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Reaction Paths in the Formation of Triangular and Cuboidal Molybdenum/Sulfur Cluster Complexes as Aqua Ions by Reduction of Molybdenum(V) Dimers

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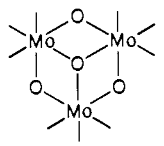
Abstract: Three different methods for the preparation of triangular Mo_3X_4 core (incomplete cuboidal) sulfido analogues of $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(H_2O)_9]^{4+}$ (A), involving reduction of $Mo^V{}_2$ are considered. The complexes prepared are $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3(H_2O)_9]^{4+}$ (B), $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_2(\mu\text{-}S)(H_2O)_9]^{4+}$ (C), $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9]^{4+}$ (D), and $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]^{4+}$ (E), all of which have a μ_3-sulfido ligand. The cuboidal mixed-valence (average oxidation state 3.25) $[Mo_4S_4(H_2O)_{12}]^{5+}$ ion F has also been obtained. Starting complexes, singly or as mixtures, are the aqua ($Mo_2O_2X_2$-type) $Mo^V{}_2$ complexes having bis(μ-sulfido), μ-oxo–μ-sulfido, and bis(μ-oxo) ligands or the related cysteinato complexes G–I, respectively. Procedures involve reduction of $Mo^V{}_2$ with $[MoCl_6]^{3-}$, electrochemically at a Hg-pool cathode, or with $NaBH_4$, followed by air oxidation in the latter two cases. Complexes B and C are best prepared by $[MoCl_6]^{3-}$ reduction of aqua $Mo^V{}_2$ ions (1 h at ca. 90 °C, N_2 atmosphere, followed by Dowex cation-exchange chromatography) in relatively clean reactions, yields 70–80%. The electrochemical and $NaBH_4$ methods, using either the cysteinato or aqua $Mo^V{}_2$ complexes, give mixes A–E depending on the identity of $Mo^V{}_2$. Yields are comparable for the two methods, but the amounts of B and C are much smaller than those obtained by the $[MoCl_6]^{3-}$ method. With use of the $NaBH_4$ method and the aqua ion of $Mo_2O_2S_2{}^{2+}$ (G) as the $Mo^V{}_2$ reactant, yields after air oxidation are typically cuboidal $[Mo_4S_4(H_2O)_{12}]^{5+}$ (~20% Mo conversion) and $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9]^{4+}$ (~30%). With use of rigorously air-free techniques orange-brown $Mo_4S_4{}^{4+}$ is identified as a precursor of green $Mo_4S_4{}^{5+}$. Prior to air oxidation orange and brown intermediate products can be identified in cation-exchange chromatography, estimated charges of 4+ and 6+, respectively, and these yield on heating in air $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9]^{4+}$ (from the organge product) and $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9]^{4+}$ and $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]^{4+}$ (from brown). The green $Mo^{IV}{}_3$ ion $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]^{4+}$ is not a primary product of the reduction. It is however formed on heating solutions of $[Mo_4S_4(H_2O)_{12}]^{5+}$ in 1 M HCl at ca. 90 °C in air for ca. 3–4 h. To maximize yields of the cube heating of the solutions obtained on reduction should therefore be minimized. Characterizations of B–F are indicated and mechanistic implications considered.

Procedures for the synthesis of cuboidal Fe_4S_4 cluster complexes,[1] as analogues of the biologically important ferredoxins,[2] and more recently of $MoFe_3S_4$ complexes[3] have attracted much attention. No aqua ions of Fe_4S_4 have been prepared however, and the few water-soluble Fe_4S_4 complexes that have been reported[4-6] are not noted for their stability except over a very limited range of pH.

It is now apparent that the aqueous solution chemistry of early-transition-metal ions as Mo is dominated by structures having more than one metal[7] and that many of these have metal–metal bonds.[8] A recent development is the identification by X-ray crystallography of triangular and cuboidal Mo/S cluster complexes having $Mo_3S_4{}^{4+}$[9-11] and $Mo_4S_4{}^{5+}$[12-14] core structures, respectively. Cubane clusters $[Mo_4S_4R_4]$, where R is cyclopentadiene or a substituted cyclopentadiene, have also been reported.[15,16] The metal–metal bonded triangular $Mo^{IV}{}_3$ aqua ion $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(H_2O)_9]^{4+}$ (A), which has an apical (as opposed to in plane) μ_3-oxo ligand, is now a well-established prototype of the trimeric ion.[17-19] Mixed oxo–sulfido triangular clusters have also been reported. Possible preparative routes into this aqueous solution chemistry involve the reduction of aqua and cysteinato μ-sulfido $Mo^V{}_2$ complexes,[11,20,21] reacting $[Mo(CO)_6]$ with Na_2S in refluxing acetic anhydride (followed by hydrolysis),[12] and via the disulfido complex $[Mo_3S_4(S_2)_3]^{2-}$ prepared by Müller et al.[22] The latter two methods have been employed by Cotton in recent studies.[12,23] Here we consider three procedures in the first category using (a) $[MoCl_6]^{3-}$ as reductant, (b) electrochemical reduction, and (c) $NaBH_4$ as a reductant. Sulfido analogues of the $Mo^{IV}{}_3$ aqua ion $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(H_2O)_9]^{4+}$ (A), formulas as in B–E are obtained. These structures are referred to subsequently as $Mo_3O_4{}^{4+}$ (A), $Mo_3(S)O_3{}^{4+}$ (B), $Mo_3(S)O_2S^{4+}$ (C), $Mo_3(S)OS_2{}^{4+}$ (D), and



A

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(1) Holm, R. H.; Ibers, J. A. In *Iron-Sulfur Proteins*; Lovenberg, W., Ed.; Academic: New York, 1977; pp 205–281. Ibers, J. A.; Holm, R. H. *Science (Washington, D.C.)* **1980**, *209*, 223.

(2) Lovenberg, W., Ed. *Iron-Sulfur Proteins*; Academic: New York, 1973–1977; Vols. I–III.

(3) Armstrong, W. H.; Mascharak, P. K.; Holm, R. H. *Inorg. Chem.* **1982**, *21*, 1699.

(4) Carrell, H. L.; Glusker, J. P.; Job, R. C.; Bruce, T. C. *J. Am. Chem. Soc.* **1977**, *99*, 3683.

(5) Hill, C. L.; Renaud, J.; Holm, R. H.; Mortenson, L. E. *J. Am. Chem. Soc.* **1977**, *99*, 2549.

(6) Henderson, R. A.; Sykes, A. G. *Inorg. Chem.* **1980**, *19*, 3103.

(7) Richens, D. T.; Sykes, A. G. *Comments Inorg. Chem.* **1981**, *1*, 141.

(8) Muller, A.; Jostes, R.; Cotton, F. A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 875.

(9) Cotton, F. A.; Dori, Z.; Llusar, R.; Schwotzer, W. *Inorg. Chem.* **1986**, *25*, 3654.

(10) Muller, A.; Jostes, R.; Eltzner, W.; Nie Chong-Shi; Diemann, E.; Bogge, H.; Zimmerman, M.; Dartmann, M.; Reinsch-Vogell, U.; Che Shun; Cyvin, S. J.; Cyvin, B. N. *Inorg. Chem.* **1985**, *24*, 2872.

(11) Shibahara, T.; Kuroya, H. *Polyhedron* **1986**, *5*, 357.

(12) Cotton, F. A.; Dori, Z.; Llusar, R.; Schwotzer, W. *Inorg. Chem.* **1986**, *25*, 3529.

(13) Müller, A.; Eltzner, W.; Bogge, H.; Jostes, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 795.

(14) Shibahara, T.; Kuroya, H.; Matsumoto, K.; Ooi, S. *J. Am. Chem. Soc.* **1984**, *106*, 789.

(15) Bandy, J. A.; Davies, C. E.; Green, J. C.; Green, M. L. H.; Prout, K.; Rodgers, D. P. S. *J. Chem. Soc., Chem. Commun.* **1983**, 1395.

(16) Williams, P. D.; Curtis, M. D. *Inorg. Chem.* **1986**, *25*, 4562.

(17) Bino, A.; Cotton, F. A.; Dori, Z. *J. Am. Chem. Soc.* **1978**, *100*, 5252.

(18) Schlemper, E. O.; Hussain, M. S.; Murmann, R. K. *Cryst. Struct. Commun.* **1982**, *11*, 89.

(19) Rodgers, K. R.; Murmann, R. K.; Schemper, E. O.; Shelton, M. E. *Inorg. Chem.* **1985**, *24*, 1313.

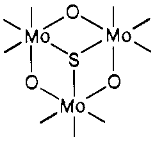
(20) Kathirgamanathan, P.; Martinez, M.; Sykes, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, *953*.

(21) Shibahara, T.; Yamada, T.; Kuroya, H.; Hills, E. F.; Kathirgamanathan, P.; Sykes, A. G. *Inorg. Chim. Acta* **1986**, *113*, L19.

(22) Muller, A.; Sarkar, S.; Bhattacharyya, R. G.; Pohl, S.; Dartmann, M. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 535.

(23) Cotton, F. A.; Dori, Z.; Llusar, R.; Marler, D. O.; Schwotzer, W. *Inorg. Chim. Acta* **1985**, *102*, L25.

0002-7863/87/1509-4615$01.50/0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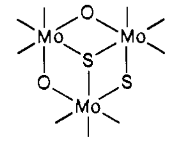
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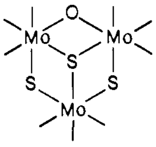
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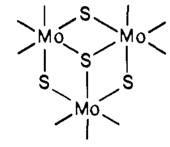
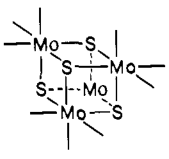
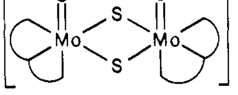

E

$Mo_3S_4^{4+}$ (E). The cuboidal $[Mo_4S_4(H_2O)_{12}]^{5+}$ ion, hereafter $Mo_4S_4^{5+}$ (F), is also obtained in the latter two procedures.


F

Experimental Section

Preparation of Mo(V)$_2$ Complexes. The cysteinato complexes sodium bis(μ-sulfido)bis[(L-cysteinato)oxomolybdate(V)] tetrahydrate, $Na_2[Mo_2O_2S_2(cys)_2]\cdot 4H_2O$, sodium ($\mu$-oxo)($\mu$-sulfido)bis[(L-cysteinato)oxomolybdate(V)] tetrahydrate, $Na_2[Mo_2O_3S(cys)_2]\cdot 4H_2O$, and sodium bis($\mu$-oxo)bis[(L-cysteinato)oxomolybdate(V)] pentahydrate, $Na_2[Mo_2O_4(cys)_2]\cdot 5H_2O$, formulas G–I, respectively, were prepared and stored as stable orange solids. Complex G was obtained by a procedure involving bubbling H_2S through sodium molybdate (VI), $Na_2[MoO_4]\cdot 2H_2O$,[24] H by a procedure involving by bubbling H_2S through molybdenum(V) pentachloride [$MoCl_5$] in 3 M HCl,[22] and I by a procedure involving sodium dithionite, hydrated [$Na_2S_2O_4$] (BDH Reagent Grade), reduction of a mixture of $Na_2[MoO_4]\cdot 2H_2O$ and L-(+)-cysteine hydrochloride (Sigma Chemicals) at 50 °C.[25] These procedures were followed (where necessary) by addition of cysteine as in the existing literature.[22,24] UV–vis absorption spectra for G–I in H_2O were as previously reported.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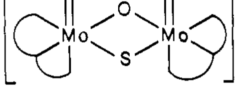
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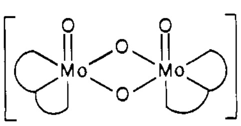
I

The procedure for obtaining the aqua ion of G, peak at 370 nm (ϵ 1940 M^{-1} cm^{-1}), has been described previously.[27] (Absorption coefficients (ϵ) throughout the paper are given per mole of complex, i.e., per dimer, trimer, or tetramer, except as stated.) In the case of H the cysteinato complex (1.25 g) was dissolved in H_2O (60 mL) and 5 M HCl (15 mL) added. After being filtered to remove any solid, this was loaded onto a Sephadex G-10 column (Sigma Chemicals; 40 cm × 1 cm diameter) and the aqua ion eluted with 1 M HCl. The spectrum of this aqua ion, prepared for the first time, alongside those for G and I, is shown in Figure 1. Absorbance peaks (λ/nm (ϵ/M^{-1} cm^{-1})): 220 (sh) (5805), 276 (3704), 312 (2990), 460 (sh) (52). The aqua ion $Mo_2O_4^{2+}$, peak at 384 nm (ϵ 103 M^{-1} cm^{-1}), has been extensively studied and was prepared by hydrazine hydrochloride reduction of $Na_2[MoO_4]\cdot 2H_2O$ in 10 M HCl at 80 °C and subsequent dilution with water.[28] The aqua dimers are assumed to have six H_2O's attached.

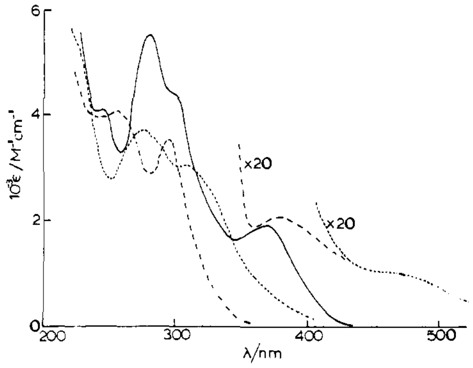

Figure 1. UV–vis spectra of aqua ions of Mo^V_2 dimers $Mo_2O_2S_2^{2+}$ (G) (—), $Mo_2OS_3^{2+}$ (H) (···), and $Mo_2O_4^{2+}$ (I) (---) in 1 M HCl.

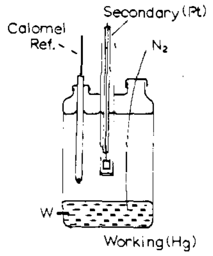

Figure 2. Cell used for electrochemical reduction of Mo^V_2, capacity 100 mL.

Reduction with $[MoCl_6]^{3-}$. The procedure is similar to one described for the preparation of the Mo^{IV}_3 ion $Mo_3O_4^{4+}$ [25] and involves heating Mo^V_2 aqua ions (4×10^{-3} M) with a 2:1 mole ratio excess of the Mo^{III} complex $K_3[MoCl_6]$ (Climax Molybdenum Co.) (air stable as solid) in 2 M HCl or 2 M HPTS (p-toluenesulfonic acid; Sigma Chemicals) for ca. 1 h on a steam bath at 80–90 °C under N_2. The reaction can be represented by (1), where [Mo(IV)] is a transient which yields Mo^{IV}_3 or

$$Mo^V_2 + 2Mo^{III} \rightarrow Mo^{IV}_3 + [Mo(IV)] \qquad (1)$$

becomes reoxidized to Mo^V_2. After the mixture is diluted to 0.5 M [H^+], the product is left to aquate any remaining chlorides (ca. 5 h) and the final purification carried out by using cation-exchange chromatography on a Dowex 50W-X2 resin (Sigma Chemicals). For this method only the aqua ions of G and H were used. The major band with $Mo_2O_2S_2^{2+}$ as reactant is gray in color (some contributing green/violet dichroism is observed) and is assigned the formula $Mo_3(S)O_2S^{4+}$ (see below), structure C. With $Mo_2O_3S^{2+}$ as the Mo^V_2 reactant a red product assigned the formula $Mo_3(S)O_3^{4+}$, structure B, is the dominant product. Yields are good with 70–80% conversion of moles of Mo^V_2 to chromatographically pure product.

Electrochemical Reduction. Both the cysteinato and aqua Mo^V_2 forms can be used. The cysteinato complex (or a mix of cysteinato complexes as required), for example, $Na_2[Mo_2O_2S_2(cys)_2]\cdot 4H_2O$ (3 g) in 2 M HCl (100 mL), is reduced under N_2 (or Ar) at a Hg-pool cathode by using a constant potential (−1.1 V vs. SCE) for 12 h (Figure 2). Subsequently, if triangular products rather than cuboidal $Mo_4S_4^{5+}$ are required, the dark brown solution is heated on a steam bath (ca. 90 °C) for 8–9 h in air, until a green solution (plus some brown solid) is obtained. After filtration and dilution to [H^+] = 0.3 M, or alternatively adding 2 L of 0.5 M HPTS the solution was loaded onto a Dowex 50W-X2 column (40 cm × 1 cm diameter). Columns were washed with 250 mL of 0.5 M HCl (or 0.5 M HPTS), and elution was with first 1 M HCl (2 M HPTS) and then 2 M HCl (4 M HPTS). The product pattern is more complex than previously indicated,[18] and the yields of pure products are less. In the electrolytic reduction of the aqua ions a solution of Mo^V_2 (10^{-2} M) in 2 M HCl (100 mL) is reduced for 6–7 h at −0.7 V (vs. SCE). A higher potential is required in the case of the cysteinato complexes because of the adverse effects of a precipitate which forms. At the lower potential less Cl_2 is evolved at the anode. Again, depending on the products required (see Discussion), the brown solution can be heated in air at 90 °C for 3–4 h or such a time as to optimize formation of a dark green color. After 10-fold dilution with H_2O the products are loaded onto a Dowex 50W-X2 column and the procedure as described previously is adopted. Initial column work was generally in HCl after which a switch to HPTS (a poor complexing ligand) was possible if required. Elution is generally slower in HPTS. With 1 M HCl chloride complexing is not

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[24] Ott, V. R.; Swieter, D. S.; Schultz, F. A. *Inorg. Chem.* **1977**, *16*, 2538.
[25] Kay, A.; Mitchell, P. C. H. *J. Chem. Soc. A* **1970**, *2421*.
[26] Spivack, B.; Dori, Z. *Coord. Chem. Rev.* **1975**, *17*, 99.
[27] Armstrong, F. A.; Shibahara, T.; Sykes, A. G. *Inorg. Chem.* **1978**, *17*, 189.
[28] Richens, D. T.; Sykes, A. G. *Inorg. Synth.* **1985**, *23*, 130.

Table I. UV–Visible Absorption Spectra of Triangular Mo^{IV}_3 and Cuboidal Mo(III,III,III,IV) Mo/S Cluster Complexes as Aqua Ions in 2 M HPTS

	λ, nm	ε,[a] M^{-1} cm^{-1}
$[Mo_3O_4(H_2O)_9]^{4+}$ (A)	505	189
$[Mo_3(S)O_3(H_2O)_9]^{4+}$ (B)	512	153
$[Mo_3(S)O_2S(H_2O)_9]^{4+}$ (C)	572	202
$[Mo_3(S)OS_2(H_2O)_9]^{4+}$ (D)	590	280
$[Mo_3S_4(H_2O)_9]^{4+}$ (E)	602	351
$[Mo_4S_4(H_2O)_{12}]^{5+}$ (F)	645	470

[a] ε's are expressed per mole of trimer or tetramer.

sufficiently extensive or persistent to give different charged products, and separate bands on columns, as is observed for example with $Mo_3O_4^{4+}$ equilibrated in 4 M HCl. To bring about satisfactory separation of some products, e.g., $Mo_3S_4^{4+}$ and $Mo_3(S)OS_2^{4+}$, a second column using Sephadex G-10 is employed. To concentrate eluted fractions a further Dowex column is used.

Reduction with $NaBH_4$. The procedure was essentially as described by Shibahara and colleagues using cysteinato complexes.[24] Typically $NaBH_4$ (1 g, 25 mmol) was added to (1–2) × 10^{-2} M cysteinato Mo^V_2 in 0.03 M HCl (200–250 mL) under N_2, reaction time 5–10 min. Concentrated HCl (30–40 mL) was then added to give a final $[H^+]$ of ca. 1.5 M, which removes any excess $NaBH_4$ and the solution left air-free overnight at ca. 4 °C. As above depending on the product required, the brown solution obtained can be heated in air at this stage for 8–9 h. The procedure was basically the same for the Mo^V_2 aqua ions, concentrations (3–6) × 10^{-3} M, in 0.05 M HCl (500–700 mL). Solutions were however heated for only 4–5 h. Column chromatography on product solutions was as in the previous section. To determine the percentage of Mo conversion, yields were averaged for five preparations.

Analyses and Characterization. Solutions in HPTS had first to be ion-exchanged and eluted with HCl. The Mo content was determined by oxidizing solutions in HCl (10^{-3} M, 2 mL) with a 2:1 mixture of concentrated HCl/HNO_3 and heating to dryness. This was followed by addition of $Br_2(l)$ and again heating to dryness. The above procedure (both steps) was repeated two or three times. The Mo(VI) was then dissolved in 1–2 M HCl and reduced to Mo^V_2 with hydrazinium sulfate at 80 °C.[29] Excess hydrazine was removed by boiling for ca. 10 min and the Mo^V_2 determined by titration with Ce(IV) using ferroin as indicator. The Mo was also checked by atomic absorption using a Perkin-Elmer 2380 spectrometer. Sulfur was determined as $BaSO_4$ after oxidation with HNO_3/Br_2 (as above) or with a 10-fold excess of 100 v H_2O_2 under alkaline conditions. The Mo/S ratios determined were within ±3% of formulas indicated n C–E and ±6% for B. Analysis for the $Mo_4S_4^{5+}$ aqua ion gave an Mo/S ratio of 0.98 ± 0.02. UV–vis absorption spectra gave peaks in the 500–650-nm region as indicated in Table I. These are in satisfactory agreement with values previously reported. All the trimeric complexes exhibit a peak in the range 300–400 nm, the magnitude of which depends on anions present: 300 (sh) (A), 332 (B), 335 (C), 312 (D), 365 nm (E).

Since crystals of aqua ions are difficult to obtain, further characterization is based on X-ray crystal structures of derivative complexes. Interconversion reactions of aqua ions characterized spectrophotometrically are therefore important. For example in the case of $[Mo_4S_4(H_2O)_{12}]^{5+}$ addition of edta and adjustment of pH or slow elution from a Dowex cation-exchange column with an edta solution gave $[Mo_4S_4(edta)_2]^{3-}$, which was identified spectrophotometrically peak at 636 nm (ε 632 M^{-1} cm^{-1} per tetramer). Treatment of the edta complex with 3 M HPTS over 60 h gave a solution containing $Mo_4S_4^{5+}$. Some decomposition also occurs over this time span. Relevant X-ray crystal structures are $Ba[Mo_3(S)O_3(Hnta)_3]\cdot 10H_2O$ (B),[30] $(pyH)_5[Mo_3(S)O_2S(NCS)_9]\cdot 2H_2O$ (C),[21] $Ba[Mo_3(S)OS_2(ida)_3]\cdot 7H_2O$ (D),[31] $Cs_2[Mo_3S_4(C_2O_4)_3(H_2O)_3]\cdot 3H_2O$,[32] $K_5[Mo_3S_4(CN)_9]\cdot 2H_2O$,[10] $Ca[Mo_3S_4(ida)_3]\cdot 11.5H_2O$ (E),[11] and $Ca_3[Mo_4S_4(edta)_2]\cdot 28H_2O$ (F).[14]

Stability of Clusters. All the aqua ions $Mo_3(S)O_3^{4+}$, $Mo_3(S)O_2S^{4+}$, $Mo_3(S)OS_2^{4+}$, $Mo_3(S)OS_2^{4+}$, $Mo_3S_4^{4+}$, and $Mo_4S_4^{5+}$, at concentration >0.1 mM in 2 M HPTS, can be stored under N_2 at 4 °C for weeks. In air the complexes are less stable, and after any period of storage (even under N_2) repurification by chromatography is advisable. It is of interest that in air $Mo_4S_4^{5+}$ is less stable in 2 M HCl than in 2 M HPTS.

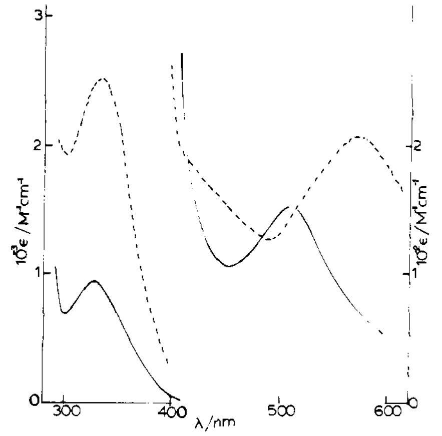

Figure 3. UV–vis spectra of aqua ions of the Mo^{IV}_3 clusters $Mo_3(S)O_3^{4+}$ (—) and $Mo_3(S)O_2S^{4+}$ (- - -) in 2 M HPTS.

Results

Two new synthetic routes using $[MoCl_6]^{3-}$ as reductant are described. From the Mo^V_2 reactant $Mo_2O_3S^{2+}$, the aqua ion of H, a red product, Mo/S ratio of 3:1 is obtained. The spectrum is shown in Figure 3, and from analyses and X-ray crystallography the dominant (possibly only) sulfido product is $Mo_3(S)O_3^{4+}$ (B). With the Mo^V_2 reactant $Mo_2O_2S_2^{2+}$, the aqua ion of G, the product is gray in color, UV–vis spectrum as in Figure 3. Analyses are consistent with the formula $Mo_3(S)O_2S^{4+}$, and structure C has been confirmed. In both cases one dominant product is obtained in good yield. Some Mo^V_2 is present in final solutions, and traces of $Mo_3O_4^{4+}$ are sometimes observed. Details of the further involvement of the Mo, referred to as [Mo(IV)] in eq 1 and relating to the stoichiometry, have not been studied.

Color changes observed in the electrochemical and $NaBH_4$ reductions are similar by using both aqua and cysteinato Mo^V_2 complexes G–I. Thus for G a brown coloration precedes formation of the green color obtained on air oxidation. Cysteine ligands are aquated in conditions of high $[H^+]$ (ca. 1 M), and aqua ion products are obtained (see below however). With the cysteinato complexes some (unwanted) black solid material is deposited during the reduction. In recent work yields are (overall) better with use of the Mo^V_2 aqua ions.

A particularly striking feature is that substantial amounts of $Mo_3(S)OS_2^{4+}$ (as much as 55% in the electrochemical method), much greater than $Mo_3S_4^{4+}$, are obtained as final product from the Mo^V_2 reactant $Mo_2O_2S_2^{2+}$. Also in the electrochemical method no additional color changes corresponding to reactions of Mo/S clusters with the Hg electrode were detected. We confirm from separate experiments that green $Mo_3S_4^{4+}$ under N_2 reacts with Hg to generate an intense purple colored product (λ_{max} 556 nm) (ε 9010 M^{-1} cm^{-1}), within minutes, which Shibahara and coworkers report to be cuboidal $HgMo_3S_4^{4+}$ or a closely related species.[33] In our studies no similar interaction of Hg with $Mo_3(S)OS_2^{4+}$ is observed. It can be concluded therefore that $Mo_3S_4^{4+}$ is not a primary product in the electrolytic procedure, and is obtained only after air oxidation over long periods (or with heating). In both the electrochemical and $NaBH_4$ preparations from $Mo_2O_2S_2^{2+}$ small amounts of $Mo_3(S)O_2S^{4+}$ are obtained. Yields from the (five) most recent $NaBH_4$ preparations from aqua $Mo_2O_2S_2^{2+}$ are $Mo_4S_4^{5+}$ (21 ± 4%), $Mo_3OS_3^{4+}$ (28 ± 6%), $Mo_3S_4^{4+}$ (ca. 3%), and $Mo_3O_2S_2^{4+}$ (ca. 1%) expressed as conversion of Mo to products.

Air-free chromatographic separation of brown solutions (left overnight in the $NaBH_4$ case) gave orange-brown $Mo_4S_4^{4+}$ as a product. The products identified in such a preparation from aqua $Mo_2O_2S_2^{2+}$ are in order of elution from a Dowex 50W-X2 column; [HCl] gradient 0.5–3.0 M; first any unreacted Mo^V_2 (Figure 4),

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(29) Rao, G. G.; Swyanavayana, Z. *Anal. Chem.* **1959**, *168*, 177.

(30) Shibahara, T.; Hattori, H.; Kuroya, H. *J. Am. Chem. Soc.* **1984**, *106*, 2710.

(31) Shibahara, T.; Miyake, H.; Kobayashi, K.; Kuroya, H. *Chem. Lett.* **1986**, 139.

(32) Cotton, F. A.; Dori, Z.; Llusar, R.; Schwotzer, W. *J. Am. Chem. Soc.* **1985**, *107*, 6734.

(33) Shibahara, T. Paper 4-426, Japanese Chemical Society Meeting, Kyoto, April, 1986, and personal communication.

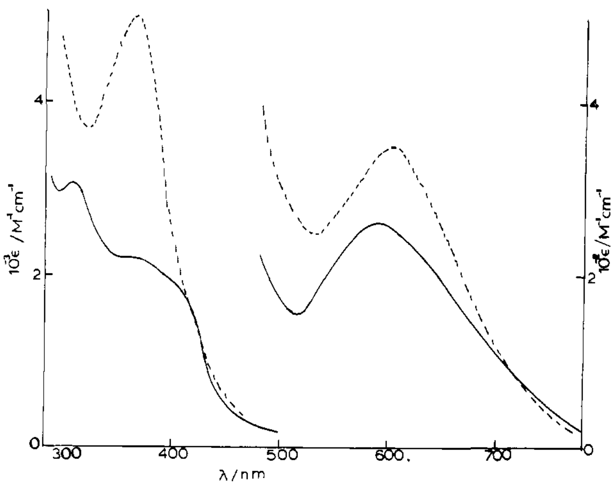


Figure 4. UV-vis spectra of aqua ions of the Mo^{IV}_3 clusters $Mo_3(S)OS_2^{4+}$ (—) and $Mo_3S_4^{4+}$ (---) in 2 M HPTS.

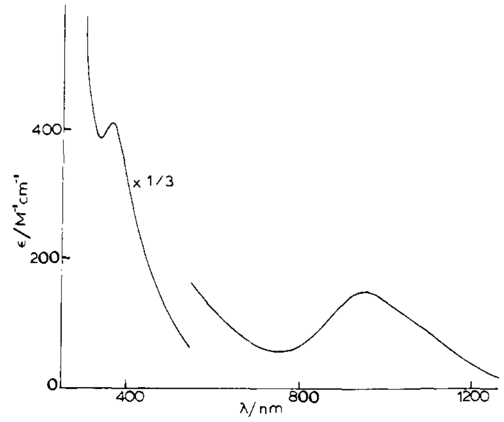


Figure 5. UV-vis-near-IR spectrum of orange intermediate, ε's approximate only, in 1 M HCl.

an orange band with peaks at 936 nm (ε 150 M^{-1} cm^{-1} per Mo) and 358 nm (ε 1200 M^{-1} cm^{-1} per Mo) (Figure 5), orange-brown $Mo_4S_4^{5+}$ (Figure 6), and finally a brown complex (dilute because of its high charge), which exhibits increasing absorbance toward the UV with a shoulder at 360 nm. Similar results are obtained on eluting with HPTS. On leaving a solution of $Mo_4S_4^{4+}$ exposed to air for an overnight period green $Mo_4S_4^{5+}$ is formed. The products obtained prior to air oxidation we refer to as primary products.

We have not further characterized the orange and brown fractions, but the products obtained on further air oxidation are particularly informative. Slow air oxidation of the orange solution over ca. 2–3 days at room temperature gives green $Mo_3(S)OS_2^{4+}$ as the sole product. The brown fraction also air oxidizes very slowly to give a green solution (ca. 4 h on heating to ca. 90 °C), which is a mixture of $Mo_3S_4^{4+}$ and $Mo_3(S)OS_2^{4+}$ (Figure 4). The latter process appears to be one source of $Mo_3S_4^{4+}$ in the procedures described. Also on heating a solution of $Mo_4S_4^{5+}$ in 2 M HCl for 3–4 h at ca. 90 °C, a color change from the original green to a different green was observed. On column purification it was found that quantitative conversion to trimeric $Mo_3S_4^{4+}$ had occurred. The heating has to be limited, or else some decomposition of $Mo_3S_4^{4+}$ to $Mo_3OS_3^{4+}$ or $Mo_3O_2S_2^{4+}$ is observed.

So far comments relate to the aqua and cysteinato Mo^V_2 reactant $Mo_2O_2S_2^{2+}$ (G). Mixes of Mo^{IV}_3 products including products with fewer sulfides are obtained when other Mo^V_2 reactants, H and I, are used. With a mixture of $Mo_2O_2S_2^{2+}$ and $Mo_2O_4^{2+}$ the range of Mo^{IV}_3 products after air oxidation is particularly extensive and separation of pure products become increasingly difficult. All of the Mo^{IV}_3 products (Table I), with the possible exception of $Mo_3(S)O_3^{4+}$ (little if any), as well as $Mo_4S_4^{5+}$ are obtained. With the Mo^V_2 reactant $Mo_2O_3S^{2+}$ there are two products, $Mo_3(S)O_3^{4+}$ and $Mo_3(S)O_2S^{4+}$, but no $Mo_3O_4^{4+}$ (or cuboidal) product is detected. We have not been able to confirm an earlier claim to have obtained the μ_3-oxo isomers of B–D (one in each case),[34] and, if these are formed, it is in small amounts, which are difficult to detect in the chromatographic procedures alongside other 4+ products.

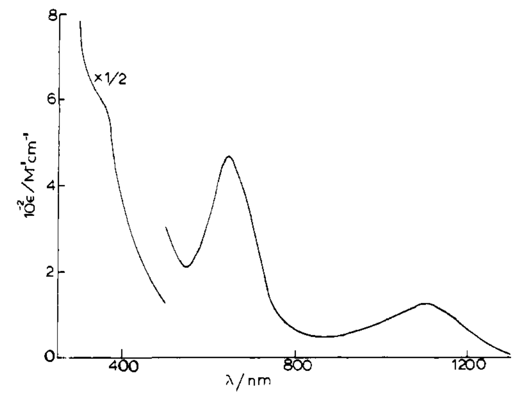
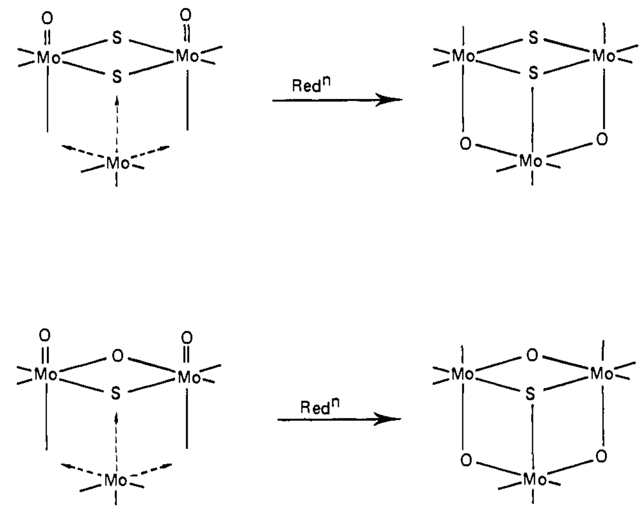


Figure 6. UV-vis-near-IR spectrum of the aqua ion of the Mo(III,III,III,IV) cuboidal $Mo_4S_4^{5+}$ in 2 M HPTS.

Scheme I



When the Mo^V_2 reactant is $Mo_2O_4^{2+}$, large amounts (ca. 60%) of red $Mo_3O_4^{4+}$ are formed. In the subsequent chromatographic separation, using the cysteinato Mo^V_2 complex as reactant, a brown component, peak at 404 nm (ε 1100 M^{-1} cm^{-1} per Mo), is obtained.[35] In our recent work this product is not confirmed as the $Mo_4O_4^{5+}$ oxo analogue of $Mo_4S_4^{5+}$ but has been shown to contain cysteine and is most likely a Mo(V), or possibly Mo(IV), cysteinato complex. Of interest is its apparent stability in up to 4 M HCl.

Discussion

The $[MoCl_6]^{3-}$ reduction of aqua Mo^V_2 ions of G and H gives 70–80% conversion of Mo^V_2 to the Mo^{IV}_3 products $Mo_3(S)O_2S^{4+}$ and $Mo_3(S)O_3^{4+}$, respectively. These are the best yields of chromatographically pure Mo^{IV}_3 complexes obtained for members of the $Mo_3O_xS_{4-x}^{4+}$ series. The reactions proceed by aquation of chloride and Mo(III) attachment to the Mo^V_2. Bridging μ-sulfido ligands in the Mo^V_2 reactant are retained as indicated Scheme I. The observation that the μ_3-oxo isomeric form of B is absent or present in only small amounts indicates a marked preference for μ_3-sulfido formation, which is a feature also of the other procedures. Use of cysteinato complexes G–I in the $[MoCl_6]^{3-}$ procedure gives much smaller yields (ca. 20%), the cysteine ligands presumably hindering reaction. For this reason

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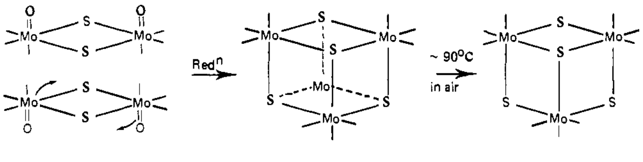
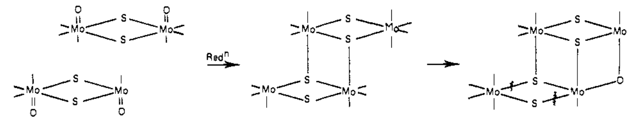
[34] Kathirgamanathan, P.; Martinez, M.; Sykes, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 1437.

[35] Armstrong, G. D.; Sykes, A. G., unpublished work.

Scheme II



Scheme III



an alternative route to that in Scheme I, with incorporation of the terminal oxo ligands of the $Mo^V{}_2$ reactant as bridging ligands, is not thought to make a significant contribution.

The successful use of aqua $Mo^V{}_2$ ions in the above, as well as the detection (following column chromatography) of cysteinato products in the electrochemical or $NaBH_4$ reductions of cysteinato $Mo_2O_4{}^{2+}$, leads us to explore the more extensive use of the aqua $Mo^V{}_2$ reactants. With the $Mo_2O_2S_2{}^{2+}$ reactant, prior to air oxidation, orange-brown cuboidal $Mo_4S_4{}^{4+}$ is detected as a primary product in the electrochemical and $NaBH_4$ procedures. This readily air oxidises to green $Mo_4S_4{}^{5+}$. From the five most recent $NaBH_4$ preparations the yield of $Mo_4S_4{}^{5+}$ is ~20%. The formation of $Mo_3(S)OS_2{}^{4+}$ and not $Mo_3S_4{}^{4+}$ as a major product is unexpected. After air oxidation of both the orange and brown products, as much as 35% ($NaBH_4$) and 55% (electrochemical) of $Mo_3(S)OS_2{}^{4+}$ have been identified. The complex $Mo_3S_4{}^{4+}$ is best obtained in a pure state by heating chromatographically pure solutions of $Mo_4S_4{}^{5+}$ (preferably in 2 M HCl) for 3–4 h at ca. 90 °C. It is also formed on heating the brown complex. The 936-nm peak of the orange product suggests a mixed-valence form by analogy with the spectrum of the Mo(III,III,IV) complex obtained from $Mo_3O_4{}^{4+}$.[36] However in separate experiments, it was found that $NaBH_4$ and Zn/Hg do not reduce $Mo_3(S)OS_2{}^{4+}$, and on this evidence the orange product does not have the same structure but may be a closely related form. One possibility (as in Scheme III below) is a mixed-valence (noncuboidal) Mo_4 species, which on air oxidation gives $Mo_3(S)OS_2{}^{4+}$.

The formation of $Mo_4S_4{}^{4+}$ as a primary product suggests that a cuboidal complex is formed following the initial reduction of $Mo^V{}_2$ to oxidation states intermediate to or as low as $Mo^{III}{}_2$. Because all four μ-sulfido ligands are retained the cuboidal adduct is believed to be generated as in Scheme II, which can then be converted to $Mo_3S_4{}^{4+}$. However, formation of $Mo_3(S)OS_2{}^{4+}$ rather than $Mo_3S_4{}^{4+}$ is so prominent a feature of the preparation from $Mo_2O_2S_2{}^{2+}$ that an alternative dimerization process has to be considered. We suggest that this occurs as in Scheme III. Such an Mo_4 "ladder" structure for the orange intermediate is able to account for the formation of $Mo_3(S)OS_2{}^{4+}$ on heating. The brown intermediate is more complex, possibly Mo_6, to account for the formation of $Mo_3(S)OS_2{}^{4+}$ and $Mo_3S_4{}^{4+}$ on air oxidation. No mixed S/O cuboidal Mo_4 species have been detected in these studies which suggests a possible size incompatability. This incompatibility may also explain the absence of a reaction of Hg with $Mo_3(S)OS_2{}^{4+}$ to give cuboidal $HgMo_3(S)OS_2{}^{4+}$ as well as the difficulty in obtaining triangular μ_3-oxo complexes.

Finally we conclude by summarizing the best methods for preparing the triangular and cuboidal Mo/S ions under discussion. Without question $Mo_3(S)O_3{}^{4+}$ and $Mo_3(S)O_2S^{4+}$ should be prepared from aqua $Mo^V{}_2$ forms of H and G, respectively, by the $[MoCl_6]^{3-}$ method. In choosing between the electrolytic reduction and $NaBH_4$ methods, it is relevant that an electrolytic cell of volume ca. 100 mL as in this study imposes restrictions, and to this extent the $NaBH_4$ method is preferred. Cleaner products and better yields are obtained by using the aqua $Mo^V{}_2$ complexes as reactants. However an extra column is required to convert the cysteinato complexes to the corresponding aqua ion, and larger volumes can be involved. An easier route for preparing the aqua ion $Mo_2O_2S_2{}^{2+}$ would be helpful. With the cysteinato $Mo^V{}_2$ complexes it is possible to work on a larger scale, and the procedure is overall quicker, although reactions are not as clean or as productive. To prepare $Mo_3(S)OS_2{}^{4+}$ (sacrificing some yield in the interests of speed) and also $Mo_4S_4{}^{5+}$, it is better to proceed to the chromatography after air oxidation and without heating. The $Mo_3S_4{}^{4+}$ complex is most readily obtained pure by first isolating $Mo_4S_4{}^{5+}$ and then heating in air followed by column purification.

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[36] Richens, D. T.; Sykes, A. G. *Inorg. Chem.* **1982**, *21*, 418.