H_2 (on acid hydrolysis, 72 h in 6 M HCl at 100 °C):B:P = 10.0:3.98:1.03 (molar ratio). Calcd for $B_4H_8 \cdot PH_3$: 10.0:4.0:1.0.

C. Reaction of $B_4H_8 \cdot PH_3$. (a) With PH_3. A sample of $B_4H_8 \cdot PH_3$, which had been prepared by the procedure described in section B(c) with use of 0.49 mmol of B_5H_{11}, was dissolved in 1.5 mL of dichloromethane, and the solution was mixed with 2.46 mmol of PH_3. The ^{11}B spectra of the mixture were examined in a temperature range from −80 to −30 °C. Only the signals of $B_4H_8 \cdot PH_3$ were observed.

(b) With $P(CH_3)_3$. A sample of $B_4H_8 \cdot PH_3$ prepared from 0.60 mmol of B_5H_{11} was dissolved in 1 mL of dichloromethane, and the solution was treated with 3.04 mmol of $P(CH_3)_3$ at −80 °C. The ^{11}B NMR spectrum of the mixture indicated the formation of $B_4H_8 \cdot 2P(CH_3)_3$. When a $B_4H_8 \cdot PH_3$ sample was treated with approximately 1 molar equiv of $P(CH_3)_3$, $B_4H_8 \cdot P(CH_3)_3$ and a small amount of $B_4H_8 \cdot 2P(CH_3)_3$ were produced.

D. Reaction of $BH_3 \cdot PH_3$ with $P(CH_3)_3$. A 0.5-mmol sample of $P(CH_3)_3$ was condensed at −197 °C above a 2-mL dichloromethane solution containing about 0.5 mmol of $BH_3 \cdot PH_3$ and was mixed into the solution at −95 °C. Below −50 °C no change could be detected in the ^{11}B spectrum of the solution. At −50 °C the signal of $BH_3 \cdot P(CH_3)_3$ was detected. At −40 °C the $BH_3 \cdot P(CH_3)_3$ signal grew slowly at the expense of the $BH_3 \cdot PH_3$ signal.

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(18) Because of the instability of $B_4H_8 \cdot PH_3$, the analytical samples were not weighed. The amount of vaporization loss of $B_4H_8 \cdot PH_3$ that occurred during the removal of $BH_3 \cdot PH_3$ from the product mixture was dependent upon the length of pumping time and ranged from 10 to 25% under the conditions employed for the preparation of the samples. Therefore, only the ratio (H_2:B:P) obtained for each sample was meaningful. The NMR data of the product and the formation of B_4H_8 adducts by treatment with $P(CH_3)_3$ further supported the formulation $B_4H_8 \cdot PH_3$ for the compound.

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Aqueous Molybdenum–Iron–Sulfur Chemistry: Enzyme-Mediated Assembly of [Mo₂Fe₆S₈(SCH₂CH₂OH)₉]³⁻ from Molybdate and Thiosulfate

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Iron–sulfur and molybdenum–iron–sulfur clusters in proteins have stimulated a large number of investigations aimed at synthesizing structural, electronic, and catalytic analogues of the biological clusters. Two prototypical "thiocubane" clusters that form by "spontaneous self-assembly" from simple iron salts, thiolates, and either sulfur or tetrathiomolybdate are $[Fe_4S_4$-$(SR)_4]^{2-}$ [1] and $[Mo_2Fe_6S_8(SR)_9]^{3-}$.[2] (Schematic structures are shown in Chart I.) The former cluster is a synthetic analogue of those occurring in many iron–sulfur proteins. The latter "double-cubane" cluster is not an analogue of any known biological cluster, but some structural and electronic features of the $MoFe_3S_4$ core approach those of the iron–molybdenum cofactor of nitrogenase.[3] A synthetic analogue of this cofactor has so far proven elusive.

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Chart I

$[Fe_4S_4(SR_4)]^{2-}$ $[Mo_2Fe_6S_8(SR)_9]^{3-}$
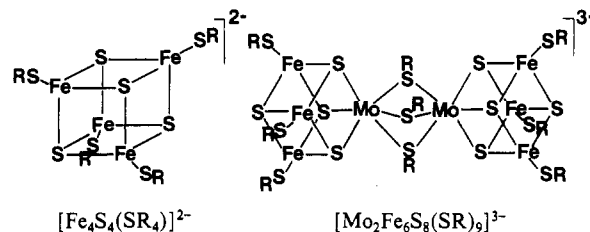
Recent results from this laboratory[4] have shown that salts of the water-soluble cluster $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$ can be prepared in high yields from aqueous solutions containing iron salts and thiols. Sulfur, sulfide, or the outer sulfur of thiosulfate can be used as the source of core sulfide. The sulfurtransferase rhodanese (thiosulfate:cyanide sulfurtransferase, EC 2.8.1.1) catalyzes the reduction of the outer sulfur of thiosulfate in the presence of thiols, especially dithiols:[5]

$$*SSO_3^{2-} + 2RSH \rightarrow *SH^- + RSSR + HSO_3^- \qquad (1)$$
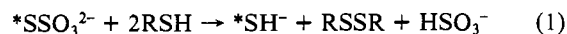
We have used the rhodanese/thiosulfate/dithiol system to show that the assembly of $[Fe_4S_4(SCH_2CH_2OH)_4]^{2-}$ can be enzyme-mediated.[4] We have also reported that reactions of MoS_4^{2-} with salts of Fe(II) in aqueous solution can, depending on the conditions, lead to formation of either the "double-cubane" cluster $[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]^{3-}$ or the novel "linear" tetranuclear cluster $[(MoO_2S_2)_2Fe_2S_2]^{4-}$.[6] This latter cluster represents trapping of an intermediate in a previously undescribed process, namely, the Fe^{2+}-accelerated hydrolysis of MoS_4^{2-}.

Since MoO_4^{2-} is the only known biological uptake and transport form of molybdenum in nitrogen-fixing bacteria,[7] we sought an aqueous system for synthesis of Mo–Fe–S clusters using MoO_4^{2-} as the source of molybdenum. Starting from MoO_4^{2-} rather than MoS_4^{2-} would also allow the exploration of various sources of cluster sulfide, which could, in turn, influence the product distribution. Herein we report and briefly discuss some results of such explorations.

Experimental Section

Rhodanese was isolated from bovine liver according to a published procedure[8] and stored at 0–4 °C as a crystalline suspension in 2 mM sodium thiosulfate, 2 M ammonium sulfate, pH 7.6. This suspension was added as such for cluster assembly reactions, as described below. Millimolar concentrations of ammonium sulfate were thus introduced into the rhodanese-containing reaction mixtures. Concentrations and thiosulfate reductase activities of rhodanese were determined, and solutions of D,L-dihydrolipoate were prepared by previously described procedures.[4] Sodium thiosulfate and sodium sulfide were added as 1 M stock solutions in either 0.2–0.3 M Tris–sulfate or NaTAPS, pH 9.0–9.2.[9] These buffers were used for all reactions. Aqueous solutions were prepared from distilled, deionized water. Methanol was distilled from magnesium and iodine. 2-Propanol was distilled from calcium hydride.

All reactions were performed at room temperature, under a purified Ar atmosphere in either Schlenk-type glassware or septum-capped vials. Solutions were added and transferred via steel tubing or gastight syringes.

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(9) Abbreviations used: Tris, 2-amino-2-(hydroxymethyl)propane-1,3-diol; NaTAPS, sodium 3-[[tris(hydroxymethyl)methyl]amino]propanesulfonate.

(n-Bu$_4$N)$_3$[Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$]. **Method a.** A 0.48-g (3.8-mmol) sample of FeCl$_2$ was added to a stirred solution of 0.33 g (1.3 mmol) of (NH$_4$)$_2$MoS$_4$[10] and 1.6 mL (23 mmol) of HSCH$_2$CH$_2$OH in 160 mL of aqueous 0.2 M Tris–sulfate pH 9.1. The color of the solution changed immediately from red to dark green-brown. This reaction mixture was stirred for 90 min and filtered through a Celite pad. Then 5.15 g (16.0 mmol) of n-Bu$_4$NBr was added to the filtered reaction mixture, which resulted in the precipitation of a green-brown microcrystalline solid. After overnight refrigeration this solid was collected by filtration, washed with 2-propanol, and dried under dynamic vacuum. The solid was recrystallized twice from methanol/2-propanol. The yield after recrystallization was 0.89 g (65%). Anal. Calcd for C$_{66}$H$_{153}$N$_3$S$_{17}$Fe$_6$Mo$_2$: C, 35.95; H, 6.99, N, 1.906. Found: C, 35.44; H, 6.68; N, 2.15. The UV–vis absorption and ^{1}H NMR spectra (except for n-Bu$_4$N$^+$ resonances) of the recrystallized solid in acetonitrile and DMSO-d_6, respectively, were in excellent agreement with those previously reported for (Et$_4$N)$_3$[Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$].[11] The crude solid had an additional minor ^{1}H NMR resonance at ~12 ppm downfield of TMS due to [Fe$_4$S$_4$(SCH_2CH$_2$OH)$_4$]$^{2-}$,[4] which disappeared upon recrystallization.

Method b. Typically 0.0918 g (0.234 mmol) of Fe(NH$_4$)$_2$(SO$_4$)$_2$· 6H$_2$O was added to a solution of 0.0819 g (0.0781 mmol) of Na$_2$Mo-O$_4$·2H$_2$O, 0.155 g (0.625 mmol) of Na$_2$S$_2$O$_3$·5H$_2$O, 0.0542 g (0.351 mmol) of dithiothreitol, and 0.30 mL (4.3 mmol) of HSCH$_2$CH$_2$OH in 20 mL of aqueous TAPS buffer pH 9.0. When the ferrous salt had dissolved completely, usually after about 30 min, 0.5 mL of rhodanese suspension was added. After 2.5 h, the reaction mixture was filtered and 0.644 g (2.00 mmol) of n-Bu$_4$NBr was added to the filtrate. After overnight refrigeration the resulting green-brown precipitate was collected by filtration, washed with 2-propanol, and dried overnight under dynamic vacuum. The resulting solid was characterized by UV–vis absorption and ^{1}H NMR spectroscopy, as described under method a, but no further purification was attempted. Reactions were sometimes scaled to total volumes of 50 or 100 mL. The relatively small scales of these reactions (in order to conserve rhodanese) prevented obtainment of accurate weight yields. The reagent ratios were varied from those listed above as stated in the text and figure captions. The starting concentration of molybdate was normally fixed at ~4 mM.

Physical Measurements. All spectra were obtained with samples under an Ar atmosphere. UV–vis absorption spectra were obtained on a Perkin-Elmer Lambda Array Model 3840 spectrophotometer using 0.01-cm-path cylindrical cells equipped with tight-fitting rubber septa. NMR spectra were obtained at 22 °C on a Nicolet NT-300 spectrometer. The signal due to the residual hydrogen atoms in DMSO-d_6 at 2.49 ppm downfield of the Me$_4$Si resonance was used as the chemical shift reference. Chemical shifts downfield of Me$_4$Si are reported as positive.

Results and Discussion

The UV–vis absorption time course for the reaction of (N-H)$_4$MoS$_4$, FeCl$_2$, and HSCH$_2$CH$_2$OH in 0.2 M Tris–sulfate pH 9.1 (included as supplementary material) consists of maxima only at 277 nm and 380 nm. The spectrum is well-formed within 1.5 min after mixing, and in less than 2 h the ratio A_{277}/A_{380} = 1.49. These spectral parameters closely resemble those previously published for (Et$_4$N)$_3$[Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$] in acetonitrile (A_{280}/A_{386} = 1.49, ϵ_{386} = 38 100 M^{-1} cm^{-1}).[11] With these parameters, a spectrophotometric yield of [Mo$_2$Fe$_6$S$_8$-(SCH$_2$CH$_2$OH)$_9$]$^{3-}$ exceeding 80% was calculated. Addition of n-Bu$_4$NBr to the filtered mixture after ~2 h of reaction caused precipitation of a solid that was shown by ^{1}H NMR to be predominantly (n-Bu$_4$N)$_3$[Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$]. Recrystallization as described in the Experimental Section (method a) produced analytically pure (n-Bu$_4$N)$_3$[Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$] in 65% yield. An equation for this reaction can be written as

$$2MoS_4{}^{2-} + 6Fe^{2+} + 11HOCH_2CH_2S^- \rightarrow$$
$$[Mo_2Fe_6S_8(SCH_2CH_2OH)_9]^{3-} + (SCH_2CH_2OH)_2 \quad (2)$$

The previously reported synthesis of (Et$_4$N)$_3$[Mo$_2$Fe$_6$S$_8$-(SCH$_2$CH$_2$OH)$_9$] in methanol calls for a reaction time of 20 h and gives only a slightly higher yield.[11] Our usages of an aqueous reaction medium and/or relatively reducing conditions, namely, Fe^{2+} instead of Fe^{3+}, and an ~4-fold molar excess of HSCH$_2$C-
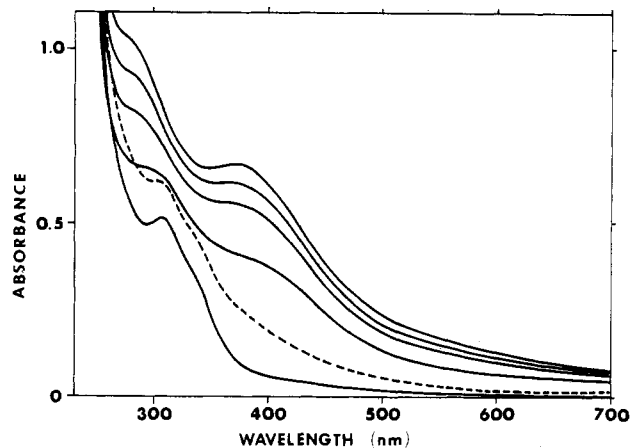
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Figure 1. UV–vis absorption time courses for reactions in 0.2 M Na-TAPS, pH 9.1, of 12 mM Fe(NH$_4$)$_2$(SO$_4$)$_2$, 3.9 mM Na$_2$MoO$_4$, 31 mM Na$_2$S$_2$O$_3$, 18 mM dithiothreitol, 210 mM HSCH$_2$CH$_2$OH, and 6 μM rhodanese. The reaction was mixed and monitored as described in the Experimental Section (method b). The bottom spectrum was obtained prior to addition of rhodanese. Following addition of rhodanese, spectra from lowest to highest absorbance were obtained at 30, 60, 90, and 150 min. The dashed spectrum represents the control solution without rhodanese after 180 min.
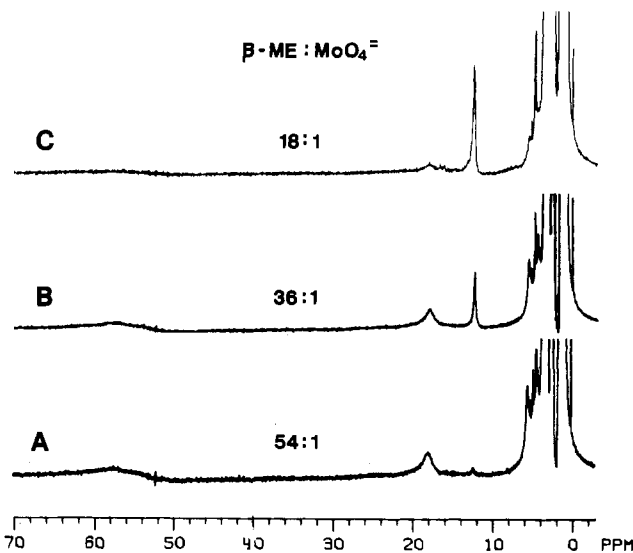

Figure 2. ^{1}H NMR spectra of unrecrystallized solids isolated from reactions such as those described in Figure 1 and method b in the Experimental Section. Solids were isolated following additions of n-Bu$_4$NBr. Part A is from the same reaction mixture as that of Figure 1. Parts B and C are from reactions performed in a manner identical with that described in the legend to Figure 1 except [HSCH$_2$CH$_2$OH] = 140 and 70 mM, respectively.

H$_2$OH above that required by eq 2 may be responsible for the relatively rapid cluster assembly. According to eq 2, at least one Mo–S bond per MoS$_4$$^{2-}$ must be broken, and Mo(VI) must be formally reduced to Mo(III) or Mo(IV).[3] Under our conditions, we note no reaction between MoS$_4$$^{2-}$ and HSCH$_2$CH$_2$OH until Fe^{2+} is added. However, even in as short a time as 1.5 min after mixing according to method a, no trace of the characteristic absorption maximum of MoS$_4$$^{2-}$ at 467 nm (ϵ ~ 12 000 M^{-1} cm^{-1})[10] is evident. Both reduction of molybdenum by thiol and acceleration of thiomolybdate hydrolysis by Fe^{2+}[6] may contribute to the relatively rapid cluster assembly.

[Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$]$^{3-}$ can also be synthesized in aqueous buffer by using molybdate in place of tetrathiomolybdate. Figures 1–3 show results obtained when the rhodanese/thiosulfate/thiol system was used as the source of core sulfide according to eq 1 and method b in the Experimental Section. Prior to addition of rhodanese the spectrum of Figure 1 resembles that of [Fe(SCH$_2$CH$_2$OH)$_4$]$^{2-}$, which we have previously character-
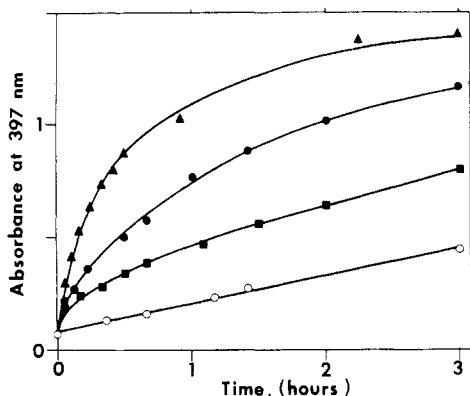
Figure 3. Plots of absorbance at 397 nm vs time for solutions containing 12.5 mM Fe(NH$_4$)$_2$(SO$_4$)$_2$, 4 mM MoO$_4^{2-}$ (as ammonium molybdate), 50 mM Na$_2$S$_2$O$_3$, 214 mM HSCH$_2$CH$_2$OH, and 18 mM dithiothreitol in 0.3 M NaTAPS, pH 9.0, incubated at 25 °C without rhodanese (open circles), or after addition of rhodanese to a concentration of 0.35 (squares), 0.7 (filled circles), or 1.4 (triangles) μM. Final reaction volumes were usually 50 mL. ^{1}H NMR spectra of the reaction products isolated after the longest time point (following addition of *n*-Bu$_4$NI) showed at least 76 mol % [Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$]$^{3-}$ vs [Fe$_4$S$_4$-(SCH$_2$CH$_2$OH)$_4$]$^{2-}$.

ized.[12] Upon addition of rhodanese, a UV–vis absorption spectrum characteristic of [Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$]$^{3-}$ developed in less than 3 h. The spectrum of the control solution shows that very little reaction has occurred over the same time period in the absence of rhodanese. Addition of *n*-Bu$_4$NBr after ∼3 h of reaction yielded a solid, whose ^{1}H NMR spectrum in DMSO-d_6 is shown in Figure 2A. The isotropically shifted resonances near 18 and ∼56 ppm are due to the Mo–SCH_2 and Fe–SCH_2 hydrogens, respectively, of [Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$]$^{3-}$.[11] The weak resonance at ∼12 ppm signifies contamination by [Fe$_4$S$_4$(SCH$_2$CH$_2$OH)$_4$]$^{2-}$.[4] From integrations of the 18 (due to six equivalent hydrogens) and 12 ppm (due to eight equivalent hydrogens) resonances in this latter spectrum, a mole ratio of [Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$]$^{3-}$ to [Fe$_4$S$_4$(SCH$_2$CH$_2$OH)$_4$]$^{2-}$ of 9:1 was calculated. When all other conditions were held constant, and the concentrations of HSCH$_2$CH$_2$OH was lowered from 210 mM (method b) to 140 mM, the spectral time course (not shown) had a lower overall absorbance and lower final ratio of A_{277}/A_{380}. These lower values are consistent with greater contamination by [Fe$_4$S$_4$(SCH$_2$CH$_2$OH)$_4$]$^{2-}$ (A_{296}/A_{374} = 1.35, ϵ_{374} = 15 400 M^{-1} cm^{-1}.[13] In this case addition of *n*-Bu$_4$NBr after ∼3 h of reaction yielded a solid whose ^{1}H NMR spectrum is shown in Figure 2B. Integrations of the appropriate resonances indicated a mole ratio of [Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$]$^{3-}$ to [Fe$_4$S$_4$(SCH$_2$CH$_2$OH)$_4$]$^{2-}$ of 1.8:1. On the basis of several additional comparisons of UV–vis absorption spectra with ^{1}H NMR spectra, the unrecrystallized solids obtained by our procedure are representative of the mole ratio of [Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$]$^{3-}$ to [Fe$_4$S$_4$-(SCH$_2$CH$_2$OH)$_4$]$^{2-}$ in solution at ≥3 h of reaction. Further lowering of the concentration of HSCH$_2$CH$_2$OH to 70 mM yielded a solid whose ^{1}H NMR spectrum (Figure 2C) indicates that the mole ratio now greatly favors [Fe$_4$S$_4$(SCH$_2$CH$_2$OH)$_4$]$^{2-}$ over [Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$]$^{3-}$. Figure 2 pictorially represents an important result, namely, *higher thiol concentrations favor obtainment of* [*Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$*]$^{3-}$ *over* [*Fe$_4$S$_4$-(SCH$_2$CH$_2$OH)$_4$*]$^{2-}$. Presumably this dependence reflects the requirement for either a two- or three-electron reduction of molybdenum on passing from MoO$_4^{2-}$ to [Mo$_2$Fe$_6$S$_8$-(SCH$_2$CH$_2$OH)$_9$]$^{3-}$.[3]

Figure 3 shows that the reaction rate, as judged by absorbance at 397 nm, increased as the concentration of rhodanese was increased. Figure 3 also illustrates that the rates of formation and yields of [Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$]$^{3-}$ and [Fe$_4$S$_4$-(SCH$_2$CH$_2$OH)$_4$]$^{2-}$ were much lower when rhodanese was omitted.[14] The results of Figures 1–3 are representative of an extensive set of experiments whose results are tabulated in the supplementary material. These latter results include substitution of D,L-dihydrolipoate for dithiothreitol and also ferric salts for ferrous salts. Omission of dithiol resulted in somewhat lower mole ratios of [Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$]$^{3-}$ to [Fe$_4$S$_4$-(SCH$_2$CH$_2$OH)$_4$]$^{2-}$ and lower rates, but not lower overall yields. Substitution of solid sulfur (20 mM) for rhodanese/thiosulfate also resulted in lower mole ratios of [Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$]$^{3-}$ to [Fe$_4$S$_4$(SCH$_2$CH$_2$OH)$_4$]$^{2-}$ as well as lower rates and yields. *Under our conditions, no* [*Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$*]$^{3-}$ *was obtained when 20–90 mM sodium sulfide was substituted for rhodanese/thiosulfate.* Lowering the starting concentration of Fe^{2+} from 12 to 6 mM did not affect this result. In these sulfide-containing reaction mixtures [Fe$_4$S$_4$(SCH$_2$CH$_2$OH)$_4$]$^{2-}$ formed rapidly and in high yield when sufficiently high concentrations of HSCH$_2$CH$_2$OH (360 mM) and dithiol (20 mM) were used, whereas intractable black solids (presumably FeS) often formed in the absence of dithiol. These effects, which we have observed previously,[4] are presumably due to complexation of Fe^{2+} by thiolate.

Summary and Conclusions

The salient results of this work are that [Mo$_2$Fe$_6$S$_8$-(SCH$_2$CH$_2$OH)$_9$]$^{3-}$ in aqueous solution (i) spontaneously and rapidly self-assembles in high yield from ferrous salts, tetrathiomolybdate, and 2-mercaptoethanol, (ii) can use molybdate (plus an appropriate core sulfide donor) as the source of molybdenum in place of tetrathiomolybdate, (iii) can use thiosulfate as the source of core sulfide with the rate and yield of assembly *greatly* enhanced in the presence of catalytic concentrations of the sulfurtransferase rhodanese,[15] (iv) *cannot* use Na$_2$S as a source of core sulfide under our conditions, and (v) assembles concurrently with [Fe$_4$S$_4$(SCH$_2$CH$_2$OH)$_4$]$^{2-}$ whose proportion can be varied in a controlled fashion; e.g., higher thiol concentrations favor formation of [Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$]$^{3-}$. These results, together with our previous results,[4,6] delineate the development of a tractable and flexible system for explorations of the factors governing assembly of biological Fe–S and Mo–Fe–S clusters and for reconstitutions of such centers in proteins.

Supplementary Material Available: A plot of the UV–vis absorption–time course for the reaction of (NH$_4$)$_2$MoS$_4$, FeCl$_2$, and HSCH$_2$CH$_2$OH in 0.2 M Tris–sulfate, pH 9.1, and a table listing mole ratios, overall yields, and rates of formation of [Mo$_2$Fe$_6$S$_8$(SCH$_2$CH$_2$OH)$_9$]$^{3-}$ and [Fe$_4$S$_4$(SCH$_2$CH$_2$OH)$_4$]$^{2-}$ using MoO$_4^{2-}$ under various conditions (3 pages). Ordering information is given on any current masthead page.

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(14) Because of long reaction times (>14 h) and low yields, the extents of reaction at the lowest and zero rhodanese concentrations were difficult to quantitate. Under the conditions of Figure 3 rhodanese appears to be gradually inactivated over the course of several hours. Omission of iron leads to production of MoS$_4^{2-}$, but on a time scale much slower than that depicted in Figures 1 or 3. For these reasons, we have been unable to further delineate the role of rhodanese (including its reaction order) in cluster assembly.

(15) In this regard we note the recent report that the iron–molybdenum cofactor of nitrogenase contains one or more thiosulfate-like moeities in addition to bridging sulfides.[16]

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