ClO_4)_2$
$[(L^2)MX]^+$	293 (51) [67] {95}	357 (92) [98]	298 (100) [100] {100}	406 (14) {15}
$[(L^2-H)MX]^+$	292 (5) [6] {8}	356 (2) [8]	297 (7) [2] {1}	
$[(L^2-2H)MX]^+$	291 (2) [4] {5}	355 (4) [10]	296 (5) [4] {3}	
$[(L^2)M]^+$	258 (47) [36] {47}	258 (72) [94]	263 (23) [48] {41}	307 (100) {100}
$[(L^2-H)M]^+$	257 (100) [100] {100}	257 (100) [100]	262 (39) [58] {36}	306 (20) {13}
$[(L^2-2H)M]^+$	256 (50) [44] {47}	256 (49) [60]	261 (40) [43] {45}	305 (26) {18}
$[(L^2-3H)M]^+$	255 (24) [26] {20}	255 (24) [25]	260 (7) [11] {9}	304 (7) {1}
$[(L^2-4H)M]^+$	254 (7) [6] {7}	254 (9) [8]	259 (5) [3] {6}	303 (4) {2}

[a]Mass (m/z) of the lowest peak of the cluster (intensity, isotope corrected); matrix: ( ) glycerol; [ ] thioglycerol; { } m-NBA.

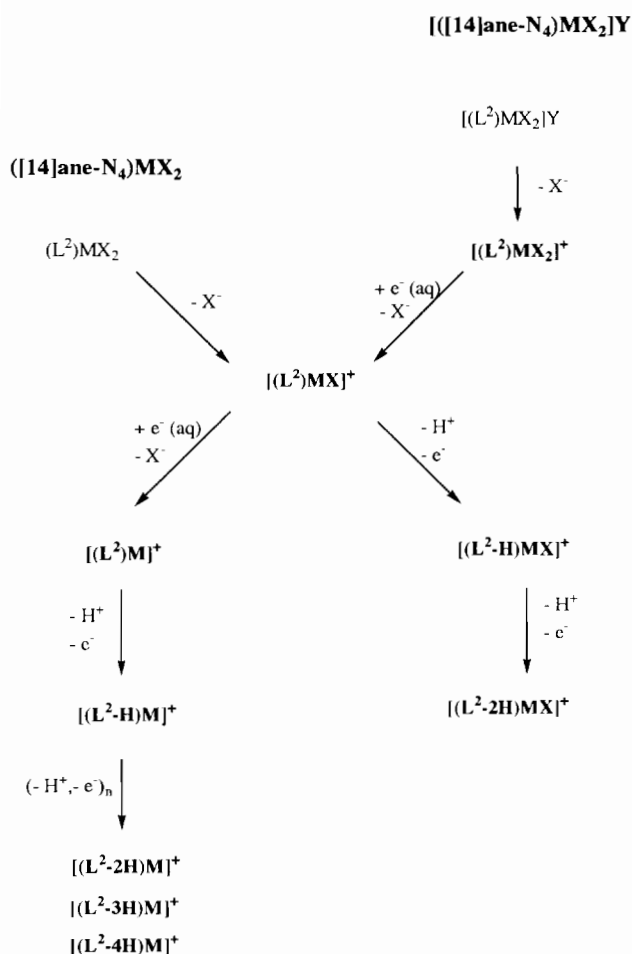TABLE 4. FAB-MS fragmentation of [14]ane-N_4 metal complexes $(L^2)MX_2Y$[a]

Ions	Complex							
	$(L^2)CoCl_3$	$(L^2)CoCl_2NO_3$	$(L^2)Co(N_3)_2ClO_4$	$(L^2)Co(SCN)_3$	$(L^2)MnCl_3$	$(L^2)FeCl_3$	$(L^2)Fe(SCN)_3$	$(L^2)RhCl_3$
$[(L^2)MX_2]^+$	329 (100) [100] {100}	329 (100) [100]	343 (8) [6]	375 (100) [100] {100}	325 (51) {50}	326 (54)	372 (65) [50] {78}	373 (100) [100] {100}
$[(L^2)MX]^+$	294 (51) [45] {30}	294 (57) [55]	301 (5) [4]	317 (60) [44] {40}	290 (100) {100}	291 (100)	314 (100) [100] {100}	338 (12) [8] {5}
$[(L^2-H)MX]^+$	293 (14) [8] {9}	293 (21) [8]	300 (2) [2]	316 (11) [5] {7}	289 (67) {65}	290 (47)	313 (39) [26] {44}	337 (3) [2] {1}
$[(L^2-2H)MX]^+$	292 (20) [15] {15}	292 (20) [14]	299 (2) [1]	315 (15) [10] {10}	288 (44) {70}	289 (28)	312 (24) [23] {39}	336 (4) [4] {3}
$[(L^2)M]^+$	259 (4) [6] {5}	259 (10) [7]	259 (10) [8]	259 (15) [6] {14}	255 (1) {−}	256 (3)	256 (2) [12] {12}	303 (8) [3] {2}
$[(L^2-H)M]^+$	258 (16) [14] {24}	258 (29) [30]	258 (64) [96]	258 (46) [17] {31}	254 (2) {2}	255 (1)	255 (16) [11] {20}	302 (20) [10] {5}

(continued)

TABLE 4. (continued)

Ions	Complex							
	$(L^2)CoCl_3$	$(L^2)CoCl_2NO_3$	$(L^2)Co(N_3)_2ClO_4$	$(L^2)Co(SCN)_3$	$(L^2)MnCl_3$	$(L^2)FeCl_3$	$(L^2)Fe(SCN)_3$	$(L^2)RhCl_3$
$[(L^2-2H)M]^+$	257 (27) [15] {15}	257 (42) [24]	257 (100) [100]	257 (41) [19] {23}	253 (2) {1}	254 (1)	254 (23) [13] {16}	301 (18) [12] {9}
$[(L^2-3H)M]^+$	256 (22) [7] {8}	256 (28) [10]	256 (51) [40]	256 (28) [9] {13}	252 (1) {-}		253 (24) [4] {9}	300 (13) [8] {10}
$[(L^2-4H)M]^+$	255 (6) [10] {10}	255 (12) [14]	255 (23) [20]	255 (10) [4] {8}			252 (11) [7] {10}	299 (11) [6] {6}

^{a}Mass (m/z) of the lowest peak of the cluster (intensity, isotope corrected); matrix: ( ) glycerol; [ ] thioglycerol; { } m-NBA.

Scheme 2. FAB induced fragmentation of [14]ane-N₄ (L²) metal complexes. Peaks observed in the mass spectra are given in bold.

Experimental

1,4,7-triazacyclononane ([9]ane-N₃) and 1,4,8,11-tetraazacyclotetradecane ([14]ane-N₄) were purchased from Aldrich and used as received. Metal complexes were synthesized according to previously published procedures [20, 24].

The FAB mass spectra were measured with a HSQ30-BEQQ system and a MAT900 instrument (Finnigan MAT, Bremen), both equipped with a cesium gun from AMD Intectra GmbH, Harpstedt and Finnigan, respectively. To analyse the isotopic clusters 20–50 spectra of a limited mass range were sampled, averaged and then corrected; all intensity values given in the tables are isotope corrected.

The samples were dissolved in water and mixed on the probe with glycerol (vol./vol. 1:1) or were dissolved in methanol to carry out the measurements in thioglycerol and m-nitrobenzyl alcohol; the concentration was in the range of 15–100 nmol/measurement.

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