

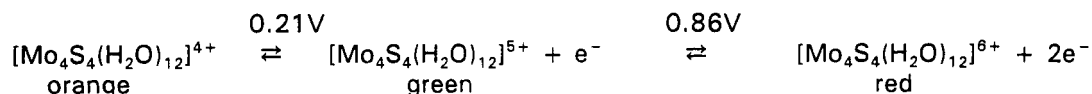
## Mechanistic studies on novel Mo–S containing cluster complexes in aqueous solution

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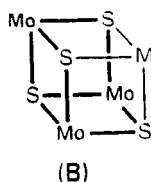
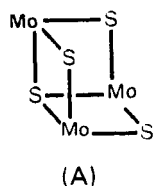
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**Abstract:** Studies on Mo-S cluster complexes including cuboidal  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{n+}$  ( $n = 4, 5, 6$ ) and heterometallic  $[\text{Mo}_3\text{MS}_4(\text{H}_2\text{O})_x]^{4+}$  ( $x = 10, 12$ ) complexes are described. Such cubes are stable in aqueous solution, and provide a ready means of studying redox and substitution reactions not possible in the case of e.g.  $\text{Fe}_4\text{S}_4$  complexes. Here the emphasis is on substitution reactions. Studies on two heterometallic cubes  $M = \text{Ni}, \text{Cr}$  obtained from  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$  are reported. Whereas  $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$  contains tetrahedral Ni, the  $[\text{Mo}_3\text{CrS}_4(\text{H}_2\text{O})_{12}]^{4+}$  cluster has octahedral Cr. Using the tridentate 1,4,7-triazacyclononane ligand, 9-aneN<sub>3</sub>, the cube  $[\text{Mo}_3\text{Ni}(9\text{-aneN}_3)\text{S}_4(\text{H}_2\text{O})_9]^{4+}$  has been prepared containing an octahedral and inert Ni. The case for a Ni<sup>0</sup> assignment is considered. The crystallographically characterised  $[\text{Mo}_3\text{S}_7\text{Br}_6]^{2-}$  has been converted to a new aqua ion  $[\text{Mo}_3\text{S}_7(\text{H}_2\text{O})_6]^{4+}$ . With  $\text{P}(\text{C}_6\text{H}_4\text{SO}_3)_3^{3-}$  in 2M Hpts the latter gives  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ . Two stages are observed in substitution studies with  $\text{NCS}^-$ .

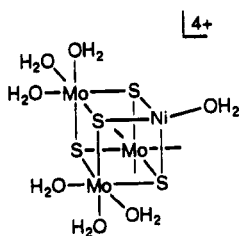
Cuboidal Mo-S complexes are prepared via the dimeric di- $\mu$ -sulfido molybdenum(V) complex  $[\text{Mo}_2\text{O}_2(\mu\text{-S})_2(\text{Cys})_2]^-$ , where Cys is the cysteinato ligand,  $\text{NH}_2\text{CH}(\text{CH}_2\text{S}^-)\text{CO}_2^-$ , (1). Using  $\text{BH}_4^-$  as reductant, the cuboidal  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$  mixed-valence (3.25) product can be isolated in normally ~15% yields. The reaction involves the (facial) linking-up of two  $\text{Mo}(\text{S})_2\text{Mo}$  rings in a reduced state to generate a cube. Although the 5+ cube is the most readily accessed, two other oxidation states 4+ and 6+ respectively can be obtained, (2).



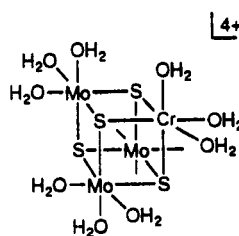
By heating a solution of  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$  to ~90°C in air for 2h one of the Mo's is removed, and the trinuclear Mo(IV)<sub>3</sub> incomplete cube  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$  (A) is obtained, (3). Heterometal atoms can be introduced into the latter to regenerate a cube and give a whole new series of cluster complexes (B), (3)-(4).



Details of the aqueous solution chemistry of heterometallic cubes with  $M = \text{Ni}$  and  $\text{Cr}$  are considered, (5),(6). Whereas the  $\text{Ni}$  in the heterocube (C) is tetrahedral, the  $\text{Cr}$  in (D) is

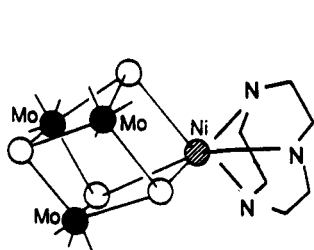


(C)

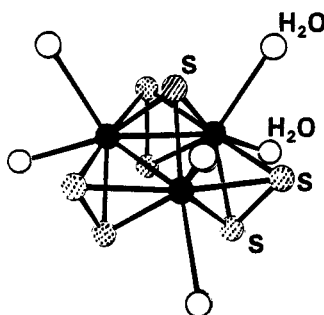


(D)

octahedral (as are the  $\text{Mo}$ 's). However when (A) is reacted with  $[\text{Ni}(\text{9-aneN}_3)\text{Cl}_2] \cdot 2.5\text{H}_2\text{O}$ , (7), where 9-ane $\text{N}_3$  is the tridentate ligand 1,4,7-triazacyclononane, the  $\text{Ni}$  in the product (E)



(E)



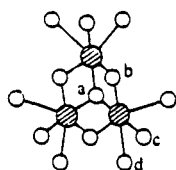
(F)

is octahedral, and it is of interest to explore the effect on reactivity.

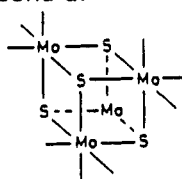
A different and entirely novel type of aqua ion  $[\text{Mo}_3\text{S}_7(\text{H}_2\text{O})_6]^{4+}$  (F) has been prepared for the first time from the previously characterised  $[\text{Mo}_3\text{S}_7\text{Br}_6]^{2-}$ , (8). Structural features of the  $[\text{Mo}_3\text{S}_7\text{X}_6]^{2-}$  ( $\text{X} = \text{Cl}^-$ ,  $\text{Br}^-$ ) clusters, are the orientation of the three disulfide groups, (8),(9). The upper S-atom is in the same (equatorial) plane defined by the three  $\text{Mo}$ 's, but is more distant to the  $\text{Mo}$  ( $2.48\text{\AA}$ ) than the second (axial) S-atom ( $2.39\text{\AA}$ ), (10). Also the two halide ligands to each  $\text{Mo}$  replaced by  $\text{H}_2\text{O}$  in (F), are non-identical and cis and trans respectively to the single apical  $\mu_3\text{-S}$  group.

It has been established from studies on ligand substitution reactions of the incomplete cuboidal complex  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ , e.g.  $\text{NCS}^-$  for  $\text{H}_2\text{O}$ , that there are two well defined stages, (11). The first monitored by stopped-flow corresponds to replacement of  $\text{H}_2\text{O}$  at the d position (trans  $\mu_2\text{S}$ ) in (G), and the second a much slower conventional time range study to reaction at c. Rate constants for substitution at d can be expressed as  $a + b[\text{H}^+]^{-1}$ , where from NMR studies, (12), b is assigned as the effect of conjugate-base formation at

one d position on substitution at the second d.



(G)



(H)

The c-H<sub>2</sub>O does not give any evidence for acid dissociation in the range of [H<sup>+</sup>] explored, (12).

### Substitution Reactions of [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>n+</sup> Clusters

All the core sulfides in the Mo<sub>4</sub>S<sub>4</sub> cube (H) are μ<sub>3</sub>-S, and coordinated H<sub>2</sub>O's are all of the c type as defined in (G). Substitution reactions are understandably slower therefore. The reactions of the 4+ and 5+ cubes are independent of [H<sup>+</sup>] in the range 0.4-2.0M studied, (13). Of the reactions with common anions NCS<sup>-</sup> gives the bigger absorbance changes and is the easiest therefore to monitor.

In the reaction of [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>4+</sup>, which has four identical Mo(III)'s, NCS<sup>-</sup> in >10-fold excess, the first stage of reaction gives equilibration kinetics  $k_{\text{eq}} = k_f[\text{NCS}^-]/4 + k_b$ , and the second (independent of [NCS<sup>-</sup>]) corresponds to isomerisation,  $k_{\text{isom}} = 3.6 \times 10^{-5}\text{s}^{-1}$ . The latter most probably corresponds to isomerisation of Mo-SCN to the more stable Mo-NCS form. Rate constants for the first stage with cube in excess differ from those with NCS<sup>-</sup> in excess by the statistical factor of 4, corresponding to the number of equivalent Mo's, and the forward and back rate constants are  $k_f = 1.95\text{M}^{-1}\text{s}^{-1}$  and  $k_b = 1.44 \times 10^{-3}\text{s}^{-1}$ .

Two [NCS<sup>-</sup>]-dependent reactions are observed in the overall slower substitution reaction on [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>5+</sup>. These are assigned as concurrent processes. For the first a statistical factor of 3 applies, and the rate constant  $k_{1f}$  is assigned as substitution at each of the three Mo(III)'s. For the second there is no statistical factor, and  $k_{2f} = 0.0166\text{M}^{-1}\text{s}^{-1}$  is assigned to reaction at the single Mo(IV). There is therefore evidence for an electron distribution which approximates to Mo(III)<sub>3</sub>Mo(IV). What may be happening is that the equilibration process with NCS<sup>-</sup>, leading to ion-pairing at each Mo, is faster than any interchange of oxidation state in Mo(III)<sub>3</sub>Mo(IV), thus registering a difference in behaviour of the Mo(III) and Mo(IV) centres. Studies with Cl<sup>-</sup> as the substituting anion are both thermodynamically ~10<sup>3</sup> less favourable, and absorbance changes are much smaller. As a consequence one stage only, presumably that giving the bigger absorbance change, is observed. By analogy with the NCS<sup>-</sup> reaction this can be assigned to reaction at the Mo(IV).

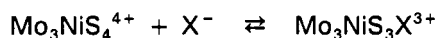
The reaction of NCS<sup>-</sup> with [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>6+</sup> has some unexpectedly different features, (14). The reaction is monophasic, and is upto ~10<sup>3</sup> times faster than the above 4+ and 5+ reactions, in spite of the higher 6+ charge. Thus rate constants are in the stopped-flow range, and unlike the 4+ and 5+ cubes exhibit an [H<sup>+</sup>]<sup>-1</sup> dependence. At 25°C the [H<sup>+</sup>] dependence is of the kind  $k_f = a + b[\text{H}^+]^{-1}$ , where  $a = 13.3\text{M}^{-1}\text{s}^{-1}$  and  $b = 5.1\text{s}^{-1}$ , these observations, and the statistical factor of two, suggest that the formally Mo(III)<sub>2</sub>Mo(IV)<sub>2</sub> metal centres may behave as two identical delocalised Mo(III)Mo(IV) pairs. The  $a + b[\text{H}^+]^{-1}$  dependence for both  $k_f$  and  $k_b$  may relate to the electron count of 10, since 12 electrons (as in the case of the 4+ ion) are required for a fully Mo-Mo bonded structure. Thus one

possibility is that in solution there may be a lengthening of one of the Mo-Mo bonds, thereby introducing  $\mu$ -S as opposed to  $\mu_3$ -S character, with some resultant acid dissociation occurring as in the case of  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ . An alternative interpretation might involve acid dissociation and substitution at the Mo(IV)'s with no involvement of the Mo(III)'s. However no similar effects are observed in the case of the 5+ cube which has a single Mo(IV) site.

### Substitution Reactions of $\text{Mo}_3\text{Ni}$ Cubes

The green-blue heterometallic cube  $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$  is prepared by  $\text{BH}_4^-$  reduction of a 1:10 solution of  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$  and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  in 0.5M HCl, and purified using Dowex 50W-X2 cation exchange chromatography.

In earlier work (5) the complexing equilibrium process,



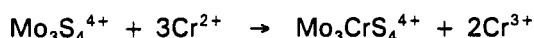
was studied by stopped-flow spectrophotometry, and gave forward and back rate constants for  $\text{X}^- = \text{Cl}^-$  of  $k_f = 9.4\text{M}^{-1}\text{s}^{-1}$ ,  $k_b = 0.099\text{s}^{-1}$ , and for  $\text{X}^- = \text{NCS}^-$  of  $k_f = 45\text{M}^{-1}\text{s}^{-1}$ ,  $k_b = 0.062\text{s}^{-1}$ . The reaction is assigned as substitution at the Ni, but as has been noted the reaction is unusually slow for substitution at tetrahedrally coordinated Ni(II), (15), and is indeed slower than substitution on  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ , (16).

The above investigations have now been extended to include three other anions, and give  $k_f/\text{M}^{-1}\text{s}^{-1}$  values for  $\text{Br}^-$  (14.6),  $\text{I}^-$  (30), and the water soluble phosphine  $\text{PR}_3^{3-}$  (51), where R is the 3-sulfonatophenyl group  $\text{C}_6\text{H}_4\text{SO}_3^-$ . In these studies  $\text{Na}_3[\text{PR}_3] \cdot 4\text{H}_2\text{O}$  was obtained from Strem Chemicals. Also relevant are the equilibrium constants  $K/\text{M}^{-1}$  which are for  $\text{Cl}^-$  (97),  $\text{NCS}^-$  (720),  $\text{Br}^-$  (150),  $\text{I}^-$  (215),  $\text{PR}_3^{3-}$  (5530). The first point to make is that there is a large thermodynamic affinity for  $\text{PR}_3^{3-}$ , not previously observed in the case of  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ . It is however consistent with the observation that carbon monoxide binds to the Ni to give  $[\text{Mo}_3\text{NiS}_4(\text{CO})(\text{H}_2\text{O})_9]^{4+}$ , (17). Secondly rate constants  $k_f$  give a narrow spread of values within a factor of 6 which suggests an  $\text{I}_d$  dissociative interchange mechanism. Previously a dissociative mechanism (possibly D) has been proposed for substitution on  $[\text{Ni}(\text{CO})_4]$ , (18). There is a case therefore for considering the Ni as approximating to  $\text{Ni}^0$  in the  $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$  cluster. A second slower stage is observed in the reaction with  $\text{NCS}^-$  which is assigned to substitution at the Mo's.

Some of the above features are confirmed in studies on the  $[\text{Mo}_3\text{Ni}(\text{9-aneN}_3)\text{S}_4(\text{H}_2\text{O})_9]^{4+}$  cluster, where 9-aneN<sub>3</sub> is the 1,4,7-triazacyclononane ligand. The cube was prepared by syphoning  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$  onto a mixture of violet  $[\text{Ni}(\text{9-aneN}_3)\text{Cl}_2] \cdot 2.5\text{H}_2\text{O}$ , (7), and  $\text{Na}[\text{BH}_4]$ . The product was purified by Dowex 50W-X2 chromatography and is stable in air. The 9-aneN<sub>3</sub> ligand closes down the Ni site to further complexation, and with  $\text{NCS}^-$  only the slower reaction corresponding to substitution at the Mo's is observed. Similarly in redox studies with hexaaqua-Fe(III) there are no contributions from the inner-sphere reaction of  $[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  at the Ni site, as is observed in the case of  $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ .

### Substitution Studies on $[\text{Mo}_3\text{Cr}_4(\text{H}_2\text{O})_{12}]^{4+}$

The Cr containing  $\text{Mo}_3\text{Cr}$  heterometallic cube is obtained by reacting  $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$  with  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ , (6). In the reaction,



$\text{Cr}^{2+}$  serves as a reducing agent and no  $\text{BH}_4^-$  is required. Whereas substitution on  $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$  gives no  $[\text{H}^+]$  dependence in the 0.1-2.0M range studied, a quite different situation applies in the case of the  $\text{Mo}_3\text{Cr}$  cube. Stopped-flow complexation studies with  $\text{NCS}^-$  are assigned as 1:1  $\text{NCS}^-$  for  $\text{H}_2\text{O}$  substitution occurring at the Cr. The  $a + b[\text{H}^+]^{-1}$  dependence indicates contributions from a conjugate-base pathway. For such a mechanism to be effective the Cr has to have at least two waters attached, and three seems probably to give  $[\text{Mo}_3\text{CrS}_4(\text{H}_2\text{O})_{12}]^{4+}$ . The 4+ charge is confirmed by the stoichiometry of the redox process,



and quantitative (spectrophotometric) determination of the  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$  produced. As already indicated the  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{4+}$  analogue gives no  $[\text{H}^+]^{-1}$  dependence in the reaction with  $\text{NCS}^-$ , (13). This behaviour parallels substitution studies on  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$  ( $3d^3$ ) and  $[\text{Mo}(\text{H}_2\text{O})_6]^{3+}$  ( $4d^3$ ), where in the Cr but not the Mo case an  $[\text{H}^+]^{-1}$  dependence has been observed, (19). From the properties so far identified it is concluded that the Cr approximates to and is best described as Cr(III). The three coordinated  $\mu_3$ -sulfido ligands give a labilisation effect. Similar effects due to a single sulfide in  $[\text{Cr}(\text{H}_2\text{O})_5\text{SH}]^{2+}$  have been reported previously, (20). In contrast the  $\mu_3$ -sulfido ligands have little effect on substitution of the Mo(III)<sub>4</sub> cube which has a similar rate constant as that for  $[\text{Mo}(\text{H}_2\text{O})_6]^{3+}$ . The relative sizes of 3d and 4d orbitals and their abilities to interact with  $\text{S}^{2-}$  are relevant.

#### Preparation and Reactivity of $[\text{Mo}_3\text{S}_7(\text{H}_2\text{O})_6]^{4+}$

The preparation involves adding 4.0 Hpts (Hpts = p-toluenesulfonic acid) to the orange coloured  $\text{Et}_4\text{N}^+$  salt of  $[\text{Mo}_3\text{S}_7\text{Br}_6]^{2-}$ , and leaving to stand for 4h at room temperature. After dilution to 0.50M acid the product can be exchanged as a single band onto a Dowex 50W-X2 cation-exchange column. This is eluted at the more concentrated acid levels 2.0M Hpts and above, consistent with a 4+ charge.

On heating a solution of  $[\text{Mo}_3\text{S}_7(\text{H}_2\text{O})_6]^{4+}$  in 4M Hpts (10mL) with concentrated HBr (10mL), and then adding solid  $\text{Et}_4\text{NBr}$  (0.2g), orange crystalline  $[\text{Et}_4\text{N}]_2[\text{Mo}_3\text{S}_7\text{Br}_6]$  is obtained, consistent with retention of the  $\text{Mo}_3\text{S}_7^{4+}$  core. Also as part of the characterisation procedure the reaction with  $\text{PR}_3^{3-}$  was studied. A rapid yellow to green colour change is observed, and the UV-VIS spectrum obtained is that of the well characterised  $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ .



The reaction is uniphasic and gives a rate constant of  $\sim 8\text{M}^{-1}\text{s}^{-1}$  at  $25^\circ\text{C}$  in 2.0M Hpts. There are two possible interpretations (a) statistical kinetics apply with concurrent reaction at all three disulfides, (13), or (b) reaction at the first disulfide is rate determining and that at the second and third disulfides is fast. In further studies the aim will be to distinguish between these two possibilities. From isotopic labelling experiments it has been demonstrated that the equatorial S-atoms are removed in this reaction, (21).

The substitution properties of the  $\text{H}_2\text{O}$  ligands of  $[\text{Mo}_3\text{S}_7(\text{H}_2\text{O})_6]^{4+}$  have also been explored. The reaction with  $\text{NCS}^-$  gives UV-VIS spectrophotometric changes corresponding to  $\text{H}_2\text{O}$

replacement. Two stages of reactions are observed. The latter can be interpreted in terms of concurrent substitution at the three cis (to the  $\mu_3$ -S) H<sub>2</sub>O's, which occurs at a different rate to substitution at the three trans H<sub>2</sub>O's. This is consistent with the preparation of the partially substituted product [Mo<sub>3</sub>S<sub>7</sub>Br<sub>3</sub>(NH<sub>2</sub>Ph)<sub>3</sub>]<sup>+</sup>, the structure of which has been determined, (22). These and other M<sub>3</sub> analogues are being investigated further.

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