Structure of Amorphous MoS₃

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Received: January 4, 1995; In Final Form: March 23, 1995

The amorphous compound MoS₃ has been investigated by monochromatic X-ray photoemission (XPS) and vibrational spectroscopy, as well as by chemical extrusion aimed at identifying structural units inside MoS₃. XPS shows that all molybdenum in MoS₃ occurs in the 4+ oxidation state, while sulfur is present in at least two states, including S²⁻ and S⁷⁻ ligands in different types of coordination. This composition corresponds to a formal charge state of Mo⁴⁺(S⁷⁻)(S²⁻)⁻. The emission infrared spectrum of MoS₃ exhibits characteristic vibrations that are also encountered in the spectra of triangular Mo⁴⁺S₃ cluster compounds. Three of such cluster compounds, i.e. (NH₄)₂[Mo⁴⁺S₃]H₂O, K₃[Mo₃S₆(CN)₆]2H₂O, and (NEt₄)₂[Mo⁴⁺S₃Cl₆] can be extruded from MoS₃ by reactions that are essentially destructive. On the basis of these results it is proposed that MoS₃ is essentially an aggregation of Mo⁴⁺—sulfur cluster types.

Introduction

Molybdenum sulfides are widely used as catalysts for hydroprocessing, where hydrodesulfurization (HDS), the removal of sulfur from crude oil, is one of the most important examples. HDS catalysts are prepared as highly dispersed molybdenum oxides (MoO₃ type structures) on a high surface area carrier and subsequently converted into the catalytically active molybdenum sulfides (MoS₂ type structures) via sulfidation, typically in H₂S/H₂ atmospheres at temperatures between 300 and 400 °C. During the sulfidation, sulfur rich phases with stoichiometries of nearly 1 Mo:3 S have been observed, and consequently, MoS₃ has been assumed to be a relevant intermediate in sulfidation reaction:

\[ \text{MoO}_3 \rightarrow \text{MoS}_3 \rightarrow \text{MoS}_2 \]  (1)

At present, the knowledge about the reaction steps involved in the oxide—sulfide phase conversion is fragmentary, and also the structures of the oxidic precursor and the active sulfide are not precisely known. While crystalline Mo(VI) oxides provide convenient references for the determination of structural features of the oxidic and sulfided states, respectively, of the supported catalyst, a well-structured analogue for MoI" can provide convenient references for the determination of structural features of the oxidic and sulfided states, respectively. This model includes a chainlike arrangement of molybdenum atoms, which have a trigonal prismatic coordination of six sulfur atoms.

MoS₃ is typically prepared from (NH₄)₂Mo⁴⁺S₄, either by acidification of an aqueous solution or by thermal decomposition in an inert gas atmosphere at temperatures between 260 and 300 °C. Above 310 °C, MoS₃ decomposes to microcrystalline MoS₂, which is the thermodynamically most stable Mo⁴⁺—sulfur solid-state compound. The final product of the decomposition reaction

\[ (\text{NH}_4)_2 \text{Mo}^{\text{IV}} \text{S}_4 \rightarrow \text{MoS}_3 \rightarrow \text{Mo}^{\text{IV}} \text{S}_2 \]  (2)

is essentially the same as that of the sulfidation of molybdenum oxides (reaction 1), while the reduction of Mo⁴⁺ → Mo⁴⁺ is a common feature in both reactions. The formation of amorphous MoS₃ and its further reaction to microcrystalline MoS₂ as given in (2) thus mimics to some extent the chemistry of the sulfidation of molybdenum oxides. The well-defined structure of the (NH₄)₂MoS₃ complex and the fact that only sulfur ligands are involved lead to a reduction of complexity and make this reaction suitable for a structural chemical study.

The structure of MoS₃ has been the subject of several studies. The earliest results suggested that MoS₃ was not an individual compound but a mixture of MoS₂ and noncrystalline sulfur. Analysis of X-ray radial distribution functions (RDF) indicated that MoS₃ may be considered as a genuine compound and a structure with a metal—sulfur short-range order similar to the W₁₃S₄—anion was proposed. Later, a new structural model for MoS₃ was proposed by Liang et al., based on extended X-ray absorption fine structure (EXAFS), high-resolution RDF, X-ray photoelectron spectroscopy (XPS), vibrational spectroscopy, and magnetic susceptibility measurements. These data were interpreted in terms of the structures of the crystalline trichalcogenides of the group IVB and VB elements, and a similar structure was proposed for MoS₃ (structure 1). This model includes a chainlike arrangement of molybdenum atoms, which have a trigonal prismatic coordination of six sulfur atoms.

Whereas diffraction and spectroscopy provide direct structural probes, important information on the nature of structural units...
can also be obtained chemically by cluster extrusion. Two of such extrusion experiments, in which MoS$_3$ was treated with aqueous solutions of NH$_3$ and KCN, yielded the (NH$_4$)$_2$-[MoIV$_6$S$_{13}$]H$_2$O$^{25}$ and the K$_4$[MoIV$_5$S$_4$(CN)$_2$]2H$_2$O$^{22}$ cluster compounds, respectively. As both compounds contain MoIV in a triangular geometry, their formation from MoS$_3$ under essentially destructive reaction conditions is impossible to explain on the basis of the MoV chainlike structure MoS$_3$ proposed by Liang et al.$^{18,19}$ (structure 1). Reinvestigation of the MoS$_3$ structure therefore becomes necessary.

In this paper we report on the formation and the structure of amorphous MoS$_3$, as investigated with three spectroscopic techniques, monochromatic XPS and in situ Raman and infrared emission spectroscopy (IRES). We refer to the literature for further information on these methods.$^{23-25}$ A new extrusion experiment yields the (NEt$_4$)$_2$[MoIV$_5$S$_4$Cl$_6$] (Et $=$ C$_2$H$_5$) cluster compound and gives valuable information regarding the quantification of structural units within the MoS$_3$ solid. This extrusion experiment, as well as the ones mentioned above, suggests a close relationship between the structure of amorphous MoS$_3$ and the structures of Mo(IV)$_3$-sulfur cluster compounds. Therefore, we also studied the extrusion products, in particular (NH$_4$)$_2$[MoS$_3$]H$_2$O, as reference compounds. We propose a new structural model for MoS$_3$ which explains the results reported here and is also compatible with spectroscopic data from the literature.

### Experimental Section

**Sample Preparation and Cluster Extrusion.** (NH$_4$)$_2$MoS$_4$,$^{26}$ and (NH$_4$)$_2$[MoS$_3$]H$_2$O$^{27}$ were prepared as described in the literature. MoS$_3$ was prepared according to ref 21 from a solution of 1.0 g of freshly made (NH$_4$)$_2$MoS$_4$ in 30 mL of degassed water, which was treated with 2 mL of concentrated HCl under stirring. The precipitated dark brown product was filtered and washed several times with H$_2$O, CH$_3$OH, CS$_2$, and diethyl ether, respectively, dried in an argon stream, and finally stored under argon to prevent oxidation. Since the preparation of MoS$_3$ by thermal decomposition of (NH$_4$)$_2$MoS$_4$ depends critically on the temperature and only in a narrow interval, between 280 and 300 $^\circ$C, is a phase with the correct stoichiometry obtained,$^{28}$ we used this type of reaction only for the spectroscopic characterization of decomposition intermediates. This was done in situ in the respective measuring cells.

For the extrusion of the (NEt$_4$)$_2$[MoS$_3$Cl$_6$] cluster compound, 0.65 g of MoS$_3$ was suspended in 35 mL of concentrated hydrochloric acid. The reaction mixture was boiled for 1 h under argon and filtered while hot. After adding 0.5 g of NEt$_4$Cl, an orange solid precipitated from the yellow-green solution within 2 days with a yield of 90 mg (i.e. 9.3% related to the amount of Mo in MoS$_3$). Characterization was done by comparing the infrared spectrum of the extrusion product with that of (NEt$_4$)$_2$[MoS$_3$Cl$_6$]H$_2$O as prepared from (NH$_4$)$_2$-[MoS$_3$]H$_2$O.$^{29}$

**Techniques.** XPS spectra were obtained with a VG Escalab 200 spectrometer equipped with a monochromated Al K$_\alpha$ source (1486.3 eV) and a hemispherical analyzer connected to a five-channel detector. Measurements were done at 20 eV pass energy. Charging was corrected for by using the C 1s peak at 284.6 eV as a reference. The spectra of MoS$_3$ were measured after pressing the compound in indium foil, while (NH$_4$)$_2$-[MoS$_3$]H$_2$O was deposited on the surface of a stainless steel sample holder from a solution in N,N-dimethylformamide (DMF) and subsequent evaporation of the solvent. All steps of the XPS sample preparation were done under inert conditions using a glovebox and a special transport vessel for introducing the samples into the UHV chamber of the spectrometer.

Raman spectra were obtained with a Spex Ramalog V (triple monochromator) and a Coherent Innova 70/4 Ar$^+$ laser. The 514.5 nm line was employed at 100 mW incident power. Before measurement, (NH$_4$)$_2$MoS$_4$ was pressed into a wafer with a KBr back, which was mounted in the in situ cell.$^{30}$ The latter was purged with argon. To study the thermal decomposition product of (NH$_4$)$_2$MoS$_4$, the cell was heated to 260 $^\circ$C for 5 min. The spectra were measured at room temperature in Ar with a spectral resolution of 8 cm$^{-1}$.

Infrared spectra were obtained with a Bruker IFS 113v spectrometer equipped with a pyroelectric DTGS detector, and with different beam splitters for the far and mid infrared region. Infrared spectra of (NH$_4$)$_2$MoS$_4$, (NH$_4$)$_2$[MoS$_3$]H$_2$O, and of our extrusion product were measured in CsI in the absorption mode. The spectra of MoS$_3$ and of the thermal decomposition intermediate of (NH$_4$)$_2$MoS$_4$ were measured in the emission mode in a cell that is very similar to the one described by Diemann et al.,$^{31}$ but was modified to fit in the Bruker spectrometer. Emission infrared spectroscopy was chosen because MoS$_3$ samples can conveniently be prepared and spectra of superior quality are obtained. MoS$_3$ and (NH$_4$)$_2$MoS$_4$ were applied as thin layers on the furnace of the cell as follows. Approximately 2 mg of the sample and 5 mL of 2-propanol were shaken in a vibrating mill. The resulting suspension was spread on the surface of the sample deposition area, and the liquid was slowly evaporated. The emission cell was purged with argon and heated up to 260 $^\circ$C. The spectrum of MoS$_3$ and of the thermal decomposition intermediate of (NH$_4$)$_2$MoS$_4$ were measured with a spectral resolution of 8 cm$^{-1}$ after a period of 15 min to achieve thermal equilibration. Each spectrum is the sum of 500 scans, while the emission of the empty sample holder served as a background spectrum.

### Results

We start with a discussion of the photoemission results. Figure 1 shows the monochromatic Mo 3d XPS spectra of (NH$_4$)$_2$[MoS$_3$]H$_2$O (Figure 1a) and of MoS$_3$ (Figure 1b). The Mo 3d$_{5/2}$ binding energy (see Table 1) of the cluster compound (229.0 eV) corresponds to the expected value for Mo(IV)–sulfur compounds, i.e. (NH$_4$)$_2$[MoS$_3$]H$_2$O$^{32}$ and MoS$_2$. Note that the sulfur ligands in both compounds differ, but do not affect the Mo 3d$_{5/2}$ binding energy. The Mo 3d XPS spectrum of MoS$_3$ (Figure 1b) shows, in principle, the same binding energy (229.1 eV). We therefore assign molybdenum in MoS$_3$ the same
formal oxidation state as in \((NH_4)_2[Mo_3S_4]H_2O\) and MoS$_2$, namely, 4+. This assignment is also reasonable in view of our discussion of the extrusion experiments (vide infra). As will be discussed in detail elsewhere, the S 2p spectrum of \((NH_4)_2[Mo_3S_4]H_2O\), as shown in Figure 2a, contains three doublets corresponding to the bridging and terminal S$_2^{2-}$ ligands and to the \(\mu_3\) (apical) S$_2^{2-}$ ligand of the cluster anion. The S 2p$_{3/2}$ binding energies are given in Table 1, along with the value for MoS$_2$. Note that the basal plane S$_2^{2-}$ ligands of MoS$_2$ have the same binding energy as the terminal disulfide ones. The S 2p spectrum of MoS$_3$ (Figure 2b) consists of at least two doublets at 162.9 and 161.6 eV with an intensity ratio of 5:4. The doublet with the higher binding energy is consistent with the presence of bridging S$_2^{2-}$ and/or apical S$_2^{2-}$ ligands and the other with either terminal S$_2^{2-}$, S$^{2-}$, or both. The fact that different kinds of sulfur ligands have the same binding energy in XPS makes an accurate relative quantification impossible. We will return to this point later.

The XPS spectra of MoS$_3$ and \((NH_4)_2[Mo_3S_4]H_2O\) strongly resemble each other and point to certain similarities in the structure of the two compounds. We conclude that MoS$_3$ contains molybdenum in the 4+ oxidation state, which implies that the formation of Mo$^{IV}$S$_3$ from \((NH_4)_2Mo^{VI}S_4\) is accompanied by molybdenum-sulfur redox processes, which lead to reduction of molybdenum, Mo$^{VI}$, and consequently to oxidation of S$^{2-}$ ligands of the MoS$_3^{2-}$ anion.

The infrared spectra of \((NH_4)_2[Mo_3S_4]H_2O\) and MoS$_3$ are shown in Figure 3. The spectrum of \((NH_4)_2[Mo_3S_4]H_2O\) (Figure 3a) shows the characteristic bands of the \([Mo_3S_4]^{2-}\) cluster anion. The bands with the highest intensity are those due to the \(v(S-S)\) vibrations, i.e. the \(v(S-S)_{br}\) vibration at 544 cm$^{-1}$ and the \(v(S-S)_{term}\) vibration at 510 cm$^{-1}$. A characteristic

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**TABLE 1: XPS Data of Molybdenum Compounds**

<table>
<thead>
<tr>
<th>compound</th>
<th>Mo 3d$_{3/2}$ (eV)</th>
<th>assignment</th>
<th>S 2p$_{3/2}$ (eV)</th>
<th>assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>((NH_4)_2[Mo_3S_4])</td>
<td>229.0 ± 0.2</td>
<td>Mo$^{4+}$</td>
<td>163.1 ± 0.2</td>
<td>S$_2^{2-}$ bridging</td>
</tr>
<tr>
<td>MoS$_3$</td>
<td>229.1 ± 0.2</td>
<td>Mo$^{4+}$</td>
<td>161.7 ± 0.2</td>
<td>S$_2^{2-}$ terminal</td>
</tr>
<tr>
<td>MoS$_3^{33}$</td>
<td>229.0 ± 0.2</td>
<td>Mo$^{4+}$</td>
<td>163.0 ± 0.5</td>
<td>S$^{2-}$ apical</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>162.9 ± 0.2</td>
<td>S$_2^{2-}$ bridging</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>161.6 ± 0.2</td>
<td>S$_2^{2-}$ terminal/or S$^{2-}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>161.8 ± 0.2</td>
<td>basal plane S$^{2-}$</td>
</tr>
</tbody>
</table>

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feature of this compound is the $\nu$(Mo–S) vibration of the apical sulfur at 459 cm$^{-1}$. The bands below 400 cm$^{-1}$ are due to coupled $\nu$(Mo–S) vibrations. The infrared emission spectrum of MoS$_3$ (Figure 3b) shows features very similar to those of the IR absorption spectrum of (NH$_4$)$_2$[MoS$_{13}$]H$_2$O, although the bands of the former are considerably broader and less well resolved. We assign the bands at 545, 520, and 470 cm$^{-1}$ to the spectrum of sulfur at 459 cm$^{-1}$. The bands below 400 cm$^{-1}$ are due to coupling of the disulfide ligands. The infrared emission spectrum of a decomposition intermediate after 15 min at 260 °C possesses disulfide as well as apical sulfur at 456 and at 478 cm$^{-1}$ corresponding to the symmetric and antisymmetric $\nu$(Mo–S) vibrations of the MoS$_2^{2-}$ anion (see above). The emission infrared spectrum of the decomposition intermediate (Figure 5b), measured at 260 °C in argon directly after thermal equilibration (15 min), resembles that of MoS$_3$, as shown in Figure 3b. Its major features are broad bands around 325 and 525 cm$^{-1}$ and smaller but clearly visible contributions around 385 and 445 cm$^{-1}$. We attribute the broad band around 525 cm$^{-1}$ to the unresolved contributions of terminal and bridging S$_2^{2-}$ ligands and the two bands at 325 and 385 cm$^{-1}$ to coupled $\nu$(Mo–S) vibrations, as discussed above. The thermal decomposition product obtained after heating (NH$_4$)$_2$MoS$_4$ for 15 min at 260 °C possesses disulfide as well as apical sulfur ligands and is almost similar to that of amorphous MoS$_3$.

Figure 4 displays the Raman spectra of (NH$_4$)$_2$MoS$_4$ and of a decomposition intermediate after 5 min at 260 °C. The spectrum of (NH$_4$)$_2$MoS$_4$ (Figure 4a) contains two sharp bands at 435 and 476 cm$^{-1}$ corresponding to the symmetric (v$_1$(A$_{1g}$)) and antisymmetric (v$_2$(F$_{2g}$)) $\nu$(Mo–S) vibrations of the MoS$_2^{2-}$ anion, respectively. The spectrum of the decomposition intermediate (Figure 4b) also shows a band around 455 cm$^{-1}$, which we assign to the $\nu$(Mo–S) vibration of Mo=S$_4^{2-}$ fragments in an environment of lower symmetry compared with the MoS$_2^{2-}$ anion. However, two new, rather broad bands appear, one with a maximum around 350 cm$^{-1}$ and the other around 525 cm$^{-1}$. The shape of the latter one is slightly asymmetric due to a very weak shoulder around 550 cm$^{-1}$. The band at 525 cm$^{-1}$ and the shoulder at 550 cm$^{-1}$ are characteristic of $\nu$(S–S) vibrations of terminal and bridging S$_2^{2-}$ ligands, respectively, which are observed at 522 cm$^{-1}$ (terminal) and 553 cm$^{-1}$ (bridging) in the Raman spectrum of (NH$_4$)$_2$[MoS$_{13}$]H$_2$O.

The results described thus far concern MoS$_3$ prepared in solution. The following experiments pertain to thermally decomposed (NH$_4$)$_2$MoS$_4$ and serve to demonstrate that part of the terminal S$_2^{2-}$ ligands as present in the MoS$_2^{2-}$ anion indeed undergo oxidation to disulfide ligands.

Figure 5 shows the infrared spectra of (NH$_4$)$_2$MoS$_4$ and of a thermal decomposition intermediate. The absorption IR spectrum of (NH$_4$)$_2$MoS$_4$ (Figure 5a) contains two sharp bands at 456 and at 478 cm$^{-1}$ corresponding to the symmetric and antisymmetric $\nu$(Mo–S) vibrations of the MoS$_2^{2-}$ anion (see above). The emission infrared spectrum of the decomposition intermediate (Figure 5b), measured at 260 °C in argon directly after thermal equilibration (15 min), resembles that of MoS$_3$, as shown in Figure 3b. Its major features are broad bands around 325 and 525 cm$^{-1}$ and smaller but clearly visible contributions around 385 and 445 cm$^{-1}$. We attribute the broad band around 525 cm$^{-1}$ to the unresolved contributions of terminal and bridging disulfide ligands and the two bands at 325 and 385 cm$^{-1}$ to coupled $\nu$(Mo–S) vibrations, as discussed above. The 445 cm$^{-1}$ band with shoulders at 430 and 470 cm$^{-1}$ is probably a superposition of $\nu$(Mo–S) vibrations of Mo=S$_4^{2-}$ fragments (see above) and of the $\nu$(Mo–S) vibration of apical S$_2^{2-}$ ligands. The infrared spectrum thus indicates that the thermal decomposition product obtained after heating (NH$_4$)$_2$MoS$_4$ for 15 min at 260 °C possesses disulfide as well as apical sulfur ligands and is almost similar to that of amorphous MoS$_3$.

If MoS$_3$ is treated with boiling concentrated HCl, an extrusion product can be isolated from the reaction mixture by adding NEt$_4$Cl. The infrared spectrum of this extrusion product is shown in Figure 6. This spectrum is virtually equivalent to the one published for the (NEt$_4$)$_2$[MoS$_3$Cl$_6$]H$_2$O cluster compound.
as prepared from (NH$_4$)$_2$[Mo$_5$S$_{13}$]H$_2$O,

where also a vibrational analysis is given. The bands at 559 and 570 cm$^{-1}$ are due to $\nu$(S-S) vibrations, and the band at 461 cm$^{-1}$ corresponds to the $\nu$(Mo=S) vibration of the apical sulfur. The bands between 350 and 250 cm$^{-1}$ are due to coupled $\nu$(Mo-S) + $\nu$(Mo-Cl) vibrations; those between 250 and 200 cm$^{-1}$ mainly correspond to deformation modes mixed with external, i.e., translational and rotational, modes. The bands at low wave-numbers, i.e., at 166 and 177 cm$^{-1}$, contain significant metal—metal stretching contributions. Although the band at 528 cm$^{-1}$ has the highest intensity, it is not discussed in ref 29; we tentatively assign this band to coupled $\nu$(S-S) + $\nu$(Mo-Cl) vibrations. The fact that (NEt$_4$)$_2$[Mo$_5$S$_{13}$] can be prepared from both MoS$_3$ and (NH$_4$)$_2$[Mo$_5$S$_{13}$]H$_2$O under comparable reaction conditions again points to similarities in the structures of MoS$_3$ and the triangular Mo$_3$—S$_2$ compounds.

Discussion

The following results are essential in considering a structure for amorphous MoS$_3$.

(i) The XPS Mo 3d$_{5/2}$ binding energy of 229.1 eV indicates that MoS$_3$ contains molybdenum in a formal 4+ oxidation state.

(ii) The XPS S 2p spectrum of MoS$_3$ shows the presence of different types of sulfur ligands, which may include bridging and terminal S$_2^-$ and bridging S$_2^-$ ones.

(iii) The emission infrared spectrum of MoS$_3$ contains all the characteristic vibrations that are encountered in the infrared spectrum of the triangular cluster compound (NH$_4$)$_2$[Mo$_5$S$_{13}$]H$_2$O.

(iv) Three triangular cluster compounds, (NH$_4$)$_2$[Mo$_5$S$_{13}$]H$_2$O,$^{25}$ K$_2$[Mo$_5$S$_{13}$]CN$_3$-2H$_2$O,$^{22}$ and (NEt$_4$)$_2$[Mo$_5$S$_{13}$Cl$_6$], can be extruded from MoS$_3$ using chemical reactions that are essentially destructive.

On the basis of these results, we propose that MoS$_3$ is essentially an aggregation of Mo(VI)—sulfur cluster types, from which the $\{\text{Mo}_2\text{S}_7\}^{4+}$ and $\{\text{Mo}_3\text{S}_9\}^{4+}$ cores—the central parts of the extrusion products—can be readily abstracted under destructive reaction conditions. This particular interpretation of the extrusion experiments (an extrusion of preformed structures instead of a synthesis in the reaction mixture) is supported by a FAB-MS study of K$_2$[Mo$_5$S$_{13}$]H$_2$O, which has been extruded from a physical mixture of $^{95,97}$MoS$_3$/$^{95,97}$MoS$_2$. The mass spectrum of the extrusion product shows mainly signals due to pure $^{95,97}$Mo$_3^+$ and $^{95,97}$Mo$_2^+$—sulfur fragments.

The MoS$_3$ structure as built up from MoS$_3$ units possesses locally a relatively high degree of internal organization. How reasonable is it to assume that this kind of structure forms in a thermal decomposition of a rather simple compound as (NH$_4$)$_2$MoS$_4$?

The thermal decomposition of (NH$_4$)$_2$MoS$_4$ according to

$$\text{(NH}_4\text{)}_2\text{Mo}^{IV}\text{S}_4 \rightarrow 2\text{NH}_3 + \text{H}_2\text{S} + \text{Mo}^{IV}\text{S}_3$$

(3)

is accompanied by molybdenum—sulfur redox processes, namely, oxidation of $\text{S}_2^-$ ligands of the MoS$_2$,$^2$ anion (2$\text{S}_2^-$ $\rightarrow$ $\text{S}_2^-$ + 2e$^-$) and reduction of the metal (Mo$^{V}$ + 2e$^-$ $\rightarrow$ Mo$^{IV}$). The first elementary step in (3) may be described as a proton transfer from the two NH$_3$ cations to an S$^2-$ ligand of the MoS$_2$,$^2$ anion, leading to NH$_3$ and a neutral [S$_2$Mo(SH$_2$)] intermediate, which immediately decomposes to gaseous H$_2$S and [MoS$_2$].

Simultaneous with the release of H$_2$S, the molybdenum—sulfur redox process takes place where the ligand oxidation reaction leads to the formation of disulfide groups and provides the electrons for the reduction of the metal. This is recognized in the Raman spectrum of Figure 4b: Treating (NH$_4$)$_2$MoS$_4$ at 260 °C for 5 min forms mainly terminal disulfide ligands, suggesting that a resulting “mononuclear” [MoS$_3$] intermediate may formally be described as [(S$^2-$)—Mo$^{IV}$—(S$^2-$)]. The latter is not expected to be stable due to the low coordination number of the metal. Stabilization is achieved by aggregation of these [S—Mo—S$_2$] fragments (indicated by the band corresponding to bridging S$^2-$ ligands in the Raman spectrum), where the formation of Mo$_3$—sulfur substructures is thermodynamically favored.

The aggregation of the [S—Mo—S$_2$] units is a random process. The positions of all molybdenum and sulfur atoms at the beginning of the decomposition reaction is determined by the crystal structure of (NH$_4$)$_2$MoS$_4$. Directly after the loss of NH$_3$ and H$_2$S, the packing of the system is loose. This, in combination with the temperature of 260 °C, causes the mobility to be higher, as is usually the case within solid-state reactions, and the [S—Mo—S$_2$] fragments aggregate mainly within one plane (the ab-plane of (NH$_4$)$_2$MoS$_4$). This can be seen in the powder diffraction pattern of MoS$_3$ (cf. ref 4), which shows a reflection at 2θ = 14.5°. This reflection corresponds to a lattice plane distance of 0.63 nm and points to a “layered structure” for MoS$_3$. During the aggregation of the [S—Mo—S$_2$] fragments four different types of triangle structures (Mo—S short-range order) can be formed. There are triangles in which the three metal atoms are bonded together with only bridging S$_2^-$ and those which also include S$_2^-$ ligands between two metal atoms. Both types of triangle structures can occur with and without an apical sulfur atom. These four possibilities are depicted in structures I—IV of Figure 7. Note that these structures do not represent compounds in their own right, but the building blocks within the MoS$_3$ solid, which, however, all satisfy the requirements of stoichiometry and electroneutrality.

The MoS$_3$ structure (long-range order) is essentially an interconnection of the structure types I—IV by means of sulfur ligands. There are two possibilities for interconnections. If both molybdenum atoms of two adjacent triangles have an S$^2-$ ligand, such as the Mo atoms at the top of structures I and II, the triangles connect via the two S$^2-$ ligands in an {Mo—(S)$_2$—Mo}
bridge. If only one S\(^2\) ligand is available, as when the Mo atoms at the top of structures I and III combine, the triangles connect via an \{Mo–S–Mo\} bridge. Figure 7 shows a representative part of the MoS\(_3\) structure. Note that the interconnection of the structures I–IV preclude the presence of Mo–S fragments and also of coordinately unsaturated molybdenum atoms as structures I–IV might imply. It is conceivable that Mo atoms at the boundaries of a MoS\(_3\) particle are terminated by S\(^2\) groups (see the arrows in Figure 7), which are required for the coordinative saturation of edge metal centers, where they impede further aggregation. This effect leads to a slightly higher stoichiometry, namely, MoS\(_{3.1}\)–MoS\(_{3.2}\), which in fact was found by elemental analysis,\(^{19,20}\) in agreement with the surplus of sulfur found in the XPS spectrum.

As the oxidation state of sulfur in the \{S–Mo–S\} fragments does not change during the aggregation process, the charge state of MoS\(_3\) can formally be written as Mo\(^{4⁺}(S^{2⁻})\)(S\(^{2⁻}\)). This charge stoichiometry itself cannot be obtained from the S\(^{2p}\) spectrum (Figure 2b) without additional structural information (vide supra). However, our structural model is in full agreement with the S\(^{2p}\) spectrum of MoS\(_3\), i.e.

\[
\frac{S\,(\text{Mo}^{4⁺})}{S\,(\text{Mo}^{4⁺})} + \text{CN}⁻ \rightarrow \left\{ \text{Mo}^{4⁺}+\text{CN}⁻ \right\} + \text{NCS}⁻ \quad (4)
\]

in which the \{Mo\(^{4⁺}\)\}\(^{4⁺}\) core is formed by subsequent sulfur redox (4) and the metal–ligand substitution (5) reactions from the \{Mo\(^{4⁺}\)S\(^{2⁻}\}\}\(^{4⁺}\) (structure III) and the \{Mo\(^{4⁺}\)S\(^{2⁻}\}\}\(^{4⁺}\) core (structure IV), which means that the portion of structure IV in MoS\(_3\) is about 25%. The cyanolysis of MoS\(_3\) is often accompanied by the formation of K\(_2\)Mo\(_3\)S\(_{12}\)Cl\(_{12}\) in varying low percentages (< 3%).\(^{22}\) Since the Mo 3d XPS spectrum of MoS\(_3\) (Figure 1b) does not indicate a second molybdenum state beside Mo\(^{4⁺}\), we argue here that the \{Mo\(^{4⁺}\)\}\(^{4⁺}\) core is not a relevant local structure within the MoS\(_3\) solid.

The remaining part of the MoS\(_3\) solid (65%) can obviously not be extruded in the form of stable clusters, probably due to the absence of apical sulfur atoms (structures I and II). We therefore conclude that structures I and II together contribute to the structure of MoS\(_3\) with ca. 65% and structures III and IV with ca. 25 and 10%, respectively. Such a composition favors the interconnection of triangles by Mo–(S)\(^{2⁻}\)–Mo bridges over that by Mo–S–Mo ones.

EXAFS measurements by Cramer et al.\(^{20}\) have indicated that the spectrum of MoS\(_3\) possesses scattering contributions from two Mo–Mo distances, 0.274 and 0.314 nm, and mainly one Mo–S distance of 0.241 nm. Metal–metal and metal–sulfur distances in our structural model can be estimated using the X-ray structure data of relevant molybdenum–sulfur cluster compounds. The Mo–Mo distance in structure III should be close to that in the \{Mo\(^{4⁺}\)S\(^{2⁻}\}\}\(^{4⁺}\) anion,\(^{32}\) namely, 0.272–0.275 nm, and should be slightly longer in structure I. The distance between molybdenum atoms bonded via an S\(^2\) ligand within structures II and IV is expected to be around 0.3 nm\(^{20}\) due to
the symmetry of the triangle structure. The distances of Mo atoms of different triangles interconnected with S²⁻ ligands are expected to be longer than 0.3 nm, because here an enlargement of Mo–S–Mo bonding angles must be involved for a minimization of the sterical interaction with the atoms of neighboring triangles (cf. also the discussion in ref 21).

Metal–sulfur distances in MoS₂ should fall between 0.236 and 0.248 nm according to the X-ray data of the [Mo₃S₄(CN)₉]⁵⁻ cluster anions, which are d(Mo–S₃) = 0.236 nm, d(Mo–S₂) = 0.245 nm, and d(Mo–S₁) = 0.248 nm, while the distance between molybdenum and a bridging S²⁻ ligand is expected between 0.238 and 0.240 nm. These small differences in distance would be hard to resolve in EXAFS, and an average metal–sulfur distance of 0.24 ± 0.01 nm is expected.

We thus expect two metal–metal distances in the MoS₃ solid, a shorter one around 0.275 nm and a longer one of about 0.31 nm, and an average metal–sulfur distance between 0.236 and 0.248 nm, in good agreement with the EXAFS results of Cramer et al.²⁰ Also the magnetic measurements given in ref 18 can easily be explained, as the diamagnetic properties of MoS₃ are due to the electronic structure of Mo⁹V. The fact that two types of Mo–Mo distances are observed in MoS₃ with EXAFS has implications for the identification of intermediate phases formed during the sulfidation of molybdenum oxides. De Boer et al.⁹ encountered an MoS₃ type intermediate phase but observed only one Mo–Mo distance of 0.276 nm with EXAFS. Although this intermediate phase has the correct stoichiometry, the absence of the longer Mo–Mo distance (0.31 nm) indicates that this phase does not have the characteristic MoS₃ structure as discussed above.

Finally, any structural model for MoS₃ must be able to account for its decomposition into microcrystalline MoS₂ at elevated temperatures:

\[ \text{MoS}_3 \rightarrow \text{MoS}_2 + S^0 \]  

(6)

This reaction, which takes place in inert gas at temperatures above 310 °C, involves the reduction of bridging disulfide ligands due to reductive elimination of S²⁻ and terminal S₂⁻ ligands⁰⁻³ formally according to:

\[ \left\{ \text{Mo}^{VI}_3 \right\}^0 \rightarrow \left\{ \text{Mo}^{IV}_3 \right\} + S^0 \]  

(7)

During decomposition the preformed Mo₃ units are preserved, and after the loss of one sulfur per molybdenum center, reactive \{Mo₅S₅\} units may remain, similarly as has been shown for the thermal decomposition of (NH₄)₂[Mo₅S₅H₂O].⁴ These \{Mo₅S₅\} units are formed in every "layer" and aggregate to build up the MoS₃ lattice.

Acknowledgment. We thank J. H. M. C. van Wolput for assisting with the infrared measurements. Valuable discussions with Dr. E. Diemann (Bielefeld), Prof. Dr. J. A. R. van Veen, and Dr. V. H. J. de Beer (Eindhoven) are gratefully acknowledged. We are indebted to Prof. A. Müller, University of Bielefeld, for his kind permission to do Raman measurements in his laboratory. This work was supported by Pioneer Grant 70–154 from the Netherlands Organization for Scientific Research (NWO).

References and Notes

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JP950037J