Preparation and Solution Properties of Chalcogenide-Rich Clusters $[Mo_3Y_7(H_2O)_6]^{4+}$ (Y = S, Se): Kinetics of PR_3^{3-} Abstraction of Y from μ-(Y_2^{2-}) and H_2O Substitution by Cl^- and Br^-

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The chalcogenide-rich trinuclear Mo^{IV}_3 clusters $[Mo_3Y_7(H_2O)_6]^{4+}$, containing single μ_3-(Y^{2-}) and three μ-(Y_2^{2-}) core ligands, have been obtained for the first time from polymeric $\{Mo_3Y_7Br_4\}_x$ via $[Mo_3Y_7Br_6]^{2-}$ (Y = S, Se). ICP analyses of 2 M HCl solutions give Mo:S and Mo:Se ratios consistent with the formulas indicated, and on reaction with concentrated HBr, 85% recovery of $(Et_4N)_2[Mo_3S_7Br_6]$, the structure of which is known, has been achieved. Abstraction of S and Se with PPh_3 (two-phase system), or the water-soluble phosphine $(3\text{-}SO_3C_6H_4)_3P^{3-}$ (PR_3^{3-}), gives quantitative formation of $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_3Se_4(H_2O)_9]^{4+}$. With CN^-, both abstraction of S (or Se) and CN^- replacement of H_2O is observed, giving $[Mo_3S_4(CN)_9]^{5-}$ and $[Mo_3Se_4(CN)_9]^{5-}$ as products. It was possible to assign which atom of the sideways η^2,η^2 μ-(S_2^{2-}) and μ-(Se_2^{2-}) ligands is abstracted using the structurally characterized $[Mo_3S_4Se_3(H_2O)_6]^{4+}$ cluster. Thus it was demonstrated that with the phosphines the equatorial (to the Mo_3 plane) Se atoms of the three μ-(SSe^{2-}) groups are removed with formation of the $Mo_3S_4^{4+}$ core. Kinetic studies on the reactions of $[Mo_3S_7(H_2O)_6]^{4+}$ and $[Mo_3Se_7(H_2O)_6]^{4+}$ with PR_3^{3-} give $\sim 10^3$ faster abstraction rate constants (k_a/M^{-1} s^{-1}) for S than Se. The rate law $k_a = k_1[H^+] + k_{-1}[H^+]^{-1}$ is explained by the involvement of protonated μ-(Y_2^{2-}) (k_1) and an H_2O conjugate-base form (k_{-1}). Equilibration rate constants for $X^- = Cl^-$ and Br^- substitution of H_2O on $[Mo_3S_7(H_2O)_6]^{4+}$ and $[Mo_3Se_7(H_2O)_6]^{4+}$ are however independent of $[H^+]$ in the range 0.5−2.0 M investigated. With X^- concentrations up to 1.3 M (S cluster) and 0.3 M (Se), the uniphasic reactions are assigned as substitution of the H_2O cis to μ_3-(Y^{2-}) at each Mo. At 25 °C formation rate constants 10^4k_f/M^{-1} s^{-1} are as follows for $[Mo_3S_7(H_2O)_6]^{4+}$: Cl^- (1.83); Br^- (2.07). The same rate constants are as follows for $[Mo_3Se_7(H_2O)_6]^{4+}$: Cl^- (6.7); Br^- (33). Formation rate constants for Cl^- are surprisingly 2×10^6 times slower than for the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with Cl^-. Reactions of $Mo_3S_7^{4+}$ with three metals (Sn, Ni, In) were studied briefly.

Introduction

The Mo^{IV}_3 incomplete cuboidal cluster $[Mo_3S_4(H_2O)_9]^{4+}$ with a vacant metal subsite, first characterized in the 1980's,[1−4] has been extensively studied.[5−7] In acidic solutions the aqua ion is noted for its high stability over long periods (years!), with no tendency to lose core atoms or undergo redox changes. The selenium-containing analogue $[Mo_3Se_4(H_2O)_9]^{4+}$ has also been fully characterized.[8,9] In this paper we report the preparation of new chalcogenide-rich Mo^{IV}_3 clusters $[Mo_3S_7(H_2O)_6]^{4+}$ and $[Mo_3Se_7(H_2O)_6]^{4+}$ from polymeric chain compounds $\{Mo_3Y_7Br_4\}_x$ via the single clusters $[Mo_3Y_7Br_6]^{2-}$ (Y = S, Se). Procedures for the conversion of $\{Mo_3Y_7Br_4\}_x$, obtained by direct combination of the elements, into $[Mo_3Y_7Br_6]^{2-}$ have been described.[10−12] An X-ray structure of $(Ph_4P)_2[Mo_3S_7Cl_6]$ has been reported, and $(Ph_4P)_2[Mo_3S_7Br_6]$ is known to be isostructural.[13] Both clusters have a single μ_3-sulfido and three μ-disulfido bridging ligands orientated as in Figure 1. Each disulfido group bridges two Mo's in a sideways η^2:η^2 manner

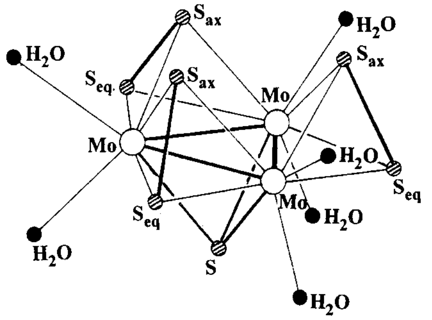

Figure 1. Structure representation of $[Mo_3S_7(H_2O)_6]^{4+}$ based on that of $[Mo_3S_7Br_6]^{2-}$ determined by X-ray crystallography.

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1997.

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with one atom equatorial and the other axial to the Mo_3 plane, distances Mo−S_{eq} 2.5 Å and Mo−S_{ax} 2.4 Å.[14] There are two nonidentical terminal ligands (H_2O in the present studies) to each Mo, which are cis and trans respectively to the μ_3-(S^{2-}) ligand. The structure of $[Mo_3Se_7(dtc)_4]$ (dtc = diethyldithiocarbamate) has also been determined,[11] and a similar core structure is indicated. We explore here the aqueous solution chemistry of the chalcogenide-rich $[Mo_3Y_7(H_2O)_6]^{4+}$ clusters, making comparisons in particular with $[Mo_3Y_4(H_2O)_9]^{4+}$, which has three terminal H_2O's to each Mo.

Experimental Section

Starting Materials. To prepare the polymeric chain compounds $\{Mo_3Y_7Br_4\}_x$ the elements were heated in a glass ampule made from Mo glass or quartz, with diameter ~2 cm, volume ~40 mL, and wall ~1 mm thick. Typical amounts were Mo (4 g), Se (7.44 g), and Br_2 (1.44 mL). The Br_2 must first be dried over concentrated H_2SO_4. The ampule was placed in a variable-temperature oven at 340−380 °C for at least 48 h. The temperature was raised gradually to 150 (~3 h), 200 °C (~3 h), etc., and the ampule was contained in a steel tube for safety. The compound $(Et_4N)_2$ $[Mo_3S_7Br_6]$ was prepared from $\{Mo_3S_7Br_4\}_x$ by first converting to $(NH_4)_2[Mo_3S_{13}]$ and then treating with concentrated HBr and Et_4NBr as described.[10] For the Se analogue $\{Mo_3Se_7Br_4\}_x$ and PPh_4Br (2 g per 1 g of complex) were melted together at 250 °C and heated for ~3 h under N_2 to obtain $(Ph_4P)_2[Mo_3Se_7Br_6]$.[11] The solid was powdered and washed with hot EtOH. The mixed S- and Se-containing cluster $(Et_4N)_2[Mo_3S_4Se_3Br_6]$ was prepared by reacting $(Et_4N)_2[Mo_3S_7Br_6]$ with Ph_3PSe (replacement of S on S_2^{2-} by Se) as described.[15] All reactions were carried out in a fumehood.

Other Reagents. These included *p*-toluenesulfonic acid (Hpts) ($CH_3C_6H_4SO_3H$), lithium carbonate (Li_2CO_3), triphenylphosphine, HBr (all from Aldrich), HCl (Fisons), and the water-soluble salt of tris(3-sulfonatophenyl)phosphine, $Na_3[(3\text{-}SO_3C_6H_4)_3P]\cdot 4H_2O$ (Strem Chemicals), here abbreviated to PR_3^{3-}, all of which were used as supplied. The latter contains 10.3% phosphine oxide,[16] which is nonreactive and was allowed for in determining concentrations of PR_3^{3-} made up by weight. Solution of Li(pts) were prepared by Li_2CO_3 neutralization of Hpts and recrystallizing. All other chemicals used were of analytical grade purity. Metals used were tin (~3 mm diameter shot; Aldrich), nickel (1 mm diameter wire; Wiggin), and indium (3 mm diameter wire; Johnson Matthey).

Elemental Analyses. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analyses for Mo and S or Se were carried out on 2 M HCl solutions.

Kinetic Studies. The temperature was 25.0 ± 0.1 °C, and *I* was adjusted to 2.00 ± 0.01 M (Lipts) for all runs. Solutions of $[Mo_3S_7(H_2O)_6]^{4+}$ and $[Mo_3Se_7(H_2O)_6]^{4+}$ were stored under N_2, to avoid a slow reaction with O_2. Kinetic runs could be carried out in air and were in agreement with experiments carried out under N_2. Stock solutions were eluted in ≥2.0 M Hpts, which limited the lower range of $[H^+]$ that could be explored. Stopped-flow time−range experiments (reactions with PR_3^{3-}) were carried out on Dionex-D110 and Applied Photophysics instruments. The latter (shorter mixing time) was essential for the faster $[Mo_3S_7(H_2O)_6]^{4+}$ studies. Rate constants were obtained on the Dionex stopped-flow using fitting procedures from On-Line Instrument Systems (OLIS, Bogart, GA) and on the Applied Photophysics instrument using a multitask software package as supplied. Individual rate constants quoted are an average of at least five traces. Conventional studies (Cl^- and Br^- substitution) were performed using a Philips-Unicam PU 8740 spectrophotometer.

Treatment of Rate Constants. Unweighted linear least-squares fitting procedures were used.

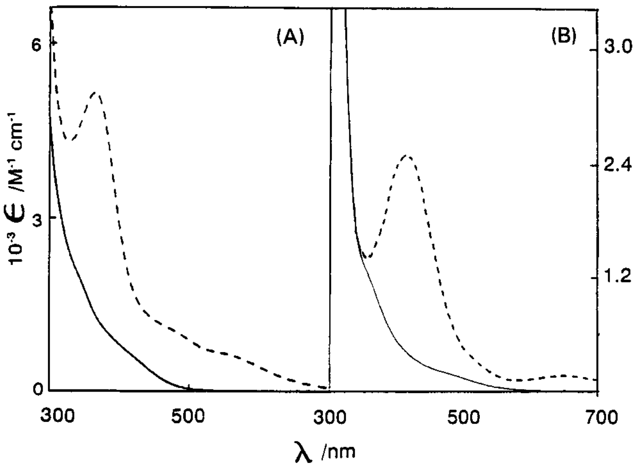

Figure 2. UV−vis spectra of (a) $[Mo_3S_7(H_2O)_6]^{4+}$ (—) and $[Mo_3S_4(H_2O)_9]^{4+}$ (- - -) and (b) $[Mo_3Se_7(H_2O)_6]^{4+}$ (—) and $[Mo_3Se_4(H_2O)_9]^{4+}$ (- - -) in 2.0 M Hpts.

Results

Preparation and Characterization of $Mo_3S_7(H_2O)_6]^{4+}$. The procedure used was to aquate the dark brick-red $(Et_4N)_2[Mo_3S_7Br_6]$ salt (0.2 g)[10] in 4 M *p*-toluenesulfonic acid (Hpts; 25 mL) for 3 h at room temperature, when a clear yellow solution was obtained.[17] This was diluted with a 3-fold volume of water and loaded onto a Dowex 50W-X2 cation-exchange resin. The compact band formed was eluted as a lemon yellow solution with ≥2 M Hpts, consistent with a 4+ charge. ICP-AES analyses on a sample eluted with 2 M HCl gave an Mo:S ratio of 3:7.3. UV−vis absorbance spectra, confirmed by quantitative conversion to $[Mo_3S_4(H_2O)_4]^{4+}$ as in (1) below, gave shoulders only at λ/nm (ε/M^{-1} cm^{-1} per Mo_3) ~350 (1800) and ~425 (500), Figure 2. Beer's Law is obeyed at 350 nm with concentrations in the range 0.06−1.9 mM investigated. Stock solutions of $[Mo_3S_7(H_2O)_6]^{4+}$ (3−4 mM) are stable for several weeks in 2.0 M Hpts or HCl under N_2 and give only ~10% decay over 12 h in air at ~20 °C. However in 2.0 M $HClO_4$ a more rapid decay is observed, yielding a precipitate which is most likely sulfur.

To characterize the $[Mo_3S_7(H_2O)_6]^{4+}$ product a solution in 2.0 M Hpts was stirred with 5% triphenylphosphine, PPh_3, in dichloromethane (5 mL). Reaction is fast, and the color becomes green in less than 1 min. The organic layer was removed, the green aqueous solution diluted 5-fold with water, and the product loaded onto a Dowex 50W-X2 column (15 × 1.2 cm diameter). After washing with 0.2 M acid (200 mL), elution was with the same 2.0 M acid. The conversion could also be achieved using the water-soluble phosphine PR_3^{3-} (R = 3-sulfonatophenyl), as the sodium salt $Na_3[(3\text{-}SO_3C_6H_4)_3P]\cdot 4H_2O$. In both cases the product was the well-characterized $[Mo_3S_4(H_2O)_9]^{4+}$, with UV−vis absorbance peak positions [λ/nm (ε/M^{-1} cm^{-1} per Mo_3)] 366 (5550) and 603 (362) in 2.0 M Hpts, Figure 2, indicating an S-abstraction process as in (1), with formation of triphenylphosphine sulfide.

$$Mo_3S_7^{\ 4+} + 3PR_3^{\ 3-} \rightarrow Mo_3S_4^{\ 4+} + 3SPR_3^{\ 3-} \qquad (1)$$

It was also possible to convert the $[Mo_3S_7(H_2O)_6]^{4+}$ product into the previously characterized $[Mo_3S_4(CN)_9]^{5-}$ by reloading onto a Dowex column (10 × 1.2 cm diameter) and after washing with H_2O (200 mL) eluting with 0.1 M KCN. The product was identified as $[Mo_3S_4(CN)_9]^{5-}$ from the UV−vis peaks at

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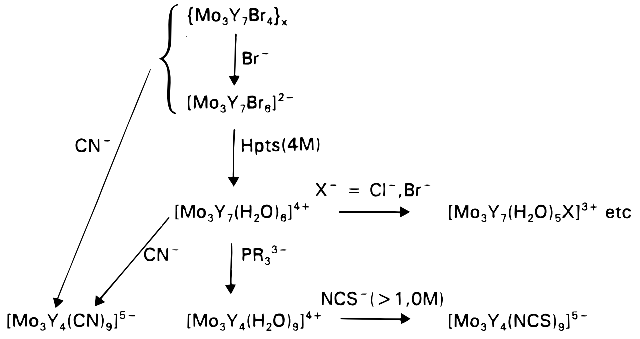
Scheme 1



247 (17 000), 280 sh, 342 (4500), 377 (5500), and 610 (500).[1] The reaction involves core S_2^{2-} abstraction (eq 2) and substitution of H_2O ligands by CN^-. Similar conversions can be carried out by treating a suspension of $\{Mo_3S_7Br_4\}_x$ (1 g in 10 mL of H_2O), or a solution of $[Mo_3S_7Br_6]^{2-}$, with KCN (1 g) for ~60 min. Reactions are summarized in Scheme 1. On addition of SCN^- (0.1 M) to $[Mo_3S_7(H_2O)_6]^{4+}$ in Hpts side reactions contribute and a cream-colored precipitate (most likely sulfur) is formed. This compares with addition of NCS^- (1 M) to $[Mo_3S_4(H_2O)_9]^{4+}$, when formation of $[Mo_3S_4(NCS)_9]^{5-}$ is observed in a clean reaction.

$$Mo_3S_7^{4+} + 3CN^- \rightarrow Mo_3S_4^{4+} + 3SCN^- \qquad (2)$$

Retention of the Mo_3S_7 core was confirmed by eluting the aqua ion with 2 M HBr, evaporating to dryness on a vacuum line, and redissolving in concentrated HBr. Only under these extreme conditions do six bromides coordinate. Addition of excess Et_4NBr resulted in the formation of orange crystals of $(Et_4N)_2[Mo_3S_7Br_6]$ (85% yield),[10] which was characterized by its infrared spectrum.

Preparation and Characterization of $[Mo_3Se_7(H_2O)_6]^{4+}$. A similar procedure applies involving in this case the aquation of brown $(PPh_4)_2[Mo_3Se_7Br_6]$ (0.5 g)[11] in 4 M Hpts (25 mL) for 10 h at room temperature. On filtration an orange solution was obtained which was diluted 5-fold with H_2O and loaded onto a Dowex 50W-X2 cation-exchange column. The compact band formed was eluted as an orange solution with 4 M Hpts. Elution was also possible with 2 M HCl. ICP analyses on the latter gave a ratio Mo:Se of 3:6.8 consistent with $[Mo_3Se_7(H_2O)_6]^{4+}$. UV−vis spectra gave shoulders at ~370 (1150) and ~480 (200), Figure 2. Solutions were stable in air for a few hours, but over longer periods red selenium was deposited. Solutions were stable under N_2 at ~20 °C for several weeks (<10% decomposition). Beer's law was obeyed at ~430 nm for solutions in the range 0.10−0.70 M investigated. Solutions of $[Mo_3Se_7(H_2O)_6]^{4+}$ were converted into $[Mo_3Se_4(H_2O)_9]^{4+}$ by procedures as described for $[Mo_3S_7(H_2O)_6]^{4+}$. The reactions with the phosphines are appreciably slower; e.g., with PPh_3 40 min is required. UV−vis peaks for $[Mo_3Se_4(H_2O)_9]^{4+}$ in 2 M Hpts are at 425 (2460) and 648 (263), Figure 2. Spectra exhibit a red shift on replacing S by Se as has been observed previously for Se-substituted [2Fe−2S] proteins.[18] Elution of $[Mo_3Se_7(H_2O)_6]^{4+}$ from a Dowex column with 0.1 M KCN gives conversion to $[Mo_3Se_4(CN)_9]^{5-}$, with UV−vis peak positions 350 (5070), 443 (5460), and 677 (730). The X-ray structure of $Cs_3[Mo_3Se_4(CN)_9]\cdot CsCl\cdot 4H_2O$ has been determined.[19] Scheme 1 indicated above applies also for Y = Se.

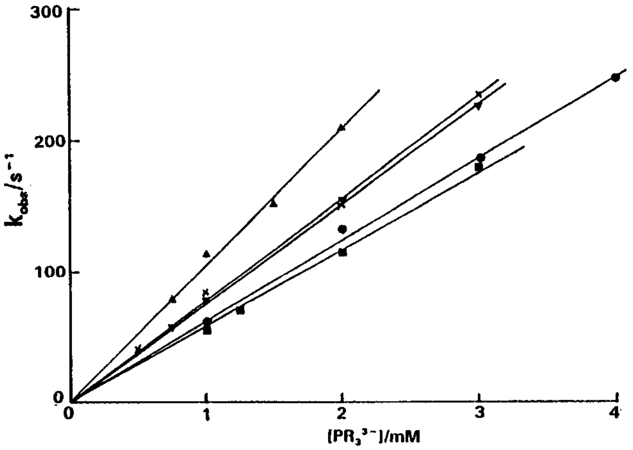


Figure 3. Dependence of first-order rate constants k_{obs} (25 °C) for the reaction of the water-soluble phosphine (PR_3^{3-}) with $[Mo_3S_7(H_2O)_6]^{4+}$ on $[PR_3^{3-}]$ (reactant in excess) at $[H^+]$/M = 2.0 (×), 1.5 (●), 1.00 (■), 0.60 (▼), and 0.30 (▲), with I = 2.00 M (Li(pts)).

Table 1. Summary of Second-Order Rate Constants k (25 °C) for the S- and Se-Abstraction Reactions of PR_3^{3-} with $[Mo_3S_7(H_2O)_6]^{4+}$, Y = S and Se [I = 2.00 M (Li(pts))]

Y = S		Y = Se	
$[H^+]$/M	$10^{-4}k_a$/M^{-1} s^{-1}	$[H^+]$/M	k_a/M^{-1} s^{-1}
2.00	7.8(3)	2.00	59(8)
1.50	6.2(2)	1.50	52(3)
1.00	5.9(1)	0.75	74(2)
0.60	7.4(1)	0.60	77(1)
0.30	9.4(5)	0.50	86(8)

Preparation and Reactivity of $[Mo_3S_4Se_3(H_2O)_6]^{4+}$ with PR_3^{3-}. The compound $(PPh_3Et)_2[Mo_3S_4Se_3Cl_6]$[18] has been prepared previously, and an X-ray structure has demonstrated the presence of μ_3-(S^{2-}) and three μ-(SSe^{2-}) core ligands, with Se in the same equatorial plane as the three Mo atoms. In this work the $(Et_4N)_2[Mo_3S_4Se_3Br_6]$ salt was used. On treatment with 4 M Hpts the aqua ion $[Mo_3S_4Se_3(H_2O)_6]^{4+}$ forms, and on reaction of a 4 mM solution (5 mL) with 3% PPh_3 (5 mL) in chloroform, the color becomes green in 1−2 min. After 1 h the green upper layer was separated, and the UV−vis spectrum was shown to be that of $[Mo_3S_4(H_2O)_9]^{4+}$. The same abstraction process is observed on elution of $[Mo_3S_4Se_3(H_2O)_6]^{4+}$ from a cation-exchange column with CN^-, when $[Mo_3S_4(CN)_9]^{5-}$ was identified as the only product from its UV−vis spectrum.

Kinetics of the Reactions of $[Mo_3S_7(H_2O)_6]^{4+}$ and $[Mo_3Se_7(H_2O)_6]^{4+}$ with PR_3^{3-}. Stopped-flow studies were on aqueous pts^- solutions, I = 2.00 M (Lipts), with $[PR_3^{3-}]$ in >10-fold excess of the trinuclear complex. The stoichiometry of the reaction is 3:1, eq 1. Some runs were carried out at less than the 10-fold excess condition in an attempt to detect a back-reaction (not observed). Uniphasic absorbance changes are observed with quantitative formation of $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_3Se_4(H_2O)_9]^{4+}$, respectively. First-order rate constants k_{obs}(25 °C) determined at 366 nm (S) and 425 nm (Se) are listed in the Supporting Information. Runs with $[Mo_3S_7(H_2O)_6]^{4+}$ were fast and at the limit of the stopped-flow range. Linear dependencies as in Figure 3 enable second-order rate constants k_a for the S and Se abstraction processes to be determined, Table 1. Variations of k_a with $[H^+]$ are illustrated in Figure 4. A two-term rate law (3) is suggested. This can be rearranged to (4). For each reaction linear plots of $k_a[H^+]$ against $[H^+]^2$ are obtained (figure in the Supporting Information). From these

$$k_a = k_1[H^+] + k_{-1}[H^+]^{-1} \qquad (3)$$

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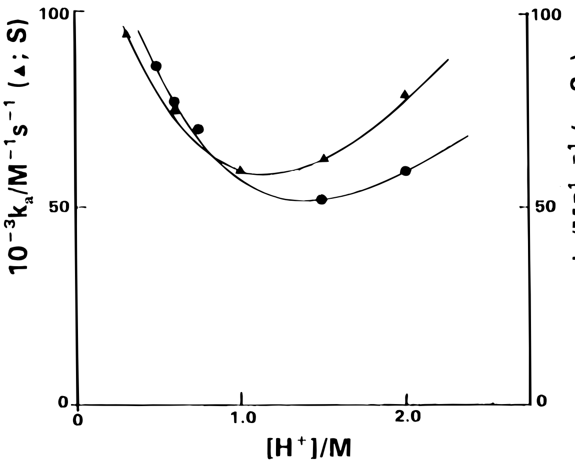

Figure 4. Variation of second-order rate constants k_a with $[H^+]$ for the PR_3^{3-} chalcogenide-abstraction reactions from $[Mo_3S_7(H_2O)_6]^{4+}$ (▲) and $[Mo_3Se_7(H_2O)_6]^{4+}$ (●), with $I = 2.00$ M (Li(pts)).

$$k_a[H^+] = k_1[H^+]^2 + k_{-1} \tag{4}$$

$k_1 = 3.14(15) \times 10^4\ M^{-2}\ s^{-1}$ and $k_{-1} = 2.78(48) \times 10^4\ s^{-1}$ for $[Mo_3S_7(H_2O)_6]^{4+}$ and $k_1 = 19.0(13)\ M^{-2}\ s^{-1}$ and $k_{-1} = 40(4)\ s^{-1}$ for $[Mo_3Se_7(H_2O)_6]^{4+}$. We cannot entirely exclude contributions from a term independent of $[H^+]$ to (3), but k_1 and k_{-1} have different origins, and the best fit of data is according to (4). For consistency with the statistical factor approach adopted elsewhere, rate constants have been divided by a factor of 3 to allow for concurrent reaction at three identical S_2^{2-} (or Se_2^{2-}) centers.[5,20] From four runs, $[PR_3^{3-}]$ in the range 0.72−1.44 mM, k_a for the reaction of $[Mo_3S_4Se_3(H_2O)_7]^{4+}$ with PR_3^{3-} is $1.48(4) \times 10^5\ M^{-1}\ s^{-1}$ in 2.0 M Hpts.

Kinetics of Cl^- and Br^- Substitution on $[Mo_3S_7(H_2O)_6]^{4+}$ and $[Mo_3Se_7(H_2O)_6]^{4+}$. Experiments already referred to, and those reported in ref 21, indicate three identical cis H_2O's at which complexation is more favorable than for the trans H_2O's. Consistent with these observations uniphasic absorbance changes were observed and monitored by conventional UV−vis spectrophotometry. The dependence of equilibration rate constants k_{eq} at 25 °C (for listing see Supporting Information) with halide (X^-) concentrations to 1.3 M (S) and 0.3 M (Se), as illustrated in Figure 5. The shape of UV−vis spectra does not change on complexing with X^- (the two shoulders are retained, Figure 2), consistent with retention of Mo_3S_7 and Mo_3Se_7 core structures. The linear dependencies in Figure 5 define formation (k_f) and aquation rate constants (k_{aq}) (eq 5). UV−vis absorbance

$$k_{eq} = k_f[X^-]/3 + k_{aq} \tag{5}$$

changes were not large enough to monitor reactions with the clusters in ≥10-fold excess of $[X^-]$. However since three cis H_2O's participate in the first phase of reaction at $I = 2.00$ M (Li(pts)), a statistical factor of 3 is included in (5), consistent with procedures established previously for substitution on e.g. $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_4S_4(H_2O)_{12}]^{5+}$.[5,20] Values of k_f and k_{aq} are listed in Table 2. No evidence was obtained for substitution at the more inert trans H_2O ligands at the $[X^-]$ values used in this study.

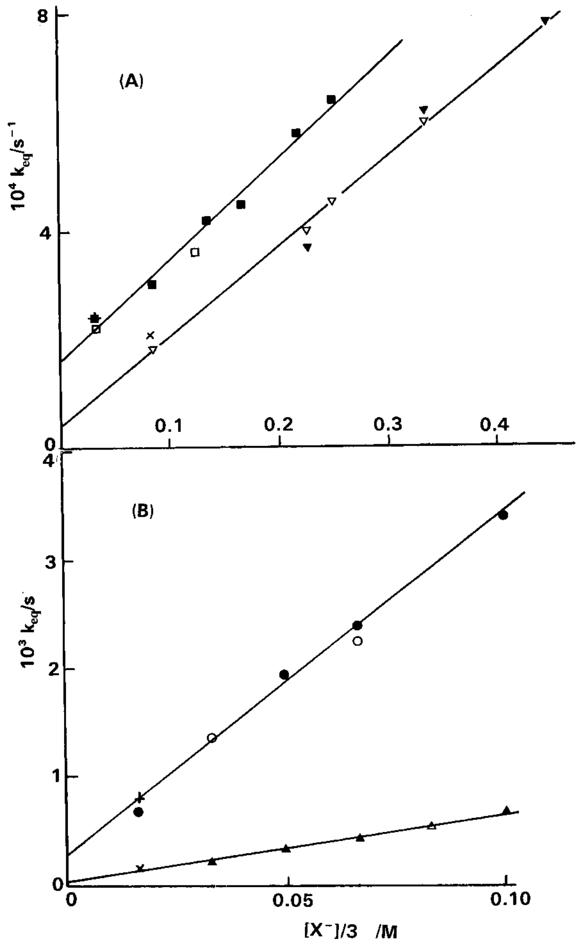

Figure 5. Dependence of equilibration rate constants k_{eq} (25 °C) on halide (X^-) concentration (reactant in excess) for the reaction of (A) $[Mo_3S_7(H_2O)_6]^{4+}$, $X^- = Cl^-$, with $[H^+]/M = 2.00$ (▼), 1.00 (▽, and 0.50 (×) and, $X^- = Br^-$, with $[H^+]/M = 2.00$ (■), 1.00 (□), and 0.50 (+), $I = 2.00$ M (Li(pts)), and (B) $[Mo_3Se_7(H_2O)_6]^{4+}$, $X^- = Cl^-$, with $[H^+]/M = 2.00$ (●), 1.00 (○), and 0.50 (×) and, $X^- = Br^-$, with $[H^+]/M = 2.00$ (●), 1.00 (○), and 0.50 (+), $I = 2.00$ M (Li(pts)).

Table 2. Summary of Formation (k_f) and Aquation (k_{aq}) Rate Constants at 25 °C from Equilibration Substitution of Cl^- and Br^- for H_2O on $[Mo_3S_7(H_2O)_6]^{4+}$ and $[Mo_3Se_7(H_2O)_6]^{4+}$ [$I = 2.00$ M (Li(pts))]

reacn	$10^4k_f/M^{-1}\ s^{-1}$	$10^4k_{aq}/s^{-1}$	$k_f/k_{aq}/M^{-1}$
$Mo_3S_7^{4+} + Cl^-$	1.83(9)	0.47(24)	3.9
$Mo_3S_7^{4+} + Br^-$	2.07(22)	1.6(2)	1.29
$Mo_3Se_7^{4+} + Cl^-$	6.7(3)	0.38(20)	17.6
$Mo_3Se_7^{4+} + Br^-$	33(1)	2.8(7)	11.8

Other Reactions. Reactions with three metals were investigated under O_2-free conditions (N_2). The reaction of $[Mo_3S_7(H_2O)_6]^{4+}$ with Sn shot gives color changes first to brown (15 min) and then a dark reddish-brown. The reaction was complete in ~8 h when the UV−vis spectrum indicated ~80% formation of $[Mo_6SnS_8(H_2O)_{18}]^{8+}$ with peak positions at 322, 372, and 543 nm.[22]

Reactions of $[Mo_3S_7Br_6]^{2-}$ in 2 M HCl with Ni (20 h at 55 °C) and In wire (15 h at 20 °C), gave 60% $Mo_3NiS_4^{4+}$ and ~100% $Mo_3InS_4^{5+}$, respectively, identified from know UV−vis spectra.[16,23,24] Evolution of H_2S was detected in all three cases, and reduction of μ-(S_2^{2-}) with S−S cleavage is indicated. Heterometal addition occurs in each case to give products previously identified.[7] If instead of a metal with $[Mo_3S_7Br_6]^{2-}$ in 2 M HCl tetrahydroborate BH_4^- is used in an attempt to

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bring about the same μ-(S_2^{2-}) → μ-(S^{2-}) conversion, the yield of $[Mo_3S_4(H_2O)_9]^{4+}$ and related Mo_3S_4 core products is only small (∼3%).

Discussion

The preparation and properties of chalcogenide-rich clusters as the aqua ions $[Mo_3S_7(H_2O)_6]^{4+}$ and $[Mo_3Se_7(H_2O)_6]^{4+}$ are described for the first time. Analyses for Mo:S and Mo:Se ratios by ICP-AES are consistent with the formulas indicated. The structures of $[Mo_3S_7Cl_6]^{2-}$ and $[Mo_3S_7Br_6]^{2-}$ have been determined,[13] and retention of the Mo_3S_7 core in the aqua ion product was confirmed by re-formation of $(Et_4N)_2[Mo_3S_7Br_6]$ (85% yield). The structure of $[Mo_3Se_7(dtc)_4]$ has also been determined.[11] The first complex with an Mo_3Te_7 core has recently been reported as the cyano complex $[Mo_3Te_7(CN)_6]^{2-}$,[25] but no route to the corresponding chloro/ bromo or aqua complexes has yet been identified. The $[Mo_3S_7(H_2O)_6]^{4+}$ and $[Mo_3Se_7(H_2O)_6]^{4+}$ aqua ions are reasonably stable in air but for storage purposes require an inert (N_2) atmosphere. Decay processes are observed on addition of NCS^- to $[Mo_3S_7(H_2O)_6]^{4+}$ in Hpts and for $[Mo_3S_7(H_2O)_6]^{4+}$ in 2 M $HClO_4$, and such conditions were therefore avoided for both the S_7 and Se_7 clusters.

As part of the characterization of $[Mo_3S_7(H_2O)_6]^{4+}$ and $[Mo_3Se_7(H_2O)_6]^{4+}$, reactions with triphenylphosphine (PPh_3) and the water-soluble tris(3-sulfonato-phenyl)phosphine (PR_3^{3-}) were studied. The products $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_3Se_4(H_2O)_9]^{4+}$ were identified from known UV−vis spectra. Elution of $[Mo_3S_7(H_2O)_6]^{4+}$ and $[Mo_3Se_7(H_2O)_6]^{4+}$ from a Dowex cation-exchange column with 0.1 M CN^- also resulted in chalcogenide abstraction, with CN^- replacement of H_2O ligands occurring to give $[Mo_3S_4(CN)_9]^{5-}$ and $[Mo_3Se_4(CN)_9]^{5-}$. These products were likewise identified from their UV−vis spectra.

The mixed-chalcogenide analogue $[Mo_3S_4Se_3(H_2O)_6]^{4+}$ has one μ_3-(S^{2-}) and three μ-(SSe^{2-}) core ligands. An X-ray crystal structure on the precursor complex $[Mo_3S_4Se_3Br_6]^{2-}$ has demonstrated that the Se atoms of the μ-(SSe^{2-}) ligands are equatorial.[15,26,27] Reaction of the aqua ion with PR_3^{3-} gives $[Mo_3S_4(H_2O)_9]^{4+}$ as the sole product, and in the case of $[Mo_3S_7(H_2O)_6]^{4+}$ and $[Mo_3Se_7(H_2O)_6]^{4+}$ abstraction of the equatorial atom of μ-(S_2^{2-}) and μ-(Se_2^{2-}) is therefore proposed. The same conclusion has been arrived at using ^{34}S isotopic labeling on $Mo_3S_7^{4+}$.[10] Thus the precise mechanism of phosphine abstraction is reasonably well established.

There have been no previous kinetic/mechanistic studies on phosphine chalcogenide abstraction reactions from Y_2^{2-}. Uniphasic kinetics are observed for the abstraction reactions $[Mo_3S_7(H_2O)_6]^{4+} \rightarrow [Mo_3S_4(H_2O)_6]^{4+}$ and $[Mo_3Se_7(H_2O)_6]^{4+} \rightarrow [Mo_3Se_4(H_2O)_6]^{4+}$, with PR_3^{3-} the reactant in large excess. Rate laws of the form $k_a = k_1[H^+] + k_{-1}[H^+]^{-1}$ are observed, which are somewhat unusual. Both terms are larger than would normally be observed for medium effects.[28] The k_1 term is therefore assigned to a process involving protonation of S_2^{2-} or Se_2^{2-}. Such a protonation may enhance electrophilic properties, with the protonated form more susceptible to nucleophilic attack by the PR_3^{3-}. The k_{-1} term on the other hand is assigned to acid dissociation of H_2O ligands cis to μ_3-(S^{2-}) or μ_3-(Se^{2-}) (see below), which we suggest has the effect of activating the S_2^{2-} or Se_2^{2-}. Although the range of $[H^+]$ values is quite extensive, no denominator terms corresponding to mass-balance considerations were observed. There is no clear-cut evidence for an $[H^+]$-independent term corresponding to simultaneous protonation and deprotonation on any one cluster. Values of k_1 and k_{-1} indicate ∼10^3 times greater reactivity of the S_7 than Se_7 cluster. This is attributed to different S_2^{2-} and Se_2^{2-} bond strengths and the relative affinities of PR_3^{3-} for S and Se. Surprisingly rate constants for PR_3^{3-} abstraction of Se from $[Mo_3S_4Se_3(H_2O)_6]^{4+}$ are 10 times faster than for S abstraction from $[Mo_3S_7(H_2O)_6]^{4+}$ in 2.0 M Hpts. Since electro-negativities for S and Se are quite similar, it would appear that S−Se bonds are weaker than S−S and Se−Se bonds to explain this increase in reactivity. No corresponding reaction of $[Mo_3Te_7(CN)_6]^{2-}$ with PR_3^{3-} (or CN^-) is observed indicating stronger Te−Te bonds.

The Cl^- and Br^- substitution reactions of one H_2O on each Mo of $[Mo_3S_7(H_2O)_6]^{4+}$ and $[Mo_3Se_7(H_2O)_6]^{4+}$ provide information as to the substitution properties of H_2O ligands. Uniphasic kinetics are observed, and reaction can occur concurrently at three equivalent H_2O's one on each Mo^{IV} as in the case of $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_3Se_4(H_2O)_9]^{4+}$.[5,9,29] No replacement of trans H_2O's is observed at the halide concentrations used in these studies. These observations are supported by the preparation of the partially substituted product $[Mo_3S_7Br_3(NH_2Ph)_3]^+$ from $[Mo_3S_7Br_6]^{2-}$ with three N-donor atoms in the cis position.[21] Selective formation of a single stereoisomer has also been observed in reactions with bidentate S, O donor ligands,[30,31] when the S-donor occupies the cis position. In the present studies concentrated HCl or HBr is required to replace the three remaining trans H_2O's. The inertness of H_2O ligands trans to core μ_3-(S^{2-}) is a well-established feature with $[Mo_3S_4(H_2O)_9]^{4+}$ [29] and applies also in the case of $[Mo_3Se_4(H_2O)_9]^{4+}$.[9] Such effects have not yet been fully explained in terms of electron distribution within the clusters but presumably reflect the different donor properties of the μ_3 and μ_2 core ligands. In the S_4 and Se_4 clusters there are two cis H_2O ligands to each Mo, and formation of a conjugate base at one is able to further enhance substitution at the other. The observation that there are no similar $[H^+]^{-1}$ dependences applying in the case of Cl^- and Br^- substitutions on $[Mo_3S_7(H_2O)_6]^{4+}$ and $[Mo_3Se_7(H_2O)_6]^{4+}$ can accordingly be explained by there being only one cis H_2O to each Mo.

The summary of rate constants, Table 2, indicates that in the case of $[Mo_3S_7(H_2O)_6]^{4+}$ k_f for Br^- is more reactive than Cl^- (but only by 13%). For Se the difference is greater, with Br^- 5 times more effective. Comparisons are possible with substitution at the Ni of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$, when k_f values for Br^- (14.6 $M^{-1}\ s^{-1}$) and Cl^- (9.4 $M^{-1}\ s^{-1}$) give a similar ratio (1.6).[16] The order of magnitude larger equilibrium constants, Table 2, for the softer halide ions (replacing H_2O) on the Se_7 as compared to S_7 cluster (Se softer than S) is consistent with soft−hard acid−base theory.[32]

Other comparisons to be made are with the substitution behavior of $[Mo_3Y_4(H_2O)_9]^{4+}$. Particularly relevant are the rate constants for Cl^- complexing to $[Mo_3S_7(H_2O)_6]^{4+}$ (1.83×10^{-4} $M^{-1}\ s^{-1}$) and $[Mo_3S_4(H_2O)_9]^{4+}$ (91 $M^{-1}\ s^{-1}$),[29] which differ by a factor of ∼2×10^6. Replacement of an H_2O cis to the μ_3-(S^{2-}) occurs in each case with $[Cl^-]$ in the range to 1.3 M.

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A similar ratio applies in the case of Y = Se, based on the Cl^- study in this paper and data for NCS^- substitution on $[Mo_3Se_4(H_2O)_9]^{4+}$.[9] These are remarkable effects of the Y_7 as opposed to Y_4 clusters, indicating that Cl^- is a much less effective nucleophile for the chalcogenide-rich clusters. The equilibrium constant (k_f/k_a) for complexing of Cl^- to $[Mo_3S_7(H_2O)_6]^{4+}$ (3.9 M^{-1}), Table 2, is very similar to that for $[Mo_3S_4(H_2O)_9]^{4+}$ (3.0 M^{-1}).[29] The high electron density on the μ-(S_2^{2-}) ligands of $[Mo_3S_7(H_2O)_6]^{4+}$, which will in part be delocalized onto the metals, appears to inhibit interaction with incoming nucleophiles for both k_f and k_{aq}. A similar but less extensive factor of ~55 has been observed for NCS^- substitution on $[Nb_2(\mu\text{-}S_2)_2(H_2O)_8]^{4+}$ as compared to $[Nb_2(\mu\text{-}S)_2(H_2O)_8]^{4+}$.[33]

Reactions of the $Mo_3S_7^{4+}$ core with three metals (Sn, Ni, In) known to give heterometallic products with $[Mo_3S_4(H_2O)_9]^{4+}$ [16,22−24] were also studied. There are at least two stages to the reactions. These are assigned to a reduction process involving the heterometal, with S−S cleavage and H_2S evolution. The heterometal then reacts with the $[Mo_3S_4(H_2O)_9]^{4+}$ to give products as previously described.[16,22−24] It is not clear whether adducts, e.g. $Mo_3SnS_7^{4+}$, are involved in these changes.

To summarize new chalcogenide-rich clusters $[Mo_3S_7(H_2O)_6]^{4+}$, $[Mo_3Se_7(H_2O)_6]^{4+}$, and $[Mo_3S_4Se_3(H_2O)_6]^{4+}$ have been prepared for the first time. Processes investigated include S and Se abstraction of the equatorial atom of dichalcogenido μ-(Y_2^{2-}) core ligands by phosphine and CN^- to give $[Mo_3Y_4(H_2O)_9]^{4+}$ and $[Mo_3Y_4(CN)_9]^{5-}$ products (Y = S, Se), respectively. Studies on $[Mo_3S_4Se_3(H_2O)_9]^{4+}$, when abstraction of equatorial Se's is observed, indicate the mechanism of abstraction. X-ray crystallographic information also favors equatorial abstraction because in e.g. the Mo_3S_7 core the $Mo-S_{eq}$ distance is 0.1 Å longer than $Mo-S_{ax}$. The $[H^+]$ dependencies of the reactions provide further behavioral insight into the aqueous solution chemistry of these chalogenide-rich clusters. The $[Mo_3S_7(H_2O)_6]^{4+}$ and $[Mo_3Se_7(H_2O)_6]^{4+}$ clusters are both (H_2O) substitution inert ($t_{1/2}$ < 1 min) at 25 °C. Rate constants for Cl^- substitution on the S-rich cluster $[Mo_3S_7(H_2O)_6]^{4+}$ are a very significant $\sim 2 \times 10^6$ times smaller than those observed for $[Mo_3S_4(H_2O)_6]^{4+}$.

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Supporting Information Available: Listings of rate constants for the PR_3^{3-} chalcogenide-abstraction reactions and Cl^- and Br^- substitution reactions and one figure relating to the PR_3^{3-} studies (11 pages). Ordering information is given on any current masthead page.

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