

Table III. Positional Parameters and Equivalent Isotropic Thermal Parameters (\AA^2) and Their Estimated Standard Deviations for $[\text{Mo}_2(\text{NCCH}_3)_{10}](\text{BF}_4)_4 \cdot 2\text{CH}_3\text{CN}$ (1)^a

atom	x	y	z	B
Mo(1)	0.0517 (1)	0.96295 (4)	0.96348 (8)	1.83 (2)
F(1)	-0.030 (1)	0.1895 (5)	0.747 (1)	7.7 (4)
F(2)	-0.022 (1)	0.1056 (5)	0.632 (1)	8.3 (4)
F(3)	0.027 (2)	0.1983 (7)	0.568 (1)	10.4 (5)
F(4)	0.181 (1)	0.1551 (6)	0.731 (1)	10.1 (4)
F(5)	0.039 (1)	0.5785 (5)	0.3372 (8)	7.3 (3)
F(6)	-0.145 (1)	0.5689 (6)	0.157 (1)	7.1 (3)
F(7)	0.053 (2)	0.6227 (5)	0.160 (1)	9.7 (5)
F(8)	0.061 (1)	0.5226 (5)	0.169 (1)	8.4 (4)
N(1)	-0.060 (1)	0.9679 (5)	0.7615 (9)	2.6 (2)
N(2)	0.226 (1)	1.0140 (5)	0.9292 (8)	2.4 (2)
N(3)	0.191 (1)	0.9311 (5)	1.1429 (9)	2.5 (2)
N(4)	-0.094 (1)	0.8912 (4)	0.9655 (8)	2.3 (2)
N(5)	0.309 (1)	0.3777 (5)	0.615 (1)	3.6 (3)
N(6)	0.086 (2)	0.263 (1)	0.274 (2)	13.2 (9)
C(1)	-0.115 (1)	0.9650 (6)	0.654 (1)	2.8 (3)
C(2)	-0.188 (2)	0.9629 (8)	0.515 (1)	5.1 (4)
C(3)	0.315 (1)	1.0382 (6)	0.904 (1)	2.4 (3)
C(4)	0.434 (1)	1.0704 (6)	0.873 (1)	3.4 (3)
C(5)	0.262 (1)	0.9124 (6)	1.240 (1)	2.5 (3)
C(6)	0.355 (2)	0.8877 (7)	1.364 (1)	4.3 (4)
C(7)	-0.169 (1)	0.8505 (6)	0.960 (1)	2.7 (3)
C(8)	-0.266 (2)	0.7975 (7)	0.953 (2)	4.7 (4)
C(9)	0.288 (1)	0.3457 (6)	0.688 (1)	3.0 (3)
C(10)	0.261 (2)	0.3024 (7)	0.783 (2)	5.0 (5)
C(11)	0.183 (3)	0.250 (1)	0.354 (2)	7.7 (7)
C(12)	0.317 (2)	0.2332 (9)	0.457 (2)	6.4 (6)
B(1)	0.038 (2)	0.1603 (9)	0.668 (2)	3.9 (4)
B(2)	0.008 (2)	0.5736 (8)	0.205 (1)	3.6 (4)

^a Anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos \gamma)\beta_{12} + ac(\cos \beta)\beta_{13} + bc(\cos \alpha)\beta_{23}]$.

the solvent molecule and resulted in the final residuals as listed in Table I.

Results and Discussion

Crystal Structure. The structure of $[\text{Mo}_2(\text{NCCH}_3)_{10}](\text{BF}_4)_4 \cdot 2\text{CH}_3\text{CN}$ (1) consists of a discrete, centrosymmetric $[\text{Mo}_2(\text{NCCH}_3)_{10}]^{4+}$ core as shown in Figure 1. The dimolybdenum core resides on an inversion center. Each molybdenum atom is bonded to the other molybdenum atom [$\text{Mo}(1)-\text{Mo}(1)' = 2.187$ (1) \AA], four nitrogen atoms of the equatorial acetonitriles [$\text{Mo}(1)-\text{N}_{\text{eq,av}} = 2.129$ (6) \AA], and one nitrogen atom in the axial position [$\text{Mo}(1)-\text{N}_{\text{ax}} = 2.600$ (13) \AA]. The BF_4^- counterions refined nicely with no apparent disorder. All Mo–N–C angles are close to 180° as expected, except $\text{Mo}(1)-\text{N}(5)-\text{C}(9)$, which is 155.3 (9) $^\circ$. A crystal packing diagram reveals that the interstitial acetonitrile molecule [$\text{N}(6)-\text{C}(11)-\text{C}(12)$] “pushes” on the weakly bonded axial acetonitrile to cause this deviation from the norm. Relevant crystallographic information is presented in Tables I–III.

Attempts have been made to determine crystallographically the structure of $[\text{Mo}_2(\text{NCCH}_3)_{10}](\text{O}_3\text{SCF}_3)_4$, but all crystals to date have been badly twinned.

Synthesis and Spectroscopic Characterization. It is of extreme importance that the acetonitrile be freshly and rigorously purified. Pure solid that is dissolved in impure acetonitrile gives either green or purple solutions that decompose to a brown solution in less than 1 day. The nature of these color changes has not been established.

The presence of only one peak in the ^1H NMR spectrum indicates that the CH_3CN ligands are labile and undergo rapid exchange with the CD_3CN solvent. This behavior has been seen in the $\text{Mo}_2(\text{O}_2\text{CCH}_3)_2(\text{NCCH}_3)_6^{2+}$ complex before.³ We attempted to record the ^1H NMR spectrum in acetone- d_6 , but complex 1 decomposed. The ^1H NMR spectrum for $\text{Mo}_2(\text{NCCH}_3)_{10}(\text{O}_3\text{CCF}_3)_4$ in acetone- d_6 was reported² to have a peak at 1.55 ppm (s). Complex 1 is again very sensitive to impurities, and on several occasions our sample dissolved in CD_3CN to give a green solution that exhibited many broad peaks in the region of 1.4–2.2 ppm and slowly decomposed to a brown solution.

Complex 1 dissolves in pure acetonitrile to give an intensely colored blue solution. This solution has an electronic absorption peak at 597 nm, which may be assigned to the $\delta-\delta^*$ transition in this unusually long Mo–Mo quadruple bond. Comparison of the values here, 597 nm and 2.187 (9) \AA , with those in the typical species¹² $\text{Mo}_2\text{Cl}_8^{4-}$, namely, 530 nm and 2.138 (4) \AA , is instructive. The IR spectrum of this solution has bands at 2360 (s), 2338 (m), 2306 (w), and 1071 cm^{-1} (s). When solutions of crude material (not recrystallized) are investigated by IR spectroscopy, peaks consistent with the presence of a bridging acetate (i.e. 1575 and 668 cm^{-1}) are evident. These acetate peaks disappear on recrystallization.

Conclusion. We have presented in this paper the first structurally characterized example of a complex containing a $[\text{Mo}_2]^{4+}$ core surrounded completely by neutral ligands. Although exhibiting an extreme sensitivity to various conditions, complex 1 has been fully characterized not only by X-ray crystallography but also by ^1H NMR, IR, and UV–vis spectroscopy. The compound's sensitivity to its environment foreshadows an exciting and varied chemistry, which is currently under investigation.

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Supplementary Material Available: Full tables of bond distances and angles and a table of the general displacement parameter expressions (5 pages); a listing of structure factors (14 pages). Ordering information is given on any current masthead page.

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Identification and Characterization of Trinuclear Molybdenum–Sulfur Clusters by Fast Atom Bombardment (FAB) Mass Spectrometry

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In the past few years, a variety of new complexes containing the cluster cores $[\text{Mo}_3\text{S}_4]^{4+}$, $[\text{Mo}_3\text{S}(\text{S}_2)_3]^{4+}$, and $[\text{Mo}_4\text{S}_4]^{n+}$ ($n = 4-6$) has been investigated.²⁻⁹ The elucidation of composition and structure is sometimes tedious, since conventional spectroscopic methods (UV–vis, NMR, IR) and elemental analysis provide only limited information. Fast atom bombardment (FAB) mass spectrometry¹⁰ has been widely used as a soft ionization technique for the identification and analysis of nonvolatile and thermally labile compounds.¹¹ For the characterization of molybdenum–sulfur clusters, mass spectrometry has occasionally been employed by Kuchen and co-workers;^{2,12} however, the authors reported that they could not obtain useful spectra by using the FAB method.¹³ In our laboratory, a variety of novel $\text{Mo}_3\text{S}(\text{S}_2)_3$ complexes has been prepared and characterized. With a 3-nitrobenzyl alcohol (3-NBA) matrix, FAB mass spectrometry has been found to be a powerful tool for the identification of the new molybdenum–sulfur clusters. In this contribution, positive (FAB⁺) and negative (FAB⁻) ion mass spectrometry of a representative series of $\text{Mo}_3\text{S}(\text{S}_2)_3$ complexes with Br^- , 8-hydroxyquinoline (Hoxq), *N,N*-diethylthiocarbamate (dtc), 2-mercaptobenzoic acid (H_2mba), and catechol (H_2cat) are discussed.

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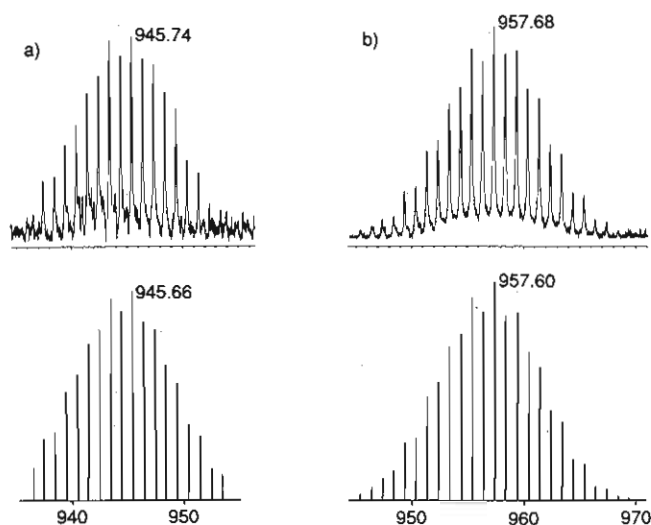


Figure 1. Measured and calculated isotope patterns for the molecular ions (a) $[\text{Mo}_3\text{S}_7(\text{oxq})_3]^+$ (average mass: 944.70) and (b) $[\text{Mo}_3\text{S}_7(\text{dtc})_3]^+$ (average mass: 957.05).

Experimental Section

Preparation of the $\text{Mo}_3\text{S}(\text{S}_2)_3$ Complexes. $[\text{NEt}_4]_2[\text{Mo}_3\text{S}_7\text{Br}_6] \cdot \frac{1}{3}\text{CH}_3\text{CN}$ was prepared as described in ref 8. $[\text{HNEt}_3]_2[\text{Mo}_3\text{S}_7(\text{mba})_3]$ (orange crystals), $[\text{Mo}_3\text{S}_7(\text{oxq})_3]\text{Br}$ (red crystals), and $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Mo}_3\text{S}_7(\text{cat})_3]$ (brown crystals) were obtained in CH_3CN by the reaction of $[\text{NEt}_4]_2[\text{Mo}_3\text{S}_7\text{Br}_6]$ or $[\text{P}(\text{C}_6\text{H}_5)_4]_2[\text{Mo}_3\text{S}_7\text{Br}_6]$ with the ligands in the presence of triethylamine according to the general procedure described earlier.⁸ A comprehensive report of the synthetic work will be published elsewhere.¹⁴ $[\text{Mo}_3\text{S}_7(\text{dtc})_3]\text{I}$ (yellow crystals) was prepared according to the method of Zimmermann¹⁵ by the reaction of $[\text{NH}_4]_2[\text{Mo}_3\text{S}_7]^{16}$ (0.3 g) with tetraethylthiuram disulfide (0.4 g) in DMF. The product was precipitated by the addition of NaI (2 g, dissolved in EtOH) and recrystallized from $\text{CH}_2\text{Cl}_2/\text{EtOH}$. All compounds were obtained with high yields ($\geq 70\%$) and satisfactory elemental analyses.

Mass Spectrometry. The samples were dissolved ($\approx 1\%$) in CH_3OH , CH_3CN , or CH_2Cl_2 . About $1 \mu\text{L}$ of this solution was mixed with $1 \mu\text{L}$ of 3-NBA on a standard stainless steel VG FAB target, and the mixture was introduced through the vacuum lock. Mass spectra were obtained by using a ZAB-VSEQ spectrometer (Vacuum Generators) with an 8-kV acceleration voltage, equipped with a VG-Cs-Ion FAB gun (35-keV, 2- μA beam current). The continuous-mode spectra (Figure 1) were measured on a cyclotron mass spectrometer CMS 47X (Spectrospin) with a 10-kV acceleration voltage and a pressure of 2×10^{-9} mbar in the ICR

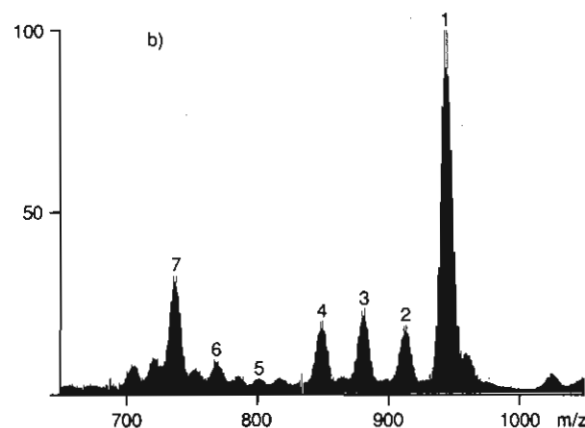
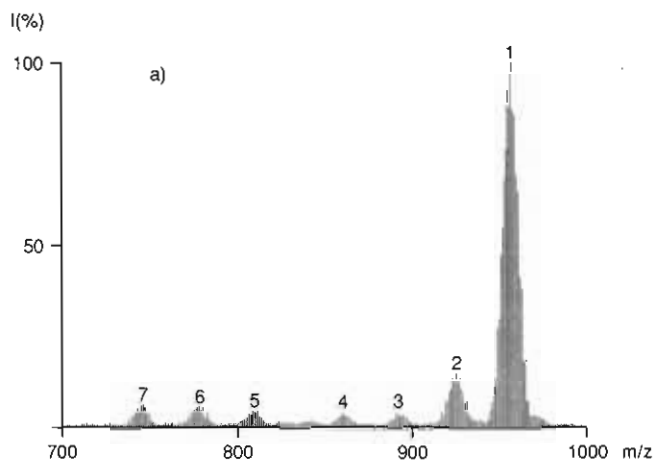


Figure 2. FAB⁺ mass spectra of (a) $[\text{Mo}_3\text{S}_7(\text{dtc})_3]\text{I}$ and (b) $[\text{Mo}_3\text{S}_7(\text{oxq})_3]\text{Br}$: (1–4) $[\text{Mo}_3\text{S}_x\text{L}_3]^+$, $7 \geq x \geq 4$; (5–7) $[\text{Mo}_3\text{S}_x\text{L}_2]^+$, $7 \geq x \geq 5$.

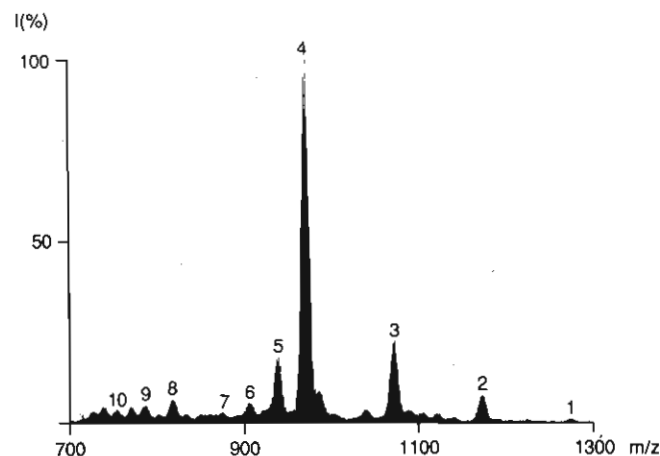


Figure 3. FAB⁺ mass spectrum of $[\text{HNEt}_3]_2[\text{Mo}_3\text{S}_7(\text{mba})_3]$: (1–4) $[(\text{HNEt}_3)_{3-x}(\text{H})_x(\text{Mo}_3\text{S}_7\text{L}_3)]^+$, $0 \leq x \leq 3$; (4–7) $[(\text{H})_3(\text{Mo}_3\text{S}_x\text{L}_3)]^+$, $7 \geq x \geq 4$; (8–10) $[(\text{H})_2(\text{Mo}_3\text{S}_x\text{L}_2)]^+$, $7 \geq x \geq 5$.

cell, equipped with a xenon beam FAB gun from Phrasor Scientific Inc. Assignments are based on the analysis of the isotope pattern (Figure 1) including all isotopes of C, N, O, S, Br, and Mo with natural abundance $\geq 0.01\%$.

Results

Depending on the charge of the ligand, cationic or anionic complexes of the $[\text{Mo}_3\text{S}(\text{S}_2)_3]^{4+}$ core are formed. In this investigation, dtc^- , oxq^- , Br^- , mba^{2-} , and cat^{2-} were used, forming $[\text{Mo}_3\text{S}_7(\text{dtc})_3]^+$, $[\text{Mo}_3\text{S}_7(\text{oxq})_3]^+$, $[\text{Mo}_3\text{S}_7\text{Br}_6]^{2-}$, $[\text{Mo}_3\text{S}_7(\text{mba})_3]^{2-}$, and $[\text{Mo}_3\text{S}_7(\text{cat})_3]^{2-}$. The mass spectra can be divided into two sections: a "lower part" ($m/z < 600$) where the counterions, the ions of the ligands or the matrix including their fragment ions, can be observed and an "upper part" ($m/z \geq 600$) with the

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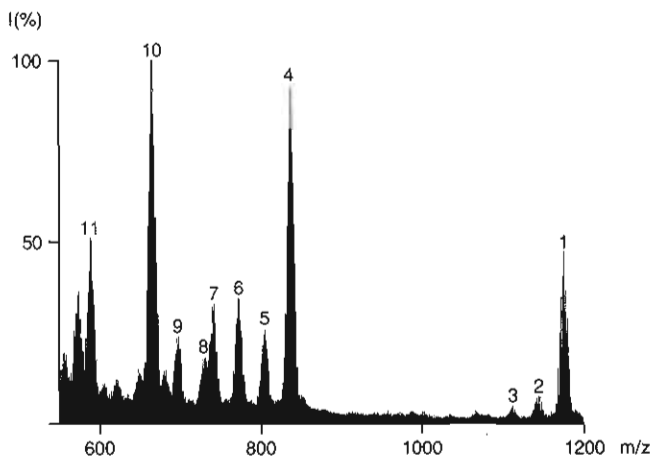


Figure 4. FAB⁻ mass spectrum of [PPh₄]₂[Mo₃S₇(cat)₃]⁻: (1–3) [(PPh₄)(Mo₃S_xL₃)]⁻, 7 ≥ x ≥ 5; (4–7) [Mo₃S_xL₃]⁻, 7 ≥ x ≥ 4; (8–10) [Mo₃S_xL₂]⁻, 7 ≥ x ≥ 5; (11) [Mo₃S₆L]⁻.

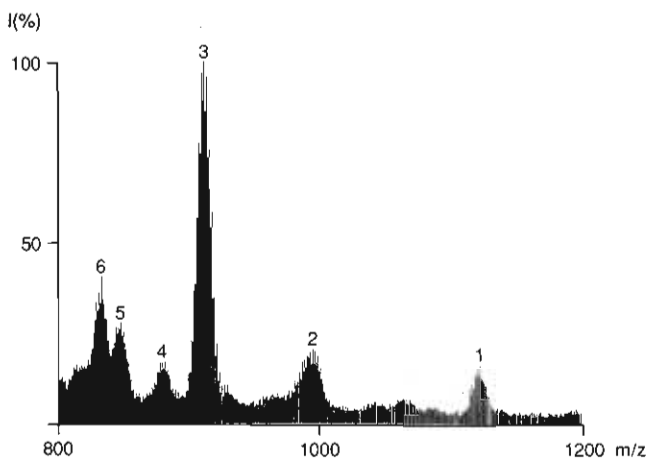


Figure 5. FAB⁻ mass spectrum of [NEt₄]₂[Mo₃S₇Br₆]⁻: (1) [(NEt₄)(Mo₃S₇Br₆)]⁻; (2) [Mo₃S₇Br₆]⁻; (3) [Mo₃S₇Br₅]⁻; (4) [Mo₃S₆Br₅]⁻; (5) [Mo₃S₅Br₅]⁻; (6) [Mo₃S₇Br₄]⁻.

characteristic multiplets of the molybdenum–sulfur clusters reflecting the polyisotopic nature of molybdenum.

FAB Mass Spectra of the Cationic Complexes. Only FAB⁺ mass spectrometry was considered. The upper part of the spectra is dominated by the molecular ions [Mo₃S₇L₃]⁺ (Figures 1 and 2). The ions of the sequence [Mo₃S₆L₃]⁺, [Mo₃S₅L₃]⁺, and [Mo₃S₄L₃]⁺ appear with lower abundance. Also, the ions of the series [Mo₃S_xL₂]⁺, 7 ≥ x ≥ 5, were observed. The lower part of the spectrum corresponds mainly to the matrix components.

FAB Mass Spectra of the Anionic Complexes. The lower part of the FAB⁺ spectra is dominated by the counterions HNEt₃⁺, NEt₄⁺, and P(C₆H₅)₄⁺. The upper section of the FAB⁺ spectrum of the mba complex is presented in Figure 3. The pseudomolecular ions [(HNEt₃)_x(H)_{3-x}(Mo₃S₇(mba)₃)]⁺ appear with decreasing abundance for increasing x (x ≤ 3). The same type of fragmentation was observed as already seen for the oxq and dtc complex: loss of sulfur and the cleavage of one ligand.

The FAB⁻ spectrum of the cat complex is shown in Figure 4. The entire complex appears as molecular ion [Mo₃S₇(cat)₃]⁻ and the ion pair [(PPh₄)(Mo₃S₇(cat)₃)]⁻. Again, the peaks of the two series [Mo₃S_x(cat)₃]⁻ (7 ≥ x ≥ 4) and [Mo₃S_x(cat)₂]⁻ (7 ≥ x ≥ 5) are visible. In addition, there is evidence for a third series [Mo₃S_x(cat)]⁻ (x = 6, 7; m/z = 588, 620), i.e. dissociation of a second ligand.

A somewhat different behavior is observed for the bromo complex. The spectra for both FAB⁺ and FAB⁻ are dominated by [Mo₃S₇Br₆]⁻, which appears in the FAB⁺ spectrum as an ion aggregate [(NEt₄)₂(Mo₃S₇Br₆)]⁺. In the FAB⁻ spectrum (Figure 5), the entire complex was observed with relatively low abundance as either [Mo₃S₇Br₆]⁻ or [(NEt₄)(Mo₃S₇Br₆)]⁻. Thus, the loss of sulfur is obviously predominated by the dissociation of Br⁻ or

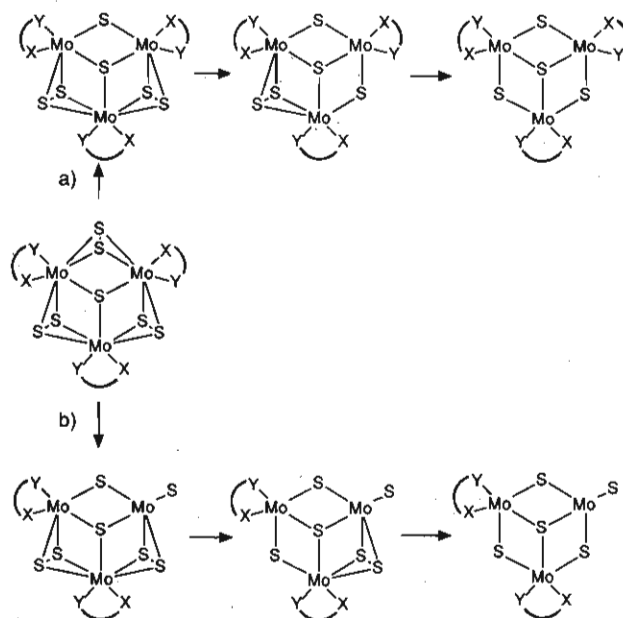


Figure 6. General fragmentation pattern of Mo₃S₇ complexes. X–Y denotes a bidentate ligand. The charges of the ions are omitted for clarity.

Br⁻, respectively. In agreement with this result, high intensities of Br⁻ and the brominated matrix could be observed in the lower part of the spectrum.

Discussion

Both FAB⁺ and FAB⁻ mass spectrometry are convenient and powerful techniques for the identification and characterization of anionic and cationic molybdenum–sulfur clusters. As demonstrated, the number of Mo atoms of an ion may directly be determined by the analysis of the isotope pattern of the observed peak (Figure 1). Moreover, only a few milligrams of the compound, dissolved in a conventional solvent, are needed for measurement, whereby rapid information about composition, structure, and reactivity of a new complex is obtained.

The general fragmentation pattern for [Mo₃S(S₂)₃]⁴⁺ complexes with bidentate ligands L is presented in Figure 6.

(a) The stepwise degradation of Mo₃S₇L₃ to Mo₃S₄L₃ obviously indicates the conversion of the three disulfido to monosulfido bridges, as already observed for many Mo₃S₇ complexes in solution.^{7,12,17} However, the intermediate Mo₃S₆ and Mo₃S₅ complexes, observed in the spectra, have not been isolated so far.

(b) The detection of the ions [Mo₃S_xL₂]⁺ (L = oxq⁻, dtc⁻), [H₂(Mo₃S_x(mba)₂)]⁺, and [Mo₃S_x(cat)₂]⁻ (5 ≤ x ≤ 7) must be explained by the loss of a neutral molecule L*, Hmba*, or cat, respectively. Therefore, this fragmentation implies a reduction of the remaining Mo–S core. Seemingly, the formation of a partially naked Mo atom is circumvented by the subsequent oxidative addition of one of the disulfido bridges. This mechanism is strongly supported by the absence of the ions [Mo₃S₄(dtc)₂]⁺, [H₂(Mo₃S₄(mba)₂)]⁺, and [Mo₃S₄(cat)₂]⁻. There is a peak, assignable to [Mo₃S₄(oxq)₂]⁺, however, with much lower abundance relative to its hypothetical parent ion [Mo₃S₅(oxq)₂]⁺. The reduction of coordinated S₂²⁻ to two S²⁻ entities is well established in solution chemistry.¹⁸ Moreover, reactions wherein both the metal and the sulfur ligand participate in the redox reaction have

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been extensively discussed in the literature as induced internal redox processes.¹⁹

The general fragmentation pattern discussed above is modulated by the individual properties of each compound.

(i) Br is much more easily detached from Mo compared to the bidentate dtc, oxq, cat, and mba. This correlated with the fact that $[\text{Mo}_3\text{S}_7\text{Br}_6]^{2-}$ undergoes facile ligand substitution in solution.⁸

(ii) There is an unusually intense peak due to the ion $[\text{Mo}_3\text{S}_5(\text{cat})_2]^-$, as shown in Figure 4. Obviously, the dissociation of *o*-quinone is particularly favored compared to other ligands, which obviously are eliminated as radicals. Moreover, only for the cat complex is the dissociation of a second ligand indicated.

(iii) Counterions, which are capable of coordinating to the cluster core, must be considered as additional ligands, as suggested

by the ions $[\text{H}(\text{Mo}_3\text{S}_6(\text{mba})_2(\text{NEt}_3)_2)]^+$ (Figure 3, $m/z = 989$) and $[\text{Mo}_3\text{S}_7(\text{oxq})_3\text{Br}]^+$ (Figure 2, $m/z = 1023$).

(iv) A partial fragmentation of dtc (dissociation of $[\text{S}=\text{C}=\text{NEt}_2]^+$) probably explains the peak $m/z = 842$ by the formation of $[\text{Mo}_3\text{S}_7(\text{dtc})_2(\text{HS})]^+$ (Figure 2).

The mass spectra of additional compounds $\text{M}_2\text{Mo}_3\text{S}_7\text{L}_3$ ²⁰ follow the same pattern as the results presented in this contribution. Hence the scheme in Figure 6 is probably valid for similar complexes containing the core $[\text{Mo}_3\text{S}(\text{S}_2)_3]^{4+}$.

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