# Characterization of Molybdenum–Sulfur–Clusters by Mass Spectrometry

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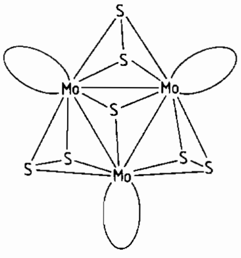
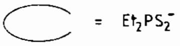
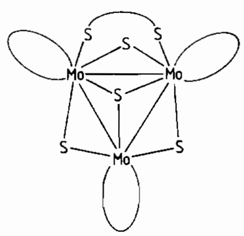
Molybdenum–sulfur–clusters are of topical interest because of their importance as model substances in bioinorganic chemistry [11]. Recently we reported the synthesis and properties of the trinuclear Mo–S–cluster–dithiophosphinates $[Mo_3Et_2PS_2)_3(S_2)_3S]^+[Et_2PS_2]^-$ *1* and $[Mo_3(Et_2PS_2)_4]S_4$ 2 [2, 3], the structures of which were confirmed by X-ray analysis. Meanwhile we succeeded in preparing another cluster $[Mo_4(Et_2PS_2)_6S_4]$ *3* [4], for which we suggest on account of spectroscopic and analytical data the tetranuclear structure *3* [5].

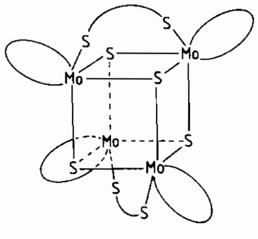


1 (cation)





2



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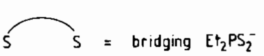

No reports can be found in the literature on the application of mass spectrometry in the characterization of the elemental composition and the molecular weight of Mo–S–clusters. Moreover, as fragmentation patterns may be helpful in identifying special characteristics, we show in this paper that the use of mass spectrometry can be of considerable value in rapid and unequivocal identification of polynuclear Mo–S–clusters with high molecular weights.

With compounds *1–3*, conventional electron impact (EI) ionization mass spectrometer failed since these compounds are of very low volatility.

However, when using ionization methods that do not require prior evaporation of the sample, like field desorption (FD) [6] or desorption chemical ionization (DCI) [7], we were able to obtain satisfactory mass spectra. The spectra exhibit very broad peak groups over a wide range of m/z values for each ion species, due to the polyisotopic character of molybdenum, but also to $^{13}C$ and $^{34}S$. This is demonstrated in Fig. 1 which shows the calculated isotope pattern for the molecular ion of *3* having the elemental composition $Mo_4C_{24}H_{60}P_6S_{16}$. Signals can be found in a range of m/z 1416–m/z 1447. This exceptionally large number of isotopes can be helpful in determining the elemental composition by isotope analysis, when there is coincidence of the calculated and experimental isotope pattern. In overlapping peak groups, like *e.g.* $[M]^{+\cdot}$ and $[M–H]^+$, however, an interpretation may be complicated.

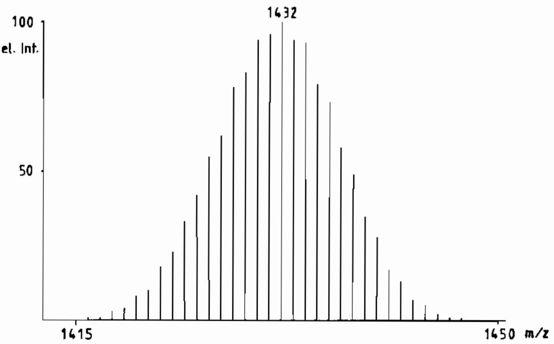

Fig. 1. Calculated isotope pattern for the molecular ion of *3*.

## DCI-Mass Spectra

The DCI-mass spectra of *1–3* have been measured using isobutane as reagent gas. The spectra of the 1:1 electrolyte *1* show the strong peak group of the cluster cation $[Mo_3(Et_2PS_2)_3(S_2)_3S]^+$ between m/z 961–m/z 983 (maximum at m/z 973, rel. Int. 23%). The latter eliminates $EtPSH_2$ leading to a group of signals at m/z 867–m/z 889 (maximum at m/z 879; 100%). Even the signal group for the complete complex *1* can be found at m/z 1130 (maximum) in very low abundance.

The spectra of *2* exhibit with low intensity the signal group of the molecular ion $[Mo_3(Et_2PS_2)_4$-

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$S_4]^{+\bullet}$ with a maximum at m/z 1029 (2.5%). $[M]^{+\bullet}$ fragments in this case by loss of the ligand $Et_2PS_2$, leading to an intensive group of signals between m/z 865–m/z 888 (maximum at m/z 877; 100%). The spectra of the tetranuclear cluster *3* are dominated by the peaks due to the 'quasi-molecular ion' $[M + H]^+$ between m/z 1416–m/z 1447 (maximum at m/z 1433; 80%) and the fragment resulting from $[M + H]^+$ by loss of $Et_2PS_2H$ (maximum at m/z 1279; 100%). It should be noted that from *2* and *3* containing bridging $Et_2PS_2^-$ complete ligands are lost, in contrast to *1* containing only chelating $Et_2PS_2^-$.

## FD-Mass Spectra

These could be obtained only with *1* and *2*. In the case of *1* they show the signal groups of the cluster cation (maximum at m/z 973) and of the fragment derived from it by loss of $EtPSH_2$ (maximum at m/z 879). With *2* the molecular ion is observed with low abundance. As on DCI-conditions, *2* fragments by loss of an intact ligand leading to an intensive group of signals with a maximum at m/z 877.

It should be mentioned that on fast atom bombardment (FAB) mass spectrometry [8], another new technique for ionization of non-volatile or thermally labile molecules by a beam of fast atoms (typically argon), no useful spectra of *1–3* were obtained.

In conclusion, as shown for Mo–S–clusters, mass spectrometry with ionization methods directly of the solid state, especially DCI-MS, may be very helpful in determining the constitution of high molecular cluster complexes.

## Experimental

FD-MS: Varian MAT 311 A, activated tungsten emitters. DCI-MS: Finnigan MAT 8200, isobutane as reagent gas. For synthesis of the compounds see loc. cit 2–4. Intensities are given as percent of the base peak (only metal containing ions in the upper mass range were considered).

## Acknowledgements

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