Crystal Structure of \((\text{NH}_4)_2[\text{Mo}_3\text{S(S}_2\text{)}_6]\) Containing the Novel Isolated Cluster \([\text{Mo}_3\text{S}_{13}]^{2-}\)

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Crystal Structure, Molybdenum, Sulfur, Cluster, Metal–Metal Bond, Disulfide Diatomic Ligands

The novel tri-nuclear metal-sulfur cluster \([\text{Mo}_2\text{S(S}_2\text{)}_6]\) can be obtained as its ammonium salt by the reaction of a \(\text{Mo}^{VI}\) containing aqueous solutions with polysulfide. Its crystal and molecular structure has been determined by a single crystal X-ray study. The crystals are monoclinic (space group \(\text{Cm}\), with \(a = 11.577(6)\) Å, \(b = 16.448(7)\) Å, \(c = 5.716(2)\) Å, \(\beta = 117.30(3)^\circ\), \(V = 967.2\) Å\(^3\), \(Z = 2\). The structure consists of isolated \([\text{Mo}_2\text{S(S}_2\text{)}_6]\) units, with three Mo atoms at the vertices of a triangle. There are bridging as well as terminal S\(^{-}\)-ligands lying above and below the Mo\(_3\) plane (bond distances: Mo–Mo = 2.722 Å, Mo–S(terminal) = 2.435, Mo–S(briding) = 2.452, Mo–S = 2.533(4) Å and S–S = 2.04 Å (mean values)).

Transition metal sulfur clusters are model compounds of bioinorganic interest [1, 2]. Isolated binary sulfur clusters were unknown until recently, though several halogen cluster compounds were reported. We were able to isolate the novel compound \((\text{NH}_4)_2[\text{Mo}_2\text{S(S}_2\text{)}_6]\) containing bridging as well as terminal S\(^{-}\)-ligands in the molybdenum-sulfur-cluster anion [2]. In this paper the crystal structure of the compound is reported.

Experimental

Preparation of \((\text{NH}_4)_2[\text{Mo}_2\text{S(S}_2\text{)}_6]\) [2]

\textbf{Method 1:} To a solution of 2.00 g (0.011 mole with respect to molybdenum) of \((\text{NH}_4)_2\text{Mo}_2\text{O}_4 \cdot 4\) H\(_2\)O, 1.50 g (0.022 mole) of NH\(_2\)OH · HCl was added. The mixture was stirred until a solution was obtained and then kept at 40–50 °C for 5 min, when a red-brown solution containing some brownish yellow precipitate was formed. After adding 30 ml of saturated ammonium polysulfide solution, the mixture was heated at ca. 90 °C for 3–4 h. Dark-red crystals separated and were filtered and washed with \((\text{NH}_4)_2\text{S}_2\text{H}_2\text{O}\) ethanol, CS\(_2\) and diethylether.

\textbf{Method 2:} To a 30 ml solution of saturated ammonium polysulfide \(1 \text{ g of solid MoCl}_2\text{py}_2\) (py = pyridine), was slowly added with continuous stirring. The reaction mixture was stirred for another 10 min, filtered from any undissolved precipitate and the filtrate kept in an oil bath at 90 °C for 1–2 h. The precipitate was washed as described under method 1.

\((\text{NH}_4)_2\text{Mo}_2\text{S}_3\) Calculated N 3.78 S 56.27, Found N 4.0 S 55.8.

Crystal Data

X-ray diffraction studies were carried out on a Syntex P2\(_i\) four-circle automated diffractometer. Crystals suitable for X-ray analysis were obtained by the methods given above and mounted in glass capillaries. Precession photographs confirmed that the crystals belonged to the monoclinic system and that the space group was \(\text{Cm}\). With an experimental density of 2.54 g/cm\(^3\) \(Z\) could only be 2. The \([\text{Mo}_2\text{S}_3]\) radical could only posses a mirror plane though the ideal symmetry should be \(\text{C}_{\text{av}}\). Crystal data are summarized in Table I.

<table>
<thead>
<tr>
<th>Identity of crystal data of ((\text{NH}_4)_2[\text{Mo}_2\text{S(S}_2\text{)}_6])</th>
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</thead>
<tbody>
<tr>
<td>Formula</td>
</tr>
<tr>
<td>Crystal system</td>
</tr>
<tr>
<td>Space group</td>
</tr>
<tr>
<td>(a), (b), (c) [Å, deg]</td>
</tr>
<tr>
<td>(\beta)</td>
</tr>
<tr>
<td>(V) [Å(^3)]</td>
</tr>
<tr>
<td>(Z)</td>
</tr>
<tr>
<td>(d_{\text{calc}}) [g/cm(^3)]</td>
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</table>

Data collection and reduction of the intensity data

A standard reflection was measured every 50 reflections and its intensity showed no significant fluctuation or evidence of decomposition of the crystal. The processing of the data was carried out as described previously [3]. An absorption correction was not applied (absorption coefficient [cm\(^{-1}\)]: 31.8; crystal dimensions [mm]: 0.12 × 0.04 × 0.03; radiation: Mo–K\(_{\alpha}\) (\(\lambda = 0.71069\) Å); scan speed [deg. min\(^{-1}\)]: 2.0–29.3 (o-29-scan method); background scan time ratio: 1:0; unique data: 800; observed data (I > 1.96 a(I)): 766; sin\(\theta_{\text{max}}/\lambda\) [Å\(^{-1}\)]: 0.572).
Structure solution and refinement

The atomic scattering factors for Mo(0), S(0), and N(0) were taken from the "International Tables" [4]. A three-dimensional Patterson synthesis [5] provided the location of the molybdenum atoms in the unit cell. Difference Fourier syntheses indicated the positions of the 13 sulfur atoms and led, after several cycles of refinement, to the location of the nitrogen atom.

The final refinement of the model converged to give residuals $R = 0.053$ and $R_w = 0.059$ for the 766 observed reflections (see Table I), using statistical weighting as described previously [3] (highest shift/error (final cycle): 0.01). Listings of final values of $(F_o)$ and $(F_c)$ are available from the authors. Atomic fractional coordinates are collected in Table II.

Results and Discussion

The crystal structure consists of discrete ($\text{Mo}_3\text{S}_{13}$)$_2^-$ units. The drawing in Fig. 1 illustrates the packing within the crystal. Bond distances and angles are given in Table III.

The cluster ($\text{Mo}_3\text{S}_{13}$)$_2^-$ (ORTEP drawing in Fig. 2)

\begin{table}[h]
\centering
\begin{tabular}{lcccc}
\hline
Atom & $x$ & $y$ & $z$ & Atom & $B_{11}$ & $B_{22}$ & $B_{33}$ & $B_{12}$ & $B_{13}$ & $B_{23}$ \\
\hline
Mo 1 & 0.00000(0) & 0.00000(0) & 0.00000(0) & Mo 1 & 2.54(11) & 1.81(10) & 2.71(11) & 0.00(0) & 1.35(9) & 0.00(0) \\
Mo 2 & 0.2287(21) & 0.08284(9) & 0.2118(42) & Mo 2 & 2.60(7) & 1.89(6) & 2.61(6) & 0.09(7) & 1.46(5) & -0.05(7) \\
S 1 & 0.43907(73) & 0.00900(0) & -0.2769(15) & S 1 & 2.49(35) & 2.72(33) & 3.86(38) & 0.00(0) & 1.72(31) & 0.00(0) \\
S 2 & 0.33884(74) & 0.00000(0) & -0.6007(14) & S 2 & 2.27(31) & 3.13(34) & 1.91(28) & 0.00(0) & 0.84(26) & 0.00(0) \\
S 3 & 0.19050(92) & 0.00000(0) & 0.4261(17) & S 3 & 4.36(48) & 2.96(37) & 3.34(37) & 0.00(0) & 1.11(35) & 0.00(0) \\
S 4 & 0.23196(85) & 0.00000(0) & 0.1146(19) & S 4 & 2.59(38) & 3.48(39) & 5.27(48) & 0.00(0) & 1.67(35) & 0.00(0) \\
S 5 & -0.0129(50) & 0.10576(31) & 0.0168(11) & S 5 & 3.34(27) & 2.02(21) & 3.01(23) & -0.25(19) & 1.48(21) & -0.35(19) \\
S 6 & -0.05912(53) & 0.10208(31) & -0.3418(10) & S 6 & 2.94(25) & 2.32(20) & 2.75(21) & -0.30(19) & 1.62(20) & -0.16(18) \\
S 7 & -0.32151(64) & 0.18171(37) & -0.0375(15) & S 7 & 4.09(31) & 3.32(27) & 4.89(32) & 0.46(23) & 2.65(27) & -0.73(24) \\
S 8 & -0.34444(61) & 0.20974(36) & -0.4107(12) & S 8 & 3.61(30) & 2.73(24) & 5.11(33) & 0.58(22) & 2.03(27) & 54.6(22) \\
S 9 & -0.15169(79) & 0.00000(0) & 0.1661(14) & S 9 & 3.33(36) & 1.80(29) & 3.12(35) & 0.00(0) & 2.00(30) & 0.00(0) \\
N 0.3518(22) & 0.1751(13) & 0.4193(43) & N & 5.62(134) & 3.95(105) & 6.76(130) & 0.82(96) & 2.87(108) & 0.40(95) \\
\hline
\end{tabular}
\caption{Positional and thermal parameters of ($\text{NH}_4$)$_2$[Mo$_3$S(S$_2$)$_6$].}
\end{table}
has three molybdenum atoms at the vertices of a triangle with a unique S-atom above its center. There are bridging as well as terminal S\textsubscript{-}ligands, which both lie above and below the Mo\textsubscript{3}-plane. Each molybdenum is coordinated to one terminal and two bridging S\textsubscript{2}-ligands as well as two other molybdenum atoms.

The directed synthesis of cluster-compounds is a current problem in transition metal chemistry [6]. For the transition elements Mo, W, Te and Re with d\textsuperscript{5} electron configurations, cluster types are expected to be dumb-bell shaped (in the case where \( n = 1 \)), triangular (\( n = 2 \)), tetrahedral (\( n = 3 \)) and octahedral (\( n = 4 \)) (therefore \( n \) also indicates the number of metal–metal bonds originating from each metal atom). Recently, the first binary species with \( n = 1 \) viz \([\text{Mo}_2\text{S}_2^2]^{2-}\) [7] has been isolated in the form of its ammonium salt. Therefore we expected the possibility of the preparation of the homologous cluster with \( n = 2 \) from a solution containing Mo\textsuperscript{IV}, which was indeed possible. From the above mentioned scheme the existence of the homologous cluster \([\text{Mo}_4\text{IIIS}_4(S_2)_6]^{4-}\) could also be predicted. The central unit \([\text{Mo}_3\text{S}_4]\) can already be found in \([\text{C}_6\text{H}_5\text{MoS}]_4\) [1] and in the solid state structures \([\text{M}_2\text{Mo}_2\text{Re}_2]\text{S}_8\) and \([\text{M}_2\text{Mo}_2\text{S}_6]\) [8] \( (\text{M} = \text{Fe, Co, Ni, Zn; M} = \text{Al, Ga}) \). Obviously the stability of these compounds is also connected with the occurrence of tri-coordinate sulfur (for the low reactivity cf. [1]) in the central units \([\text{Mo}^\text{V}(S_2)\text{Mo}^\text{Y}], [\text{Mo}^\text{IVS}(S_2)_4]\) and \([\text{Mo}^\text{IVS}_4]\). It is interesting to note that the first two units are also present in the solid state structures of \( 1/4 [\text{Mo}_2\text{S}_2^4\text{Cl}_4\text{Cl}_4/2] \) and \( 1/2 [\text{Mo}_2\text{S}_2^4\text{Cl}_4\text{Cl}_4/2] \) [9].

A comparison shows that corresponding bond distances are very similar (Table IV) even with respect to the asymmetric coordination of the S\textsubscript{4}-ligands (see Table III and ref. [7, 9]). The existence of metal–metal bonds follows from the short distance as well as from the diamagnetism of \([\text{Mo}_3\text{S}_4(S_2)_6]^{2-}\) [10]. The Mo–Mo bond distance is shorter in \([\text{Mo}_3\text{S}_4(S_2)_6]^{2-}\) than in \([\text{Mo}^\text{IVS}(S_2)_4]^2-\) as expected.

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Table IV. Comparison of bond distances of compounds with the central units \([\text{Mo}_3\text{S}_4(S_2)_6]^{2-}\) and \([\text{Mo}_2\text{S}_6]^2-\) (mean values, in Å).

<table>
<thead>
<tr>
<th></th>
<th>Mo–Mo</th>
<th>Mo–S\textsuperscript{f}</th>
<th>Mo–S\textsuperscript{term}\textsuperscript{e}</th>
<th>Mo–S\textsuperscript{bridge}\textsuperscript{e}</th>
<th>S–S\textsuperscript{term}</th>
<th>S–S\textsuperscript{bridge}</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Mo}_3\text{S}_4(S_2)_6]^{2-})</td>
<td>2.722</td>
<td>2.353</td>
<td>2.435</td>
<td>2.452</td>
<td>2.06</td>
<td>2.02</td>
</tr>
<tr>
<td>(1/4 [\text{Mo}_2\text{S}_2^4\text{Cl}_4\text{Cl}_4/2])</td>
<td>2.745</td>
<td>2.36</td>
<td>–</td>
<td>2.45</td>
<td>2.049</td>
<td>2.043</td>
</tr>
<tr>
<td>([\text{Mo}_2\text{S}_6]^2-)</td>
<td>2.827</td>
<td>–</td>
<td>2.459</td>
<td>2.444</td>
<td>2.049</td>
<td>2.043</td>
</tr>
<tr>
<td>(1/2 [\text{Mo}_2\text{S}_2^4\text{Cl}_4\text{Cl}_4/2])</td>
<td>2.853</td>
<td>–</td>
<td>–</td>
<td>2.43</td>
<td>1.980</td>
<td>1.980</td>
</tr>
</tbody>
</table>

\(\text{a}\) This work, \(\text{b}\) ref. [9], \(\text{c}\) ref. [7], \(\text{d}\) ref. [9], \(\text{e}\) average distances (term: terminal S\textsubscript{2}-groups; bridge: bridging S\textsubscript{2}-groups), \(\text{f}\) distance to the S-atom above the Mo\textsubscript{3}-plane.

[1] H. Vahrenkamp, Angew. Chem. 87, 363 (1975);
[5] All calculations were done using the "Syntex XTL Program System" and the program ORTEP from C. K. Johnson.
[10] The interpretation of the thermochemical, magnetic and spectroscopic properties (UV, VIS, XPS, IR, RAMAN, Xa-calculations) will be published later.