Preparation and Properties of Group 13 (Ga, In, Tl) Heterometallic Single and Corner-Shared Double Cube Derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$ and Related Studies

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New routes are described for the preparation of cuboidal complexes $[Mo_3InS_4(H_2O)_{12}]^{5+}$, $[Mo_3GaS_4(H_2O)_{12}]^{5+}$, and $[Mo_6InS_8(H_2O)_{18}]^{8+}$ from the incomplete cuboidal $[Mo_3S_4(H_2O)_9]^{4+}$. A comparison of the aqueous solution properties of the single cubes, $[Mo_3GaS_4(H_2O)_{12}]^{5+}$ and $[Mo_3InS_4(H_2O)_{12}]^{5+}$, and the double cubes, $[Mo_6InS_8(H_2O)_{18}]^{8+}$ and $[Mo_6TlS_8(H_2O)_{18}]^{8+}$, the total listing of group 13 derivatives, is reported. The single cube $[Mo_3InS_4(H_2O)_{12}]^{5+}$ can be quantitatively converted into the double cube by reductive (H_3PO_2 or BH_4^-) addition of $[Mo_3S_4(H_2O)_9]^{4+}$. The double cubes are O_2 sensitive, much more so in HCl than Hpts ($pts^- =$ *p*-toluenesulfonate), and are oxidized by H^+ in HCl solutions with the formation of H_2 (detected by gas chromatography). The single cubes are less reactive in air, and are only oxidized by H^+ at higher (∼4 M) levels. Stoichiometry measurements with $[Co(dipic)_2]^-$ and $[Fe(H_2O)_6]^{3+}$ as $1e^-$ oxidants were used to confirm charges on the clusters. In the absence of reduction potentials, rate constants for outer-sphere $[Co(dipic)_2]^-$ oxidations give a measure of redox properties. Oxidation of $[Mo_6InS_8(H_2O)_{18}]^{8+}$ with $[Co(dipic)_2]^-$ provides a route back to the single cube $[Mo_3InS_4(H_2O)_{12}]^{5+}$. Properties of $[W_3InS_4(H_2O)_{12}]^{5+}$ and $[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$ obtained from $[W_3S_4(H_2O)_9]^{4+}$ and $[Mo_3OS_3\text{-}(H_2O)_9]^{4+}$ are also considered. The single cube $[W_3InS_4(H_2O)_{12}]^{5+}$ is $>10^3$ times more reactive with $[Co(dipic)_2]^-$ than $[Mo_3InS_4(H_2O)_{12}]^{5+}$, consistent with reducing properties W > Mo. No evidence was obtained in these studies for $[Mo_3TlS_4(H_2O)_{12}]^{5+}$, $[Mo_6GaS_8(H_2O)_{18}]^{8+}$, or the recently proposed 6+ analogue of $[Mo_3GaS_4(H_2O)_{12}]^{5+}$.

Introduction

Of the extensive list of heterometal atoms incorporated into the Mo^{IV}_3 incomplete cuboidal cluster $[Mo_3S_4(H_2O)_9]^{4+}$ (now >20),[1,2] those of the group 13 elements (Ga, In, Tl) are the focus of the present paper and provide an interesting illustration of group properties and trends. The extent to which main group elements participate in this chemistry is a recent somewhat unexpected development. The incorporation of group 15 As,[2] as well as Sb[3] and Bi,[4] has demonstrated that nonmetallic/metalloid elements also play a part in such studies. The main group elements As,[2] Sb,[3] Bi,[4] Sn,[5−7] and Pb[8] along with Hg[9] give corner-shared double cubes, and single cubes are not as common as in the case of transition metal derivatives.[1,2] In the case of Sn a particular feature is the existence of single and double cubes $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ and $[Mo_6SnS_8(H_2O)_{18}]^{8+}$ where redox induced interconversions have been studied.[6] The isolation of the highly charged $Mo_3PbS_4{}^{6+}$ and $Mo_3BiS_4{}^{7+}$ cores has been possible using anionic ligands.[10] In the case of the group 13 elements single (Ga, In),[11,12] and double cubes (In, Tl)[13,14] have been identified, but whether this is a complete list as well as trends in the solution properties have not so far been studied in a systematic manner. X-ray crystal structures have been reported for $[Mo_3InS_4(pts)_2(H_2O)_{10}]\ (pts)_3{\cdot}13H_2O$,[12] $[Mo_6InO_2S_6(H_2O)_{18}])pts)_8{\cdot}30H_2O$,[13] $[Mo_3GaS_4(H_2O)_{12}]\ (pts)_5{\cdot}14H_2O$, and surprisingly $[Mo_3GaS_4(H_2O)_{12}](pts)_6{\cdot}17H_2O$.[11] The double cube $Mo_6InS_8{}^{8+}$ has not previously been characterized with respect to its charge and composition. New preparative work is described in the Results section. Oxidation state assignments for the $[Mo^{IV}_3S_4(H_2O)_9]^{4+}$ derivatives can be written as $[(Mo^{IV}_3S_4)Ga^{I}(H_2O)_{12}]^{5+}$, $[(Mo^{IV}_3S_4)In^{I}(H_2O)_{12}]^{5+}$, $[(Mo^{IV}_3S_4)_2In^{0}(H_2O)_{18}]^{8+}$, and $[(Mo_3S_4)_2Tl^{0}(H_2O)_{18}]^{8+}$ according to a newly suggested formalism.[2] A number of properties, in particular those involving redox changes and including reactions with H^+ (unique to group 13 derivatives) are considered. All the studies described are in aqueous solution in the presence of acids HCl or Hpts.

Experimental Section

Preparation of Clusters. Procedures previously reported include those for the green incomplete cubes $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_3OS_3\text{-}(H_2O)_9]^{4+}$ (schematic structures Figure 1) which were obtained by

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Table 1. UV−Vis Spectra Peak Positions λ/nm (ϵ/M^{-1} cm^{-1}) for Ga, In, and Tl Heterometallic Single and Corner-Shared Double Cube Aqua Ion Derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$ and $W_3S_4(H_2O)_9]^{4+}$ in 2 M HCl and 2 M Hpts As Indicated; ϵ Values per Mo_3 (Single) or Mo_6 (Double) Cube

cluster	color	λ/nm (ϵ/M^{-1} cm^{-1})	acid	ref
$Mo_6InS_8{}^{8+}$	red-orange	379 (2.18 × 10^4); 488 (6650)	2 M Hpts	this work
$Mo_6InO_2S_6{}^{8+}$	red-brown	374 (1.25 × 10^4); 1000 (633)	1 M Hpts	13
$Mo_6TlS_6{}^{8+}$	turquoise	386 (1.04 × 10^4); 667 (1.20 × 10^4)	4 M HCl	14
		380 (1.29 × 10^4); 660 (1.43 × 10^4)	4 M Hpts	14
$Mo_3GaS_4{}^{5+}$	dark brown	390 (3500); 550 (200); 762 (500)	2 M HCl	this work
		388 (2877); 537 (253); 746 (464)	2 M Hpts	this work
		548 (205); 760 (404)	0.5 M HCl	11
$Mo_3InS_4{}^{5+}$	red-brown	355 (8.3 × 10^3); 570 (210); 800 (510)	1 M HCl	12
		329 (1.05 × 10^4); 552 (192); 758 (510)	2 M Hpts	12
$W_3InS_4{}^{5+}$	indigo-blue	304 (1.4 × 10^4); 379 (1.1 × 10^4); 590 (1500)	2 M HCl	18
	purple	298 (1.3 × 10^4); 362 (6010); 591 (900)	2 M Hpts	18
$Mo_3S_4{}^{4+}$	green	370 (4995); 616 (326)	2 M HCl	21
		366 (5550); 603 (362)	2 M Hpts	
$W_3S_4{}^{4+}$	purple	317 (6100); 570 (480)	2 M HCl	18
		315 (6350); 560 (446)	2 M Hpts	18

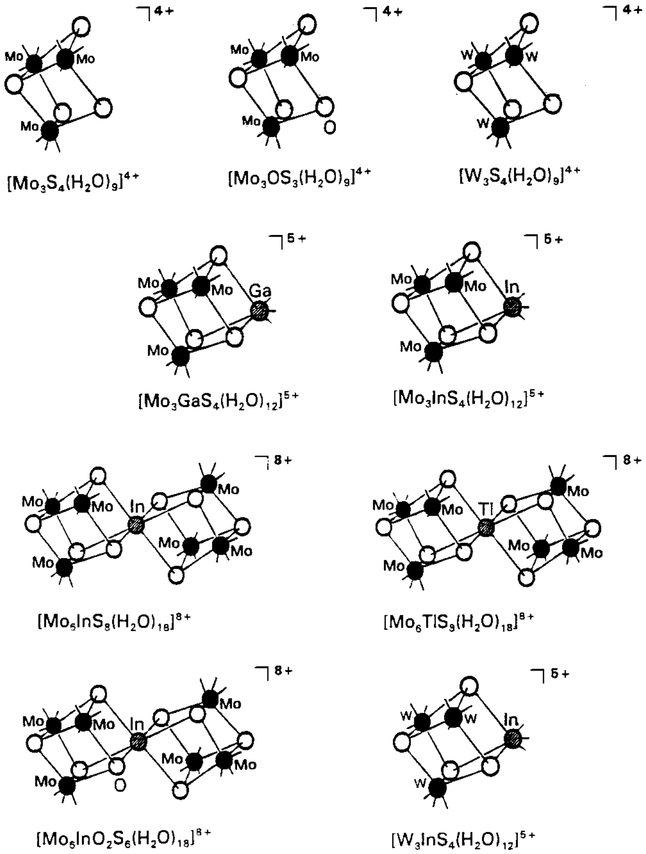

Figure 1. Schematic structures of clusters relevant to this work.

$NaBH_4$ reduction of the $Mo^V{}_2$ complex $[Mo_2O_2(\mu\text{-}S)_2(Cys)_2]^{2-}$ (Cys = cysteine).[15] The former was also obtained by an improved method from polymeric $\{Mo_3S_7Br_4\}_x$, by first converting the polymer into water-soluble $(NEt_4)_2$ $[Mo_3S_7Br_6]$.[16,17] As previously two procedures were used for the preparation of the purple $[W_3S_4(H_2O)_9]^{4+}$ analogue.[18] Conversions to heterometallic cube derivatives require air-free (N_2) conditions, and acids HCl and Hpts were used. UV−vis spectra are summarized in Table 1.

The double cube $[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$ was prepared by reacting $[Mo_3OS_3(H_2O)_9]^{4+}$ with indium wire (Johnson Matthey, Specpure 1.6 mm diameter).[13] Stock solutions of the double cube $[Mo_6TlS_8(H_2O)_{18}]^{8+}$ (1−10 mM) were obtained by reacting $[Mo_3S_4(H_2O)_9]^{4+}$ with Tl metal or with TlCl using $NaBH_4$ as reducing agent.[14] Three procedures have been described for the preparation of $[W_3InS_4(H_2O)_{12}]^{5+}$.[18] All purifications were carried out by Dowex 50W−X2 cation-exchange chromatography (Sigma; mesh size 100−400), elution in Hpts (4 M) or HCl (2 M). Fresh solutions of $[Mo_6TlS_8(H_2O)_{18}]^{8+}$ were eluted from a Dowex column with 2 M HCl, but for studies in Hpts the product from a Tl metal + $[Mo_3S_4(H_2O)_9]^{4+}$ preparation was used without further purification. In the Dowex purification of $[Mo_6TlS_8(H_2O)_{18}]^{8+}$ the column was washed free of Tl^+ using 0.5 M Hpts, even when 2 M HCl was used for the final elution (TlCl is unsoluble).[14]

Other Reagents. Hypophosphorous acid, H_3PO_2 (50% w/w H_2O solution); sodium borohydride, $NaBH_4$; *p*-toluenesulfonic acid, *p*-$CH_3C_6H_4$-SO_3H, here written as Hpts (white crystalline solid); lithium carbonate, Li_2CO_3; and lithium chloride were all obtained from Aldrich. Solutions of Lipts were prepared by Li_2CO_3 neutralization of Hpts and recrystallization (solubility ∼4 M). A solid sample of the Co^{III} oxidant NH_4-$[Co(dipic)_2]\cdot H_2O$, dipic = 2,6-dicarboxylatepyridine, peak at 510 nm (ϵ = 630M^{-1} cm^{-1}), and solution of $[Fe(H_2O)_6]^{3+}$ in 2 M Hpts from iron(III) perchlorate $Fe(ClO_4)_3\cdot 6H_2O$ (Fluka) using Dowex chromatography, were prepared as previously.[6] Reduction potentials vs nhe are for $[Co(dipic)_2]^{-/2-}$ (0.362 V, recently redetermined),[19] and $[Fe(H_2O)_6]^{3+/2+}$ (0.770 V). Solutions of ∼0.1 mM In^I in 0.02 M $HClO_4$ were prepared by anodic oxidation of an indium wire electrode as previously described.[20]

Kinetic Studies. These were at 25.0 ± 0.1 °C, ionic strength adjusted to $I = 2.00 \pm 0.01$ M with either LiCl or Lipts. Conventional time range experiments were by UV−vis spectrophotometry. Faster reactions were studied on an Applied Photophysics stopped-flow spectrophotometer.

Detection of Dihydrogen. A Phasesep model LC2 chromatograph complete with thermal conductivity detector (current 120 mA) and a 5 Å molecular sieve was used in a semiquantitative procedure used to estimate amounts of H_2 gas evolved. Air-free (N_2) samples of the cube (typically 10 mM; 20 mL) were contained in a 100 mL round-bottom flask, fitted with appropriate taps/entries. The reaction was allowed to proceed at room temperature (∼20 °C) for the required time (30 min to 3 days). Nitrogen (85 °C) was used as carrier gas for the 10 mL gas sample taken by syringe from the reaction vessel.

Results

Preparation of $[Mo_3GaS_4(H_2O)_{12}]^{5+}$. A mixture of $[Mo_3S_4$-$(H_2O)_9]^{4+}$ (10 mM; 5 mL) in 0.5 M HCl and 1 mL of Ga^{III} obtained by dissolving Ga metal (0.7 g) in 4.0 M HCl (10 mL)

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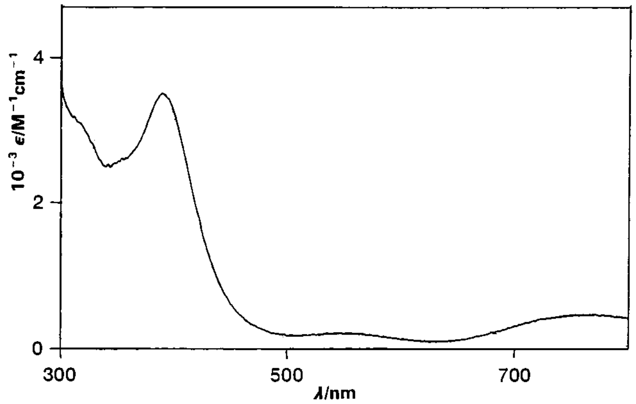

Figure 2. UV−vis spectrum of $[Mo_3GaS_4(H_2O)_{12}]^{5+}$ in 1 M HCl; absorption coefficients (ϵ) per Mo_3.

was siphoned onto $NaBH_4$ (0.14 g) under air-free conditions. The color changed to brown. After standing for ~2 h the solution was diluted 2-fold, loaded onto a Dowex 50W-X2 cation-exchange column, and washed with 0.50 M HCl. Remaining $[Mo_3S_4(H_2O)_9]^{4+}$ (~2%) was eluted with 1.0 M HCl, and $[Mo_3GaS_4(H_2O)_{12}]^{5+}$ with 2.0 M HCl (yield 94%). The reaction can be expressed as in eq 1. The 5+ charge was

$$Mo_3S_4^{\ 4+} + Ga^{III} + 2e^- \rightarrow Mo_3GaS_4^{\ 5+} \qquad (1)$$

confirmed in redox stoichiometry experiments (see below). The UV−vis spectrum is shown in Figure 2, and details are included in Table 1. An earlier procedure[11] involving the reaction of Ga metal with $[Mo_3S_4(H_2O)_9]^{4+}$ requires 1 day.

No reaction was observed on addition of $GaCl_3$ to $[Mo_3S_4(H_2O)_9]^{4+}$ in 2.0 M HCl. No UV−vis absorption changes were observed on heating an air-free solution of $[Mo_3S_3O(H_2O)_9]^{4+}$ in 2.0 M HCl at 60−80 °C for 2 h with Ga metal.

Attempted Conversion to $[Mo_6GaS_4(H_2O)_{18}]^{8+}$. Attempts to convert $[Mo_3GaS_4\ (H_2O)_{12}]^{5+}$ (2 mM; 5 mL) into a corner-shared double cube by mixing with an equivalent amount of $[Mo_3S_4(H_2O)_9]^{4+}$ (15.8 mM; 0.6 mL) in the presence of $NaBH_4$ (0.3 g) under N_2 gave no new species. Experiments were repeated with Ga^{III} (0.57 M; 0.06 mL) and $[Mo_3S_4(H_2O)_9]^{4+}$ (15.8 mM; 4.6 mL) using an excess of H_3PO_2 (available as 50% w/w H_2O solution) as reductant with the same result. In air-free column chromatography the only products identified were $[Mo_4S_4(H_2O)_{12}]^{4+}$ and $[Mo_7S_8(H_2O)_{18}]^{8+}$.[21] We have therefore no evidence for the formation of $[Mo_6GaS_8(H_2O)_{18}]^{8+}$ by reductive addition which is effective in the conversion of In (see below) and Sn[6,7] single to double cubes.

Preparation of $[Mo_3InS_4(H_2O)_{12}]^{5+}$. An earlier method[12] involved reacting indium plate with an air-free solution of $[Mo_3S_4(H_2O)_9]^{4+}$ in 4 M Hpts for 2 days. The same product is obtained on heating 34 mM $[Mo_3S_4(H_2O)_9]^{4+}$ in 2 M HCl with indium wire at 60−70 °C for 2−3 h. Formation of $[Mo_6InS_8(H_2O)_{18}]^{8+}$, eq 2,

$$2Mo_3S_4^{\ 4+} + In \rightarrow Mo_6InS_8^{\ 8+} \qquad (2)$$

is followed by reaction with $[H^+]$, eq 3,

$$Mo_6InS_8^{\ 8+} + H^+ \rightarrow Mo_3InS_4^{\ 5+} + Mo_3S_4^{\ 4+} + {}^1/_2H_2 \qquad (3)$$

to give red-brown $[Mo_3InS_4(H_2O)_{12}]^{5+}$, Figure 3. Three other procedures were identified. In the first of these In^+ was prepared,[20] and an equivalent amount was added to $[Mo_3S_4(H_2O)_9]^{4+}$ (0.22 mM; 1 mL) in an optical cell (both 0.01M $HClO_4$), when rapid quantitative formation of $[Mo_3InS_4(H_2O)_{12}]^{5+}$ was observed (eq 4).

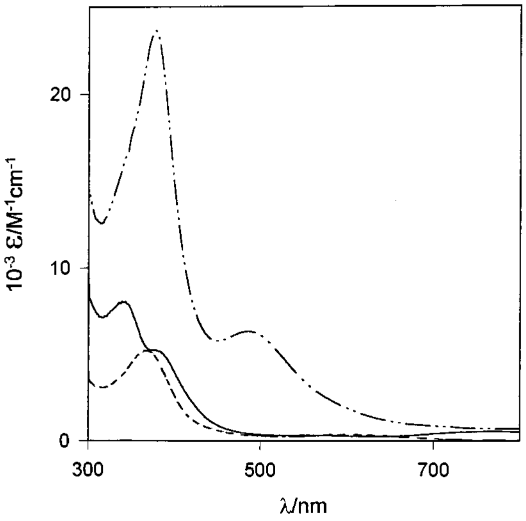

Figure 3. UV−vis spectra of $[Mo_6InS_8(H_2O)_{18}]^{8+}$ (− • • −), $[Mo_3InS_4(H_2O)_{12}]^{5+}$ (—), and $[Mo_3S_4(H_2O)_9]^{4+}$ (- - -) in 2 M HCl; absorption coefficients (ϵ) per Mo_6 in the first case, and per Mo_3 in the others.

$$Mo_3S_4^{\ 4+} + In^I \rightarrow Mo_3InS_4^{\ 5+} \qquad (4)$$

In the second an equivalent amount of In^{3+} and excess H_3PO_2 (as reductant) were added to $[Mo_3S_4(H_2O)_9]^{4+}$ (18 mM; 4 mL) in 0.5 M HCl, when $[Mo_3InS_4(H_2O)_{12}]^{5+}$ was formed within 5−10 min (eq 5).

$$Mo_3S_4^{\ 4+} + In^{3+} + 2e^- \rightarrow Mo_3InS_4^{\ 5+} \qquad (5)$$

The third procedure involved leaving indium wire (0.5 g) with a 2 M HCl solution of $(NH_2Me_2)[Mo_3S_7Br_6]$ (0.12 g; 20 mL)[16,17] for 2 days (60% yield).

Preparation of $[Mo_6InS_8(H_2O)_8]^{8+}$. Two procedures were used, both under air-free (N_2) conditions. In the first the red-brown single cube $[Mo_3InS_4(H_2O)_{12}]^{5+}$ was prepared and converted into the double cube by reacting with an equivalent of $[Mo_3S_4(H_2O)_9]^{4+}$ (0.21 mM; 20 mL) in 1 M Hpts in the presence of excess H_3PO_2 or $NaBH_4$ (0.5 g) as reductant (eq 6).

$$Mo_3S_4In^{5+} + Mo_3S_4^{\ 4+} + e^- \rightarrow Mo_6InS_8^{\ 8+} \qquad (6)$$

When $NaBH_4$ was used, 1 M HCl solutions were employed. The color changed to red-orange, and after 5 min no UV−vis bands of $[Mo_3S_4In(H_2O)_{12}]^{5+}$ remained. Assuming complete conversion to $[Mo_6InS_8(H_2O)_{18}]^{8+}$ the UV−vis spectrum (Figure 3) was obtained, with details as listed in Table 1.

The second procedure involved addition of a 1.5-fold excess of H_3PO_2 (0.06 mL) to a 0.5 M HCl solution of $[Mo_3S_4(H_2O)_9]^{4+}$ (3.6 mM; 20 mL) and stoichiometric amount of $InCl_3$ (eq 7).

$$2Mo_3S_4^{\ 4+} + In^{3+} + 3e^- \rightarrow Mo_6InS_8^{\ 8+} \qquad (7)$$

On heating at ~50 °C red-brown $[Mo_3InS_4(H_2O)_{12}]^{5+}$ first forms and gives red-orange $[Mo_6InS_8(H_2O)_{18}]^{8+}$ within 1 h. The latter is retained as long as amounts of H_3PO_2 remain.

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No Dowex cation-exchange chromatographic purification of the product was possible. First the product loaded onto a Dowex 50W-X2 column does not move on washing with 1 M Hpts. Second attempts to elute with 4 M Hpts or 2 M HCl (column thermostated at 0 °C), gave rapid decomposition due to oxidation by H^+, and $[Mo_3InS_4(H_2O)_{12}]^{5+}$ and $[Mo_3S_4(H_2O)_9]^{4+}$ products were eluted. It was necessary therefore to proceed without chromatographic purification. We note that excess BH_4^- reacts with H^+, whereas excess H_3PO_2 remains in stock solutions. In the latter case any decay of $[Mo_6InS_8(H_2O)_{18}]^{8+}$ will therefore be followed by its reformation as in eq 6. In stoichiometry determinations it was necessary to use the BH_4^- procedures.

Decay of Heterometallic Clusters in Air. Rigorous air-free (N_2) storage conditions were used for all heterometallic products. Solutions of $[Mo_3GaS_4(H_2O)_{12}]^{5+}$ were stored under N_2 at 4 °C, and gave little oxidation within 1 month. On bubbling air through a 0.5 mM solution of the cube 5% decay is observed in 2 h; heating in air leads to decomposition within a few minutes. Column chromatography of the fully oxidized solution gave 95−100% yields of $[Mo_3S_4(H_2O)_9]^{4+}$ characterized by its UV−vis spectrum.

The In-containing double cube $[Mo_6InS_8(H_2O)_{18}]^{8+}$ is air sensitive, with quantification made difficult by the accompanying reaction with H^+. Both reactions give the In-containing single cube (eq 8) which reacts more slowly (eq 9).

$$Mo_6InS_8^{\ 8+} - e^- \xrightarrow{\text{fast}} Mo_3InS_4^{\ 5+} + Mo_3S_4^{\ 4+} \qquad (8)$$

$$Mo_3InS_4^{\ 5+} - e^- \xrightarrow{\text{slow}} Mo_3S_4^{\ 4+} + In^{3+} \qquad (9)$$

Solutions of the single cube and $[Mo_3GaS_4(H_2O)_{12}]^{5+}$ (under N_2) can be stored for weeks at 4 °C. The $[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$ double cube is also air sensitive.

The double cube $[Mo_6TlS_8(H_2O)_{18}]^{8+}$ is one of the most air-sensitive heterometallic derivatives known,[14] where in air 2 M HCl solutions $\sim 1.5 \times 10^{-4}$ M undergo complete decay in 3 min in an open optical cell (with some shaking). At 4 °C solutions of $[Mo_6TlS_8(H_2O)_{18}]^{8+}$ under N_2 can be kept for 3 days without full decay. Solutions in 4 M Hpts are much more stable and can be kept for 2 weeks at 4 °C under N_2.

Stoichiometries of Redox Processes. The Co^{III} complex $[Co(dipic)_2]^-$ and $[Fe(H_2O)_6]^{3+}$ were used as oxidants. Stoichiometries were determined by titrating aliquots of oxidant from a 0.5 mL Hamilton microsyringe into a 3 mL capacity optical cell (1 × 1 cm cross-section) containing a solution of the cube. The possibility of detecting a 6+ intermediate[11] in the redox titration of $[Mo_3GaS_4(H_2O)_{12}]^{5+}$ (3.5 mM) was examined. With $[Fe(H_2O)_6]^{3+}$ (26.7 mM) in 1 M Hpts the stoichiometry determined was 1.87:1 of Fe^{III}:cube, Figure 4. A single stage was also observed for the titration with $[Co(dipic)_2]^-$ (18 mM), stoichiometry 1.98:1 of Co^{III}:cube. The reaction can therefore be expressed as in eq 10.

$$Mo_3GaS_4^{\ 5+} + 2Fe^{III} \rightarrow Mo_3S_4^{\ 4+} + Ga^{III} + 2Fe^{II} \qquad (10)$$

If a build-up of a 6+ product with virtually identical UV−vis spectrum to the 5+ cube occurs,[11] little or no absorbance change would be observed in the early stages of the reaction. The reaction is slow, and 1 h was required for reaction after addition of each aliquot.

In the case of the indium double cube a two-stage reaction is observed (eqs 11 and 12).

$$Mo_6InS_8^{\ 8+} + Co^{III} \rightarrow Mo_3InS_4^{\ 5+} + Mo_3S_4^{\ 4+} + Co^{II} \qquad (11)$$

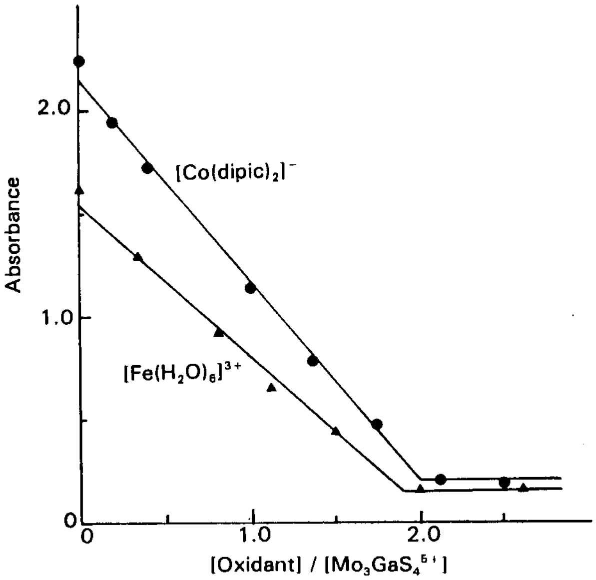


Figure 4. Titration of the $[Mo_3GaS_4(H_2O)_{12}]^{5+}$ cluster in 2 M Hpts with (a) $[Co(dipic)_2]^-$ and (b) $[Fe(H_2O)_6]^{3+}$, monitored at 745 nm. The titrations indicate uniphasic changes with consumption of close to 2 mol of oxidant per $[Mo_3GaS_4(H_2O)_{12}]^{5+}$.

$$Mo_3InS_4^{\ 5+} + 2Co^{III} \rightarrow Mo_3S_4^{\ 4+} + In^{III} + 2Co^{II} \qquad (12)$$

The second stage is again much slower, and quantitative conversion (oxidative degeneration) to the single cube (eq 11) is possible. The final product in eq 12 is In^{III} and not the more strongly reducing In^{I}, contrast eq 13 below. The stoichiometry of (11) was determined by titrating $[Mo_6InS_8(H_2O)_{18}]^{8+}$ (0.1 mM) in 0.5 M HCl with $[Co(dipic)_2]^-$ (0.9 mM). The reaction was monitored at the double cube UV−vis peak at 379 nm, and gave 1.18:1 of Co^{III}: $Mo_6InS_8^{8+}$ (average of three determinations). Both the $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_3InS_4(H_2O)_{12}]^{5+}$ products were identified (and quantified) from their UV−vis spectra. These observations indicate an 8+ charge on the double cube. The stoichiometry of the reaction of $[Mo_3InS_4(H_2O)_{12}]^{5+}$ with $[Co(dipic)_2]^-$ was determined as 1.85:1 in separate experiments.

The stoichiometry of the reaction of $[Mo_6TlS_8(H_2O)_{18}]^{8+}$ with $[Fe(H_2O)_6]^{3+}$, (eq 13), has been reported previously,[14]

$$Mo_6TlS_8^{\ 8+} + Fe^{III} \rightarrow 2Mo_3S_4^{\ 4+} + Tl^{I} + Fe^{II} \qquad (13)$$

with $[Mo_3S_4(H_2O)_9]^{4+}$ as the only product.

The stoichiometry for the titration of 1.8 mM $[W_3InS_4(H_2O)_{12}]^{5+}$ with $[Co(dipic)_2]^-$ (8.2 mM) monitored at 570 nm was found to be 2.06:1 of Co^{III}:$W_3InS_4^{5+}$, in agreement with the value obtained using $[Fe(H_2O)_6]^{3+}$, (eq 14).[18]

$$W_3InS_4^{\ 5+} + 2Co^{III} \rightarrow W_3S_4^{\ 4+} + In^{III} + 2Co^{II} \qquad (14)$$

Reactions with H^+. The Tl- and In-containing derivatives are considered first. In an earlier study on $[Mo_6TlS_8(H_2O)_{18}]^{8+}$ in 2 M HCl under air-free conditions (N_2), a decay process believed to be the reaction with H^+ was reported.[14] This has now been confirmed by GC as a reaction giving H_2. Yields of up to 56% were detected (eq 15), based on the conversion to $[Mo_3S_4(H_2O)_9]^{4+}$.

$$Mo_6TlS_8^{\ 8+} + H^+ \rightarrow 2Mo_3S_4^{\ 4+} + Tl^{I} + {}^1/_2H_2 \qquad (15)$$

Some loss of double cube in transfers (reaction with O_2) is the

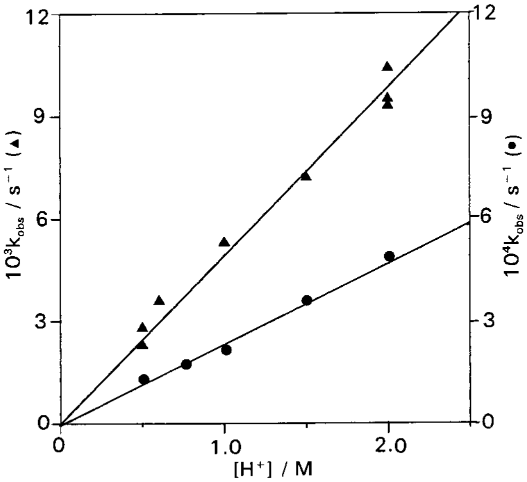


Figure 5. Dependence of first-order rate constants k_{obs} (25 °C) for the reaction of (a) (1.0−2.0) × 10^{-4} M $[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$ and (b) (1.6−1.8) × 10^{-4} M $[Mo_6TlS_8(H_2O)_{18}]^{8+}$ with [H$^+$], I = 2.00 M (LiCl).

most likely explanation of the shortfall. The Tl^{I} formed was at too low a level (<10 mM) for TlCl precipitation to occur. The reaction is much less effective in 2 M Hpts, which is the preferred acid for storage. Thus <1% absorbance change was observed in 40 min for 0.2 mM $[Mo_6TlS_8(H_2O)_{18}]^{8+}$ in 2 M Hpts, and no H_2 was detected by GC after 24 h. Both indium-containing double cubes $[Mo_6InS_8(H_2O)_{18}]^{8+}$ and $[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$ give H_2 in HCl solutions with formation of the single cube, e.g. eq 16.

$$Mo_6InS_8^{\;8+} + H^+ \rightarrow Mo_3InS_4^{\;5+} + Mo_3S_4^{\;4+} + {}^1/_2H_2 \quad (16)$$

There is little contribution from eq 17.

$$Mo_3InS_4^{\;5+} + 2H^+ \rightarrow Mo_3S_4^{\;4+} + In^{III} + H_2 \quad (17)$$

Amounts of H_2 ~80% of that predicted in eq 16 were detected experimentally. In the case of $[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$ 40% H_2 was detected after 3 h, but no H_2 was detected for experiments in Hpts solutions. In a further experiment no H_2 was detected with $[Mo_6SnS_8(H_2O)_{18}]^{8+}$ in 2 M HCl.

Kinetic studies demonstrating first-order dependencies on [H$^+$] were carried out for the reactions of $[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$ and $[Mo_6TlS_6(H_2O)_{18}]^{8+}$, I = 2.00 M (LiCl), Figure 5. Rate constants k_H (25 °C) were 4.9(1) × 10^{-3} M^{-1} s^{-1} (In), and 0.25(1) × 10^{-3} M^{-1} s^{-1} (Tl), respectively. The experiments with $[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$ relate to the conversion to $[Mo_3InOS_3(H_2O)_{12}]^{5+}$, as in eq 16, whereas in the case of $[Mo_6TlS_8(H_2O)_{18}]^{8+}$ the product is $[Mo_3S_4(H_2O)_9]^{4+}$ (eq 15).

In contrast, little if any reaction of the single cubes $[Mo_3GaS_4(H_2O)_{12}]^{5+}$, $[Mo_3InS_4(H_2O)_{12}]^{5+}$, and $[W_3InS_4(H_2O)_{12}]^{5+}$ with H$^+$ is observed under identical conditions, and no H_2 is detected by GC within 3 days. However, in 4 M HCl both $[Mo_3GaS_4(H_2O)_{12}]^{5+}$ and $[Mo_3InS_4(H_2O)_{12}]^{5+}$ react with H$^+$. For the former 10% H_2 was detected after 3 days based on eq 18,

$$Mo_3GaS_4^{\;5+} + 2H^+ \rightarrow Mo_3S_4^{\;4+} + Ga^{III} + H_2 \quad (18)$$

and in the case of the latter (same stoichiometric equation) 35% H_2 was obtained also over 3 days. No corresponding experiments were carried out with $[W_3InS_4(H_2O)_{12}]^{5+}$.

Kinetic Studies on Oxidations with $[Co(dipic)_2]^-$. Stoichiometric equations have already been indicated. First-order rate constants k_{obs} (25 °C) were determined for the reactions of single and double cubes with $[Co(dipic)_2]^-$. The latter was in large excess to conform with pseudo first-order conditions i.e., for a stoichiometry 2:1 of Co^{III}:cube a >20-fold excess of Co^{III} was used. UV−vis absorbance changes corresponding to decay of the heterometal cube were monitored. Different rate constants were obtained depending on whether Cl$^-$ or pts$^-$ solutions were used. Linear dependencies of k_{obs} on [Co^{III}] gave second-order rate constants k_a with I = 2.00 M (LiCl) and k_b with I = 2.00 M (Lipts), Table 2. As in previous studies[1,2] no dependence of k_a or k_b on [H$^+$], range 0.50−2.00 M, was observed (Figure 6). The reactions can accordingly be assigned as outer-sphere electron transfer.[1,2] In the case of $[Mo_6TlS_8(H_2O)_{18}]^{8+}$ in both Cl$^-$ and pts$^-$ solutions were too fast to study by the stopped-flow method, lower limit for rate constants ~10^5 M^{-1} s^{-1}. In the case of the indium-containing double cubes, the process monitored corresponds to formation of the single cube. Rate constants for the reactions of the single cubes were obtained in separate experiments. The single cube $[W_3InS_4(H_2O)_{12}]^{5+}$ is much more reactive than the other single cubes. Significantly uniphasic absorbance changes were observed in the oxidation of $[Mo_3GaS_4(H_2O)_{12}]^{5+}$ with $[Co(dipic)_2]^-$, Figure 7.

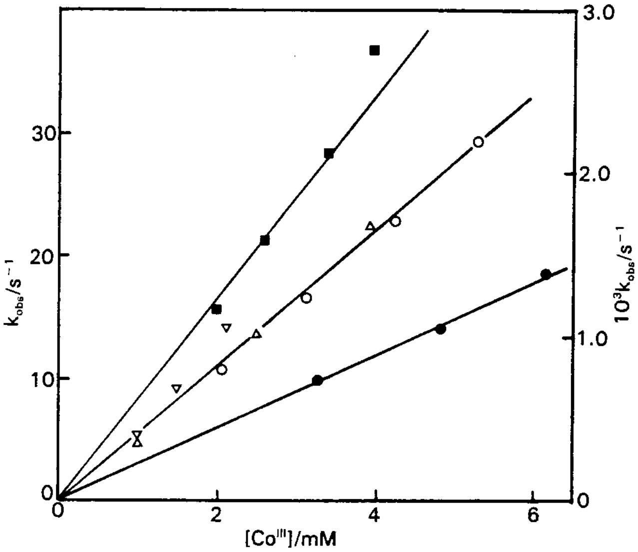


Figure 6. Dependence of first-order rate constants k_{obs} (25 °C) on $[Co(dipic)_2^-]$, reactant in >10-fold excess, for the oxidation of $[Mo_3GaS_4(H_2O)_{12}]^{5+}$ (●); $[MoInS_4(H_2O)_{12}]^{5+}$ (■) (both right-hand scale), and $[W_3InS_4(H_2O)_{12}]^{5+}$ (○), all at [H$^+$] = 2.0 M, with (△) and (▽) at [H$^+$] = 1.0 and 0.5 M, respectively, left-hand scale, I = 2.00 M (Hpts).

Table 2. A Comparison of Rate Constants (25 °C) for the Outer-Sphere Oxidation of Heterometal Containing Clusters with $[Co(dipic)_2]^-$; Rate Constants, Independent of [H$^+$] in the Range [H$^+$] = 0.50−2.00 M, Are k_a with I = 2.00 M (LiCl) and k_b with I = 2.00 M (Lipts)

cluster	k_a/M^{-1} s^{-1}	k_b/M^{-1} s^{-1}	ratio k_a/k_b
$[Mo_6InS_8(H_2O)_{18}]^{8+}$	*a*	30.9(7) × 10^3	
$[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$	*b*	322(8)	
$[Mo_6TlS_8(H_2O)_{18}]^{8+}$	v. fast[c]	v. fast[c]	
$[Mo_3GaS_4(H_2O)_{12}]^{5+}$	4.5(5)	0.231(4)	19.5
$[Mo_3InS_4(H_2O)_{12}]^{5+}$	17.5(5)	0.65(2)	26.9
$[W_3InS_4(H_2O)_{12}]^{5+}$	25.3(4) × 10^3	5.5(1) × 10^3	4.6

[a] Upper limit of stopped-flow range. [b] Reaction with H$^+$ complete in 8−15 min makes stopped-flow studies difficult. [c] Too fast for stopped-flow studies, k > 10^5 M^{-1} s^{-1}.

Discussion

With the studies reported herein the group 13 Ga, In, and Tl heterometallic derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$ provide what is

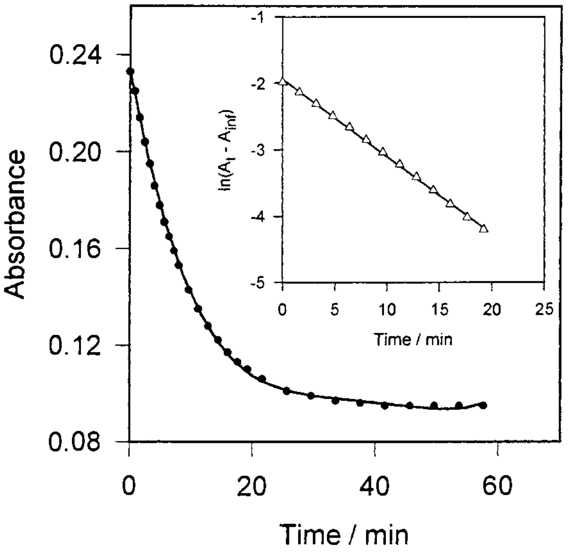
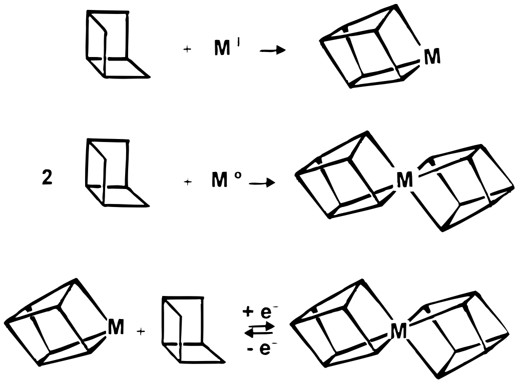


Figure 7. Absorbance decay at 750 nm with time, and corresponding first-order plot ln($A_t - A_\infty$) vs time (inset), for the oxidation of $[\mathrm{Mo_3GaS_4(H_2O)_{12}}]^{5+}$ (3.8×10^{-4} M) with $[\mathrm{Co(dipic)_2}]^-$ (8.2×10^{-3} M) in 2.0 M Hpts.

Scheme 1. Reaction Schemes



probably the most detailed information of specific group properties and trends observed in the aqueous solution chemistry of metal/chalcogenide cuboidal clusters. The single cubes consist of $[\mathrm{Mo_3GaS_4(H_2O)_{12}}]^{5+}$ and $[\mathrm{Mo_3InS_4(H_2O)_{12}}]^{5+}$ with no Tl-containing analogue. Corner-shared double cubes are $[\mathrm{Mo_6InS_8(H_2O)_{18}}]^{8+}$ (not previously characterized) and $[\mathrm{Mo_6TlS_8(H_2O)_{18}}]^{8+}$, with no Ga analogue. Relevant structures are as shown in Figure 1, and reactions are summarized in Scheme 1. Single and double cube interconversions in the indium case, as well as stoichiometry determinations, indicate quite unambiguously formation of the double cube $[\mathrm{Mo_6InS_8(H_2O)_{18}}]^{8+}$. Preparative methods have been explored using all existing procedures in search of the missing members and the existing list probably represents the complete set of group 13 derivatives. Thus controlled oxidation of $[\mathrm{Mo_6TlS_8(H_2O)_{18}}]^{8+}$ gave no evidence for the formation of a single cube, and treatment of $[\mathrm{Mo_3GaS_4(H_2O)_{12}}]^{5+}$ with $[\mathrm{Mo_3S_4(H_2O)_9}]^{4+}$ and $\mathrm{NaBH_4}$ (or $\mathrm{H_3PO_2}$) gave no evidence for a double cube by reductive addition. The reaction of $\mathrm{Tl^I}$ with $[\mathrm{Mo_3S_4(H_2O)_9}]^{4+}$ would normally be expected to yield the single cube, and Ga metal with $[\mathrm{Mo_3S_4(H_2O)_9}]^{4+}$ the double cube, but neither conforms to this pattern of behavior.

Single and double cube interconversions, have now been successfully carried out with indium and tin[6,7] as heteroatoms. The reactions, referred to as reductive addition (eq 6), and oxidative degradation (eq 11), are reversible and quantitative conversion is observed. Using a recently adopted formalism[2] the single and double cubes of indium can be written as $(\mathrm{Mo_3S_4}^{4+})\mathrm{In}^+$ and $(\mathrm{Mo_3S_4}^{4+})_2\mathrm{In}^0$ (one-electron difference), and in the tin case as $(\mathrm{Mo_3S_4}^{4+})\mathrm{Sn}^{2+}$ and $(\mathrm{Mo_3S_4}^{4+})_2\mathrm{Sn}^0$ (two-electron difference).[6] Identical oxidation state assignments can be made in the case of $[\mathrm{Mo_6InO_2S_6(H_2O)_{18}}]^{8+}$.

Background levels of $\mathrm{H^+}$ are necessary to retain aqua ligands, and trace amounts of $\mathrm{O_2}$ are difficult to exclude entirely in transfer/storage procedures as used in these studies. The In- and Tl-containing double cubes are particularly reactive with both $\mathrm{H^+}$ and $\mathrm{O_2}$, where reactions are most favorable i.e., faster in HCl solutions. With $[\mathrm{Mo_6InS_8(H_2O)_{18}}]^{8+}$ the final product is in both cases the single cube (eq 19).

$$\mathrm{Mo_6InS_8}^{8+} - e^- \rightarrow \mathrm{Mo_3InS_4}^{5+} + \mathrm{Mo_3S_4}^{4+} \qquad (19)$$

Further oxidation of the single cube $[\mathrm{Mo_3InS_4(H_2O)_{12}}]^{5+}$ by $\mathrm{H^+}$ is slow, even in 4 M HCl. With $[\mathrm{Mo_6TlS_8(H_2O)_{18}}]^{8+}$ on the other hand reaction proceeds direct to $[\mathrm{Mo_3S_4(H_2O)_9}]^{4+}$ (eq 20).

$$\mathrm{Mo_6TlS_8}^{8+} - e^- \rightarrow 2\mathrm{Mo_3S_4}^{4+} + \mathrm{Tl}^+ \qquad (20)$$

Yields of $\mathrm{H_2}$ of 80% and 56% have been observed for eqs 19 and 20, respectively. The $\mathrm{In^I}$ aqua ion is known to react with $\mathrm{H^+}$,[20,22] and it is not surprising therefore that the final product is $\mathrm{In^{III}}$. No similar reaction of $\mathrm{Tl^I}$ has been observed, and strong oxidants are generally required to generate $\mathrm{Tl^{III}}$ (reduction potential for $2e^-$ change 1.25 V vs nhe).

The $[\mathrm{Mo_6TlS_8(H_2O)_{18}}]^{8+}$ double cube is more stable to air oxidation in 2 M Hpts, and as far as reaction with $\mathrm{H^+}$ is concerned no $\mathrm{H_2}$ was detected after 1 day at 20 °C. This contrasts with the behavior in 2 M HCl solutions, where at 20 °C a 1.6 mM $[\mathrm{Mo_6TlS_8(H_2O)_{18}}]^{8+}$ solution undergoes full decay in 15 h with $\mathrm{H_2}$ evolution. At 4 °C, 3 mM solutions can be stored for 3 days without full decay, consistent with the high activation energy (79 kJ $\mathrm{mol^{-1}}$) for reaction with $\mathrm{H^+}$.[14] A possible explanation is that in Hpts solutions the cluster is protected by outer-sphere association with $\mathrm{pts^-}$, and formation of a network of H bonds as in crystal structures.[2] No similar protection is observed in HCl solutions. While chloride can complex to Mo, $\mathrm{pts^-}$ shows much less tendency to inner-sphere coordinate, and along with $\mathrm{ClO_4}-$ and $\mathrm{CF_3SO_3}-$ is one of the poorest donor groups.[23] Previously 1:1 complexing of $\mathrm{Cl^-}$ to Mo in $[\mathrm{Mo_3S_4(H_2O)_9}]^{4+}$ ($K = 3.0\mathrm{M^{-1}}$)[24] and $[\mathrm{Mo_4S_4(H_2O)_{12}}]^{4+}$ ($K = 1.98\mathrm{M^{-1}}$)[25] has been observed. In one case at least with $[\mathrm{Mo_6BiS_8(H_2O)_{18}}]^{8+}$ changes in the UV−vis spectrum in 2 M HCl suggest that $\mathrm{Cl^-}$ is able to coordinate ($K > 40\ \mathrm{M^{-1}}$) to the Bi.[4] The existence of nine-coordinate $[\mathrm{Bi(H_2O)_9}]^{3+}$,[26] provides evidence for high Bi coordination numbers. Differences in UV−vis spectra for $[\mathrm{Mo_6TlS_8(H_2O)_{18}}]^{8+}$ in 4 M HCl and 4 M Hpts are low key and there is no evidence for similar $\mathrm{Cl^-}$ complexing to Tl.[14]

The double cube $[\mathrm{Mo_6InS_8(H_2O)_{18}}]^{8+}$ has been prepared by two methods in addition to that using indium metal.[13] The new procedures have the advantage of being more rapid. Because of its reactivity (with $\mathrm{H^+}$ and $\mathrm{O_2}$) the cluster has proved difficult

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to purify by chromatography and characterize by X-ray crystallography.[11,13] One concern in monitoring reactions with H^+ and O_2 is the extent to which excess H_3PO_2 as reductant might remain and could be influential. Preparations using BH_4^- have the advantage that excess BH_4^- reacts quite rapidly with H^+ and will not therefore remain in stock solutions.

Kinetic studies were carried out for the reactions of $[Mo_6TlS_8(H_2O)_{18}]^{8+}$ and $[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$ with H^+. The rate laws, first-order in double cube and in $[H^+]$, give second-order rate constants 0.25×10^{-3} M^{-1} s^{-1} (Tl) and 4.9×10^{-3} M^{-1} s^{-1} (In). Both stoichiometric equations, e.g. eqs 15 and 16, involve uptake of one H^+. The single cubes $[Mo_3GaS_4(H_2O)_{12}]^{5+}$ and $[Mo_3InS_4(H_2O)_{12}]^{5+}$ are stable in Hpts, and show little or no reaction in 2 M HCl, but in 4 M HCl give 10% and 36% amounts of H_2 respectively in 3 days.

It has not so far been possible to prepare any other oxidation states of the heterometallic derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$ described in this paper, and with one exception (Cu as the heteroatom[27]) oxidation results in a single-stage regeneration of $[Mo_3S_4(H_2O)_9]^{4+}$. The electrochemistry is difficult, and in order to assess redox properties, oxidations with $[Co(dipic)_2]^-$ have been carried out, $I = 2.00$ M. The reactions are independent of $[H^+]$ in the range 0.50−2.00 M, and are assigned as outer-sphere electron-transfer processes. Rate constants, Table 2, confirm the greater reactivity in Cl^- than pts^-. In the case of $[Mo_6TlS_8(H_2O)_{18}]^{8+}$ reactions in both Cl^- and pts^- are very fast. With $[Mo_6InS_8(H_2O)_{18}]^{8+}$ the first stage (eq 21),

$$Mo_6InS_8{}^{8+} + Co^{III} \rightarrow Mo_3InS_4{}^{5+} + Mo_3S_4{}^{4+} + Co^{II} \quad (21)$$

is 4.6×10^4 times faster than the second stage (eq 22),

$$Mo_3InS_4{}^{5+} + 2Co^{III} \rightarrow Mo_3S_4{}^{4+} + In^{III} + 2Co^{II} \quad (22)$$

Both studies are made in 2 M pts^- solution. The double cube $[Mo_6InS_8(H_2O)_{18}]^{8+}$ reacts $\sim 10^2$ times faster than $[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$.

Oxidation of the single cubes $[Mo_3GaS_4(H_2O)_{12}]^{5+}$ and $[Mo_3InS_4(H_2O)_{12}]^{5+}$ is $\sim 10^3$ times slower than for $[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$, Figure 8. In 2 M HCl some Cl^- complexing to the heteroatom is likely (as in the case of Sn[6]), and rate constants are ~20-fold more rapid in Cl^-. Rate constants for $[W_3InS_4(H_2O)_{12}]^{5+}$ are larger than those for $[Mo_3InS_4(H_2O)_{12}]^{5+}$ by factors of 1450 (Cl^-) and 8420 (pts^-) and are larger than for $[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$. These ratios reflect the greater reducingproperties of the W as compared to Mo. Such effects W vs Mo have been reported previously.[28,29] Surprisingly the $[W_3InS_4(H_2O)_{12}]^{5+}$ cube does not react appreciably faster with H^+. A possible explanation is that the $[Co(dipic)_2]^-$ oxidation of $[W_3InS_4(H_2O)_{12}]^{5+}$ is largely via the W_3S_4 part of the cube, whereas H^+ oxidation involves the heteroatom.

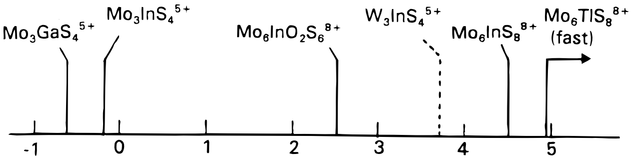

Figure 8. Summary of rate constants (as log k_a values) for the oxidation of different clusters with $[Co(dipic)_2]^-$ at 25 °C, $I = 2.00$ M (LiCl).

Finally while we have been able to prepare $[Mo_3GaS_4(H_2O)_{12}]^{5+}$ by different procedures and characterize the product as 5+, we have not been able to obtain evidence in support of a 6+ cluster as an intermediate in the oxidation to $[Mo_3S_4(H_2O)_9]^{4+}$ and Ga^{III}. Both the stoichiometric titrations, Figure 4, and kinetic studies with $[Co(dipic)_2]^-$ in large >20-fold excess, Figure 7, suggest a uniphasic process with no evidence for intermediate formation of the 6+ ion $[Mo_3GaS_4(H_2O)_{12}]^{6+}$. This behavior could be explained by the 6+ cube being more reactive than the 5+ cube. However it then becomes difficult to see how H^+ can oxidize 5+ with build-up of the 6+ cube (as has been proposed[11]), instead of proceeding through to $[Mo_3S_4(H_2O)_9]^{4+}$. Evidence for the 6+ cube comes from a crystal structure determination, presented alongside that of the 5+ cube, and from electrochemical CV data in acetonitrile.[11] Visible spectra of the 5+ and 6+ ions are however reported as very similar/identical.[11] These contradictions can be resolved if in the crystal structure containing 6 pts^- per cube, one pts^- is incorporated as Hpts (which is difficult to detect), as observed previously.[7,30] Further evidence is required for the existence of a 6+ cube as other than a transient form.

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