structure **5** is 2.0 kcal/mol higher than that of **4**. Thus, our final estimates (Table II) indicate metalation to be favored kinetically over addition by 2.7 kcal/mol, in agreement with experiment. Despite the larger thermodynamic driving force for addition ($\Delta E = -38.1$ kcal/mol), only metalation ($\Delta E = -23.4$ kcal/mol) is observed.

The α-C–Li separations in **4** and **5** are very similar, 2.083 and 2.064 Å,[9a] respectively; these values are close to the C–Li bond in lithioacetylene (1.923 Å at 6-31G*, Figure 2) indicating the C–Li interaction to be dominant in both transition states. The Li–H separation in the transition structure for addition is smaller (1.650 Å)[9a] than that in the metalation transition structure **4** (1.788 Å).

Conclusions

The mechanism for metalation of carbon acids deduced calculationally in this work is consistent with the experimental findings: the reactions proceed through the highly ionic four-membered ring transition states that have been implicated in experimental work by kinetic measurements and Hammett relationships. The transition structures are characterized by more nearly linear C–H–H geometries than have been assumed in experimental studies.

Acetylene is metalated easily (very low activation energy) in an exothermic reaction, whereas the lithiation of methane is endothermic with a high activation barrier. The experimentally known reverse process, hydrogenolysis of methyllithium, is favored instead.

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Registry No. CH_4, 74-82-8; C_2H_2, 74-86-2; HLi, 7580-67-8; CH_3Li, 917-54-4; C_2HLi, 1111-64-4.

Supplementary Material Available: Full geometry information in the form of archive entries (3 pages). Ordering information is given on any current masthead page.

Solution Chemistry of the Cuboidal Mixed-Valence (3.25) Molybdenum/Sulfido Cluster $[Mo_4S_4(H_2O)_{12}]^{5+}$

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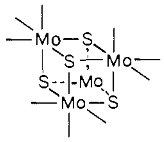
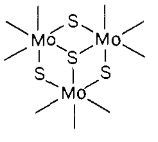
Abstract: The green aqua ion of cuboidal $Mo_4S_4^{5+}$, here designated as $[Mo_4S_4(H_2O)_{12}]^{5+}$, average oxidation state 3.25 (11 Mo valence electrons), exhibits remarkable stability in acidic solutions, *p*-toluenesulfonic acid (HPTS), and $HClO_4$, $[H^+] = 0.01$–4.0 M. At 50 °C (pH <2) in air (1 M acid), slow oxidation of $Mo_4S_4^{5+}$ ($t_{1/2} \sim 4$ days) occurs, giving 1:1 amounts of the incomplete cuboidal Mo^{IV}_3 ion, $[Mo_3S_4(H_2O)_9]^{4+}$. In 1 M HCl ($t_{1/2} \sim 10$ h at 50 °C) the reaction is used as a preparative procedure (~90 °C) for $Mo_3S_4^{4+}$. No large variations in UV–vis spectrum are observed for $Mo_4S_4^{5+}$ at pH < 2. At pH > 2, however, a purple hydrolysis product is generated, complete formation of which is observed at, e.g., pH 6.2 and 8.4. This product is stable for at least 1 h (but subsequently decomposes), and on acidification (2 M $HClO_4$) it reforms overnight $Mo_4S_4^{5+}$ (86%) along with $Mo_3S_4^{4+}$ (10%). Cyclic voltammetry of $Mo_4S_4^{5+}$ in 2 M HPTS gives two one-electron waves, and reduction potentials for $Mo_4S_4^{5+/4+}$ and $Mo_4S_4^{6+/5+}$ of 0.21 and 0.86 V, respectively (vs NHE). The orange $Mo_4S_4^{4+}$ ion obtained on constant potential reduction (−0.12V vs SCE) rapidly reoxidizes in air. At 25 °C under N_2, $I = 2.0$ M ($LiClO_4$), reduction of $Mo_4S_4^{5+}$ to $Mo_4S_4^{4+}$ with Cr^{2+} (0.61×10^3 M^{-1} s^{-1}) and V^{2+} (24.5×10^3 M^{-1} s^{-1}) occurs by outer-sphere processes, with no dependence on $[H^+]$ (0.5–1.9 M). From the Marcus equations the self-exchange rate constant for $[Mo_4S_4(H_2O)_{12}]^{4+/5+}$ is 760 M^{-1} s^{-1}. On constant potential oxidation of $Mo_4S_4^{5+}$ (+0.70 V vs SCE) for ~40 min, chromatographically separated products are $Mo_3S_4^{4+}$ (15% of Mo), the di-μ-sulfido Mo^V_2 ion (30%), unreacted $Mo_4S_4^{5+}$ (25%), and Mo^{VI}, with no evidence for $Mo_4S_4^{6+}$. With a large excess of $V(O)_2^+$ (1.0 V) as oxidant the reaction $Mo_4S_4^{5+} + 5V^V \rightarrow Mo_3S_4^{4+} + Mo^{VI} + 5V^{IV}$ occurs via a red purple intermediate. With a 2:1 molar excess of $V(O)_2$, red-purple $Mo_4S_4^{6+}$ (or a closely related hydrolyzed product) can be separated chromatographically and is stable under N_2 at 4 °C. It oxidized in air within ~12 h to give $Mo_3S_4^{4+}$. On complexing $Mo_4S_4^{5+}$ with NCS^- (~0.10 M) air oxidation gives the thiocyanato complex of $Mo_4S_4^{6+}$ overnight. The same product is formed rapidly on addition of NCS^- to $Mo_4S_4^{6+}$.

Procedures for the preparation of the aqua ion of the cuboidal mixed-valence $Mo_4S_4^{5+}$ core have been described.[1] An X-ray crystallographic study of the edta (ethylenediamine-N,N′-tetraacetate) complex, $Ca_3[Mo_4S_4(edta)_2]\cdot 28H_2O$,[2] is the basis for designating the aqua ion as $[Mo_4S_4(H_2O)_{12}]^{5+}$ The incomplete cuboidal ion $[Mo_3S_4(H_2O)_9]^{4+}$ is also known.[1] Also from crystallographic studies the $Mo_4S_4^{6+}$ core has been characterized as red $(NH_4)_6[Mo_4S_4(NCS)_{12}]\cdot 10H_2O$,[3] and structures of the edta complexes of $Mo_4S_4^{6+}$ and $Mo_4S_4^{4+}$ have been reported.[4] In contrast there have as yet been no studies on the solution chemistry of the 5+ aqua ion, including investigations as to the accessibility and stability of the corresponding 4+ and 6+ states. In view of the wide ranging occurrence of cuboidal structures in metalloproteins,[5-8] through organometallic (cyclopentadienyl) chemistry,



$[Mo_4S_4(H_2O)_{12}]^{5+}$



$[Mo_3S_4(H_2O)_9]^{4+}$

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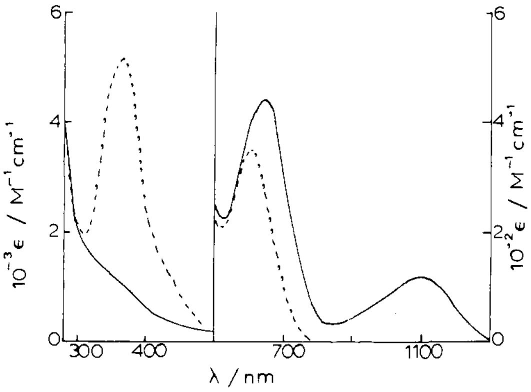

Figure 1. A comparison of UV–vis–near-infrared spectra for the green aqua ions $[Mo_4S_4(H_2O)_{12}]^{5+}$ (—) and $[Mo_3S_4(H_2O)_9]^{4+}$ (---) in 2 M HPTS; absorption coefficients (ε) are per cube and per trimer, respectively.

it seemed timely to explore such properties.

Experimental Section

Preparation of $[Mo_4S_4(H_2O)_{12}]^{5+}$. Solutions of the $Mo_4S_4^{5+}$ aqua ion (~5 mM) in HPTS (2 M) were obtained as previously described,[1] with final purification by ion-exchange chromatography. Solutions in $HClO_4$ were obtained by saturating a small Dowex 50W-X2 cation-exchange column (2 × 0.5 cm, e.g., Pasteur pipet) with the aqua ion, and washing with 0.5 M $HClO_4$ (20 mL) to remove PTS^- ions. The 5+ ion was eluted with 4 M $HClO_4$ and diluted 2-fold for storage. The visible–near-infrared range spectrum of $Mo_4S_4^{5+}$ is independent of anions (PTS^- or ClO_4^-), peaks at 645 nm (ε 435 M^{-1} cm^{-1} per cube) and 1100 nm (ε 122 M^{-1} cm^{-1} per cube) (Figure 1). However, the cube was noticeably easier to elute with HPTS as compared to $HClO_4$ of the same concentration, suggestion more extensive complexation by PTS^-. Stock solutions were typically $Mo_4S_4^{5+}$ (0.75 mM) in 2 M $HClO_4$. No decomposition of the latter solution was observed over periods of 24 h.

Studies in PTS^- and ClO_4^- were appropriate since in other circumstances the Mo(III) state is known to react with ClO_4^-.[10] In the present work no such reactions of the different Mo_4S_4 ions were observed.

Other Reagents. Perchloric acid (70%), sodium bicarbonate, and sodium thiocyanate (all BDH, Analar) were used. Lithium perchlorate (Aldrich Chemicals) was recrystallized from H_2O. A solution of chromium(III) perchlorate was prepared by H_2O_2 reduction of chromium trioxide in aqueous $HClO_4$. This was then reduced to hexaaqua Cr^{2+} (peak at 715 nm, ε = 4.82 M^{-1} cm^{-1}) by electrochemical reduction at a Hg-pool electrode. Vanadyl sulfate, as hydrated $VOSO_4$ (BDH, Lab Reagent), was first converted to the perchlorate salt with cation-exchange chromatography and was then reduced to the hexaaqua ion V^{2+} (peak 850 nm, ε = 3.22 M^{-1} cm^{-1}) by the same electrochemical procedure.[11] Solutions of the aqua cis dioxo V^V ion, $V(O)_2^+$, in 2 M HPTS were prepared by dissolving a known amount of ammonium vanadate, NH_4VO_3 (BDH, Analar), in hot water followed by the addition of an equal volume of 4 M HPTS. The concentration was determined by titration against a freshly prepared solution of Fe^{2+}, using ferroin as indicator.

Cyclic Voltammetry. Cyclic voltammograms were recorded on a Princeton Applied Research PAR173 potentiostat interfaced to an Apple II europlus microcomputer with a PAR276 unit. The working electrode was a glassy carbon disc (2.5-mm diameter; Metrohm), Pt wire was used as the secondary electrode, and a saturated calomel electrode was used as reference.

Products from the Cr^{2+} and V^{2+} Reductions of $Mo_4S_4^{5+}$. For a run at 25 °C with Cr^{2+} (2.8 mM) and $Mo_4S_4^{5+}$ (2.8 mM) in 1 M HPTS, the products were separated on an O_2-free Dowex 50W-X2 cation-exchange column. Of the initial Cr, 92% was accounted for as $[Cr(H_2O)_6]^{3+}$, peak positions λ/nm (ε/M^{-1} cm^{-1}), 408 (15.5), 574 (13.7).[11] The Mo product was 90% $Mo_4S_4^{4+}$, peak at 378 nm (ε = 1100 M^{-1} cm^{-1} per cube), with air oxidation giving 10% $Mo_4S_4^{5+}$. As a further check the Mo fractions were tested for Cr by oxidizing under alkaline conditions with H_2O_2 and checking for $[CrO_4]^{2-}$ at 372 nm (ε = 4.82 × 10^3 M^{-1} cm^{-1}). No chromatographic band corresponding to a more highly charged Mo–Cr inner-sphere reaction product was observed.

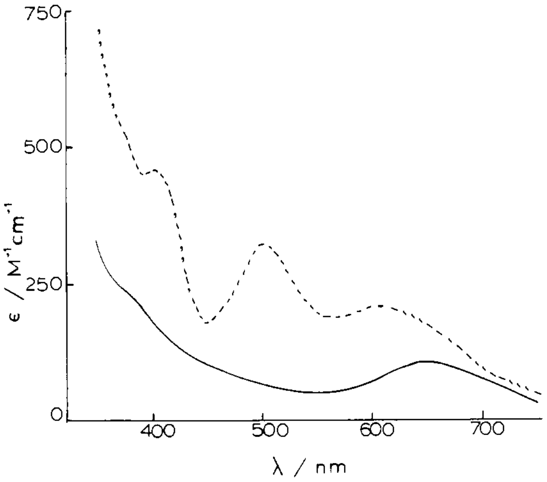

Figure 2. A comparison of UV–vis spectra for the green $[Mo_4S_4(H_2O)_{12}]^{5+}$ ion at pH <2 (—) and the purple product (---), complete formation of which is observed at pH 6.2 and 8.5; absorption coefficients (ε) are per Mo.

In the case of the V^{2+} reacton the product is $[V(H_2O)_6]^{3+}$ with no evidence for the intense brown-colored V^{III}_2 intermediate, VOV^{4+} (peak at 425 nm, ε = 6.8 × 10^3 M^{-1} cm^{-1}),[12] which would be formed if VO^{2+} were a primary product in the redox process.

All the evidence is consistent therefore with 1:1 stoichiometric reactions 1,

$$[M(H_2O)_6]^{2+} + [Mo_4S_4(H_2O)_{12}]^{5+} \rightarrow [M(H_2O)_6]^{3+} + [Mo_4S_4(H_2O)_{12}]^{4+} \quad (1)$$

where M = Cr or V.

Kinetic Studies. These were carried out using a Dionex D-110 stopped-flow spectrophotometer. Rigorous air-free conditions were observed throughout for studies on the Cr^{2+} and V^{2+} reductions. Plots of absorbance (A) changes at 645 nm, ln ($A_t - A_\infty$) against time t, were linear for 3-4 half-lives. The slopes gave first-order rate constants k_{obs}. Unweighted linear least-squares programs were used in the determination of second-order rate constants (k). Activation parameters were obtained from Eyring plots of log (k/T) against $1/T$.

Results

Stability. The aqua ion $Mo_4S_4^{5+}$ is stable indefinitely when stored O_2-free (under N_2) at ~4 °C in 2 M HPTS. No change in spectrum was detected on varying $[H^+]$ over the range 0.01–4.0 M. In air a slow conversion to the Mo^{IV}_3 ion $[Mo_3S_4(H_2O)_9]^{4+}$, peaks at 367 nm (ε 5130 M^{-1} cm^{-1} per trimer) and 602 nm (351 M^{-1} cm^{-1}) (Figure 1) is observed at 50 °C for solutions 1 M in $HClO_4$ or HPTS. We note that both the Mo_4 and Mo_3 ions are green in color. From absorbance changes over 20 h a $t_{1/2}$ of ~4 days was estimated. For solutions in 1 M HCl changes occur more rapidly, $t_{1/2}$ ~ 10 h, and a procedure involving heating at 90 °C for 2-3 h can be used to generate $Mo_3S_4^{4+}$ in good yield (~95%).[1] The identity of the product formed from the fourth Mo in each cube was not established.

Effect of pH on $Mo_4S_4^{5+}$. The $[H^+]$ of stock solutions of $Mo_4S_4^{5+}$ (0.56 mM, 2 M $HClO_4$) was adjusted by addition of saturated sodium bicarbonate (6.9 g; 100 mL of H_2O) dropwise to (mechanically) stirred solutions at 0 °C. Under less stringent conditions (using OH^-) some precipitation was observed. Over the range $[H^+]$ = 0.01–2.00 M (and up to 4.0M in other experiments), no significant shifts in the UV–vis–near-infrared spectrum were observed. However at pH >2 changes in spectrum are obtained, and at pH 6.2 and 8.5 purple solutions having identical spectra were generated. The spectrum, Figure 2, has peaks λ/nm (ε/M^{-1} cm^{-1} per Mo) at 610 (205), 492 (325), and 400 (460). At least 90% of the change in spectrum occurs prior to recording the first spectrum (within 5 min). There are subsequent (~10%) changes over 30 min the nature of which is

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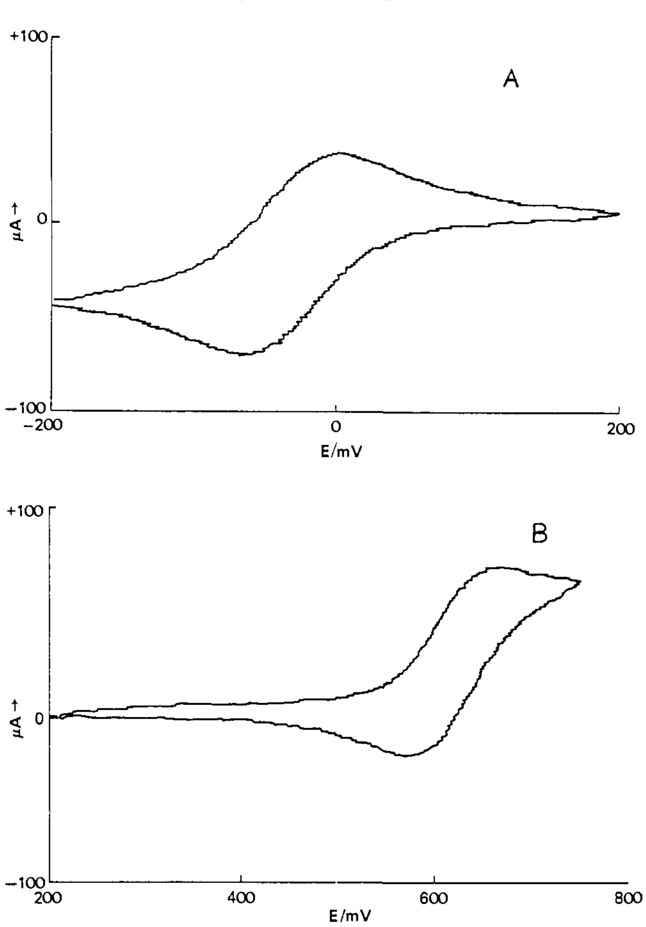

Figure 3. Cyclic voltammograms of $[Mo_4S_4(H_2O)_{12}]^{5+}$ (8 mM) at 22 °C in 2 M HPTS, scan rate 0.1 V s^{-1}, (A) for reduction to the 4+ state and (B) for oxidation to the 6+ state.

uncertain, and may be part of an oligomerization process. The purple solutions are stable for at least 1 h but subsequently decompose. On acidification (2 M $HClO_4$) of the freshly generated purple solution and leaving overnight, a green solution consisting of 86% of $Mo_4S_4^{5+}$ and 10% of $Mo_3S_4^{4+}$ was obtained. An initial intensification of the purple color was noted on addition of the acid, followed by formation of the green products.

Reduction Potentials. With $Mo_4S_4^{5+}$ as starting complex cyclic voltammograms were obtained for one-electron reduction and oxidation processes (Figure 3). Both changes exhibit reversible behavior, and analysis of the one-electron waves gives $E_{pc,1}$ = −0.062 V, $E_{pa,1}$ = 0.004 V and $E_{pc,2}$ = 0.573 V, $E_{pa,2}$ = 0.661 V. From these values reduction potentials, (2) and (3), both vs the normal hydrogen electrode were obtained.

$$Mo_4S_4^{5+} + e^- \rightleftharpoons Mo_4S_4^{4+} \quad (0.21\ V) \tag{2}$$

$$Mo_4S_4^{6+} + e^- \rightleftharpoons Mo_4S_4^{5+} \quad (0.86\ V) \tag{3}$$

Constant Potential Experiments. At a constant potential of −0.12 V (vs standard calomel electrode), the green $Mo_4S_4^{5+}$ aqua ion is reduced quantitatively at a carbon–cloth electrode (O_2-free conditions) to orange $Mo_4S_4^{4+}$, peak at 378 nm (ϵ = 1100 M^{-1} cm^{-1} per cube). Further details of this procedure and studies on the $Mo_4S_4^{4+}$ ion will be reported elsewhere.[13] On oxidation of $Mo_4S_4^{5+}$ (1 mM, 30 mL) in 2 M HPTS at a constant potential of 0.70 V (vs SCE) at a carbon–cloth electrode, the solution changed to a green-yellow color after 40 min. This was diluted to $[H^+]$ = 0.5 M and loaded onto a Dowex 50W-X2 column (1 × 8 cm). After washing with 0.5 M HPTS the products were eluted with 2 M HPTS and characterized from known spectra. These were in order of elution the di-μ-sulfido Mo(V)$_2$ ion, $[Mo_2O_2S_2(H_2O)_6]^{2+}$ (30% of initial Mo),[14] $Mo_3S_4^{4+}$ (15%), and unreacted $Mo_4S_4^{5+}$ (25%). No other products were identified, and formation of colorless Mo^{VI} accounts for the Mo imbalance.

Table I. The Variation of First-Order Rate Constants, k_{obs}, for the Reduction of $[Mo_4S_4(H_2O)_{12}]^{5+}$ with $[Cr(H_2O)_6]^{2+}$, $[H^+]$ = 1.90 M (Except as Indicated), I = 2.0 M ($LiClO_4$)

temp (°C)	$10^3[Cr^{2+}]$ (M)	$10^3[Mo_4S_4^{5+}]$ (M)	k_{obs} (s^{-1})
13.0	4.0	0.2	1.72
	6.0	0.2	2.88
	8.0	0.2	3.69
25.0	2.0	0.1	1.07
	4.0	0.1	2.43
	4.0	0.1	2.48[a]
	4.0	0.2	2.52[b]
	6.0	0.2	3.5
	6.0	0.1	3.6[c]
	8.0	0.2	4.9
	10.0	0.2	6.0
35.3	4.0	0.2	3.3
	6.0	0.2	5.2
	8.0	0.2	6.8

[a] $[H^+]$ = 0.75 M. [b] $[H^+]$ = 0.50 M. [c] $[H^+]$ = 1.0 M.

Table II. The Variation of First-Order Rate Constants, k_{obs}, for the Reduction of $[Mo_4S_4(H_2O)_{12}]^{5+}$ with $[V(H_2O)_6]^{2+}$, $[H^+]$ = 1.90 M (Except as Indicated), I = 2.0 M ($LiClO_4$)

temp (°C)	$10^3[V^{2+}]$ (M)	$10^3[Mo_4S_4^{5+}]$ (M)	k_{obs} (s^{-1})
11.2	2.0	0.2	37
	4.0	0.2	75
	6.0	0.2	119
17.5	2.0	0.2	43
	4.0	0.2	85.1
	6.0	0.2	133
25.0	1.0	0.1	23.4
	2.0	0.2	46
	2.0	0.2	47
	3.0	0.2	71
	3.0	0.1	71[a]
	4.0	0.2	93
	4.0	0.2	95
	4.0	0.2	95
	4.0	0.1	93[a]
	5.0	0.2	122
	6.0	0.2	150

[a] $[H^+]$ = 1.0 M.

Table III. The Variation of Second-Order Rate Constants k with Temperature for the Cr^{2+} and V^{2+} Reductions of Aqua $Mo_4S_4^{5+}$, I = 2.0 M ($LiClO_4$)

reductant	temp (°C)	$10^{-3}k$ (M^{-1} s^{-1})
Cr^{2+}	13.0	0.46
	25.0	0.61
	35.3	0.85
V^{2+}	11.2	19.5
	17.5	21.7
	25.0	24.5

Kinetic Studies on the Cr^{2+} and V^{2+} Reductions. First-order rate constants k_{obs} with Cr^{2+} (2–10 mM) and V^{2+} (1–6 mM) in large excess of $Mo_4S_4^{5+}$ (0.1–0.2 mM) are listed in Tables I and II. A linear dependence on reductant concentration is observed, consistent with the rate law given in (4). With Cr^{2+} little or no

$$\text{rate} = k[M^{2+}][Mo_4S_4^{5+}] \tag{4}$$

(<4%) dependence on $[H^+]$ was observed in the range 0.5–1.9 M, and with V^{2+} no dependence in the range 1.0–1.9 M. In both cases the data treatment was assuming no $[H^+]$ dependence. The temperature dependences of k were investigated (Table III), and these give for Cr^{2+} $\Delta H^‡$ = 4.0 + 0.5 kcal mol^{-1}, $\Delta S^‡$ = −32.3 + 1.7 cal K^{-1} mol^{-1} and for V^{2+} $\Delta H^‡$ = 2.3 + 0.3 kcal mol^{-1}, $\Delta S^‡$ = −30.8 + 1.2 cal K^{-1} mol^{-1}.

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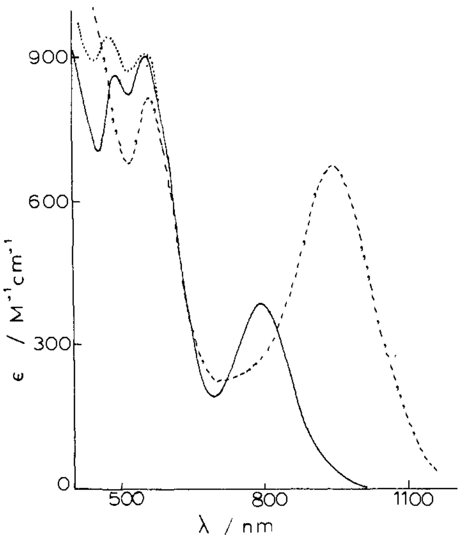

Figure 4. A comparison of the spectrum of the red-purple $Mo_4S_4^{6+}$ state aqua ion (—) in 1.0 M HPTS, isolated by Dowex column chromatography following $V(O)_2^+$ oxidation of $[Mo_4S_4(H_2O)_{12}]^{5+}$ in O_2-free 2.0 M HPTS, with that previously reported for the edta complex $[Mo_4S_4(edta)_2]^{2-}$ (- - -) in H_2O, which has been characterized by X-ray crystallography.[4] Absorption coefficients (ε) are per cube. Shifts in the aqua spectrum are indicated on increasing the H^+ from 1.0 M (—) to 3.0 M (··), (ionic strength not adjusted).

The $V(O)_2^+$ Oxidation of $Mo_4S_4^{5+}$. With $V(O)_2^+$ in >10-fold excess formation of a red-purple intermediate (~1 min) is observed, followed by rapid (5–10 min) decay to $Mo_3S_4^{4+}$ (Figure 1), eq 5. With a 2:1 molar excess, $Mo_4S_4^{5+}$ (2.5 mmM) and

$$Mo_4S_4^{5+} + 5V^{V} \rightarrow Mo_3S_4^{4+} + Mo^{VI} + 5V^{IV} \quad (5)$$

$V(O)_2^+$ (5.0 mM) in 2 M HPTS at 0 °C, the initial green solution turns red-brown within ~5 min. Products were separated on an ice-cooled Dowex 50W-X2 column under O_2-free conditions after first diluting to give $[H^+]$ ~ 1 M. The vanadium was recovered quantitatively as blue VO^{2+} (λ_{max} 760 nm, ε 17.2 M^{-1} cm^{-1}). A red-purple band of $Mo_4S_4^{6+}$ was eluted as a 4+ and not 6+ ion with 1 M HPTS. This band was closely followed by a small amount of green $Mo_3S_4^{4+}$ and finally by unreacted $Mo_4S_4^{5+}$ with 2 M HPTS.

The red-purple product is stable for days when stored under N_2 at 4 °C. Small changes in the spectrum (Figure 4) are observed on increasing the $[H^+]$ from 1 to 3 M, with relative 493 nm:555 nm peak heights increasing from ~0.96 to 1.05. Stock solutions, typically 0.1–0.2 mM, were not sufficiently concentrated to allow the acid dissociation (pK_a) to be determined. In air at room temperature conversion of a 0.1 mM solution to $Mo_3S_4^{4+}$ occurs overnight. On addition of NaNCS (solid) immediate conversion of the red-purple product to an intense red thiocyanato complex (peak at 502 nm, shoulder 360 nm), which corresponds to Cotton's $[Mo_4S_4(NCS)_{12}]^{6-}$ ion (see below),[3] was observed. It is possible to estimate ε's for the red purple product in 1 M HPTS, peak positions λ/nm (ε/M^{-1} cm^{-1} per cluster) 493 (865), 555 (905), and 795 (385) (Figure 4), from the known spectrum of $Mo_3S_4^{4+}$,[1] assuming a stoichiometric conversion $Mo_4S_4^{6+} \rightarrow Mo_3S_4^{4+}$ (with the fourth Mo converted to Mo^{VI}), and by conversion to the thiocyanato complex. The spectrum has similar features to that previously reported[4] for the edta complex of the $Mo_4S_4^{6+}$ state ion, $[Mo_4S_4(edta)_2]^{2-}$, also shown in Figure 4.

On applying a constant potential of −0.15 V (vs SCE) for ~1 h at a carbon-cloth electrode (O_2-free conditions) reduction to orange $Mo_4S_4^{4+}$ (characterized spectrophotometrically) via green $Mo_4S_4^{5+}$ was observed. On exposure of the latter to air green $Mo_4S_4^{5+}$ was regenerated.

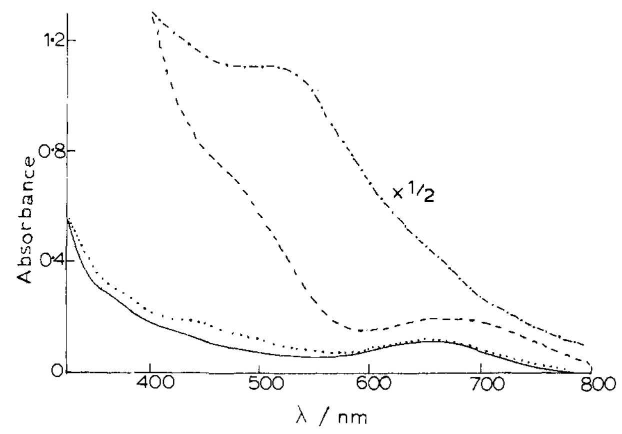

Figure 5. Effect of NCS^- on the UV–vis spectrum of $[Mo_4S_4(H_2O)_{12}]^{5+}$ in 2 M $HClO_4$. The spectrum of $[Mo_4S_4(H_2O)_{12}]^{5+}$ (0.25 mM) (—), gives the spectrum shown by dots after 2 min in the presence of NCS^- (10 mM) under N_2. After 8 h an orange solution (- - -) is obtained, which on bubbling O_2 through for 5 min gives, after an additional 8 h, a red solution (-··) corresponding to the product in the 6+ state.

Reaction with NCS^-. Changes in spectra are as indicated in Figure 5. At 25 °C, with NCS^- (10 mM) and $Mo_4S_4^{5+}$ (0.25 mM) in O_2-free 2 M $HClO_4$, a rapid reaction is observed. In a stopped-flow study it was found that secondary processes are incident before completion of the first kinetic stage. From absorbance changes at 450 nm it was possible to estimate A_∞, and hence plot ln $(A_t - A_\infty)$ against time. Assuming a first-order dependence on $[NCS^-]$ an upper limit for the formation rate constant is 2.2 M^{-1} s^{-1}, which may correspond to (6). The final

$$[Mo_4S_4(H_2O)_{12}]^{5+} + NCS^- \rightarrow [Mo_4S_4(H_2O)_{11}(NCS)]^{4+} + H_2O \quad (6)$$

equilibrated solution is orange in color. With access of O_2 oxidation to the red 6+ state occurs in ~8 h (Figure 5). Addition of a 10^3-fold excess of NCS^- (0.2 M) to $Mo_4S_4^{5+}$ (0.2 mM) in the presence of O_2 gave the same spectrum as for Cotton's $[Mo_4S_4(NCS)_{12}]^{6-}$,[3] with a peak at 502 nm, ε ~ 12000 M^{-1} cm^{-1} per tetramer, based on $Mo_4S_4^{5+}$.

Discussion

Cyclic voltammetry studies on green cuboidal $[Mo_4S_4(H_2O)_{12}]^{5+}$ provide evidence for $[Mo_4S_4(H_2O)_{12}]^{n+}$ forms (n = 4, 5, and 6), with Mo electron counts of 12, 11, and 10, respectively. Of these forms the 5+ ion is by far the most readily accessible. Reduction potentials for the $Mo_4S_4^{5+/4+}$ and $Mo_4S_4^{6+/5+}$ couples have been determined as 0.21 and 0.86 V (vs NHE), respectively, in 2 M HPTS. The reduction of $Mo_4S_4^{5+}$ to orange $Mo_4S_4^{4+}$ (which is air sensitive) presents no problem and can be achieved at a constant potential (−0.12 V vs SCE), or chemically with Cr^{2+} and V^{2+}, which reactions we return to later. Oxidation of $Mo_4S_4^{5+}$ to red-purple $Mo_4S_4^{6+}$ is less straightforward in that electrochemical and chemical (with high $V(O)_2^+$) oxidation takes the reaction past the 6+ state and yields Mo products in higher oxidation states of lower molecularity, as in eq 5. With a restricted 2-fold molar excess of $V(O)_2^+$ (reduction potential 1.0 V)[15] the yield of $Mo_4S_4^{6+}$ is optimized, and following cation-exchange chromatography the product is stable under N_2 over long periods. The product is readily converted into a thiocyanato complex, with a spectrum that agrees with that obtained for the somewhat slower air oxidation of $Mo_4S_4^{5+}$ in the presence of NCS^- (Figure 5). On reduction of the aqua ion at a constant potential of −0.15 V (vs SCE) orange $Mo_4S_4^{4+}$ is obtained via green $Mo_4S_4^{5+}$, indicating retention of the Mo_4S_4 core. Slow oxidation of $Mo_4S_4^{6+}$ (average Mo oxidation state 3.5) in air (~12 h at room temperature) gives the $Mo^{IV}{}_3$ ion $Mo_3S_4^{4+}$.

The behavior observed for the red-purple product as a 4+ ion in cation-exchange chromatography requires further comment. One possibility is that this is the result of acid dissociation as in (7), where the product may have the structure illustrated. Al-

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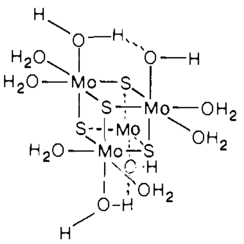
[15] Latimer, W. In *Oxidation States of the Elements and their Potentials in Aqueous Solutions*; 2nd ed.; Prentice-Hall Inc.: Englewood Cliffs, 1952. *Standard Potentials in Aqueous Solutions*; Bard, A. J., Parsons, R., Jordan, J., Eds.; International Union of Pure and Applied Chemistry: Dekker: New York, 1985.

$$[Mo_4S_4(H_2O)_{12}]^{6+} \rightleftharpoons [Mo_4S_4(H_2O)_{10}(OH)_2]^{4+} + 2H^+ \qquad (7)$$

ternatively a single acid dissociation and some anion complexation is possible. UV–vis spectrophotometric changes are observed on increasing $[H^+]$ from 1 to 3 M (Figure 4). Extensive (H_2O) acid



dissociation (K_a = 0.2–0.5 M) has been observed for the series of incomplete cuboidal $[Mo_3O_xS_{4-x}(H_2O)_9]^{4+}$ ions, with formation of a single proton-bridged structure a possible contributing factor.[16] Other examples of ligated $H_3O_2^-$ are known.[17,18] On the basis of crystal structure information,[2] the Mo–Mo separation in the present case of ~2.8 Å[3,4] is quite high for such an explanation to hold.[17] The H_2O's of a 6+ ion might be expected to exhibit acid dissociation, although the extent implied is surprising since the $Mo_4S_4^{5+}$ ion does not appear to behave in the same way.

No evidence has been obtained for accumulation of the red-purple 6+ state product in the constant potentiometric oxidation (+0.70 V vs SCE) of $Mo_4S_4^{5+}$, and further oxidation appears to occur readily under these conditions. Thus for an experiment in which ~25% of the $Mo_4S_4^{5+}$ remained after 40 min, there was no evidence from column chromatography for any $Mo_4S_4^{6+}$. The products identified were the Mo^{IV}_3 ion $Mo_3S_4^{4+}$ (15% of Mo) and the (yellow) di-μ-sulfido Mo^V_2 ion, $Mo_2S_2O_2^{2+}$ (30%). While it is reasonable that decomposition of the 6+ cube should yield Mo_3 and Mo_2 fragments with retention of μ-sulfido, such Mo^{IV}_3 and Mo^V_2 products cannot be formed in a single redox stage from the cube (average oxidation state 3.5). The remaining product is Mo^{VI}, which is formed by electrochemical oxidation of the Mo excluded from the cluster. The reactivity observed for the 6+ ion may be related to its high charge, which is alleviated by deprotonation as in (7), and also by complexing with NCS^- (see below).

Air oxidation of $Mo_4S_4^{5+}$ (0.25 mM) occurs following complexation with NCS^- (10 mM) (Figure 5). More extensive complexation occurs with 0.2 M NCS^-, when the red thiocyanato complex of $Mo_4S_4^{6+}$ has a peak at 502 nm (ϵ = 12000 M^{-1} cm^{-1} per cube). These observations agree with earlier findings of Cotton and colleagues[3] that the Mo_4S_4 cluster in $(NH_4)_6[Mo_4S_4(NCS)_{12}]\cdot 10H_2O$ is in the 6+ state. It is now accepted that the green aqua ion used as starting material in this study is in the 5+ and not the 6+ state.[4] The behavior observed suggests a relative stabilization of the 6+ state on complexing with NCS^-. Complete NCS^- complexing is not necessarily required for O_2 oxidation. Previously edta complexes of 4+, 5+, and 6+ state cubes have been prepared,[4] where the latter as $Na_2[Mo_4S_4(edta)_2]\cdot 6\cdot 5H_2O$ is also red in color. The reduction potential for the 6+/5+ state edta complexes (determined here as 0.64 V) is less than that of the aqua ions (0.86V) consistent with a greater stability of the 6+ state. We note that cyclopentadienyl complexes of the Mo_4S_4 core, e.g., $[Mo_4S_4(n\text{-}C_5H_4Pr^i)_4]^{0,1,2+}$ (corresponding to 4+, 5+, and 6+ states), have been prepared. Electrochemical studies in nonaqueous solvents[19] are not however directly comparable.

Some information has been obtained regarding the substitution properties of aqua $Mo_4S_4^{5+}$. In stopped-flow studies with excess NCS^-, spectrophotometric changes indicated multiphasic processes. From the effects observed an upper limit of 2.2 M^{-1} s^{-1} for 1:1 complexing of NCS^- with $Mo_4S_4^{5+}$ is implied. Absorbance changes were not big enough to allow studies with the $Mo_4S_4^{5+}$ reactant in large excess.

Table IV. Comparison of Rate Constants (25 °C) and Activation Parameters

	k (M^{-1} s^{-1})	ΔH^* (kcal mol^{-1})	ΔS^* (cal K^{-1} mol^{-1})	ref
$Cr^{2+} + Mo_4S_4^{5+}$	0.61×10^3	4.0	−32.3	this work
$V^{2+} + Mo_4S_4^{5+}$	2.45×10^4	2.3	−30.8	this work
Cr^{2+} + Rb[a]	1.2×10^3	0	−44	25
V^{2+} + Rb[a]	1.6×10^4	0.1	−40	25
$Cr^{2+} + [((NH_3)_5Co)_2O_2]^{5+}$	2.3×10^3	0.5	−41	24
$V^{2+} + [((NH_3)_5Co)_2O_2]^{5+}$	9.7×10^4	−1.4	−45	24

[a] Rubredoxin (Rb) undergoes a one-electron change $[Fe(SR)_4]^-$ to $[Fe(SR)_4]^{2-}$ (SR^- = thiolate).

In the present work it was possible to prepare $Mo_4S_4^{5+}$ in up to 4 M $HClO_4$, when no adverse redox (or decomposition) reactions were observed.[10] The 5+ ion does not elute from Dowex columns as readily in $HClO_4$ as in HPTS, suggesting the PTS^- may complex to some extent with $Mo_4S_4^{5+}$. This does not appear to have a significant effect on the slow ~4 day (at 50 °C) reaction of $Mo_4S_4^{5+}$ with O_2 to give $Mo_3S_4^{4+}$, which in 1 M HPTS and 1 M $HClO_4$ occurs at about the same rate (within 5%). In 2 M HCl however the reaction of $Mo_4S_4^{5+}$ to $Mo_3S_4^{4+}$ is 10× faster. Small UV–vis absorbance changes are observed in 2 M HCl, the 645 nm $Mo_4S_4^{5+}$ peak shifting to 652 nm (with a 3–4% decrease in ϵ). It has previously been noted that with the $Mo_3O_4^{4+}$ cluster,[20,21] electronic transitions within the core are not significantly perturbed on complexing with Cl^-.

From spectrophotometric studies on cuboidal $[Mo_4S_4(H_2O)_{12}]^{5+}$ no H_2O ligand acid dissociation is clearly apparent until pH >2. This does not necessarily exclude such a process, which may not be readily detected spectrophotometrically. In the case of the Mo^{IV}_3 ions, $[Mo_3O_xS_{4-x}(H_2O)_9]^{4+}$, small spectrophotometric changes have been measured,[21] and these and kinetic studies indicate extensive acid dissociation (K_a = 0.2–0.5 M).[16,21] This raises the question as to whether in this respect the cuboidal and trimeric complexes behave in the same way. An important structural difference is that whereas the incomplete cuboidal ions have μ (three) and μ_3 (one) oxo/sulfido ligands, the cuboidal ions have only μ_3-sulfido ligands. With $Mo_4S_4^{5+}$ at pH's >2 purple solutions are obtained, and some form of oligomerization to give hydroxo and/or oxo bridged (at least dimeric) cuboidal products is presumably occurring with involvement of the conjugate base. The reactions are reversible with 86% recovery of $Mo_4S_4^{5+}$ ($Mo_3S_4^{4+}$ is also formed) on addition of acid, clearly indicating that there is retention of the cuboidal structure. Interestingly, Shibahara and colleagues[22] have reported the isolation of a purple complex from $Mo_3S_4^{4+}$, the crystal structure of which indicates a double cuboidal formula $[(H_2O)_9Mo_3S_4Mo_3(H_2O)_9](PTS)_8\cdot 18H_2O$ (with one Mo common to both cubes). The spectrum is quite different, however, and in the present case the observation that $Mo_4S_4^{5+}$ is reformed on addition of acid rules out the possibility that the two products are closely related.

One-equivalent reduction of $Mo_4S_4^{5+}$ to $Mo_4S_4^{4+}$ is observed with both Cr^{2+} (−0.41 V) and V^{2+} (−0.26 V). No evidence was obtained in the Cr^{2+} case for substitution-inert Cr(III) attached to the product. Since H_2O is not a good inner-sphere bridging ligand, and there is at most only a small dependence on $[H^+]^{-1}$, an outer-sphere mechanism is dominant. Furthermore the k_V/k_{Cr} ratio of 40 is close to previous values of 50,[23] believed to be diagnostic of outer-sphere processes. The activation parameters, with small ΔH^* and high negative ΔS^* values, are similar to those obtained for the outer-sphere Cr^{2+} and V^{2+} reductions of the μ-superoxo-dicobalt(III) complex $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$,[24]

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and the metalloprotein rubredoxin (Rb) (Table IV).[25] All the indications are therefore that both $Mo_4S_4^{5+}$ reactions are outer sphere.

From the Marcus equations,[26] using the rate constant for the reaction of $[V(H_2O)_6]^{2+}$ with $[V(H_2O)_6]^{3+}$ (0.01 $M^{-1}\ s^{-1}$),[27] the self-exchange rate constant for $[Mo_4S_4(H_2O)_{12}]^{5+/4+}$ is 760 $M^{-1}\ s^{-1}$. No corrections have been made for work terms, which may be significant in view of the high charge product of the reactants.[28] The rate constant obtained indicates a favorable electron-transfer process.[13]

Finally we draw attention to the quite remarkable stability of $[Mo_4S_4(H_2O)_{12}]^{5+}$ over a wide $[H^+]$ range, 0.01–4.0 M. If stored O_2-free in 2 M HPTS the cluster is stable for weeks. It is oxidized only slowly in air, $t_{1/2} \sim 4$ days at 50 °C. This behavior contrasts with that of the biologically relevant Fe_4S_4 cube, which in aqueous solution as tetrahedrally ligated $[Fe_4S_4(SR)_4]^{2-}$ has only limited stability.[29-31]

Acknowledgment. We thank the Climax Molybdenum Co. Ltd., and the U.K. Science and Engineering Research Council for a CASE/SERC studentship (to C.S.) and the University of Newcastle upon Tyne for a Ridley Fellowship (B.-L.O.).

Registry No. $Mo_4S_4^{5+}$, 99145-05-8; $Mo_3S_4^{4+}$, 101660-28-0; $Mo_4S_4^{4+}$, 104843-16-5; $Mo_4S_4^{6+}$, 117626-49-0; $[Mo_2O_2S_2(H_2O)_6]^{2+}$, 52700-51-3; $[M(H_2O)_6]^{2+}$ (M = Cr), 20574-26-9; $[M(H_2O)_6]^{2+}$ (M = V), 15696-18-1; $V(O)_2^+$, 18252-79-4; $[Mo_4S_4(NCS)_{12}]^{6-}$, 103731-75-5; NCS^-, 302-04-5.

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Mechanism of the Substitution Reactions of the Nineteen-Electron Co(CO)$_3$L$_2$ Complex [L$_2$ = 2,3-Bis(diphenylphosphino)maleic Anhydride]

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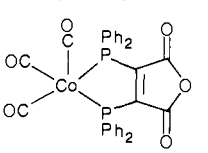
Abstract: The substitution reactions of the $Co(CO)_3L_2$ complex [L_2 = 2,3-bis(diphenylphosphino)maleic anhydride] with phosphines, phosphites, and iodide were studied. This 19-electron complex (perhaps better described as an 18-electron complex with a reduced ligand) was chosen as a model to study the substitution reactions of more reactive 19-electron complexes. Although a dissociatively activated substitution pathway seemed likely, the molecule has a square-pyramidal geometry and the possibility of associatively activated reactions was also anticipated. The complex reacted with entering ligands at room temperature in CH_2Cl_2 to form $Co(CO)_2L_2L'$ [$L' = PR_3$, $P(OR)_3$, I^-]. The derivative with $L' = PPh_3$ was structurally characterized by a single-crystal X-ray analysis. The substitution reactions followed first-order kinetics, and the rates were independent of the entering ligand concentration and the nature of the entering ligand. A dissociatively activated pathway involving loss of CO (not chelate dissociation) is proposed. Rate constants as a function of temperature yielded the following activation parameters: $\Delta H^{\ddagger} = 23.8 \pm 0.6$ kcal mol^{-1} and $\Delta S^{\ddagger} = 11.1 \pm 2.2$ cal mol^{-1} K^{-1}. For comparison purposes, the substitution reactions of the 18-electron $Co(CO)_3L_2^+$ complex were studied. No substitution reactions of this complex took place under the same conditions used for $Co(CO)_3L_2$. Thus, the lability of the latter complex can be attributed to the extra electron. ESR studies of $Co(^{13}CO)_3L_2$ showed a slight delocalization of the extra electron into ^{13}CO orbitals (orbitals that are likely Co–CO antibonding); electronic occupation of these orbitals will weaken the Co–CO bond, and we propose this is the origin of the lability.

Reactions of 17-electron organometallic radicals with 2-electron donor ligands yield 19-electron adducts.[1] Because 19-electron adducts represent a new class of organometallic complexes and because these molecules are expected to be important intermediates whenever metal radicals are formed,[2] we have begun a systematic study of their reactivity.[3]

In this paper, we report the results of our study on the substitution reactions of the $Co(CO)_3L_2$ complex [L_2 = 2,3-bis(diphenylphosphino)maleic anhydride].[8] This 19-electron complex



(perhaps better described as an 18-electron complex with a reduced ligand) was chosen for our initial substitution study for two reasons:

[†] University of Oregon.

[‡] Oregon State University.

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(3) In previous work, we showed that many 19-electron complexes are powerful reductants,[4] and we showed that this property made them key intermediates in the photochemical disproportionation reactions[5] of the $Cp_2Mo_2(CO)_6$, $Cp_2Fe_2(CO)_4$, and $Mn_2(CO)_{10}$ dimers.[6,7] In addition, we demonstrated that the 19-electron complexes could be used to reduce a wide variety of organic, inorganic, and organometallic complexes; even complexes with reduction potentials more negative than −1.5 V (vs SCE) are reduced with ease.[4]

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