Complete Synthesis of the Series of Triangular Oxo/Sulphido Bridged Molybdenum(IV) Complexes as Aqua Ions

P. Kathirgamanathan, Manuel Martinez, and A. Geoffrey Sykes*

Department of Inorganic Chemistry, The University, Newcastle upon Tyne NE1 7RU, U.K.

Electrochemical reduction of pairs of $Mo^V{}_2$ complexes from $[Mo_2O_4(cys)_2]^{2-}$, $[Mo_2O_3S(cys)_2]^{2-}$, and $[Mo_2O_2S_2(cys)_2]^{2-}$ (cys = cysteinato) in equimolar amounts, has enabled triangular oxo/sulphido $Mo^{IV}{}_3$ complexes (eight in all) to be synthesised.

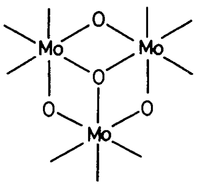
Triangular metal–metal bonded oxo/sulphido bridged $Mo^{IV}{}_3$ complexes of which the apical μ_3-oxo ion $[Mo_3O_4(H_2O)_9]^{4+}$ (**1**) is now a well established prototype,[1—3] can be of the symmetrical (**1**)—(**4**) or unsymmetrical type (**5**)—(**8**). The synthesis and characterisation of complexes (**2**), (**4**), (**7**), and (**8**), including *X*-ray crystal structure determinations, have recently been completed.[4—8] Here we report a procedure which gives all eight complexes, and has enabled complexes (**3**), (**5**), and (**6**) to be identified for the first time. The method employed has mechanistic implications and is important because it demonstrates that cubic complexes, possessing an additional Mo only in the inner core, are the precursors of the triangular complexes.

The procedure for the preparation of (**6**) is typical of those used. A solution of the cysteine complex $Na_2[Mo_2O_4(cys)_2]\cdot 5H_2O$ (**A**) (1 g), and the di-μ-sulphido complex $Na_2[Mo_2O_2S_2(cys)_2]\cdot 3H_2O$ (**B**) (1 g),[9–11] in 2 M HCl (100 ml) was filtered and electrolysed at -0.95 V (*vs.* normal hydrogen electrode, n.h.e.) at a Hg cathode for 12 h. The solution was filtered and diluted to 2 l with 0.3 M *p*-toluene

Table 1. U.v.–visible spectra of triangular oxo/sulphido clusters.

		$\lambda_{max.}$ /nm	ε^a /M^{-1} cm^{-1}	$\lambda_{max.}$ /nm	ε^a /M^{-1} cm^{-1}
$[Mo_3O_4(H_2O)_9]^{4+}$	**(1)**	505	189	300(sh)	1560
$[Mo_3O_3S(H_2O)_9]^{4+}$	**(5)**	511	—	332	—
$[Mo_3O_3S(H_2O)_9]^{4+}$	**(2)**	512	153	333	930
$[Mo_3O_2S_2(H_2O)_9]^{4+}$	**(6)**	545	188	327	2490
$[Mo_3O_2S_2(H_2O)_9]^{4+}$	**(7)**	568	207	335	2330
$[Mo_3OS_3(H_2O)_9]^{4+}$	**(3)**	580	206	332	2500
$[Mo_3OS_3(H_2O)_9]^{4+}$	**(8)**	588[b]	263	332	2980
$[Mo_3S_4(H_2O)_9]^{4+}$	**(4)**	602[c]	351[c]		

[a] Absorption coefficients per trimer. [b] Shoulders at 410 and 370 nm. [c] Ref. 5, see footnote†.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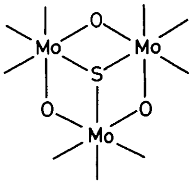
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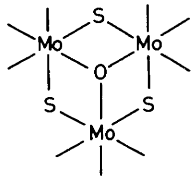
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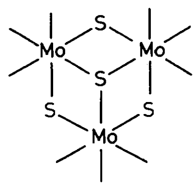
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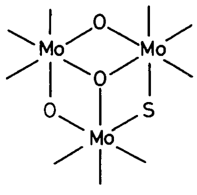
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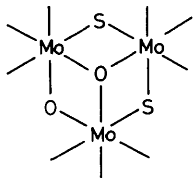
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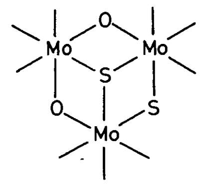
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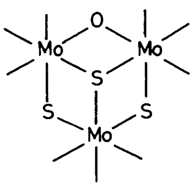
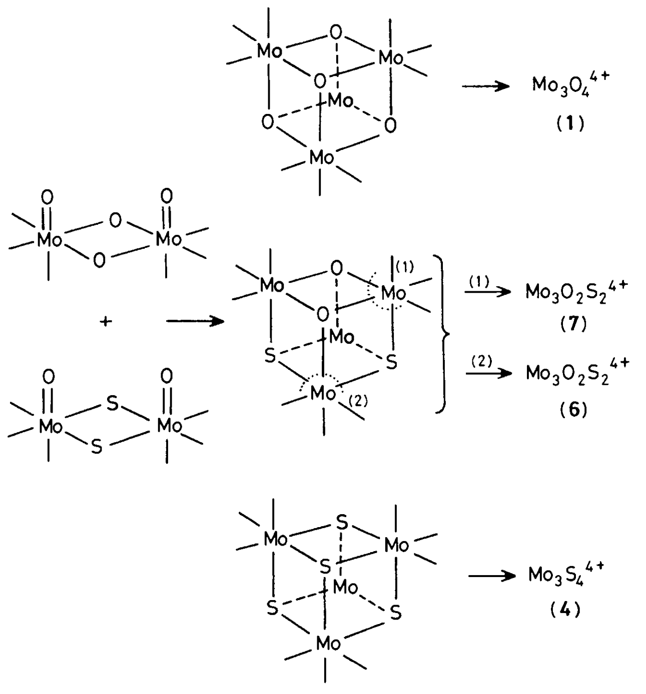

(8)

sulphonic acid (HPTS), which is a suitably strong acid (and poor donor ligand). After air oxidation (~12 h) the solution was loaded onto a Dowex 50W X2 column, and washed with 0.5 M HPTS (when unreacted Mo^V was collected) and then 1.0 M HPTS to separate the different 4+ bands which were eluted with 1.5 M acid in the order $Mo_3O_4^{4+}$ (red, 0.29%), $Mo_3O_2S_2^{4+}$ **(7)** (grey-violet, 4.2%), a previously uncharacterised fraction (pink-violet, 6%), and $Mo_3S_4^{4+}$ (green, 15%). Mixed oxo/sulphido cubic complexes of higher charge were held at the top of the column. The previously uncharacterised fraction, Mo/S ratio 1.43 by analyses, was re-loaded onto a Dowex 50W X2 column and after washing with 0.5 M HCl eluted as a thiocyanato complex using a solution of 1 M NaNCS in 0.5 M HCl. A crystalline sample of the tetramethylammonium salt of the thiocyanato complex was obtained {Calc. for $(Me_4N)_5[Mo_3O_2S_2(NCS)_9]$: H, 4.9; C, 26.6; N, 15%. Found: H, 4.5; C, 27.5; N, 14.6}. An *X*-ray crystal structure determination has characterised the isomeric $Mo_3O_2S_2^{4+}$ form as **(7)**.[7]



Scheme 1

Complexes **(3)** and **(5)** were prepared by similar procedures using equimolar amounts of **(B)** and the μ-sulphido complex $Na_2[Mo_2O_3S(cys)_2]\cdot 4H_2O$ **(C)**,[12] and equimolar amounts of **(A)** and **(C)** respectively. U.v.–visible spectra of the completed series of eight oxo/sulphido complexes are listed in Table 1. On using ethylenediaminetetra-acetate (edta) complexes, *e.g.* $[Mo_2O_3S(edta)]^{2-}$, for **(C)**,[13] a greater proportion of the μ_3-oxo product appears to be formed.

Previously[6] the triangular and cubic ions $Mo_3S_4^{4+}$ (60%) and $Mo_4S_4^{5+}$ (30%) have been obtained in high yield in a single electrochemical reduction of complex **(B)** on its own, and the method is applicable also to the preparation of $Mo_3O_4^{4+}$ and $Mo_4O_4^{5+}$, reduction of **(A)**, and other analogue clusters containing selenido and tellurido bridges.[14]

The experimental procedures adopted and products obtained raise important mechanistic questions, which have not previously been addressed, namely how are the triangular complexes generated? As an example we consider the electrolytic reduction of the di-μ-sulphido $Mo^V{}_2$ complex **(B)** to give $Mo_3S_4^{4+}$ and $Mo_4S_4^{5+}$. Clearly the $Mo_4S_4^{5+}$ cube can be generated by sideways approach of two Mo_2S_2 dimer units. To obtain the triangular complexes by a route not involving the cube, two possibilities may be considered. The first requires a mole of dimer to break down into monomer units,

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† Some decomposition to **(3)** occurs in the presence of mercury.

one of which then adds on to a second mole of dimer. The second involves the end-on approach of one dimer unit to the Mo_2S_2 plane of another (with subsequent loss of Mo from the approaching dimer). Both are unsatisfactory because they are unable to generate the required number of μ-sulphido ligands. Formation of a cube with subsequent elimination of a Mo is on the other hand able to explain all the necessary features, and in particular the different products obtained when two Mo^{V}_2 dimers are used. This is illustrated in Scheme 1, which applies to the procedure described in this paper. Since the 5+ cubes with the four Mo's in oxidation states of III, III, III, and IV are known to be stable over long periods,[6] the triangular complexes must be formed from cubes of different charge. The 6+ analogues of $Mo_4S_4^{5+}$ and $Mo_4O_4^{5+}$ obtained by electrochemical oxidation are being further studied.

It is of interest that in ferredoxin related chemistry the dimerisation of [2Fe–2S] to [4Fe–4S] clusters has been observed.[15,16]

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References

1 A. Bino, F. A. Cotton, and Z. Dori, *J. Am. Chem. Soc.*, 1978, **100**, 5252.
2 D. T. Richens and A. G. Sykes, *Inorg. Chem.*, 1982, **81**, 418.
3 K. R. Rodgers, R. K. Murmann, E. O. Schlemper, and M. E. Shelton, *Inorg. Chem.*, 1985, **24**, 1313.
4 T. Shibahara, H. Hattori, and H. Kuroya, *J. Am. Chem. Soc.*, 1984, **106**, 2710.
5 T. Shibahara and H. Kuroya, Abstracts 5th International Conference on the Chemistry and Uses of Molybdenum, 1985, p. 59.
6 P. Kathirgamanathan, M. Martinez, and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, 1985, 953.
7 T. Shibahara, T. Yamada, H. Kuroya, E. F. Hills, P. Kathirgamanathan, and A. G. Sykes, preparation, *X*-ray structure, and characterisation of $Mo_3O_2S_2^{4+}$ (**7**), unpublished work.
8 T. Shibahara, preparation, *X*-ray structure, and characterisation of $Mo_3OS_3^{4+}$ (**8**), personal communication.
9 A. Kay and P. C. H. Mitchell, *J. Chem. Soc. (A)*, 1970, 2421.
10 B. Spivack and Z. Dori, *Chem. Commun.*, 1970, 1416.
11 F. A. Armstrong, T. Shibahara, and A. G. Sykes, *Inorg. Chem.*, 1978, **17**, 189.
12 V. R. Ott, D. S. Swieter, and F. A. Schultz, *Inorg. Chem.*, 1977, **16**, 2538.
13 Y. Sasaki and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1974, 1468.
14 P. Kathirgamanathan, M. Martinez, and A. G. Sykes, Abstracts, 5th International Conference on the Chemistry and Uses of Molybdenum, 1985, p. 133.
15 W. O. Gillum, L. E. Mortenson, J.-S. Chen, and R. H. Holm, *J. Am. Chem. Soc.*, 1977, **99**, 584.
16 J. Cambray, R. W. Lane, A. G. Wedd, R. W. Johnson, and R. H. Holm, *Inorg. Chem.*, 1977, **16**, 1565.