Synthesis and Reactivity of New Chalcogen-rich Aqua Ions $[Mo_3S_7(H_2O)_6]^{4+}$ and $[Mo_3Se_7(H_2O)_6]^{4+}$

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The aqua ions $[Mo_3Y_7(H_2O)_6]^{4+}$ (Y = S, Se) containing μ_3-Y and μ-Y_2 core ligands have been prepared for the first-time, enabling chalcogen-transfer reactions with an H_2O-soluble phosphine to generate the well-characterised $[Mo_3Y_4(H_2O)_9]^{4+}$, reactions with Cl^- to give substitution of H_2O ligands (which are of two different types), and heterometallic Sn^{II} addition reactions to be studied.

The $Mo^{IV}{}_3$ incomplete cuboidal cluster $[Mo_3S_4(H_2O)_9]^{4+}$ with an Mo_3S_4 core and vacant metal subsite has been much studied since its first preparation in the mid 1980's.[1-3] The cluster is stable indefinitely in air at room temperature, with no tendency to lose core atoms. Although less extensively studied the selenium containing analogue $[Mo_3Se_4(H_2O)_9]^{4+}$ has also been prepared and fully characterised.[4,5] The existence of cuboidal Fe_3S_4 and Fe_4S_4 clusters in biology, and a whole range of analogous complexes with thiolate ligands, is well recognised.[6] Less well understood are the properties of sulfur-rich clusters of the kind encountered in nitrogenase.[7]

Here we report the preparation of new chalcogenide-rich trinuclear complexes as aqua ions $[Mo_3Y_7(H_2O)_6]^{4+}$. Polymeric chain compounds, written here as $\{Mo_3Y_7Br_4\}_x$ are prepared by direct combination of the elements.[8] Procedures have been described for the conversion of the latter into molecular complexes *e.g.* $[Mo_3Y_7Br_6]^{2-}$.[8] Both types of compound contain clusters with a single μ_3-chalcogenido and three μ-dichalcogenido bridging ligands orientated as shown in Fig. 1.[8,9] One Y-atom of each μ-dichalcogenido group is in the same plane as the three Mo-atoms. There are two non-identical terminal ligands to each Mo-atom.

To prepare the new aqua ion $[Mo_3S_7(H_2O)_6]^{4+}$ aqueous 4.0 M toluene-*p*-sulfonic acid, *p*-$MeC_6H_4SO_3H$ (Hpts), (25 ml) was added to the orange $(Et_4N)_2[Mo_3S_7Br_6]$ (0.2 g) and the mixture left for 4 h at room temperature. The halide cluster is of low solubility, and conversion to a lemon–yellow solution is observed as the reaction proceeds. The solution obtained was diluted to 0.5 M Hpts and exchanged onto a Dowex 50W-X2 cation-exchange resin. Elution required acid levels of 2.0 M Hpts and above, consistent with a 4+ charge. Alternatively elution with trifluoromethanesulfonate, CF_3SO_3H(triflic acid), or HCl could be employed. In the latter case elution occurs with 0.5–1.0 M HCl indicating some complexing by the Cl^-. An Mo : S ratio of 3 : 7.3 was obtained on analysis of a 1.0 M HCl solution by inductively coupled plasma (ICP) emission spectroscopy consistent with an $Mo_3S_7{}^{4+}$ core. The product has a featureless UV–VIS absorbance spectrum, Fig. 2. Similar observations hold in the case of the preparation and purification of the $Mo_3Se_7{}^{4+}$ analogue.

The new aqua ions $[Mo_3S_7(H_2O)_6]^{4+}$ and $[Mo_3Se_7(H_2O)_6]^{4+}$ are stable in both 2.0 M Hpts and HCl solutions under a dinitrogen atmosphere, and give only a 10% change in absorption over 12 h in air at room temperature. However in 2.0 M $HClO_4$ decomposition is observed, presumably as a result of some oxidation of sulfur or selenium.

Retention of the Mo_3S_7 core in the aqua ion was demonstrated by first eluting with 2.0 M HBr. The HBr solution was then evaporated to dryness on a vacuum line and redissolved in concentrated HBr. Addition of excess Et_4NBr resulted in the formation of orange crystals of $(Et_4N)_2\,[Mo_3S_7Br_6]$, which was characterised by its IR spectrum (85%).[10]

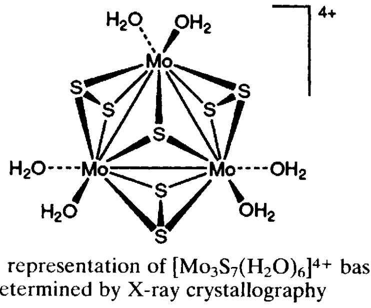

Fig. 1 Structure representation of $[Mo_3S_7(H_2O)_6]^{4+}$ based on that of $[Mo_3S_7Br_6]^{2-}$ determined by X-ray crystallography

As part of the characterisation of $[Mo_3S_7(H_2O)_6]^{4+}$ the reaction with the water-soluble phosphine $PR_3{}^{3-}$ (R = 3-sulfonatophenyl group), as the sodium salt $Na_3[(3\text{-}SO_3\text{-}C_6H_4)_3P]\cdot 4H_2O$ (Strem Chemicals), was investigated. A fast uniphasic conversion with change in colour from yellow to green was observed, where the final UV–VIS absorbance spectrum, Fig. 2, is that of the well characterised $[Mo_3S_4(H_2O)_9]^{4+}$ trinuclear cluster, λ/nm (ε/M^{-1} cm^{-1} per Mo_3) for peaks at 366 (5550), 603 (362) in quantitative yield.[3] The conversion of three μ-S_2 to μ-S core ligands is summarised in eqn (1).

$$Mo_3S_7{}^{4+} + 3\,PR_3{}^{3-} \rightarrow Mo_3S_4{}^{4+} + 3\,SPR_3{}^{3-} \qquad (1)$$

The rate constant (25 °C) for **1** is (1–2) × 10^{-4} M^{-1} s^{-1} in 2.0 M Hpts (I = 2.0 M). The reaction with $[Mo_3Se_7(H_2O)_6]^{4+}$ is also quantitative, yielding $[Mo_3Se_4(H_2O)_9]^{4+}$ with peaks at 425 (2462) and 648 (263),[4] and corresponding rate constants are being determined.

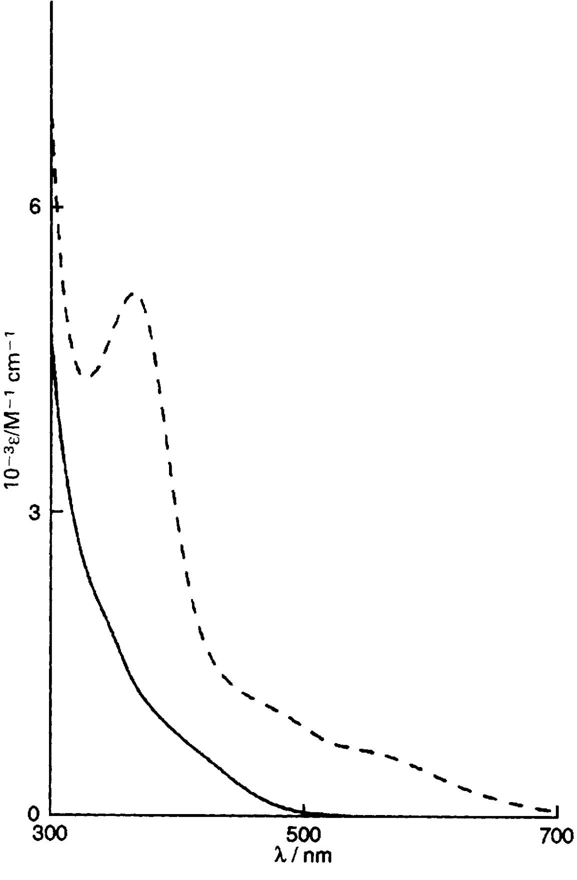

Fig. 2 The UV-VIS spectrum of $[Mo_3S_7(H_2O)_6]^{4+}$ (—) and of $[Mo_3S_4(H_2O)_9]^{4+}$ (---) obtained by the desulfurisation reaction with the water-soluble phosphine $PR_3{}^{3-}$

The reaction of $[Mo_3S_7(H_2O)_6]^{4+}$ with a >10-fold excess of Cl^- gives biphasic kinetics indicating substitution at two different types of H_2O to each Mo. At 25 °C rate constants for the second stage, 6×10^{-4} M^{-1} s^{-1} are independent of $[H^+]$ in the range 0.5–2.0 M, and for the first stage the rate constant is 0.45 M^{-1} s^{-1}. Two stages are observed also in the reaction of $[Mo_3Se_7(H_2O)_6]^{4+}$ with Cl^-. The two stages for these substitution reactions can be interpreted in terms of concurrent substitution of the three *cis* H_2O's (relative to the μ_3-S) (Fig. 1), which occurs at a different rate to substitution at the three *trans* H_2O's. This is consistent with the preparation from $[Mo_3S_7Br_6]^{2-}$ of the partially substituted product $[Mo_3S_7Br_3(NH_2Ph)_3]^+$,[11] with three N-donor atoms in the *cis* position, and the selective formation of one single stereoisomer with the sulfur donor atom in *cis* position during substitution with bidentate S,O donor ligands.[12]

In further studies we have demonstrated that reactions with heterometal atoms can occur. Thus a reaction of $[Mo_3S_7(H_2O)_6]^{4+}$ (0.15 mM) in 2 M Hpts with a 50-fold excess of tin(II) chloride is observed. Spectrophotometric changes indicate formation of a heterometallic cluster with peak positions λ/nm (ε/M^{-1} cm^{-1}) at 347 (9070) and 414(sh) (4680). These are diagnostic of the previously reported $Mo_3SnS_4^{6+}$ aqua ion.[13] However the spectrum intensifies (*ca.* 30%) on addition of the water soluble phosphine PR_3^{3-}, suggesting that only at this stage is there completion of the reaction.

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References

1 T. Shibahara, *Adv. Inorg. Chem.*, 1991, **37**, 143.

2 M. Martinez, B.-L. Ooi and A. G. Sykes, *J. Am. Chem. Soc.*, 1987, **109**, 4615.

3 B.-L. Ooi and A. G. Sykes, *Inorg. Chem.*, 1989, **28**, 3799.

4 M. Nasreldin, G.Henkel, G. Kampmann, B. Krebs, G. J. Lamprecht, C. A. Routledge and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1993, 737.

5 G. J. Lamprecht, M. Martinez, M. Nasreldin, C. A. Routledge, N. Al-Shatti and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1993, 747.

6 R. H. Holm, *Adv. Inorg. Chem.*, 1992, **38**.

7 D. C. Rees, M. K. Chan and J. Kim, *Adv. Inorg. Chem.*, 1993, **40**, 89.

8 V. P. Fedin, M. N. Sokolov, O. A. Geras'ko, A. V. Virovets, N. V. Podberezskaya and V. Ye. Fedorov, *Inorg. Chim. Acta.*, 1991, **187**, 81; V. P. Fedin, M. N. Sokolov, K. G. Myakishev, O. A. Geras'ko, V. Ye. Fedorov and J. Macichek, *Polyhedron*, 1991, **10**, 1311; A. V. Virovets, Yu. L. Slovohotov, Yu. T. Struchkov, V. Ye. Fedorov, N. G. Naumov, O. A. Geras'ko and V. P. Fedin, *Koord. Khim.*, 1990, **16**, 332.

9 M. D. Meienberger, K. Hegetschweiler, H. Rüegger and V. Gramlich, *Inorg. Chim. Acta.*, 1993, **213**, 157 and references cited therein.

10 V. P. Fedin, M. N. Sokolov, Yn. V. Mironov, B. A. Kolesov, S. V. Tkachev and V. Ye. Fedorov, *Inorg. Chim. Acta*, 1990, **167**, 39.

11 V. P. Fedin, Yu. V. Mironov, A. V. Virovets, N. V. Podberezskaya and V. Ye. Fedorov, *Polyhedron*, 1992, **11**, 2083.

12 K. Hegetschweiler, T. Keller, H. Zimmermann, W. Schneider, H. Schmalle and E. Dubler, *Inorg. Chim. Acta*, 1990, **169**, 235; K. Hegetschweiler, T. Keller, M. Bäumle, G. Rihs and W. Schneider, *Inorg. Chem.*, 1991, **30**, 4342.

13 H. Akashi and T. Shibahara, *Inorg. Chem.*, 1989, **28**, 2906.

14 V. P. Fedin, G. J. Lamprecht and A. G. Sykes, to be published.