Characterization of Amorphous Substances by Studying Isotopically Labelled Compounds with FAB–MS: Evidence for Extrusion of Triangular Mo_3^{IV} Clusters from a Mixture of $^{92}MoS_3$ and $^{100}MoS_3$ by Reaction with OH^-

Achim Müller,*[a] **Vladimir Fedin,**[a] **Kaspar Hegetschweiler**[b] **and Walter Amrein**[c]

[a] *Fakultät für Chemie, Lehrstuhl für Anorganische Chemie I, Postfach 8640, D-4800 Bielefeld 1, Germany*
[b] *Laboratorium für Anorganische Chemie,* [c] *Laboratorium für Organische Chemie, ETH Zentrum, CH-8092 Zürich, Switzerland*

As the extrusion of $^{92}Mo_3$ and $^{100}Mo_3$ cluster species is the absolutely dominating pathway for the reaction of a mixture of amorphous $^{92}MoS_3$ and $^{100}MoS_3$ with an aqueous solution of KOH, it can be concluded that the material is built up by Mo_n ($n \geqslant 3$) cluster units.

The molybdenum–sulfur compound MoS_3 is a material of general interest and can only be prepared in amorphous form, a property that has hindered its structural characterization. Stimulated in part by the fact that MoS_3 can be used as cathode material to construct a high-energy-density alkali metal battery and that it has special catalytic properties, a variety of methods have been used for the structural characterization of this material.[1–7] The lack of direct physical methods for the investigation of amorphous compounds has stimulated us to search for new methods for their characterization.

The reaction of MoS_3† with a 5% solution of KOH in degassed water under argon at room temp. (48 h) yields red $K_2[Mo_3S_{13}]{\cdot}nH_2O$ salt‡ in a rather high yield (52% referring to Mo and 75% referring to S) [eqn. (1)].

$$MoS_3 + OH^- \rightarrow [Mo_3S_{13}]^{2-} \qquad (1)$$

One can explain the formation of the cluster species according to eqn. (1) by two different reaction pathways: (*a*) Cluster units Mo_n ($n \geqslant 3$) are already present in the amorphous MoS_3 and only trinuclear clusters Mo_3 are extruded *via* a nucleophilic attack of OH^-. (*b*) The formation of $[Mo_3S_{13}]^{2-}$ clusters takes place (only) in solution, for example, from mononuclear Mo or dinuclear Mo_2 fragments, formed from MoS_3.

To prove the validity of (*a*) or (*b*) we studied the reaction of an equimolar mixture of $^{92}MoS_3$ (95% of ^{92}Mo isotope) and $^{100}MoS_3$ (95% of ^{100}Mo isotope) with an aqueous solution of KOH. The determination of the composition of the isotopomeric products was done by the FAB^+–MS method. As it is difficult to get high quality mass spectra for the alkali salt $K_2[Mo_3S_{13}]{\cdot}nH_2O$ the compound was transformed into $Mo_3S_7(dtc)_4$ (dtc = S_2CNEt_2) by the well-known reaction [eqn. (2)].[11–14]

$$[Mo_3S_{13}]^{2-} \xrightarrow{HBr} [Mo_3S_7Br_6]^{2-} \xrightarrow{dtc^-} Mo_3S_7(dtc)_4 \qquad (2)$$

Fig. 1 shows the FAB^+–MS spectrum of $Mo_3S_7(dtc)_4$,§ which was obtained from the products of the reaction of an equimolar mixture of $^{92}MoS_3$ and $^{100}MoS_3$ with an aqueous solution of KOH at room temperature. The FAB^+–MS study showed that the intensity of $[^{92}Mo_3S_7(dtc)_3]^+$ and $[^{100}Mo_3S_7(dtc)_3]^+$ [Fig. 1(*a*)] exceeds the intensity of $[^{92}Mo_2{}^{100}MoS_7(dtc)_3]^+$ and $[^{92}Mo^{100}Mo_2S_7(dtc)_3]^+$ ions by a factor of five.

This result proves that the extrusion of Mo_3^{IV} clusters is the absolutely dominant pathway of eqn. (1) as the clusters with mixed isotopes can only be formed in solution.

There are two possible explanations for the formation of the 'mixed' cluster species: it may be due to the existence of incomplete trinuclear clusters on the 'surface' of the MoS_3 particles or due to a possible fragmentation of the Mo_n ($n > 3$) clusters. For example, for Mo_4 type clusters one possibility is [eqn. (3)]:

$$3^{92}Mo_4 + 3^{100}Mo_4 \rightarrow 3^{92}Mo_3 + 3^{100}Mo_3 + {}^{92}Mo_2{}^{100}Mo + {}^{92}Mo^{100}Mo_2 \qquad (3)$$

The method described here can be used for the characterization of other amorphous or crystalline materials—for instance chalcogenides of the early transition elements built up by metal clusters, too. The method has now been validated using crystalline compounds of known structure[17] [eqns. (4), (5); solvents: H_2O and MeCN, respectively]:

$$^{92}Mo_3S_7Cl_4 + {}^{100}Mo_3S_7Cl_4 \xrightarrow{(NH_4)_2S_x} (NH_4)_2{}^{92}Mo_3S_{13} + (NH_4)_2{}^{100}Mo_3S_{13} \xrightarrow[\text{ii Nadtc}]{\text{i HBr}} {}^{92}Mo_3S_7(dtc)_4 + {}^{100}Mo_3S_7(dtc)_4 \qquad (4)$$

$$^{92}Mo_6Te_8 + {}^{100}Mo_6Te_8 \xrightarrow[(PPh_4)Cl]{Cl_2} (PPh_4)_2{}^{92}Mo_6Cl_{14} + (PPh_4)_2{}^{100}Mo_6Cl_{14} \qquad (5)$$

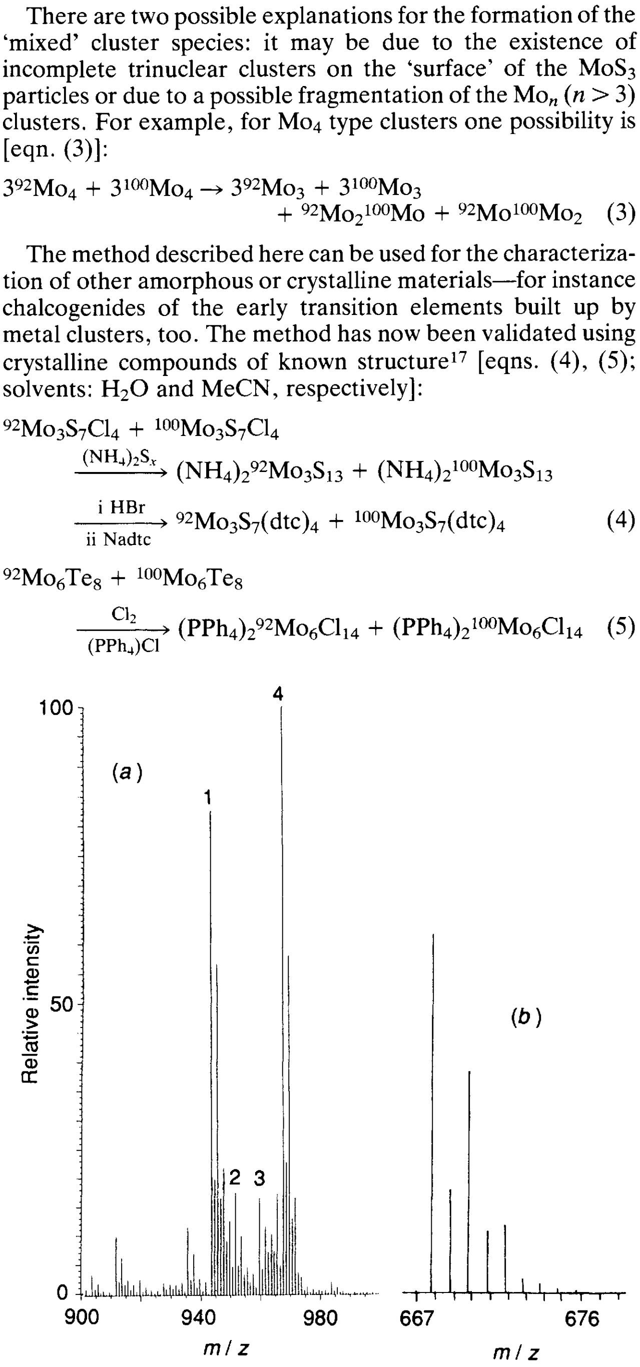

Fig. 1 FAB^+ spectrum of $Mo_3S_7(dtc)_4$ obtained from the reaction product of a mixture of $^{92}MoS_3$ and $^{100}MoS_3$ with KOH at room temp. (*a*): **1** $[^{92}Mo_3S_7(dtc)_3]^+$; **2** $[^{92}Mo_2{}^{100}MoS_7(dtc)_3]^+$; **3** $[^{92}Mo^{100}Mo_2S_7(dtc)_3]^+$; **4** $[^{100}Mo_3S_7(dtc)_3]^+$). The calculated isotope distribution for $[S_7(dtc)_3]$ using the natural abundance of the isotopes of C, H, N and S for the purpose of comparison (*b*).

---

† MoS_3 used in this study was prepared by the reaction of an aqueous solution of $(NH_4)_2MoS_4$ with hydrochloric acid.[7]

‡ The IR spectrum of this compound is rather characteristic and corresponds to the IR spectrum of $(NH_4)_2[Mo_3S_{13}]$.[8–10]

§ Details of FAB^+–MS experiments and the mass spectrum of $Mo_3S_7(dtc)_4$ with natural contents of isotopes are given in ref.[15]

According to FAB$^+$ and FAB$^-$–MS methods equimolar mixtures of the trinuclear cluster compounds $^{92}Mo_3S_7(dtc)_4$ and $^{100}Mo_3S_7(dtc)_4$ [eqn. (4)] as well as of the hexanuclear ones $(PPh_4)_2{}^{92}Mo_6Cl_{14}$ and $(PPh_4)_2{}^{100}Mo_6Cl_{14}$ [eqn. (5)] were obtained and practically no cluster species with different molybdenum isotopes.

The use of isotopes for proving cluster extrusion from amorphous or crystalline materials¶ has an important advantage: the possibility of cluster formation in solution from 'smaller' fragments can be excluded (see interpretation of reaction of MoS_3 with CN^- giving $[Mo_3S_4(CN)_9]^{5-}$).[7] This method can probably be widely used for the characterization of amorphous materials for instance for the mineral jordisite (MoS_2) using model compounds and hydrodesulfurization catalysts M_xMoS_{2+x} (M = Co, Ni).

We .thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support, the Alexander von Humboldt-Stiftung for a fellowship (V. F.) and Rolf Häfliger for technical assistance.

Received, 23rd June 1992; Com. 2/03320H

References

1 R. R. Chianelli, *Int. Rev. Phys. Chem.*, 1982, **2**, 127.

2 S. P. Cramer, K. S. Liang, A. J. Jacobson, C. H. Chang and R. R. Chianelli, *Inorg. Chem.*, 1984, **23**, 1215.

3 E. Diemann, *Z. Anorg. Allg. Chem.*, 1977, **432**, 127.

4 K. S. Liang, J. P. deNeufville, A. J. Jacobson, R. R. Chianelli and F. Betts, *J. Non-Cryst. Solids*, 1980, **35–36**, 1249.

5 A. J. Jacobson, R. R. Chianelli, S. M. Rich and M. S. Whittingham., *Mater. Res. Bull.*, 1979, **14**, 1437.

6 K. S. Liang, S. P. Cramer, D. C. Johnston, C. H. Chang, A. J. Jacobson, J. P. deNeufville and R. R. Chianelli, *J. Non-Crystl. Solids*, 1980, **42**, 345.

7 A. Müller, R. Jostes, W. Eltzner, C.-S. Nie, E. Diemann, H. Bögge, M. Zimmermann, M. Dartmann, U. Reinsch-Vogell, S. Che, S. J. Cyvin and B. N. Cyvin, *Inorg. Chem.*, 1985, **24**, 2872.

8 A. Müller, V. Wittneben, E. Krickemeyer, H. Bögge and M. Lemke, *Z. Anorg. Allg. Chem.*, 1991, **605**, 175.

9 A. Müller and E. Krickemeyer, *Inorg. Synth.*, 1990, **27**, 47.

10 A. Müller, R. Jostes and F. A. Cotton, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 875.

11 V. P. Fedin, M. N. Sokolov, Yu. V. Mironov, B. A. Kolesov, S. V. Tkachev and V. Ye. Fedorov, *Inorg. Chem. Acta*, 1990, **167**, 39.

12 V. P. Fedin, M. N. Sokolov, O. A. Geras'ko, A. V. Virovets, N. V. Podberezskaya and V. Ye. Fedorov, *Inorg. Chim. Acta*, 1992, **192**, 153.

13 H. Zimmermann, K. Hegetschweiler, T. Keller, V. Gramlich, H. W. Schmalle, W. Petter and W. Schneider, *Inorg. Chem.*, 1991, **30**, 4336.

14 K. Hegetschweiler, T. Keller, H. Zimmermann, W. Schneider, H. Schmalle and E. Dubler, *Inorg. Chim. Acta*, 1990, **169**, 235.

15 K. Hegetschweiler, T. Keller, W. Amrein and W. Schneider, *Inorg. Chem.*, 1991, **30**, 873.

16 S. C. Lee and R. H. Holm, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 840.

17 V. E. Fedorov, A. V. Mishchenko and V. P. Fedin, *Russ. Chem. Rev.*, 1985, **54**, 408.

¶ For cluster extrusion from crystalline solids see also ref.[16,17]