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Preparation and properties of the heterometallic cube $[Mo_3CdS_4(H_2O)_{12}]^{4+}$ and the reaction with H^+

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The orange–brown cadmium-containing heterometallic cube $[Mo_3CdS_4(H_2O)_{12}]^{4+}$ has been prepared by reacting $[Mo_3S_4(H_2O)_9]^{4+}$ in 2.0 M HCl with Cd^{2+} in the presence of H_3PO_2 as reductant for ~1 h at 20 °C. Alternatively, it can be obtained by heating a solution of $[Mo_3S_4(H_2O)_9]^{4+}$ in 0.5 M Hpts ($pts^- = p$-toluenesulfonate) with Cd metal for ~1 h at 70 °C. The cube reacts with H^+ in a process which is inhibited by the replacement of Cl^- with pts^-. Purification by elution from a Dowex cation-exchange column was carried out at low $[H^+]$ using a mixture of 2.9 M Lipts and 0.1 M Hpts. On titration with $[Co(dipic)_2]^-$, the incomplete cube $[Mo_3S_4(H_2O)_9]^{4+}$ is reformed, and two equivalents of Co^{III} oxidant are consumed per cube, consistent with the equation $Mo_3CdS_4^{4+} + 2Co^{III} \longrightarrow Mo_3S_4^{4+} + Cd^{2+} + 2Co^{II}$. Reaction with $[H^+]$ in the range 0.5–1.5 M, $I = 2.0$ M (Lipts) gives H_2, which was determined quantitatively by gas chromatography. The kinetics of the decay $Mo_3CdS_4^{4+} + 2H^+ \longrightarrow Mo_3S_4^{4+} + Cd^{2+} + H_2$ give a rate law $k_H[Mo_3CdS_4^{4+}][H^+]^2$, with $k_H = 4.6 \times 10^{-4}\ M^{-2}\ s^{-1}$ at 25 °C, $I = 2.00$ M (Lipts). In 1 M HCl, $I = 2.0$ M (Lipts), the half-life of 0.3 mM solutions is ~5 min.

Introduction

The aim of this paper is to report procedures for the formation of a heterometallic derivative by incorporating Cd into the incomplete (metal-depleted) $[Mo_3S_4(H_2O)_9]^{4+}$ cube,[1] and comment on the unusual sensitivity of the cube towards reaction with H^+. Of the group 12 elements, Hg has been studied most and provides the only example to date of a fully characterised heterometallic derivative of $[Mo_3S_4(H_2O)_9]^{4+}$.[2–4] Reaction with Hg metal occurs readily, with the formation of the intensely coloured purple double cube $[Mo_6HgS_8(H_2O)_{18}]^{8+}$.[2] In 4 M HCl, the double cube changes colour (purple ⟶ blue), giving a tetrachloro-substituted derivative, $[Mo_6HgS_8(H_2O)_{14}Cl_4]^{4+}$, the crystal structure of which has also been determined as a component of a cucurbituril supramolecular assembly.[3,4] Details of the preparation of the Cd-containing double cubes $[Mo_6CdS_8(dtp)_8(CH_3CN)_2]$ (dtp = diethyl-dithiophosphate) and $[Mo_6CdS_8(Hnta)_6]^{4-}$ (nta = nitrilo-triacetate) from non-aqueous and neutral aqueous solutions, respectively, have been reported,[5] but no Zn-containing derivative has yet been identified. A Cd-containing single cube is of considerable interest, since the group 12 elements border the B and C categories previously defined.[1] Hexaaquacadmium(II) has an extensive solution chemistry.[6] Aqueous solutions of 10^{-3} mM Cd^{I}_2 have recently been prepared.[7]

Experimental

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

Stock solutions of the green Mo^{IV}_3 incomplete cube $[Mo_3S_4(H_2O)_9]^{4+}$ in 2 M HCl or 2 M Hpts were prepared from polymeric $\{Mo_3S_7Br_4\}_x$, as previously described.[8,9] Details of the UV-Vis absorption peak positions are λ/nm (ε/M^{-1} cm^{-1} per Mo_3) 370 (5.0×10^3), 616 (330) in 2 M HCl and 366 (5.5×10^3), 603 (360) in 2 M Hpts.[10] Purification and concentration of the product were carried out by Dowex 50W-X2 cation-exchange chromatography using standard procedures.

Other materials

Hypophosphorous acid, H_3PO_2 (50% w/w H_2O solution), p-toluenesulfonic acid, p-$CH_3C_6H_4SO_3H$ (Hpts; white crystalline solid), lithium carbonate, Li_2CO_3, and lithium chloride were all from Aldrich, as were methylsulfonic acid (CH_3SO_3H) and sodium methylsulfonate ($NaCH_3SO_3$). Solutions of Lipts were prepared by Li_2CO_3 neutralisation of Hpts and recrystallisation from water (solubility ~4 M). Lanthanum p-toluenesulfonate, $La(pts)_3$, was prepared by neutralisation of La_2O_3 (50 g; Rare-earth Products Ltd., 99.5%) with aqueous 4.0 M Hpts at ~80 °C, until the equivalent point is reached (pH ~4).[11] The solution was then filtered, the white product recrystallised three times from water and washed with acetone. A solid sample of the Co^{III} oxidant $NH_4[Co(dipic)_2]\cdot H_2O$ (dipic = 2,6-dicarboxylatopyridine), which shows a UV-Vis peak at 510 nm (ε = 630 M^{-1} cm^{-1}), was prepared as described previously.[12] A reduction potential for the $[Co(dipic)_2]^{-/2-}$ couple (0.362 V *vs.* NHE) has been determined.[13]

Instrumentation and techniques

A Phasesep Model LC2 chromatograph complete with thermal conductivity detector (current 120 mA) and a 5 Å molecular sieve was used for the quantitative determination of H_2. Metal analyses were carried out by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using an ATI Unicam Model 701 instrument. Applied Photophysics SX-17MV stopped-flow and Perkin-Elmer Lambda 9 UV-Vis spectrophotometers were used. For kinetic studies, ionic strengths were adjusted to I = 2.0 M with Lipts.

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Treatment of kinetic data

Errors in kinetic data were obtained by unweighted least-squares fitting procedures.

Results

Preparation of $[Mo_3CdS_4(H_2O)_{12}]^{4+}$

In the first procedure, stock $[Mo_3S_4(H_2O)_9]^{4+}$ (2.5 mM; 40 mL) in 2.0 M HCl was diluted 4-fold and $CdCl_2$ (0.2 g, 0.001 mmol; BDH) added prior to making the solution O_2-free by bubbling N_2 through for ~30 min. An excess of hypophosphorous acid reductant (0.3 mL of a 50% solution; Aldrich) was added, and the solution left at 20 °C for ~1 h. Larger amounts of H_3PO_2 bring about precipitation. The colour of the solution changed from green to orange–brown (eqn. 1).

$$Mo_3S_4^{4+} + Cd^{2+} + 2e^- \longrightarrow Mo_3CdS_4^{4+} \qquad (1)$$

Any reaction of the product with H^+ at this stage results in a regeneration of $[Mo_3CdS_4(H_2O)_9]^{4+}$, since Cd^{2+} and H_3PO_2 are present in excess. The product solution was diluted to 0.3 M HCl and loaded onto an ice-cooled Dowex 50W-X2 column under N_2. After washing with 0.10 M Hpts (100 mL) to remove excess H_3PO_2, washing was continued with 0.10 M Lipts + 0.10 M Hpts (150 mL) and 0.40 M Lipts + 0.10 M Hpts (150 mL) to remove excess Cd^{2+}. Elution of the orange–brown $[Mo_3CdS_4(H_2O)_{12}]^{4+}$ was initially by the displacement method using 0.30 M La(pts)$_3$ + 0.10 M Hpts.[11] However, because quantitative studies were more difficult in the presence of the 3 :1 electrolyte, this procedure was superceded by one using a solution of 2.9 M Lipts and 0.10 M Hpts for elution. Under these conditions, no $[Mo_3S_4(H_2O)_9]^{4+}$ band was observed and yields approaching 100% were obtained. In the presence of higher concentrations of H^+ and with the addition of Cl^-, a decay process yielding $[Mo_3S_4(H_2O)_9]^{4+}$ and H_2 becomes increasingly important.

In a second procedure, Cd granules (1 g; 30–80 mesh; Aldrich) were added to $[Mo_3S_4(H_2O)_9]^{4+}$ in 0.50 M Hpts and the solution heated (~70 °C) for 1 h to give an orange–brown solution (eqn. 2).

$$Cd + Mo_3S_4^{4+} \longrightarrow Mo_3CdS_4^{4+} \qquad (2)$$

The Cd cube was again purified by Dowex chromatography and eluted with 2.9 M Lipts + 0.1 M Hpts. UV-Vis spectra indicated 100% conversion to $Mo_3CdS_4^{4+}$. With this procedure, possible interference from H_3PO_2 and chloride (which can affect kinetic studies) is avoided.

Solutions of $Mo_3CdS_4^{4+}$ stored at ~4 °C under air-free conditions (N_2) age quickly, with deposition of a fine brown powder. It is necessary to prepare fresh solutions after 2 days.

Attempts to prepare a corner-shared double cube

Conditions were as used previously for the conversion of the single cube, *e.g.* $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ to $[Mo_6SnS_8(H_2O)_{18}]^{8+}$.[10] A solution of $[Mo_3CdS_4(H_2O)_{12}]^{4+}$ (3 mM; 5 mL) in 1.9 M Lipts + 0.1 M Hpts was mixed with $[Mo_3S_4(H_2O)_9]^{4+}$ (3 mM; 5 mL) in 0.1 M Hpts and excess H_3PO_2 (1 mL of a 50% w/w H_2O solution), added under O_2-free conditions. The mixture was left for ~1 h. No colour change was observed and on carrying out Dowex chromatography, only the starting materials were identified.

Stability in air and characterisation

On exposure of a solution of the cube in 1.9 M Lpts + 0.1 M Hpts to air with some shaking, ~60% decay is observed in 5 min, with the reformation of $[Mo_3S_4(H_2O)_9]^{4+}$ and Cd^{2+}. Storage was under N_2 at 4 °C and all experiments were carried out in O_2-free conditions. Metal analyses were carried out by ICP-AES. For this technique, solutions in HCl are generally preferred to Hpts. However, since the cube readily decays in HCl, a methylsulfonate solution was used here. The solution eluted with 1.9 M CH_3SO_3Na + 0.1 M CH_3SO_3H gave a ratio Mo : Cd of 3.0 to 0.8. This suggests some decay of the Cd product during elution, with loss of Cd^{2+}. The UV-Vis spectrum of a solution of $Mo_3CdS_4^{4+}$ in 1.9 M Lipts + 0.1 M Hpts was recorded. After reaction with O_2, the final spectrum was identified as $[Mo_3S_4(H_2O)_9]^{4+}$, with peaks at 366 and 603nm (details as above). From this information, ε values for $Mo_3CdS_4^{4+}$ were calculated, Fig. 1, which has peak positions at λ/nm (ε = M^{-1} cm^{-1} per Mo_3) 374 (4580); 554sh (331); 866 (420). A variety of procedures were used in attempts to obtain crystals. The sensitivity of $Mo_3CdS_4^{4+}$ to H^+ precludes the use of cucurbituril (soluble in 1–2 M HCl) to induce crystallisation.[3] Assuming that the Cd is six-coordinate, the formula $[Mo_3CdS_4(H_2O)_{12}]^{4+}$ applies.

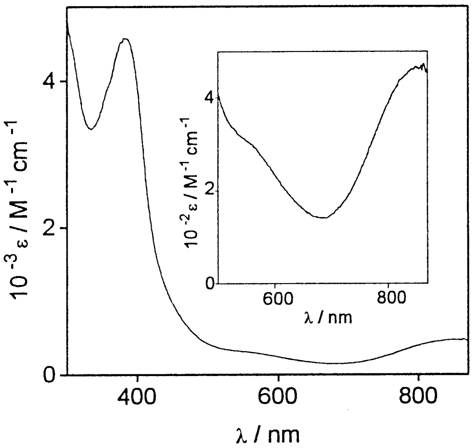

Fig. 1 UV-Vis spectrum of $[Mo_3CdS_4(H_2O)_{12}]^{4+}$ in 1.90 M Lipts + 0.10 M Hpts aqueous solution. The inset shows an enlargement of the 500–850 nm region.

Reaction with $[Co(dipic)_2]^-$

The stoichiometry was determined by titrating 0.10 mL aliquots (Hamilton micro-syringe) of $[Co(dipic)_2]^-$ (2.21 × 10^{-3} M) into a solution of the $Mo_3CdS_4^{4+}$ cube (1.60 mL; 5.0 × 10^{-4} M), both in 1.90 M Lipts + 0.10 M Hpts. A plot of the absorbance at 866 nm against $[Co(dipic)_2^-]/[Mo_3CdS_4^{4+}]$ (inset to Fig. 2) gave a ratio of 2.08 at the end point. This indicates a 2 : 1 stoichiometry (eqn. 3) with ~4% uncertainty in $[Mo_3CdS_4^{4+}]$.

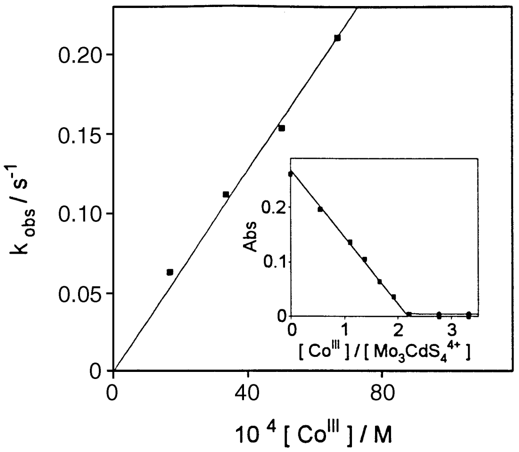

Fig. 2 Rate constants for the $[Co(dipic)_2]^-$ oxidation of $[Mo_3CdS_4(H_2O)_{12}]^{4+}$ in aqueous 1.9 M Lipts + 0.10 M Hpts solution. The inset illustrates absorbance changes on titrating $[Co(dipic)_2]^-$ from a micro-syringe into $[Mo_3CdS_4(H_2O)_{12}]^{4+}$, I = 2.00 M (Lipts).

$$Mo_3CdS_4^{4+} + 2Co^{III} \longrightarrow Mo_3S_4^{4+} + Cd^{2+} + 2Co^{II} \quad (3)$$

One equivalent of $[Mo_3S_4(H_2O)_9]^{4+}$ is released, confirming the charge on $[Mo_3CdS_4(H_2O)_{12}]^{4+}$ as 4+.

The kinetics were monitored by studying the absorbance decay of the cube at 866 nm by stopped-flow spectrophotometry. First-order rate constants k_{obs} were obtained for the oxidation of $Mo_3CdS_4^{4+}$ (~0.15 mM) with $[Co(dipic)_2]^-$ (1.8–6.7 mM). The $[Co(dipic)_2]^-$ concentration was varied at $[H^+]$ = 0.10 M, I = 2.00 M (Lipts). A ≥ 20-fold excess of oxidant (≥ 3.6mM) is required to meet pseudo-first-order conditions for eqn. 3. From Fig. 2, a first-order dependence on $[Co(dipic)_2^-]$ applies, with the rate law as in eqn. 4.

$$\text{Rate} = k_{Co}[Mo_3CdS_4^{4+}][Co^{III}] \quad (4)$$

The slope gives a second-order rate constant k_{Co} = 31.5(5) $M^{-1}\ s^{-1}$. From two runs at a higher $[H^+]$ of 0.20 M, no dependence of k_{Co} on $[H^+]$ was observed. This suggests an outer-sphere reaction as in the reactions of other cube derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$, all of which give $[H^+]$-independent rate laws over a wider range of $[H^+]$ (0.5–2.0 M).[1,8,10]

Reaction of $[Mo_3CdS_4(H_2O)_{12}]^{4+}$ with H^+

Hydrogen gas is released and was identified and determined quantitatively by gas chromatography. A solution of $[Mo_3CdS_4(H_2O)_{12}]^{4+}$ (2.09 mM; 15 mL) in 1.00 M Lipts + 0.10 M Hpts in a three-necked flask was made O_2-free by passing N_2 gas through at 15.4 mL min^{-1} for ~20 min. The $[H^+]$ was adjusted to 1.00 M and $[Cl^-]$ = 0.9 M, I = 2.00 M. The solution was stirred and heated to ~50 °C. A brown to green colour change was observed. The evolution of H_2 was monitored by sampling the N_2 stream after 1 min, and every subsequent 2 min for 30 min. Calibration was using a 1.03% H_2 sample. The amount of H_2 evolved was 3.110×10^{-5} mol (0.6969 mL), which compares with the calculated amount of 3.135×10^{-5} mol from eqn. 5.

$$Mo_3CdS_4^{4+} + 2H^+ \longrightarrow Mo_3S_4^{4+} + H_2 + Cd^{II} \quad (5)$$

Kinetic studies were carried out on the reaction of $[Mo_3CdS_4(H_2O)_{12}]^{4+}$ (0.188–0.383 mM), in pts^- solutions, $[H^+]$ = 0.5–1.5 M, I = 2.00 M (Lipts), by conventional UV-Vis monitoring at 866 nm. Care was required to obtain reproducible data due to the aging of stock solutions. First-order rate constants k_{obs} (25 °C) were determined from the slope of plots of absorbance (A) changes, $\ln(A_t - A_\infty)$ *vs.* time. The inset to Fig. 3 suggests a dependence of k_{obs} *vs.* $[H^+]^2$, as in eqn. 6

$$k_{obs} = k_H\,[H^+]^2 \quad (6)$$

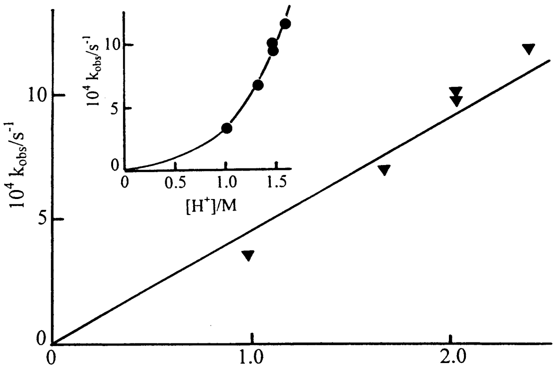

Fig. 3 First-order rate constants k_{obs} (25 °C) for the reaction of H^+ with $[Mo_3CdS_4(H_2O)_{12}]^{4+}$ (~0.3 mM) and the $[H^+]^2$ dependence, I = 2.00 M (Lipts).

which gives $k_H = 4.6(2) \times 10^{-4}\ M^{-2}\ s^{-1}$. Smaller contributions from a first-order $[H^+]$ term cannot be ruled out, where a fit to the dependence $k_{obs} = a[H^+]^2 + b[H^+]$ was tested by plotting $k_{obs}/[H^+]$ *vs.* $[H^+]$. This gives $a \approx 2.8 \times 10^{-4}\ M^{-2}\ s^{-1}$ and $b \le 0.80 \times 10^{-4}\ M^{-1}\ s^{-1}$ (uncertainty in extrapolation), *i.e.* the first-order rate constants for the reactions carried out are dominated (~80%) by an $[H^+]^2$-dependent term.

Reaction of $[Mo_3CdS_4(H_2O)_{12}]^{4+}$ with H^+ in the presence of Cl^-

The reaction with H^+ is faster in the presence of added LiCl. The dependence on $[Cl^-]$ was explored with $[Mo_3CdS_4(H_2O)_{12}^{4+}]$ in the range 0.23–0.48 mM, $[Cl^-]$ = 0.5–1.5 M, I = 2.00 M (Lipts). At $[H^+] \le 0.20$ M, contributions from eqn. 5 are small. The variation of k_{obs} with $[Cl^-]$ (Fig. 4) indicates a dominant $[Cl^-]^2$ term. This at first suggests Cl^- complexing to the Cd, but an alternative interpretation is possible, as considered below. From exploratory experiments, the $[Cl^-]^2$ term has a dependence on $[H^+]$ in the range 0.10–0.20 M, with an $[H^+]^2$ term again dominant.

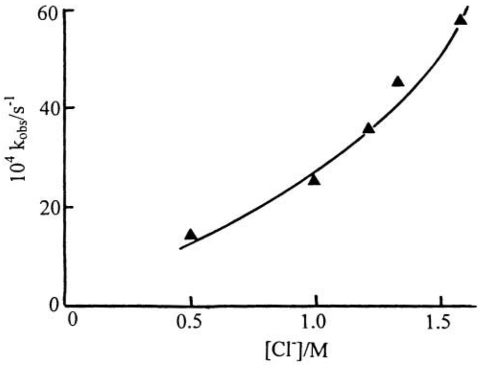

Fig. 4 The variation of first-order rate constants k_{obs} (25 °C) for the reaction of H^+ with $[Mo_3CdS_4(H_2O)_{12}]^{4+}$ in the presence of $[Cl^-]$, $[H^+]$ = 0.20 M.

Discussion

In these studies, a cadmium single cube derivative of $[Mo_3S_4(H_2O)_9]^{4+}$ has been prepared for the first time. From ICP-AES analyses, the double cube structure $Mo_6CdS_8^{8+}$ (6 : 1 ratio Mo : Cd) is ruled out, and the 3 : 1 ratio reported suggests a core structure $Mo_3CdS_4^{4+}$. The 2 : 1 stoichiometry (eqn. 3) for the oxidation with $[Co(dipic)_2]^-$ confirms the 4+ charge. The cube is also oxidised by O_2 (a common occurrence), and by H^+ (which is relatively rare); in all three redox processes, $[Mo_3S_4(H_2O)_9]^{4+}$ and Cd^{2+} are formed. In the reaction with H^+ (eqn. 5), replacement of pts^- with Cl^- produces a significant increase in the rate. Following the recently adopted formalism, the cube is written as $Mo_3S_4^{4+},Cd^o$.[14] The coordination number of the Cd has not been determined, but is assumed to be octahedral, which allows coordination of H^+, and possibly also Cl^-, to take place.

The rate law (eqn. 4) for the 2 : 1 $[Co(dipic)_2]^-$ oxidation of $[Mo_3CdS_4(H_2O)_{12}]^{4+}$ indicates that the reaction with the first $[Co(dipic)_2]^-$ is rate determining. In Table 1, rate constants are compared with those of other cubes,[15–17] and $Mo_3CdS_4^{4+}$ is seen to be mid-range in terms of redox reactivity. It has been shown that the group 13 cubes $[Mo_3GaS_4(H_2O)_{12}]^{5+}$ and $[Mo_3InS_4(H_2O)_{12}]^{5+}$ are ~20 times more reactive with $[Co(dipic)_2]^-$ in 2.0 M HCl as compared to 2.0 M Hpts,[17] while group 13 and 14 double cubes are ~150 times more reactive.[18] The most reasonable explanation is that in 2.0 M pts^-, outer-sphere association occurs with hydrogen bonding of adjacent pts^- ions, giving a protective sheath around the cluster, as observed in the crystal structures.[18] In the case of $[Mo_3CdS_4(H_2O)_{12}]^{4+}$, addition of Cl^- increases the rate of reaction with H^+. Coordination of Cl^- to

Table 1 A comparison of rate constants (25 °C) for the outer-sphere oxidation of some heterometallic derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$ in 2.0 M (Lipts), except where otherwise stated

Cluster	$k_{Co}/M^{-1}\ s^{-1}$	Ref.
$[Mo_3CdS_4(H_2O)_{12}]^{4+}$	31.5	This work
$[Mo_3GaS_4(H_2O)_{12}]^{5+}$	0.23	17
$[Mo_3InS_4(H_2O)_{12}]^{5+}$	0.65	17
$[Mo_3FeS_4(H_2O)_{10}]^{4+}$	87[a]	15
$[Mo_3NiS_4(H_2O)_{10}]^{4+}$	0.35[a]	16
$[Mo_6InS_8(H_2O)_{18}]^{8+}$	30.9	17
$[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$	322	17
$[Mo_6TlS_8(H_2O)_{18}]^{8+}$	fast	17

[a] I adjusted to 2.0 M with $LiClO_4$.

$[Cd(H_2O)_6]^{2+}$ is more favourable by an order of magnitude as compared to other transition metal ions.[19]

The oxidation of heterometallic derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$ with H^+ has been observed previously,[17] but is a relatively rare occurrence confined to group 12 and 13 heteroatoms. Evolution of H_2 gas has been monitored in all cases by gas chromatography.[17] Reactions of the corner-shared double cubes $[Mo_6TlS_8(H_2O)_{18}]^{8+}$ ($k_H = 0.25 \times 10^{-3}\ M^{-1}\ s^{-1}$) and $[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$ ($k_H = 4.9 \times 10^{-3}\ M^{-1}\ s^{-1}$) with $[H^+]$ have been studied in the range 0.5–2.0 M, I = 2.00 M (LiCl). In both cases, a first-order dependence on $[H^+]$ is observed. A similar decay process is observed with $[Mo_6InS_8(H_2O)_{18}]^{8+}$.[17] The reaction of $[Mo_6TlS_8(H_2O)_{18}]^{8+}$ with H^+ occurs in a single stage (eqn. 7)

$$Mo_6TlS_8^{8+} + H^+ \longrightarrow 2Mo_3S_4^{4+} + Tl^+ + 1/2H_2 \qquad (7)$$

and the reaction of $[Mo_6InS_8(H_2O)_{18}]^{8+}$ occurs in two steps (eqn. 8 and eqn. 9).[17]

$$Mo_6InS_8^{8+} + H^+ \longrightarrow Mo_3InS_4^{5+} + Mo_3S_4^{4+} + 1/2H_2 \qquad (8)$$

$$Mo_3InS_4^{5+} + 2H^+ \longrightarrow Mo_3S_4^{4+} + In^{3+} + H_2 \qquad (9)$$

The reaction of the In^+ aqua ion with H^+ gives a first-order dependence on $[H^+]$.[20,21] In all these reactions, the behaviour observed contrasts with the dominant $[H^+]^2$ rate law term observed for eqn. 10.

$$Mo_3CdS_4^{4+} + 2H^+ \longrightarrow Mo_3S_4^{4+} + Cd^{2+} + H_2 \qquad (10)$$

It is probably no coincidence that the hydride chemistry of group 12 and 13 metals has been investigated.[22] The hydride ZnH_2[23] is more stable than CdH_2 and HgH_2, which decompose rapidly, even below 0 °C.[24] The formation of $InHCl_2$, InH_2Cl and the gallium analogues has also been reported.[25] In the present studies, the formation of a dihydride by the reaction of two H^+ with the Cd of $Mo_3CdS_4^{4+}$ is possible. The effect of Cl^- can be summarised as a dominant $[Cl^-]^2$ dependence, which may, in some part, be due to inner-sphere complexation to the Cd. However, in view of the pts^- *vs.* Cl^- effects already noted for the group 13 and 14 cubes with $[Co(dipic)_2]^-$,[17,18] inhibition by hydrogen-bonded outer-sphere pts^- ions is a more likely interpretation. Such a protective sheath is a common feature in crystal structures of pts^- salts.[3] In solution, on replacing Cl^- with pts^-, the inhibition of the reaction of the heterometallic cube with H^+ (or $[Co(dipic)_2]^-$) is accounted for by this decreased access. There are two different ways in which an activated complex of $[Mo_3CdS_4(H_2O)_{12}]^{4+}$ and two H^+ ions can be assembled. Both H^+ can coordinate to the Cd as hydrido groups. Alternatively, direct attack of H^+ on an existing hydride ligand is possible.

Electrochemical and kinetic evidence has been obtained for protonation of μ-S groups of Fe–S clusters.[26,27] As yet, however, no UV-Vis spectrophotometric evidence for protonation of μ-S groups in Mo–S clusters has been obtained.[1] In studies on [3Fe–4S] clusters in *Desulfovibrio africanus*, uptake of heterometals (M = Fe, Zn, Co and Cd) has been observed.[26] Reversible interconversion of $Fe_3S_4^{o}$ and $Fe_3CdS_4^{2+}$ occurs on addition of Cd^{2+}, while $Fe_3S_4^+$ and the hyper-reduced (all Fe^{II}) cluster $Fe_3S_4^{2-}$ have little affinity for M. In studies[27] on the oxidation of $Fe_3S_4^{2-}$, a net uptake of three protons (pHs at or close to 7.0) has been reported. No H_2 evolution is observed in any of these, in contrast to hydrogenase enzymic reactions.[28]

A further question is concerned with the role of Cl^- and whether a step involving a direct interaction with the Cd is relevant instead of (or alongside) the Cl^- *vs.* pts^- effect already considered. The most obvious argument in favour of Cl^- catalysis is based on electrostatics, with H^+ more readily able to approach the Cd when it is coordinated to chloride. Equilibrium constants (K/M^{-1}) for the formation of monochloro complexes at the heterometal of $[Mo_3MS_4(H_2O)_{10}]^{4+}$ have been reported for M = Fe (560),[15] and M = Ni (97).[16] The main group metal Sn in $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ has an even greater affinity for Cl^-, with the formation of $[Mo_3(SnCl_3)S_4(H_2O)_9]^{3+}$ approaching completion at 0.05 M Cl^-.[11] Complexation of Cl^- to the Mo atoms of $[Mo_4S_4(H_2O)_{12}]^{5+}$ ($K = 1.98\ M^{-1}$)[29] and $[Mo_3S_4(H_2O)_9]^{4+}$ ($K = 3.0\ M^{-1}$) is much less at 25 °C, I = 2.00 M ($LiClO_4$).[30] Overall however, in view of the earlier comments, it would be surprising if Cl^- complexation to the heteroatom made other than minor contributions.

To summarise, the single cube $[Mo_3CdS_4(H_2O)_{12}]^{4+}$ has been prepared and characterised. Oxidation decay processes are observed with both O_2 and H^+, when $[Mo_3S_4(H_2O)_9]^{4+}$ and Cd^{2+} are formed. Rate constants for the oxidation of $[Mo_3CdS_4(H_2O)_{12}]^{4+}$ with $[Co(dipic)_2]^-$ are mid-range ($31.5\ M^{-1}\ s^{-1}$) for heterometallic derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$. The reaction with H^+ has novel features, in particular the dominant $[H^+]^2$ dependence of the rate law. In the presence of Cl^- for pts^- the cube is more exposed to direct attack by H^+; half-life in 1 M HCl ~5 min. The inhibition by pts^- is attributed to its tendency to form a protective outer sphere layer. The reactions of the Cd, Ga, In and Tl heterometallic derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$ with H^+ provides an interesting development in the chemistry of this type of cube.

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