plot for the complex $[(bpy)_2ClRu(pyr)RuCl(bpy)_2]^{3+}$ has been constructed by Meyer et al.[31] In this case, we calculated that the theoretical slope was 3.2 and the measured slope was 4.3. The excellent agreement between theory and experiment for Meyer's experiments and the poor agreement obtained in the present work may be a reflection of the degree of adiabaticity in the systems. In other words, the influence of noncontinuum contributions becomes relatively more important as the degree of electronic coupling between the metal centers decreases. This was also observed in spectral measurements of IT bands performed under high pressures. We have reported[42] the effect of pressure on the IT band of the spiro binuclear complex I. A large red shift occurred as the pressure was increased from 1 to 1500 bar, indicating that significant interactions with the medium were occurring. For a strongly coupled system, the Creutz-Taube ion, II, no shift of the IT band could be observed over this pressure range.[43] Experiments are under way to test the generality of these observations.

II

Acknowledgment. We are grateful to the National Institutes of Health (Grant No. GM 36857) for generous support of this work.

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Solution Properties and Reactivity of the Aqua Ion of the Mo^{IV}_3 Incomplete Cuboidal Mo/S Cluster $[Mo_3S_4(H_2O)_9]^{4+}$

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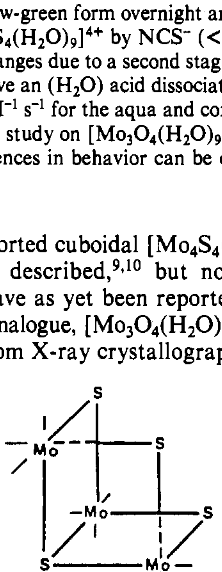
The green sulfido-bridged Mo^{IV}_3 ion $[Mo_3S_4(H_2O)_9]^{4+}$, prepared by decomposition of cuboidal $[Mo_4S_4(H_2O)_{12}]^{5+}$, exhibits solution behavior strikingly different from that of the previously studied red $[Mo_3O_4(H_2O)_9]^{4+}$. It is stable indefinitely in acidic solutions of pH < 1 and, unlike the μ-oxo analogue, does not react overnight with O_2 and ClO_4^-. It does however react (<1 min) with air-free solutions of aqua M^{2+} under reducing conditions ($NaBH_4$ or electrochemical) to yield mixed-metal cuboidal (or related) complexes $[Mo_3MS_4(H_2O)_{10}]^{4+}$ (e.g. M = Fe, Ni, Cu), whereas no corresponding reactions of $[Mo_3O_4(H_2O)_9]^{4+}$ are observed. In this reaction the three exposed μ-sulfido groups of Mo_3S_4 are activated by reduction of Mo^{IV}_3, and M^{2+} is incorporated (order not specified). No permanent electrochemical or chemical reduction of $[Mo_3S_4(H_2O)_9]^{4+}$ is observed, again in contrast to $[Mo_3O_4(H_2O)_9]^{4+}$, which is readily reduced to the Mo^{III}_3, and $Mo^{III}_2Mo^{IV}$ states. Similarly, by reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with $[Mo(H_2O)_6]^{3+}$ in the presence of $NaBH_4$, $[Mo_4S_4(H_2O)_{12}]^{5+}$ can be regenerated. The cube is also regenerated by first converting $[Mo_3S_4(H_2O)_9]^{4+}$ to the double cube $Mo_7S_8^{8+}$ and then leaving it to stand in 2 M HCl for a few days, when the cube and trimer are obtained in equal amounts. With 1 M NCS^- substitution to $[Mo_3S_4(NCS)_9]^{5-}$ occurs and yellow-green and red products can be separated chromatographically. From previous crystallographic studies the yellow-green product is assigned the N-bonded thiocyanato structure. The minority red product (~1% yields after chromatography) converts to the yellow-green form overnight and is possibly an S-bonded isomer. Stopped-flow kinetic studies on the 1:1 substitution of H_2O in $[Mo_3S_4(H_2O)_9]^{4+}$ by NCS^- ($<2 \times 10^{-3}$ M) were monitored at an isosbestic point at 362 nm, thereby avoiding contributions from small changes due to a second stage of reaction, isomerization of S- to N-bonded thiocyanate. The kinetics at 25 °C, $I = 2.00$ M ($LiClO_4$), give an (H_2O) acid dissociation constant $K_a = 0.22$ M for $[Mo_3S_4(H_2O)_9]^{4+}$ and formation rate constants k_1 and k_2 of 108 and 1120 $M^{-1}\ s^{-1}$ for the aqua and conjugate-base forms, respectively, $I = 2.00$ M ($LiClO_4$). These compare with values for the corresponding study on $[Mo_3O_4(H_2O)_9]^{4+}$, $I = 2.00$ M (LiPTS), for which k_2 is 230-fold less and no contribution from k_1 is observed. Differences in behavior can be explained by the electron-rich properties of the μ-S core ligands.

Introduction

The cyano complex $[Mo_3S_4(CN)_9]^{5-}$, obtained by treating $(NH_4)_2[Mo_3S(S_2)_6]$ with excess KCN,[1] was the first Mo_3S_4 core complex to be prepared.[1] Since then, others have been reported,[2-5] including the aqua ion $[Mo_3S_4(H_2O)_9]^{4+}$.[6-8] The procedure for the latter involves heating 1-2 M HCl solutions of cuboidal $[Mo_4S_4(H_2O)_{12}]^{5+}$.[8] The structure has been confirmed as $[Mo_3S_4(H_2O)_9]^{4+}$ by X-ray crystallographic structures on derivative complexes $Ca[Mo_3S_4(ida)_3]\cdot 11.5H_2O$ (ida = iminodiacetate) and $Cs_2[Mo_3S_4(C_2O_4)_3(H_2O)_3]\cdot 3H_2O$.[6,7] Solution properties of the distorted cuboidal $[Mo_4S_4(H_2O)_{12}]^{n+}$ ions (n = 4, 5, 6) have been described,[9,10] but no similar studies on $[Mo_3S_4(H_2O)_9]^{4+}$ have as yet been reported.

The Mo^{IV}_3 μ-oxo analogue, $[Mo_3O_4(H_2O)_9]^{4+}$, has been studied extensively.[11-14] From X-ray crystallography the $Mo_3S_4^{4+}$ and



$Mo_3S_4^{4+}$

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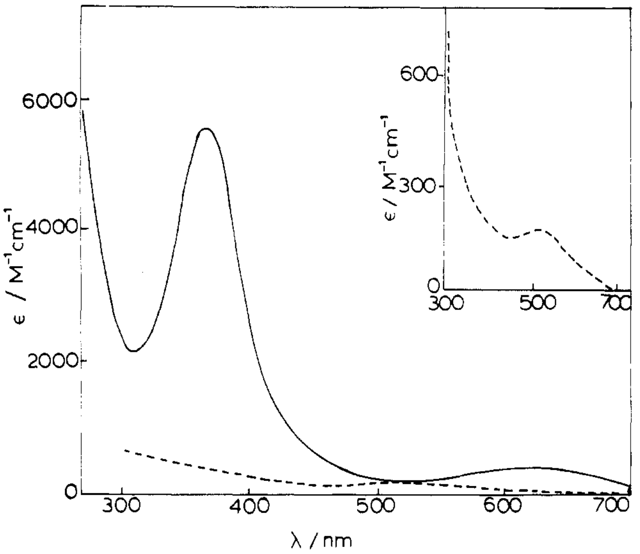

Figure 1. Comparison of UV-visible spectra of $[Mo_3S_4(H_2O)_9]^{4+}$ (—) and $[Mo_3O_4(H_2O)_9]^{4+}$ (- - -) in 3 M HPTS.

$Mo_3O_4^{4+}$ cores are structurally similar, having one μ_3- and three μ-sulfido/oxo ligands, the former apical with respect to the three Mo's.[6,7,12,14] An appropriate description of the trimers is incomplete cuboidal. The Mo^{IV}_3 oxidation state of $Mo_3S_4^{4+}$ is higher than that of the structurally related cuboidal $[Mo_4S_4(H_2O)_{12}]^{n+}$ ions (n = 4, 5, 6), average oxidation states 3, 3.25, and 3.5, respectively.[9,10] Each Mo(IV) of the Mo_3S_4 cluster is in a distorted octahedral coordination. The average Mo–Mo bond length of 2.77 Å[6] is longer than that in $[Mo_3O_4(H_2O)_9]^{4+}$ (2.48 Å).[14]

Experimental Section

Preparation of $[Mo_3S_4(H_2O)_9]^{4+}$. Solutions of cuboidal $[Mo_4S_4(H_2O)_{12}]^{5+}$ (~8 mM) in 2 M HCl were obtained by $NaBH_4$ reduction of the cysteinato bis(μ-sulfido) Mo^V_2 complex $Na_2[Mo_2O_2S_2(cys)_2]\cdot 4H_2O$ as previously described.[8,10] Conversion of cyclic Mo_2S_2 to cuboidal Mo_4S_4 occurs during this reduction. On heating of $[Mo_4S_4(H_2O)_{12}]^{5+}$ in 1–2 M HCl on a steam bath (~90 °C) for 3–4 h, there is essentially quantitative 1:1 formation of $[Mo_3S_4(H_2O)_9]^{4+}$. Solutions of $[Mo_3S_4(H_2O)_9]^{4+}$ were purified by Dowex 50W-X2 cation-exchange chromatography using a short column (4 cm × 1.2-cm diameter). The solution was diluted to 0.5 M acid to exchange onto this column. After loading, the column was washed with 1 M $HClO_4$ (or 0.5 M HCl), which separated $[Mo_3S_4(H_2O)_9]^{4+}$ from any remaining $[Mo_4S_4(H_2O)_{12}]^{5+}$, and the 4+ ion was eluted with 3 M $HClO_4$ (or 2 M HCl). Solutions of $[Mo_3S_4(H_2O)_9]^{4+}$ were standardized spectrophotometrically at the 603-nm peak (ϵ = 362 M^{-1} cm^{-1} per trimer at 25 °C) (see below). Stock solutions were typically 4 mM complex in 3 M $HClO_4$.

Other Reagents. Sodium thiocyanate, 70% perchloric acid (BDH, AnalaR), and *p*-toluenesulfonic acid (HPTS; Sigma) were used as supplied. Lithium perchlorate (Aldrich) was recrystallized twice from water. Concentrations of sodium thiocyanate, perchloric acid, and lithium perchlorate, and the [H$^+$] content of $[Mo_3S_4(H_2O)_9]^{4+}$ stock solutions, were determined by ion-exchange chromatography and/or titration for [H$^+$].

UV–Vis Spectrum. The absorption spectrum of $[Mo_3S_4(H_2O)_9]^{4+}$ in 3 M $HClO_4$ has three absorption maxima λ/nm (ϵ/M^{-1} cm^{-1} per trimer) at 603 (362), 366 (5550), and 248 (8219), on the basis of Mo and S analyses by inductively coupled plasma (ICP) atomic emission spectroscopy (Jobin Yvon JY38 VHR ICP instrument, Servei d Espectroscopic de la Universitat de Barcelona). The spectrum is compared with that of $[Mo_3O_4(H_2O)_9]^{4+}$ (Figure 1).

Electrochemistry. Cyclic voltammetry was carried out on a Princeton Applied Research PAR 173 potentiostat interfaced with an Apple II Europlus microcomputer using a PAR 276 unit. The working electrode was a glassy-carbon disk (Metrohm, 2.5-cm diameter); a Pt wire was used as the counter electrode, and a calomel electrode, as reference. Solutions of $[Mo_3S_4(H_2O)_9]^{4+}$ (~4 mM) in 2 M $HClO_4$ or HPTS were used.

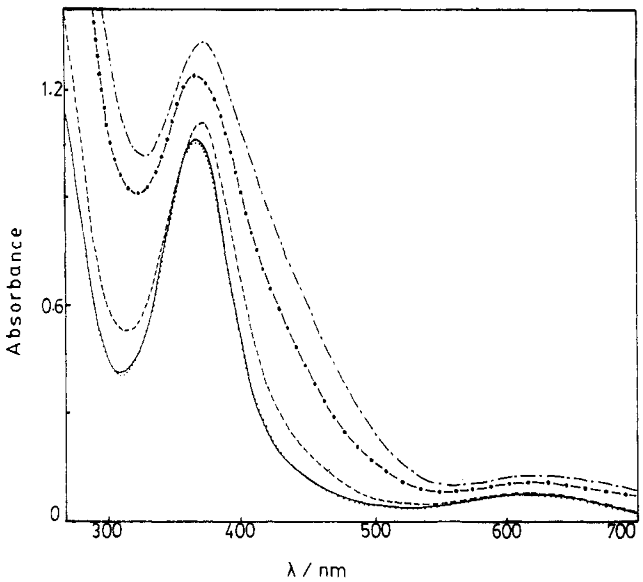

Figure 2. Effect of pH variation on the UV-visible spectrum of $[Mo_3S_4(H_2O)_9]^{4+}$ (~0.02 mM) in aqueous (perchlorate) solutions: [H$^+$] = 0.3–3.0 M (···), 0.1 M (—); pH = 2.3 (- - -), 5.4 (-·-), 6.9 (– – –).

Kinetic Studies. The equilibration of $[Mo_3S_4(H_2O)_9]^{4+}$ with thiocyanate at 25 °C, I = 2.0 M ($LiClO_4$), was studied by using a Dionex D-110 stopped-flow spectrophotometer. With NCS$^-$ in large (>10-fold) excess, and in the range appropriate for 1:1 complex formation, a slower second stage was observed with an isosbestic point at 362 nm (Figure 2). This second stage may be due to isomerization of S- to N-bonded thiocyanate. To minimize contributions from the second step, absorbance changes were monitored at 362 nm. Even at the isosbestic point runs at the higher [NCS$^-$] show some secondary biphasic behavior that becomes more pronounced at the lower [H$^+$]'s. The concentration of NCS$^-$ was restricted to <2 × 10^{-3} M. With the Mo reactant in excess no second stage was observed and many of these runs were monitored at 465 nm. The range of $[Mo_3S_4(H_2O)_9{}^{4+}]$ used (<1 mM) was limited by the concentration of stock solutions. Absorbance–time data were treated "online" by using programs from OLIS (Jefferson, GA).

Treatment of Data. Unweighted linear least-squares programs were used.

Results

Stability. Over >2 weeks in air 2 M HPTS and 2 M $HClO_4$ solutions of $[Mo_3S_4(H_2O)_9]^{4+}$ give no reaction with either O_2 or ClO_4^-. Variations in temperature have (reversible) effects on the UV–vis spectrum. Thus, when the temperature is increased from 10 to 40 °C at [H$^+$] = 2.0 M ($HClO_4$), a 5% decrease in absorbance is observed at 603 nm, and two well-defined isosbestic points are observed at 557 and 673 nm. Such behavior can be attributed to temperature-dependent absorption coefficients (which are rare) and/or chemical changes, in this case acid dissociation or anion complexing. Similar temperature effects are observed with $[Mo_3O_4(H_2O)_9]^{4+}$. Addition of 2 M Cl$^-$ shifts the 603 nm peak to 620 nm with a decrease in ϵ of ~10%.

Attempts were made to determine the acid dissociation constant K_{aM} for $[Mo_3S_4(H_2O)_9]^{4+}$ (eq 1) from spectrophotometric changes

$$Mo_3S_4^{4+} \rightleftharpoons Mo_3S_4(OH)^{3+} + H^+ \qquad (1)$$

with [H$^+$] and $[Mo_3S_4(H_2O)_9{}^{4+}]$ at 0.25 mM, I = 2.0 M ($LiClO_4$). Such a dissociation has been detected in the kinetics described below. However, changes over the range [H$^+$] = 0.1–2.0 M were too small for precise measurements (Figure 3). At pH > 1.2, absorbance changes are too large to be attributed to deprotonation and oligomerization occurs. On adjustment of the pH (slow addition of saturated sodium bicarbonate with efficient stirring), the color changes from green to yellow and over longer periods becomes brown. No precipitation was observed until pH > 7.

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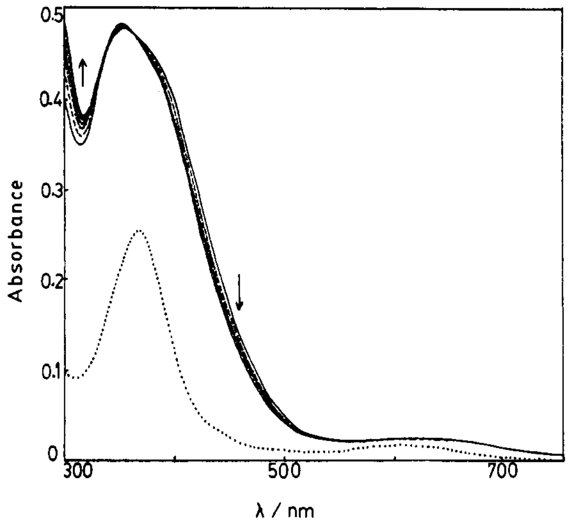
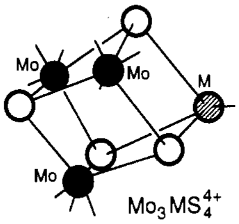


Figure 3. Reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ (4.5 × 10^{-5} M) with NCS^- (2.0 × 10^{-3} M) at 25 °C, I = $[H^+]$ = 2.00 M $HClO_4$. The spectrum (—) recorded after 45 s showed a rapid increase from the initial spectrum (···) with no NCS^- present. Subsequent changes at 1-min intervals (sequence as indicated by arrows) are shown.

Formation of Mixed-Metal Cuboidal Clusters. Rapid (<1 min) color changes are observed on transferring air-free 0.5 M HCl solutions of $[Mo_3S_4(H_2O)_9]^{4+}$ (~5 mM) containing a 10-fold excess of M^{2+} (M = Fe, Ni, Cu) to a flask containing a 100-fold excess of solid $NaBH_4$. Alternatively, in an electrochemical procedure, a constant potential of −0.7 V (vs SCE) can be applied for ~3 h to the same solution in 2 M HPTS (Cl_2 is produced with HCl). A carbon-cloth electrode and electrolytic cell as described in ref 9 were used. The products were loaded onto a Dowex 50W-X2 column. After excess M^{2+} was washed off with 0.5 M HCl, the product can be eluted with 2 M HCl. The whole procedure was carried out under N_2. The colors produced are Fe (gray/purple), Ni (green), and Cu (orange). The reactions can be summarized by (2).

$$Mo_3S_4^{4+} + M^{2+} + 2e^- \rightarrow Mo_3MS_4^{4+} \qquad (2)$$



The products ($Mo_3S_4^{4+}$) are the same as those reported by Shibahara and colleagues for the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with the corresponding metals (eq 3).[15-17]

$$Mo_3S_4^{4+} + M \rightarrow Mo_3MS_4^{4+} \qquad (3)$$

The reverse reactions occur with O_2 (eq 4), when reaction times

$$Mo_3MS_4^{4+} + \tfrac{1}{2}O_2 + 2H^+ \rightarrow Mo_3S_4^{4+} + M^{2+} + H_2O \qquad (4)$$

are minutes for Fe, hours for Ni, and minutes for Cu. Similar reactions occur with Co^{2+} and Hg^{2+} (and the metals) to yield dark brown (Co) and purple (Hg) products. These elute from cation-exchange columns more slowly than $[Mo_3S_4(H_2O)_9]^{4+}$ (whereas the $[Mo_3MS_4(H_2O)_{10}]^{4+}$ ions elute more rapidly), consistent with higher charges. The Hg product has been shown to be a double cube about a central Hg atom[18] and is presumably formed as in (5), although $Mo_3HgS_4^{4+}$ has not yet been characterized.

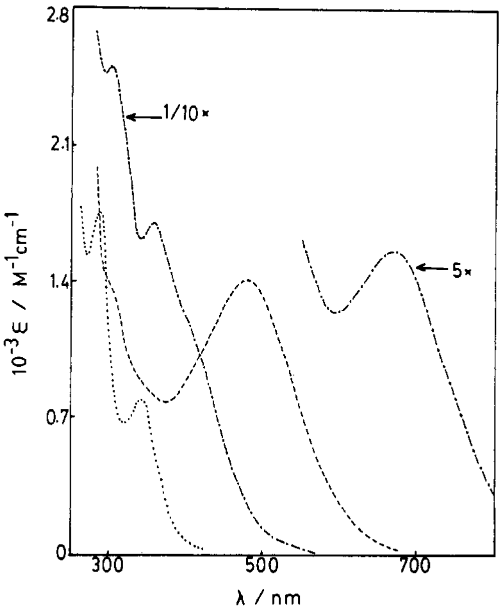
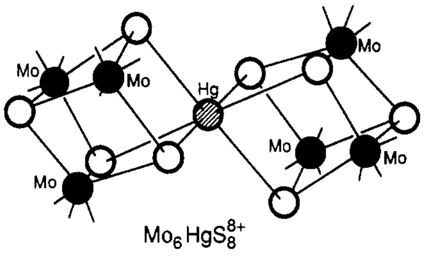


Figure 4. Spectra of the yellow-green (–·–) and red (---) thiocyanato products obtained from the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with 1 M NCS^- followed by column chromatography. The spectrum obtained on further reaction of the red product (to give yellow-green) is also shown (···). Extensive and possibly complete replacement of H_2O by NCS^- is observed under these conditions.



$$Mo_3HgS_4^{4+} + Mo_3S_4^{4+} \rightarrow Mo_6HgS_8^{8+} \qquad (5)$$

Regeneration of $[Mo_4S_4(H_2O)_{12}]^{5+}$ from $[Mo_3S_4(H_2O)_9]^{4+}$. This can be achieved by adopting the above procedure with $NaBH_4$ and using $[Mo(H_2O)_6]^{3+}$ instead of hexaaqua M^{2+}. Concentrated (>0.5 M) $[Mo(H_2O)_6]^{3+}$ was generated from the sodium salt of the formato complex $Na_3[Mo(CO_2CH)_6]$.[19] After mixing with $[Mo_3S_4(H_2O)_9]^{4+}$ in 0.3 M HCl (under N_2), the solution was heated to ~50 °C and transferred to the $NaBH_4$. The reaction can be expressed as in (6). The yield of cuboidal $[Mo_4S_4(H_2O)_{12}]^{5+}$ was ~15% after column chromatography.

$$Mo_3S_4^{4+} + Mo^{3+} + 2e^- \rightarrow Mo_4S_4^{5+} \qquad (6)$$

In a second procedure the trimer $[Mo_3S_4(H_2O)_9]^{4+}$ in 2 M HCl was first converted into the purple double cube $[(H_2O)_9Mo_3S_4MoS_4Mo_3(H_2O)_9]^{8+}$ by addition of Mg to initiate reduction.[20] The same double cube identified by its spectrum λ_{max}/nm (ϵ/M^{-1} cm^{-1} per Mo) at 950 (606), 635 (1266), 518 (1469), 480 (sh, 1295), 416 (1027), and 360 (770) is obtained by addition of $NaBH_4$ (100-fold excess) to a 2–5 mM solution of $[Mo_3S_4(H_2O)_9]^{4+}$, followed by air oxidation. On standing in

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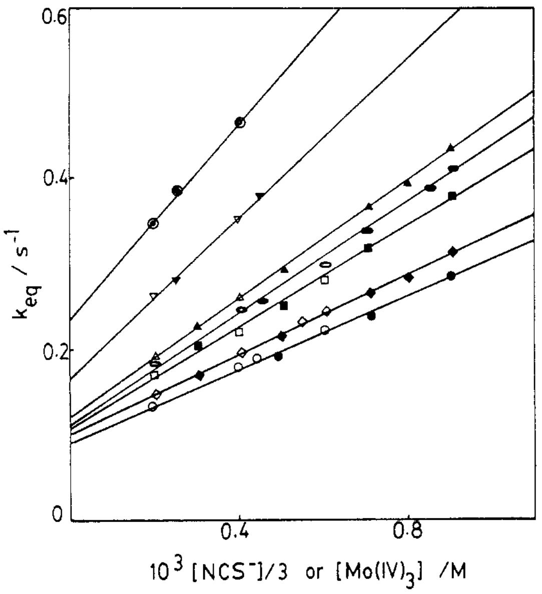

Figure 5. First-order rate constants k_{eq} (25 °C) for the equilibration of $[Mo_3S_4(H_2O)_9]^{4+}$ with NCS^-. Points with NCS^- in excess (open) and Mo in excess (closed) are indicated (I = 2.00 M ($LiClO_4$)): $[H^+]$/M = 0.25 (⊙), 0.40 (▽, ▼), 0.75 (△, ▲), 0.80 (open oval, closed oval), 0.92 (□, ■), 1.50 (◇, ◆), 1.96 M(○, ●).

2 M HCl for a few days (several weeks in 4 M HPTS), solutions of the purple double cube produce equal amounts of green $[Mo_4S_4(H_2O)_{12}]^{5+}$ and $[Mo_3S_4(H_2O)_9]^{4+}$. A possible reaction scheme involves initial production of $[Mo_4S_4(H_2O)_{12}]^{4+}$ as in (7),

$$Mo_7S_8^{8+} \rightarrow Mo_4S_4^{4+} + Mo_3S_4^{4+} \tag{7}$$

which then becomes air oxidized to $[Mo_4S_4(H_2O)_{12}]^{5+}$. Alternatively oxidation may precede breakup of the double cube.

Products of the Reaction with 1 M Thiocyanate. A solution of $[Mo_3S_4(H_2O)_9]^{4+}$ (5 mM in 4 M $HClO_4$; 60 mL) was diluted to $[H^+]$ ~ 0.5 M and loaded onto an ice-cooled Dowex 50W-X2 column (15 cm × 1-cm diameter). After washing with 0.5 M $HClO_4$ (100 mL), slow elution with NCS^- (1 M) in $HClO_4$ (0.1 M) was carried out. Two bands formed, the first a dark yellow-green color (peaks at 299 and 354 nm) and the second red (peak at 475 nm) (Figure 5). Absorption coefficients are based on analyses for Mo by ICP spectroscopy (one determination only for each product). Values for the red product are approximate only. The red band (~1% after elution) turns yellow-green on standing overnight with no further spectrophotometric changes after 2 days. The spectrum obtained (Figure 4) is that of the yellow-green eluted product. In 1 M NCS^- there is extensive and possibly complete replacement of the coordinated H_2O's by NCS^-.

Kinetics of the 1:1 Equilibration with NCS^-. The dependence of first-order equilibration rate constants k_{eq} (Table I) on $[NCS^-]$ and $[Mo_3S_4^{4+}]$ was investigated at $[H^+]$ = 0.25–1.96 M (Figure 5). As in previous studies on $[Mo_3O_4(H_2O)_9]^{4+}$, it is necessary to plot k_{eq} vs $[NCS^-]/3$ so that rate constants agree with those obtained with the $Mo(IV)_3$ reactant in large (10-fold) excess.[21a] In other words, a statistical factor is required, relating to the number of equivalent reaction sites.[21b] With NCS^- in large (10-fold) excess, assuming three equivalent sites, the approach to equilibrium is governed by (8). In the presence of excess

$$k_{eq} = k_f[NCS^-]/3 + k_{aq} \tag{8}$$

$[Mo_3S_4(H_2O)_9]^{4+}$ the relationship (9) holds. Values of k_f and

$$k_{eq} = k_f[Mo_3S_4^{4+}] + k_{aq} \tag{9}$$

k_{aq} for formation and aquation steps, involving $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_3S_4(H_2O)_8(NCS)]^{3+}$, respectively, are listed in Table II.

Table I. First-Order Equilibration Rate Constants k_{eq} (25 °C) for the Reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with NCS^- in Excess Monitored at 362 nm or with $[Mo_3S_4(H_2O)_9]^{4+}$ in Excess at 465 nm, I = 2.00 M ($LiClO_4$)

$[H^+]$, M	$10^3[Mo_3S_4^{4+}]$, M	$10^3[NCS^-]$, M	$10k_{eq}$, s^{-1}
0.25	0.25	0.07	3.83
	0.02	0.60	3.45
	0.04	1.20	4.62
0.40	0.25	0.07	2.79
	0.45	0.10	3.80
	0.02	0.60	2.63
	0.04	1.20	3.50
0.75	0.30	0.07	2.28
	0.50	0.10	2.90
	0.71	0.10	3.66
	0.80	0.10	3.95
	0.90	0.10	4.35
	0.02	0.60	1.91
	0.02	1.20	2.60
0.80	0.45	0.10	2.52
	0.70	0.10	3.35
	0.85	0.10	3.90
	0.90	0.10	4.15
	0.02	0.60	1.84
	0.04	1.20	2.46
	0.04	1.80	2.94
0.98	0.30	0.07	2.04
	0.50	0.10	2.50
	0.71	0.10	3.20
	0.90	0.10	3.80
	0.02	0.60	1.71
	0.04	1.20	2.20
	0.04	1.80	2.80
1.50	0.30	0.07	1.65
	0.50	0.10	2.15
	0.71	0.10	2.64
	0.80	0.10	2.80
	0.90	0.10	3.13
	0.02	0.60	1.47
	0.04	1.20	1.98
	0.04	1.65	2.33
	0.04	1.80	2.46
1.96	0.50	0.10	1.92
	0.71	0.10	2.38
	0.90	0.10	2.84
	0.02	0.60	1.33
	0.04	1.20	1.80
	0.04	1.35	1.89
	0.04	1.80	2.22

Table II. Formation (k_f) and Aquation (k_{aq}) Rate Constants (25 °C) for the Equilibration of $[Mo_3S_4(H_2O)_9]^{4+}$ with NCS^- Corresponding to the Slope and Intercept, Respectively, in Figure 5, I = 2.00 M ($LiClO_4$)

$[H^+]$, M	k_f, M^{-1} s^{-1}	$10k_{aq}$, M^{-1} s^{-1}	$[H^+]$, M	k_f, M^{-1} s^{-1}	$10k_{aq}$, M^{-1} s^{-1}
0.25	573 ± 50	2.35 ± 0.15	0.98	296 ± 11	1.08 ± 0.06
0.410	469 ± 22	1.65 ± 0.08	1.50	233 ± 7	1.00 ± 0.04
0.75	344 ± 5	1.22 ± 0.03	1.96	212 ± 7	0.92 ± 0.04
0.80	327 ± 15	1.11 ± 0.09			

A graph of k_f against $[H^+]^{-1}$ is curved (Figure 6). The reaction scheme (8)–(11), with $[Mo_3S_4(H_2O)_9]^{4+}$ written as Mo_3^{4+}, and

$$Mo_3^{4+} \rightleftharpoons Mo_3OH^{3+} + H^+ \quad (K_{aM}) \tag{10}$$

$$Mo_3^{4+} + NCS^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Mo_3(NCS)^{3+} \tag{11}$$

$$Mo_3OH^{3+} + NCS^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Mo_3OH(NCS)^{2+} \tag{12}$$

$$Mo_3(NCS)^{3+} \rightleftharpoons Mo_3OH(NCS)^{2+} + H^+ \quad (K_{aMT}) \tag{13}$$

the conjugate-base form as Mo_3OH^{3+}, gives a satisfactory fit to the data. The formation rate constant can be expressed as in (14).

$$k_f = \frac{k_1[H^+] + k_2K_{aM}}{[H^+] + K_{aM}} \tag{14}$$

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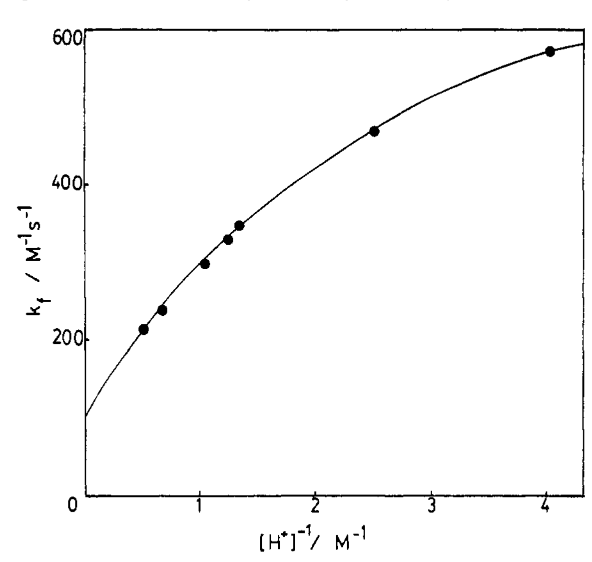

Figure 6. Dependence of k_f (25 °C) on $[H^+]^{-1}$ for the 1:1 complexing of $[Mo_3S_4(H_2O)_9]^{4+}$ with NCS^-, $I = 2.00$ M ($LiClO_4$).

A plot of $k_f([H^+] + K_{aM})$ against $[H^+]$ is linear, using estimates of K_{aM} in the range 0.1–0.3 M. From the slope and intercept K_{aM} can be refined in an iterative manner to give a best fit with $k_1 = 108 \pm 4$ M^{-1} s^{-1}, $k_2 = 1120 \pm 55$ M^{-1} s^{-1}, and $K_{aM} = 0.22 \pm 0.03$ M.

Similarly, the aquation rate constant k_{aq} can be described as in (15). A plot of k_{aq} against $[H^+]^{-1}$ gives a satisfactory straight

$$k_{aq} = \frac{k_{-1}[H^+] + k_{-2}K_{aMT}}{[H^+] + K_{aMT}} \qquad (15)$$

line fit, but the data obtained are less precise. Thus, from k_{aq} (Table II) and (15), $k_{-1} \sim 7 \times 10^{-2}$ s^{-1}, $k_{-2} > 1$ s^{-1}, and K_{aMT} of the order 10^{-3} M are obtained in the same way as for k_1, k_2, and K_{aM} by using (14).

Discussion

Whereas overnight the oxo analogue $[Mo_3O_4(H_2O)_9]^{4+}$ is extensively oxidized by air-free 2 M $HClO_4$, and in 2 M HPTS ~10% by air, $[Mo_3S_4(H_2O)_9]^{4+}$ is stable indefinitely to both ClO_4^- and O_2 at pH <1. A similar but more extreme situation applies in the case of the cuboidal analogues, where $[Mo_4S_4(H_2O)_{12}]^{5+}$ is stable in air and is only oxidized to $[Mo_3S_4(H_2O)_9]^{4+}$ on heating on a steam bath for 3–4 h.[8,10] In contrast, $[Mo_4O_4(H_2O)_{12}]^{5+}$ has not yet been isolated and if formed in analogous preparative procedures involving reduction of bis(μ-oxo) Mo^V_2, decays rapidly to $[Mo_3O_4(H_2O)_9]^{4+}$.

A particularly interesting property of $[Mo_3S_4(H_2O)_9]^{4+}$ not observed with $[Mo_3O_4(H_2O)_9]^{4+}$ is its ability to react rapidly with a wide range of metal ions M^{2+} under reducing conditions ($NaBH_4$ or electrochemical) to generate cuboidal $[Mo_3MS_4(H_2O)_{10}]^{4+}$ (tetrahedral M = Fe, Ni, Cu) or in the case of the Hg the (double cube) $[Mo_6HgS_8(H_2O)_{18}]^{8+}$. Incorporation of M^{2+} stabilizes a lower oxidation state of $Mo_3S_4^{4+}$. If M^{2+} coordinates with $Mo_3S_4^{4+}$ prior to reduction, the extent of coordination is not extensive and is not detected spectrophotometrically. Also possible is the attachment of M^{2+} to the electron-rich μ-sulfido ligands of a transient reduced form of $Mo_3S_4^{4+}$. The incomplete cube has three such exposed (ring) μ-sulfido ligands. Reduction of $[Mo_3S_4(H_2O)_9]^{4+}$ to a lower oxidation state has not yet been observed. Thus, in cyclic voltammetry experiments on $[Mo_3S_4(H_2O)_9]^{4+}$ in 2 M $HClO_4$ or HPTS, no peak is obtained in the region 0 to −0.6 V (vs SCE) at a glassy-carbon electrode. Likewise, in constant potentiometry experiments (−0.7 V) no permanent reduction is observed. This contrasts with the behavior of $[Mo_3O_4(H_2O)_9]^{4+}$, which can be reduced chemically and electrochemically to well-defined Mo^{III}_3 and $Mo^{III}_2Mo^{IV}$ states.[22,23] It has however been established that in neutral solution $[Mo_3S_4(ida)_3]^{2-}$ (ida = iminodiacetate) can be reduced to the $Mo^{III}_2Mo^{IV}$ and $Mo^{III}Mo^{IV}_2$ states in cyclic voltammetry.[6] The latter experiments suggest that $[Mo_3S_4(H_2O)_9]^{4+}$ may be reduced but at pH < 1 (with no M^{2+} ions added) is rapidly reoxidized by H^+. In related studies we have noted that oxidation of the Mo^{III}_4 complex $[Mo_4S_4(edta)_2]^{4-}$ occurs in acidic solutions, but it is not yet proven that this is a reaction with H^+.[24]

The $[Mo_3S_4(H_2O)_9]^{4+}$ cluster has also been reported to react directly with the metals M = Fe, Ni, Cu and Hg.[15-18] No reductant is required, but the reactions appear to be slower than those described here. The single cubes $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ and $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ have been characterized by X-ray crystallography, as have a dimer form of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ and the double cube $[Mo_6HgS_8(H_2O)_{18}]^{8+}$.[15-18] The products M = Hg and Co are both more strongly held on a Dowex column, consistent with higher charges. An X-ray crystal structure of the Co complex is under way.[25] In the absence of M^{2+}, the double cube $[(H_2O)_9Mo_3S_4MoS_4Mo_3(H_2O)_9]^{8+}$ is obtained. Further characterization and studies on the solution chemistry of these complexes is in progress.

In the preparative procedure for $[Mo_3S_4(H_2O)_9]^{4+}$ decomposition of cuboidal $[Mo_4S_4(H_2O)_{12}]^{5+}$ (3.25 state) occurs by a process involving air oxidation of Mo(III) to Mo(IV), with release of one of the Mo's.[8] In the present work the reverse reaction involving the conversion of $Mo_3S_4 \rightarrow Mo_4S_4$ has been achieved for the first time, by the reduction of $[Mo_3S_4(H_2O)_9]^{4+}$ in the presence of $[Mo(H_2O)_6]^{3+}$. The relative inertness of $[Mo(H_2O)_6]^{3+}$ as compared to hexaaqua M^{2+},[26] its higher positive charge, and the short life of $NaBH_4$ in acidic solutions are believed to be responsible for the lower yield (~15%). An interesting feature of the mixed-metal structures is that whereas Mo as an early transition metal exhibits octahedral coordination, late transition metals (including Fe) are tetrahedral. A previous example of this is Holm's complex $[Fe_3VS_4(Cl)_3(DMF)_3]$, in which V is octahedral and Fe tetrahedral.[27] The formation of mixed-metal clusters in this work is similar to the conversion of metalloprotein Fe_3S_4 clusters to Fe_3MS_4 (M = Zn, Co), and there are similarities also in the regeneration of Fe_4S_4.[28,29] For the trimeric Mo/S and Fe/S clusters to be stable an oxidation state higher than that for the related cuboidal forms is required. This can be rationalized in terms of the greater μ-S to metal electron donation occurring for μ-S as opposed to μ_3-S ligands.

Replacement of oxo by sulfido ligands in the trimer (red and green, respectively) produces a shift toward the red in the UV–vis absorbance spectrum (Figure 1), consistent with trends in the spectrochemical series.[30] The $[Mo_3S_4(H_2O)_9]^{4+}$ ion exhibits small changes in the visible range in 0.1–2.0 M chloride, indicating complexing with Cl^-, and large changes in the UV region on complexing with NCS^-. From the kinetic studies there is substantial acid dissociation of $[Mo_3S_4(H_2O)_9]^{4+}$, $K_a = 0.22$ M, but very small accompanying changes in UV–visible absorbance as $[H^+]$ is varied, which precludes a precise determination of K_a by this method.

The reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with 1 M thiocyanate generates two multiply substituted products having strikingly different colors, yellow-green (major) and red, respectively.[31] Two isomers may also be formed in kinetic studies at lower $[NCS^-]$ such that 1:1 complexing is dominant, and there is need to work at an

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isosbestic at 362 nm. This is the first time in NCS^- substitution studies on Mo ions that evidence consistent with formation of an S-bonded isomer has been obtained.[11,26,32] We have checked and confirm that within limits of detection $[Mo_3O_4(H_2O)_9]^{4+}$ gives only one product. Although X-ray crystallographic studies, on $[Mo_3O_4(NCS)_8(H_2O)]^{4-}$ and $[Mo_3(S)O_2S(NCS)_9]^{5-}$,[13b,33] have indicated N-bonded thiocyanate, an S-bonded form is not unreasonable in the case of $[Mo_3S_4(H_2O)_9]^{4+}$, in view of the greater number of S^{2-} ligands, making the trimer core softer (or more class b)[34] and more likely to yield the S-bonded thiocyanato product. What is perhaps surprising is that more of the S-bonded isomer is not obtained. Previously S-bonded complexes of core Mo_3S_4 have been prepared that are also red, for instance $[Mo_3S(S_2)_6]^{2-}$.[4] The red product obtained on elution of $[Mo_3S_4(H_2O)_9]^{4+}$ with 1 M NCS^- was not at a sufficiently high concentration (<0.5 mM), or sufficiently long-lived, to allow for its isolation and further study.

From the kinetics of thiocyanate ($<2 \times 10^{-3}$ M) substitution on $[Mo_3S_4(H_2O)_9]^{4+}$, an acid dissociation constant of 0.22 M is obtained, which can be compared with K_{aM} values of 0.42 M (kinetics), 0.24 M (spectrophotometry), and 0.31 M (^{17}O NMR study) for $[Mo_3O_4(H_2O)_9]^{4+}$.[11a,14] Formation of an $H_3O_2^-$ bridge involving H_2O's trans to μ-O ligands on adjacent Mo's has been suggested as a possible explanation, since the K_a's appear high for Mo(IV)'s already extensively bonded to oxo ligands.[14,32] An Mo–Mo bond distance of 2.48 Å for $[Mo_3O_4(H_2O)_9]^{4+}$ [14] may be acceptable for $H_3O_2^-$ bridging, but one of 2.77 Å for the $Mo_3S_4^{4+}$ core[6] is much less so.[35] Therefore, in view of the similar K_{aM} values, $H_3O_2^-$ bridging might seem less likely. An alternative explanation is that each acid dissociation involves one H_2O ligand only, which in the case of $[Mo_3O_4(H_2O)_9]^{4+}$ (from ^{17}O NMR) is one of the H_2O's trans μ-O and not trans μ_3-O.[14]

An interesting feature of the kinetics is that an $[H^+]$-independent term is observed in the rate law for the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$, whereas the reaction of $[Mo_3O_4(H_2O)_9]^{4+}$ proceeds solely via the conjugate base. As already indicated, acid dissociation constants (K_a) for the two complexes are very similar, and this does not provide an explanation. The presence of four S^{2-} ligands in the trimer core activates substitution on the aqua ion itself. Rate constants for NCS^- substitution on $[Mo_3S_4(H_2O)_9]^{4+}$ are $k_1 = 108$ M^{-1} s^{-1} and $k_2 = 1120$ M^{-1} s^{-1} for the aqua and conjugate-base forms, respectively. The ratio $k_2{:}k_1$ of $\sim$10 favors the conjugate base but is relatively less favorable than in the case of $[Mo_3O_4(H_2O)_9]^{4+}$. The replacement of four μ-oxo by four μ-sulfido ligands results in a 230-fold labilization effect on the basis of a k_2 of 4.8 M^{-1} s^{-1} for NCS^- substitution on the conjugate base of $[Mo_3O_4(H_2O)_9]^{4+}$.[11a] The latter study was in $I = 2.00$ M (LiPTS), since no full study has been carried out in perchlorate, taking into account K_a. From existing information we might expect that in perchlorate k_2 would be about one-third of 4.8 M^{-1} s^{-1},[21a] assuming that K_a remains unchanged. This decreases the net μ-S labilization to $\sim 10^2$. We have previously reported[32] that replacement of μ_3-O of $[Mo_3O_4(H_2O)_9]^{4+}$ by μ_3-S slows down substitution by a factor of $\sim$10. Introduction of the three μ-S ligands therefore gives a $\sim 10^3$-fold increase in rate constants.

Small absorbance changes from a second stage were minimized by working at the 362-nm isosbestic point. The existence of different H_2O's, and crystallographic evidence for those trans to the μ_3 group being significantly shorter (and more inert),[6,7] is the same as for $[Mo_3O_4(H_2O)_9]^{4+}$.[14,21a] The kinetics reported with NCS^- in excess are therefore believed to be for substitution of H_2O's (two to each Mo) trans to the μ-S ligands. Some formation of the bis(thiocyanato) complex as well as isomerization of S- to N-bonded thiocyanate may also contribute to the second stage.

Substitution reactions of hexaaqua metal ions have been extensively studied[36,37] and ratios k_2/k_1 illustrating the effectiveness of conjugate-base pathways noted. For the III state ions Fe, Al, and Ga with higher electron populations, the conjugate base is very much more reactive with k_2/k_1 values $>10^3$. A similar but less-marked dominance applies in the case of Cr. With V (d^2) and Ti (d^1) however, which have empty t_{2g} orbitals, no conjugate-base pathway is detected even though acid dissociation of the hexaaqua ion occurs. Similarly for d^3 Mo(III) no contribution from the conjugate-base pathway is observed, and I_a processes are assigned to these low-electron-population metal ions.[26] In the case of $[Mo_3O_4(H_2O)_9]^{4+}$ the dominance of the conjugate-base path is consistent with an I_d mechanism, which is favored because metal–metal bonding gives a coordination number of 8 at each Mo, decreasing the possibility of an associative process. The same argument should hold for $[Mo_3S_4(H_2O)_9]^{4+}$. However, the electron-rich S^{2-} ligands are able to donate extra electron density to the Mo's, with the same net effect as in a conjugate-base process, and in this way participation of the aqua ion in an I_d process can be understood.

To summarize, replacement of core oxo by sulfido ligands in $[Mo_3O_4(H_2O)_9]^{4+}$ to give $[Mo_3S_4(H_2O)_9]^{4+}$ significantly alters the solution properties of the clusters with respect to stability, incorporation of a fourth metal, redox change (as indicated by the electrochemical behavior), and substitution (of coordinated H_2O). Shifts in electron density resulting from the electron-donating properties of μ-S as compared to μ-O are believed to be important.

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Registry No. $[Mo_3S_4(H_2O)_9]^{4+}$, 101660-28-0; $[Mo_4S_4(H_2O)_{12}]^{5+}$, 99145-05-8; $[Mo_3S_4(NCS)_9]^{5-}$, 99155-06-3; $[Mo_3S_4(SCN)_9]^{5-}$, 122020-66-0; $[Mo_3FeS_4(H_2O)_{10}]^{4+}$, 122020-67-1; $[Mo_3NiS_4(H_2O)_{10}]^{4+}$, 122020-68-2; $[Mo_3CuS_4(H_2O)_{10}]^{4+}$, 122020-69-3; $[(H_2O)_9Mo_3S_4MoS_4Mo_3(H_2O)_9]^{8+}$, 108168-24-7; NCS^-, 302-04-5.

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