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# Preparation, Structure, and Properties of the Corner-Shared Double Cubes $[Mo_6HgQ_8(H_2O)_{18}]^{8+}$ (Q = S, Se) and Tungsten Analogues

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The purple corner-shared double cube $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ derivative of green $[Mo_3S_4(H_2O)_9]^{4+}$, obtained under air-free conditions by the reaction with $Hg^0$ (metal), is also formed with $Hg^{I}_2$. The $Hg^{I}_2$ reaction is accounted for by the disproportionation $Hg^{I}_2 \rightleftharpoons Hg^0 + Hg^{II}$, which is a source of $Hg^0$. X-ray crystallographic information on the blue partially $Cl^-$ substituted cucurbituril supramolecular assemblies $[Mo_6HgQ_8Cl_4(H_2O)_{14}](C_{36}H_{36}N_{24}O_{12})Cl_4{\cdot}14H_2O$ (**1**) and of the Se analogue $[Mo_6HgSe_8Cl_4(H_2O)_{14}](C_{36}H_{36}N_{24}O_{12})Cl_4{\cdot}14H_2O$ (**2**) have been determined. The product $[W_6HgSe_8Cl_4(H_2O)_{14}](C_{36}H_{36}N_{24}O_{12})Cl_4{\cdot}14H_2O$ (**3**) has also been obtained, but there is no evidence for $[W_6HgS_8(H_2O)_{18}]^{8+}$ and related forms. The formation of $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ by the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with $Hg^0$ under anaerobic conditions maximizes after ∼40 h in 2.0 M HCl, but requires longer reaction time (∼120 h) in 2.0 M Hpts (*p*-toluenesulfonic acid) and in 2 M $HClO_4$ (∼6 days). In 2.0 M HCl there is little absorbance increase until $[Mo_3S_4(H_2O)_9]^{4+}$ exceeds $1.2 \times 10^{-3}$ M, which is explained by a dependence of the formation $K$ (265 $M^{-1}$) on $[Mo_3S_4(H_2O)_9{}^{4+}]^2$. Furthermore, on dilution of column-purified $[Mo_6HgS_8(H_2O)_{18}]^{8+}$, Beer's law is not obeyed and equilibria involving $2[Mo_3S_4(H_2O)_9]^{4+}$ are apparent. The kinetics of formation of $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ is first-order in $[Mo_3S_4(H_2O)_9]^{4+}$, consistent with rate-determining formation of the single cube $[Mo_3HgS_4(H_2O)_x]^{4+}$. The oxidations of $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ with $[Fe(H_2O)_6]^{3+}$ and $[Co(dipic)_2]^-$ are complicated by the release of $[Hg(H_2O)_6]^{2+}$, which also functions as an oxidant. Similar results are obtained for $[Mo_6HgSe_8(H_2O)_{18}]^{8+}$ and the less extensively studied $[W_6HgSe_8(H_2O)_{18}]^{8+}$.

## Introduction

The mercury-containing corner-shared $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ double cube is prepared by the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ (0.1 M) in 4 M Hpts (*p*-toluenesulfonic acid) with mercury (∼3 g).[1] Crystals of $[Mo_6HgS_8(H_2O)_{18}](pts)_8{\cdot}20H_2O$ have indicated a corner-shared $\mu_6$-Hg double-cube structure $[Mo_6HgS_8(H_2O)_{18}]^{8+}$,[2] and the formalism $(Mo_3S_4{}^{4+})_2Hg^0$ has been introduced.[3] However, there is as yet no evidence for the single cube, i.e., $(Mo_3S_4{}^{4+})Hg^0$, where unlike the group 13−15 derivatives the heteroatom has the same oxidation state as in the double cube. The aqueous solution chemistry has the potential therefore for different behavior as compared to other heterometallic derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$,[4] as well as Fe−S clusters.[5,6] The ability of other incomplete cubes $[M_3Q_4(H_2O)_9]^{4+}$ (M = Mo, W; Q = S, Se) to form heterometallic Hg-containing derivatives has also been explored. A communication referring to some of the work has appeared.[7]

The properties of mercury in aqueous solution are relevant to the present studies. Redox properties of $[Hg(H_2O)_6]^{2+}$ (p$K_a$ = 3.7)[8] and the mercury(I) aqua dimer $Hg_2{}^{2+}$ (p$K_a$ = 5.0)[9] are summarized by eqs 1−3,[10,11]

$$2Hg^{II} + 2e^- \rightleftharpoons Hg^{I}{}_2 \qquad E^{\circ\prime} = 0.920\ \mathrm{V} \tag{1}$$

$$Hg^{II} + 2e^- \rightleftharpoons Hg^0 \qquad E^{\circ\prime} = 0.855\ \mathrm{V} \tag{2}$$

$$Hg^{I}{}_2 + 2e^- \rightleftharpoons 2Hg^0 \qquad E^{\circ\prime} = 0.789\ \mathrm{V} \tag{3}$$

(reduction potentials vs nhe). Also important is the tendency of the mercury(I) dimer to disproportionate (eq 4),[12,13]

$$Hg^{I}{}_2 \rightleftharpoons Hg^{II} + Hg^0 \tag{4}$$

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with $K = [Hg^{II}]/[Hg^{I}_2] = 0.0061$.[10,14] At equilibrium $Hg_2^{2+}$ solutions contain 0.6% of $Hg^{2+}$ (and $Hg^0$). The upper limit of the equilibrium constant for eq 5 is $10^{-7}$ M,[15] but no evidence

$$Hg_2^{2+} \rightleftharpoons 2Hg^+ \qquad (5)$$

has been obtained for this step in redox studies.[16] The solubility of $Hg^0$ (metal) in $H_2O$ is estimated to be $2.8 \times 10^{-7}$ M.[17]

## Experimental Section

**Preparation of $[Mo_3S_4(H_2O)_9]^{4+}$.** The green $Mo^{IV}_3$ incomplete cube $[Mo_3S_4(H_2O)_9]^{4+}$ was prepared by two procedures, one from $[Mo_2O_2(\mu\text{-}S)_2(Cys)_2]^{2-}$ (Cys = cysteine)[18] and the other from polymeric $\{Mo_3S_7Br_4\}_x$.[19-21] Purification was carried out using Dowex 50W-X2 cation-exchange chromatography, final elution with 2 M HCl, Hpts, or $HClO_4$ as required. The $[Mo_3S_4(H_2O)_9]^{4+}$ product has UV−vis peak positions $\lambda$/nm ($\epsilon$/$M^{-1}$ $cm^{-1}$ per $Mo_3$) at 370 (4995), 616 (326) in 2 M HCl, and 366 (5550), 603 (362) in 2 M Hpts, with peaks slightly shifted to 367 and 605 in 2 M $HClO_4$. A crystalline sample of $[Mo_3S_4(H_2O)_9](pts)_4{\cdot}9H_2O$ was prepared.

**Preparation of Other $[M_3Q_4(H_2O)_9]^{4+}$ Trinuclear Clusters.** Solutions of yellow-brown $[Mo_3Se_4(H_2O)_9]^{4+}$ were prepared from polymeric $\{Mo_3Se_7Br_4\}_x$ as previously described, UV−vis peak positions in 2 M HCl $\lambda$/nm ($\epsilon$/$M^{-1}$ $cm^{-1}$) at 433 (5250), 682 (580). Likewise purple $[W_3S_4(H_2O)_9]^{4+}$, peaks at 317 (6100), 570 (480);[22] and green $[W_3Se_4(H_2O)_9]^{4+}$, peaks at 360 (6950), 625 (500) (both in 2 M HCl), were prepared by procedures already described.[23]

**Other Reagents.** High-purity $Hg^0$ metal (Aldrich, 99.99%) and redistilled $Hg^0$ were used. Solutions of aqua $Hg^{I}_2$ and $[Hg(H_2O)_6]^{2+}$ in the required acid were prepared from newly opened samples of mercury(I) perchlorate, $Hg_2(ClO_4)_2{\cdot}4H_2O$, and mercury(II) perchlorate, $Hg(ClO_4)_2{\cdot}3H_2O$, both >99% purity (Strem Chemicals). Crystalline (white) *p*-toluenesulfonic acid and lithium chloride were obtained from Aldrich. The annular-shaped cavitand molecule cucurbituril ($C_{36}H_{36}N_{24}O_{12}$) was prepared by procedures already described.[24] A sample of the bis-dipicolinatocobaltate(III) complex, $(NH_4)[Co(dipic)_2]{\cdot}H_2O$ (dipic = 2,6-carboxylatopyridine), peak at 510 nm (630 $M^{-1}$ $cm^{-1}$), and solutions of $[Fe(H_2O)_6]^{3+}$ in 2 M Hpts or 2 M $HClO_4$ were prepared as in earlier studies.[4] Dowex 50W-X2 cation-exchange resin (mesh size 200−400) was obtained from Sigma Chemicals. Air-free ($N_2$) conditions were used throughout.

**Precautions.** It was necessary to wash all glassware with concentrated $HNO_3$ to remove traces of Hg from the glass surface. Dowex 50W-X2 cation-exchange resin was not reused in other studies. Normal precautions were observed in handling mercury metal.

**Preparation of Hg-Containing Derivatives.** On addition of high (≈10 mM) concentrations of air-free $[Mo_3S_4(H_2O)_9]^{4+}$ in 2 M HCl or Hpts to Hg metal, formation of the intense purple colored $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ is observed, eq 6. In order to monitor reactions by UV−vis

$$2Mo_3S_4^{\ 4+} + Hg^0 \rightleftharpoons Mo_6HgS_8^{\ 8+} \qquad (6)$$

spectrophotometry smaller concentrations (~1 mM) were used. Literature peak positions $\lambda$/nm ($\epsilon$/$M^{-1}$ $cm^{-1}$ per $Mo_6$) at 372−375 ($13.0 \times 10^3$) and 556−600 ($18.8 \times 10^3$) were used throughout.[1] When the preparation is carried out with $[Mo_3S_4(H_2O)_9]^{4+}$ in 4 M HCl, or 2 M HCl + 4 M LiCl, a dark (royal) blue $Cl^-$-substituted product is obtained. Equilibrium constants $K = [Mo_6HgS_8^{\ 8+}]/[Mo_3S_4^{\ 4+}]^2$ defined by eq 6 were obtained. The same preparative route was used for the Se-containing analogues $[M_3Se_4(H_2O)_9]^{4+}$ (M = Mo, W). No reaction was observed with $[W_3S_4(H_2O)_9]^{4+}$.

**Techniques.** UV−vis spectra were recorded on Shimadzu 2101PC or Perkin-Elmer Lambda 9 spectrophotometers. Quantitative aspects of eq 6 in different acids (Hpts, HCl, and $HClO_4$) are considered in this paper. Elemental analyses for Mo and Hg, as well as S and Se (both less accurate), were carried out by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an ATI Unicam 701 instrument. To calibrate for S and Se, solutions of $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_3Se_4(H_2O)_9]^{4+}$ in 2 M HCl were used.

**Stability in Air.** Under $N_2$ with no Hg metal present, purple solutions containing $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ (0.5 mM) were stored for ~1 month. On bubbling air through solutions with no Hg metal present, green $[Mo_3S_4(H_2O)_9]^{4+}$ re-forms, eq 7. With excess $Hg^0$, recycling of the $[Mo_3S_4(H_2O)_9]^{4+}$ occurs as in eq 6.

$$2Mo_6HgS_8^{\ 8+} + O_2 + 4H^+ \rightarrow 4Mo_3S_4^{\ 4+} + 2Hg^{II} + 2H_2O \qquad (7)$$

**Crystal Structure Determinations.** Preparative procedures and analyses for cucurbituril ($C_{36}H_{36}N_{24}Q_{12}$) supramolecular assemblies have been described.[7] Crystallographic refinement data for $[Mo_6HgQ_8Cl_4(H_2O)_{14}](C_{36}H_{36}N_{24}O_{12})Cl_4{\cdot}14H_2O$ (Q = S, **1**; and Q = Se, **2**) have been reported.[7] Crystals of $[W_6HgSe_8Cl_4(H_2O)_{14}](C_{36}H_{36}N_{24}O_{12})Cl_4{\cdot}14H_2O$ (**3**) were small, and cell parameters only were determined. Structures were solved by direct methods and refined using the SHELX-97 program set.[25]

A check on the crystal structure of $[Mo_3S_4(H_2O)_9](pts)_4{\cdot}9H_2O$ was carried out. A 3D analysis gave the same unit cell as previously with no evidence for short S···S contacts between two adjacent clusters.[26] Substantially shorter S···S distances (3.37 Å) have been observed for $[Mo_3S_4(H_2O)_6Cl_3][Mo_3S_4(H_2O)_7Cl_2]$ (pyH) $(C_{36}H_{36}N_{24}O_{12})Cl_4{\cdot}17H_2O$, as compared to the sum of van der Waals radii (~3.6 Å).[27]

## Results

**Double Cube Structures.** The isostructural $[M_6HgQ_8Cl_4(H_2O)_{14}](C_{36}H_{36}N_{24}O_{12})Cl_4{\cdot}14H_2O$ (M = Mo, Q = S, **1**; M = Mo, Q = Se, **2**; M = W, Q = Se, **3**) compounds have six carbonyl O atoms above and six below the ring of the cucurbituril molecule, which hydrogen bond to $H_2O$ ligands of the double cube. Four chlorides are coordinated to M, and four chlorides act as counterions. The interaction of $[Mo_6HgS_8Cl_4(H_2O)_{14}]^{4+}$ with a cucurbituril molecule of **1** is illustrated in Figure 1. The cation lies in a special position of space group $C2/m$ and has $C_{2h}$ point symmetry. The cations $[Mo_6HgQ_8Cl_4(H_2O)_{14}]^{4+}$ are sandwiched between two cucurbituril units, and the cation and cucurbituril alternate with each other to give linear chains. These structures have *pseudohexagonal* packing typical of rodlike structures. Bond distances for **1** and **2** are given in Table 1. The Mo−Mo distances 2.7125−2.733 Å for **1** and 2.762−2.799 Å for **2** are short and consistent with Mo−Mo bonding. The Mo−Hg separations are ~1 Å longer and nonbonding. Two symmetrical $\{Mo_3Q_4Cl_2(H_2O)_7\}^{2+}$ species in **1** and **2** (Q = S, Se, respectively) are weakly coordinated to the mercury atom by rather long Hg−Q bonds. For Q = S (**1**)

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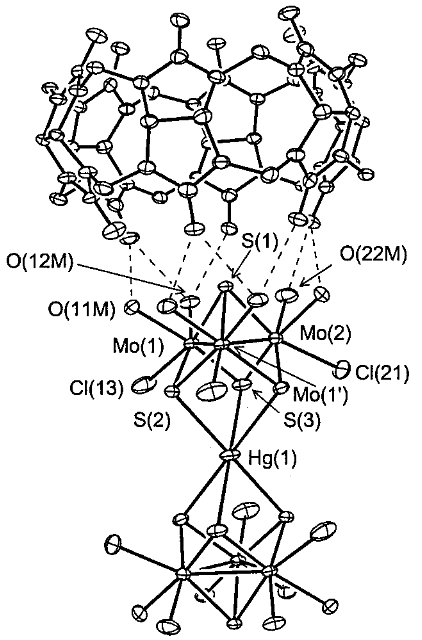

**Figure 1.** Crystal structure of **1** showing the cluster cation and cucurbituril molecule. The O···O contacts less than 3 Å are shown as dashed lines. The positions of Cl(13) and Cl(21) are occupied by $^{2}/_{3}$Cl and $^{1}/_{3}$H$_2$O. Metal−metal bonding Mo−Mo is indicated. The numbering scheme for compound **2** is similar.

**Table 1.** Selected Bond Distances (Å) in Compounds **1** and **2**

| compound **1** | | compound **2** | |
|---|---|---|---|
| Hg(1)−S(2) | 2.768(2) | Hg(1)−Se(2) | 2.7951(12) |
| Hg(1)−S(3) | 2.9029(17) | Hg(1)−Se(3) | 2.9682(9) |
| Mo(1)−Mo(1′) | 2.7326(11) | Mo(1)−Mo(1′) | 2.7986(14) |
| Mo(1)−Mo(2) | 2.7116(9) | Mo(1)−Mo(2) | 2.7622(12) |
| Mo(1)−S(1) | 2.3301(18) | Mo(1)−Se(1) | 2.4578(11) |
| Mo(1)−S)2) | 2.2955(18) | Mo(1)−Se)2) | 2.4210(12) |
| Mo(1)−S(3) | 2.2907(17) | Mo(1)−Se(3) | 2.4147(11) |
| Mo(1)−O(11M) | 2.214(4) | Mo(1)−O(11M) | 2.231(5) |
| Mo(1)−O(12M) | 2.185(4) | Mo(1)−O(12M) | 2.189(5) |
| Mo(1)−Cl(13)[a] | 2.482(3) | Mo(1)−Cl(13)[a] | 2.490(3) |
| Mo(2)−S(1) | 2.340(2) | Mo(2)−Se(1) | 2.4595(15) |
| Mo(2)−S(3) | 2.2918(19) | Mo(2)−Se(3) | 2.4218(11) |
| Mo(2)−Cl(21)[a] | 2.476(3) | Mo(2)−Cl(21)[a] | 2.476(4) |
| Mo(2)−O(22M) | 2.181(5) | Mo(2)−O(22M) | 2.188(6) |

[a] This position is statistically occupied by $^{2}/_{3}$Cl and $^{1}/_{3}$O.

there are two shorter Hg−S at 2.768(2) Å and four longer at 2.9029(17) Å. These are in good agreement with the value of 2.84(12) Å reported for [Mo$_6$HgS$_8$(H$_2$O)$_{18}$](pts)$_8$·20H$_2$O.[1] The Hg−Se distances in **2** are also rather long, two at 2.7951(12) Å and four at 2.968(9) Å. To assess these with respect to values from other structures, a statistical analysis of Hg−Q (Q = S, Se) bond distances using the Cambridge Structural Database was made.[28] The resulting histograms show that values cover a wide range. The distribution for Q = S (875 bonds in 353 structures) has a wide spread with maximum between 2.32 and 2.59 Å. In the case of Q = Se (198 bonds in 49 structures) the distribution is sharper, with a narrow peak between 2.62 and 2.69 Å. The Hg−Q distances in **1** and **2** correspond to the upper limit of these distributions.

The cluster cation is disordered over three positions around pseudo-3-fold axes, resulting in partial occupancy Cl:O = $^{2}/_{3}$:$^{1}/_{3}$ for the Cl(13) and Cl(21) positions. All chlorine ligands lie trans to the $\mu_3$-Q position, leaving the cis positions for six coordinated water molecules. The latter form complementary hydrogen bonds with six portal atoms of cucurbituril molecules. The O···O distances are 2.665−2.768 Å in **1** and 2.679−2.797 Å in **2**.

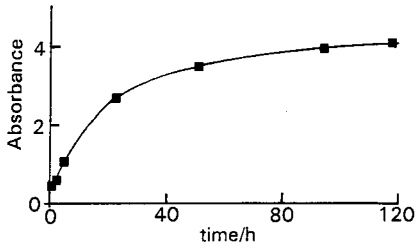

**Figure 2.** UV−vis absorbance change (556 nm) with time for the air-free equilibration of [Mo$_3$S$_4$(H$_2$O)$_9$]$^{4+}$ (1.36 × 10$^{-3}$ M) in 2.0 M Hpts with Hg$^0$ metal at ~20 °C. Absorbance readings adjusted to 1 cm path length.

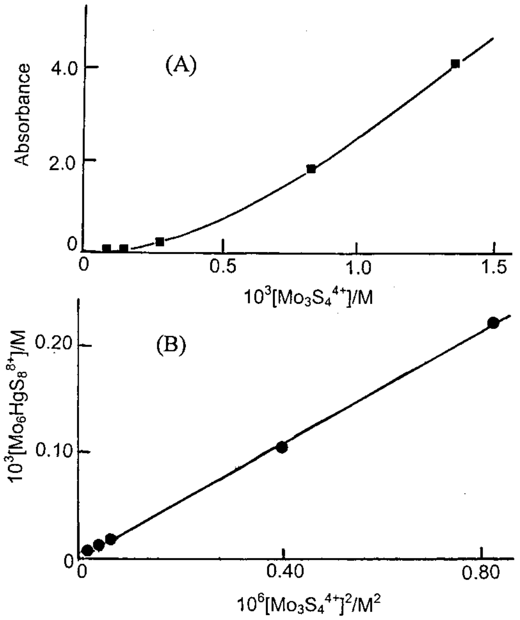

**Figure 3.** (A) The UV−vis absorbance at 556 nm of [Mo$_6$HgS$_8$(H$_2$O)$_{18}$]$^{8+}$ formed by equilibration of different initial concentrations of [Mo$_3$S$_4$(H$_2$O)$_9$]$^{4+}$ in 2.0 M Hpts with Hg$^0$ for ~120 h at ~20 °C. (B) The linear dependence of [Mo$_6$HgS$_8$(H$_2$O)$_{18}$$^{8+}$] from final absorbance readings in plot A vs [Mo$_3$S$_4$(H$_2$O)$_9$$^{4+}$]$^2$. Absorbance readings adjusted to 1 cm path lengths.

**Effect of Different Acids on the Formation of [Mo$_6$HgS$_8$(H$_2$O)$_{18}$]$^{8+}$.** Different concentrations of [Mo$_3$S$_4$(H$_2$O)$_9$]$^{4+}$ in the range (0.07−1.36) × 10$^{-3}$ M, in 2.0 M Hpts (under N$_2$), were added to Hg metal (0.5 mL). Air-free solutions were at ambient temperature (~20 °C), and shaking was intermittent (every 15−30 min for 8 h; then less frequently). UV−vis absorbance changes (2 mm path length cell) were monitored at the ~556 nm peak for [Mo$_6$HgS$_8$(H$_2$O)$_{18}$]$^{8+}$. Little or no reaction was observed until concentrations of [Mo$_3$S$_4$(H$_2$O)$_9$]$^{4+}$ exceeded 0.25 × 10$^{-3}$ M. After 2 h, color changes were clearly visible at the higher [Mo$_3$S$_4$(H$_2$O)$_9$]$^{4+}$ concentrations, and maximum absorbance changes were observed after 120 h, Figure 2. For a series of runs a plot of final absorbance readings vs [Mo$_3$S$_4$(H$_2$O)$_9$$^{4+}$] is shown in Figure 3A. Absorbance readings at the 556 nm peak ($\epsilon$ = 18.8 × 10$^3$ M$^{-1}$ cm$^{-1}$ per Mo$_6$) can be converted to concentrations of [Mo$_6$HgS$_4$(H$_2$O)$_{18}$]$^{8+}$. A linear plot of [Mo$_6$HgS$_8$(H$_2$O)$_{18}$$^{8+}$] vs [Mo$_3$S$_4$(H$_2$O)$_9$$^{4+}$]$^2$ for equilibrated solutions, Figure 3B, gives a slope $K$ = 265(10) M$^{-1}$.

Similar behavior is observed for 2.0 M HCl solutions of [Mo$_3$S$_4$(H$_2$O)$_9$]$^{4+}$ in the range (0.87−2.64) × 10$^{-3}$ M. No

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reaction is apparent until $[Mo_3S_4(H_2O)_8]^{4+}$ exceeds $\sim 1.2 \times 10^{-3}$ M. Maximum absorbance changes are obtained in about one-third the time (~40 h), and $K \sim 600$ $M^{-1}$.

Solutions of $1.79 \times 10^{-4}$ M $[Mo_3S_4(H_2O)_9]^{4+}$ in 2 M $HClO_4$ require a longer period, ~6 days, to reach equilibrium and were not further studied. The kinetic and thermodynamic effects $Cl^- > pts^- > ClO_4^-$ reflect the extent of anion coordination and influence on electrostatics.

**Purple and Blue Forms: UV–Vis Spectra.** Solutions of $2.25 \times 10^{-3}$ M $[Mo_3S_4(H_2O)_9]^{4+}$ in 2.0 M HCl were diluted with 6 M LiCl/2 M HCl to give $[Cl^-]$ levels ranging from 2.0 to 6.0 M. Each solution was reacted with $Hg^0$ metal for 40 h. Dominant colors were purple (peak at 560 nm) with $[Cl^-] \leq 4$ M and blue (574 nm) for $[Cl^-] \geq 4$ M. Spectra have the same shape, indicating similar transitions. The purple → blue color change is accounted for by the coordination of up to $4Cl^-$ to the Mo atoms of the double cube (eq 8), as in the structure of

$$[Mo_6HgS_8(H_2O)_{18}]^{8+} + 4Cl^- \rightleftharpoons [Mo_6HgS_8Cl_4(H_2O)_{14}]^{4+} + 4H_2O \quad (8)$$

$[Mo_6HgS_8Cl_4(H_2O)_{14}](C_{36}H_{36}N_{24}O_{12})Cl_4 \cdot 14H_2O$. Shibahara et al. have reported $\lambda$/nm ($\epsilon$/$M^{-1}$ $cm^{-1}$ per $Mo_6$) values of 372 ($13.0 \times 10^3$) and 556 ($18.8 \times 10^3$) for the purple crystalline product in 2 M Hpts.[1] In the present work the largest $\epsilon$/$M^{-1}$ $cm^{-1}$ values per $Mo_6$ in 2.0 M Hpts (solutions not recolumned) were at 372 ($15.4 \times 10^3$) and 556 ($13.0 \times 10^3$), but were often considerably less due to equilibration and incomplete formation of the double cube (eq 9).

$$2Mo_3S_4^{\ 4+} + Hg^0 \rightleftharpoons Mo_6HgS_8^{\ 8+} \quad (9)$$

The purity of $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ can be judged by the relative absorbance at the 372 and 556 nm peaks. In 2.0 M Hpts with $[Mo_3S_4(H_2O)_9]^{4+}$ present, peaks at 366 (5550) and 603 (362), the lower wavelength absorbances become relatively more intense. Addition of excess $[Mo_3S_4(H_2O)_9]^{4+}$ to obtain more $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ is not therefore an advantage as far as determination of the UV–vis spectrum is concerned. The green-blue Se analogue $[Mo_6HgSe_8(H_2O)_{18}]^{8+}$ was prepared by equilibrating $[Mo_3Se_4(H_2O)_9]^{4+}$ (2.12 mM) in 2.0 M HCl with $Hg^0$ metal under $N_2$ for 1 day. Here peak positions $\lambda$/nm ($\epsilon$/$M^{-1}$ $cm^{-1}$) at 445 (13500) and 604 (16340) were indicated.

**Dowex Chromatography.** Solutions of purple $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ prepared by reacting $1.7 \times 10^{-3}$ M $[Mo_3S_4(H_2O)_9]^{4+}$ in 2 M HCl with $Hg^0$ metal under $N_2$ were diluted to 0.5 M HCl and loaded onto a short Dowex 50W-X2 cation-exchange column (7 cm × 1 cm diameter). After washing with 0.5 M HCl and a small amount of 1.0 M HCl (10 mL), elution was carried out with 2.0 M HCl. Fractions of green $[Mo_3S_4(H_2O)_9]^{4+}$ followed by purple $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ were collected. If the column is turned off after elution of the $[Mo_3S_4(H_2O)_9]^{4+}$, further purple → green changes occur consistent with further re-equilibration. ICP-AES analyses on the purple solutions give a high Hg content, corresponding to release of $Hg^0$ during the column procedure. When blue solutions at high $[Cl^-]$ are diluted to 0.5 M levels, they became purple (or green). A column loaded with purple double cube can be eluted with $\geq 4$ M $Cl^-$ solutions as the blue product.

**Alternative Preparative Routes.** The most interesting of these involves mixing $[Mo_3S_4(H_2O)_9]^{4+}$ (2 mM; 10 mL) in 2 M Hpts or 2 M HCl with a solution of the mercury(I) dimer as a perchlorate salt (0.92 mM; 12 mL) under $N_2$. An immediate color change to purple is observed (eq 10).

$$2Mo_3S_4^{\ 4+} + Hg^I_{\ 2} \rightarrow Mo_6HgS_8^{\ 8+} + Hg^{II} \quad (10)$$

The reaction involves disproportionation of $Hg^I_2$ (eq 11)

$$Hg^I_{\ 2} \rightleftharpoons Hg^0 + Hg^{II} \quad (11)$$

and further reaction of $Hg^0$ with $[Mo_3S_4(H_2O)_9]^{4+}$ as in eq 6.

An alternative procedure involves reduction of a solution of $[Mo_3S_4(H_2O)_9]^{4+}$ (2 mM; 20 mL) in 2 M HCl containing $Hg^{II}$ (1 mM) with excess $H_3PO_2$. An immediate color change to purple is observed together with some black precipitate.

**Beer's Law Plot.** A solution of $[Mo_3S_4(H_2O)_9]^{4+}$ ($1.7 \times 10^{-3}$ M) was equilibrated with $Hg^0$ metal in 2.0 M HCl for 40 h. A sample of solution was then systematically diluted with 2.0 M HCl, and the 560 nm absorbance of re-equilibrated solutions monitored. On dilution, absorbance readings (Figure 4) decrease as a result of dissociation of $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ to give $2[Mo_3S_4(H_2O)_9]^{4+}$. The slope at low absorbances $\epsilon \sim 180$ $M^{-1}$ $cm^{-1}$ indicates a dominance of $[Mo_3S_4(H_2O)_9]^{4+}$ ($\epsilon = 326$ $M^{-1}$ $cm^{-1}$ at the 616 nm peak).

**Kinetics of $[Mo_3Q_4(H_2O)_9]^{4+}$ (Q = S, Se) with $Hg^0$.** Experiments were carried out in optical cells of path length 0.20 cm (volume ~1 mL) and 1 cm (volume ~3 mL). In each case sufficient $Hg^0$ (liquid) was used to cover the bottom of the cell. Air-free conditions were maintained by slow bubbling of $N_2$, which also served to keep solutions homogeneous. The incomplete cubes $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_3Se_4(H_2O)_9]^{4+}$, concentrations in the range $(4.0-8.0) \times 10^{-4}$ M, were made up in 2.0 M HCl, and the increase in absorbance was monitored at the double cube peaks at 560 nm (Figure 5) and 607 nm, respectively. First-order plots of $\ln(A_\infty - A_t)$ vs time were linear to ~2 half-lives, and from the slopes equilibration rate constants (25 °C) were determined. These are $0.70 \times 10^{-4}$ $s^{-1}$ for $[Mo_3S_4(H_2O)_9]^{4+}$ and $1.42 \times 10^{-4}$ $s^{-1}$ for $[Mo_3Se_4(H_2O)_9]^{4+}$. Only small variations in rate constants (±5%) were observed on varying the surface area of the Hg (determined by the two sizes of optical cell), and as a result of, e.g., evaporation. First-order and not second-order dependences on the concentration of $[Mo_3Q_4(H_2O)_9]^{4+}$ favor a route $Mo_3Q_4^{4+} \rightarrow Mo_3HgQ_4^{4+} \rightarrow Mo_6HgQ_8^{8+}$, rather than $Mo_3Q_4^{4+} \rightarrow (Mo_3Q_4^{4+})_2 \rightarrow Mo_6HgQ_8^{8+}$ (Q = S, Se). The existence of dimer forms $(Mo_3Q_4^{4+})_2$ in crystal structures[7] has suggested the latter as a possible route (see Discussion).

**Formation of Red Product.** A solution of $[Mo_3S_4(H_2O)_9]^{4+}$ (2 mM; 5 mL) and $Hg^{II}$ perchlorate (0.92 mM; 5 mL) in 2 M

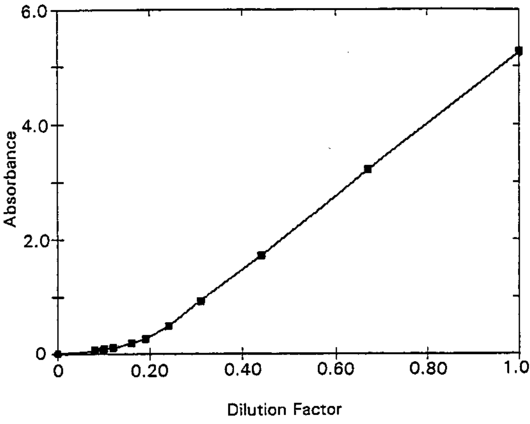

**Figure 4.** Nonapplicability of Beer's law at 560 nm on diluting purple solution obtained by equilibrating $1.7 \times 10^{-3}$ M $[Mo_3S_4(H_2O)_9]^{4+}$ in 2.0 M HCl for 40 h with $Hg^0$ metal. Initially ~35% of $[Mo_3S_4(H_2O)_9]^{4+}$ is present as $[Mo_6HgS_8(H_2O)_{18}]^{8+}$. Absorbance readings in a narrow cell were adjusted to 1 cm light path.

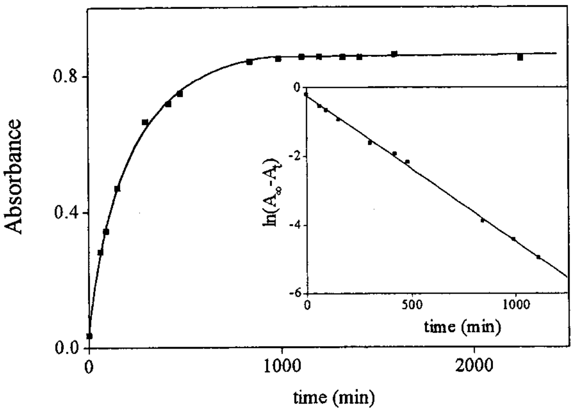

**Figure 5.** Absorbance vs time plot for the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ $= 8.0 \times 10^{-4}$ M in 2.0 M HCl with $Hg^0$ monitored at 560 nm in 0.2 cm optical cell, and (inset) first-order kinetic dependence. Slow bubbling of $N_2$ through the solution maintained homogeneity.

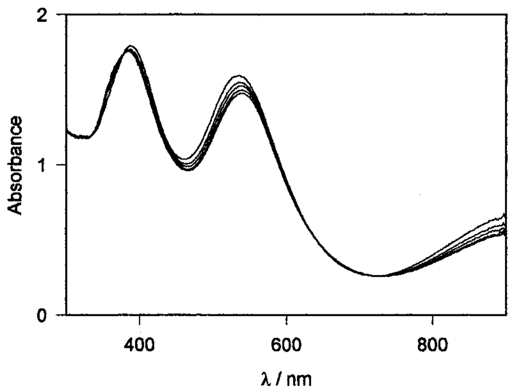

**Figure 6.** UV−vis decay of red (peak at 536 nm) to purple form of double cube on diluting with 2.0 M HCl in air. Scan spectra recorded at 90 s intervals.

Hpts or HCl was siphoned onto $NaBH_4$ (0.4 g) under air-free conditions. An immediate color change to red is observed, UV−vis peak positions 385 and 536 nm. The same red color is observed on adding $BH_4^-$ to a solution of purple $[Mo_6HgS_8(H_2O)_{18}]^{8+}$. No reaction is observed with $H_3PO_2$, and with a large excess of $H_3PO_2$ a blue precipitate was obtained. Purification of the red solution was attempted by Dowex chromatography at 0 °C. However, on washing with 0.5 M acid the red band turned to purple followed by formation of $[Mo_3S_4(H_2O)_9]^{4+}$. In air the red → purple color change gives isosbestic points at 377, 650, and 720 nm, Figure 6, and the behavior observed suggests that the red product is a reduced form, e.g., $[Mo_6HgS_8(H_2O)_{18}]^{7+}$, not previously observed.

**Heteroatom-Exchange Reaction.** To a solution of purple $[Mo_6HgS_4(H_2O)_{18}]^{8+}$ (∼1 mM) in 2 M Hpts under $N_2$ was added an excess of $SnCl_2 \cdot 2H_2O$. An immediate color change to yellow $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ was observed.[29] The overall reaction can be written as in eq 12

$$Mo_6HgS_8^{\ 8+} + 2Sn^{II} \rightarrow 2Mo_3SnS_4^{\ 6+} + Hg^0 \qquad (12)$$

and most likely occurs with intermediate formation of $[Mo_3S_4(H_2O)_9]^{4+}$ (eq 13),

$$Mo_6HgS_8^{\ 8+} \rightleftharpoons 2Mo_3S_4^{\ 4+} + Hg^0 \qquad (13)$$

followed by eq 14.

$$Mo_3S_4^{\ 4+} + Sn^{II} \rightarrow Mo_3SnS_4^{\ 6+} \qquad (14)$$

No meaningful absorbance changes were detected on mixing $[Mo_6SnS_8(H_2O)_{18}]^{8+}$ (0.37 mM) with excess $Hg^{II}$, but a black precipitate (probably Hg) was noted.

Similarly it is possible to replace the Hg of $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ with Ge and In. To a 2.0 M HCl solution of $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ (0.15 mM), in a spectrophotometric cell, was added an excess of $GeCl_3$ solution, when the color changed to yellow brown. After 1 day, the red-purple color of $[Mo_6GeS_8(H_2O)_{18}]^{8+}$ was obtained with peaks at 390 and 536 nm. Similarly on addition of solid InBr (3 mg) to $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ (1 mM; 1 mL), after 5 min with some shaking the spectrum showed quantitative conversion to $[Mo_3InS_4(H_2O)_{12}]^{5+}$.

**Reaction of $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ with $Hg^{II}$.** On addition of $Hg^{II}$ to purple $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ a rapid decay to $[Mo_3S_4(H_2O)_9]^{4+}$ is observed (eq 15). The stoichiometry was determined in 2 M $HClO_4$ by titration of $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ (0.6 mM) in a 2 mm path length cell, with $Hg^{II}$ (9.2 mM) from a Hamilton microsyringe. The titration monitored at 560 nm gave a $Mo_6HgS_8^{8+}$:$Hg^{II}$ ratio of 1:0.95 in satisfactory agreement with eq 15. The reduction potential of the $Hg^{2+}/Hg^I_2$ couple is 920 mV.[11]

$$Mo_6HgS_8^{\ 8+} + Hg^{2+} \rightarrow 2Mo_3S_4^{\ 4+} + Hg^I_{\ 2} \qquad (15)$$

**Oxidation of $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ with $[Fe(H_2O)_6]^{3+}$.** The stoichiometry of the reaction was determined by addition of excess $[Fe(H_2O)_6]^{3+}$ (18 mM; 1 mL) to $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ (0.6 mM; 2 mL) under $N_2$. After 1−2 days, 2 mL of the solution was transferred to a separating funnel, and sodium acetate was added to give a pH of ∼3.5, followed by isoamyl acetate and 4,7-diphenyl-1,10-phenanthroline (L-L).[30] The $Fe^{II}$ product was extracted by the organic solvent as red $[Fe(L\text{-}L)_3]^{2+}$ ($\epsilon = 17.8 \times 10^3$ M$^{-1}$ cm$^{-1}$ at 534 nm). The ratio of $[Mo_6HgS_8^{8+}]$ to $[Fe^{III}]$ consumed of 1:1.09(10) (three determinations) is consistent with eqs 16−17, with overall reaction as in eq 18.

$$Mo_6HgS_8^{\ 8+} + 2Fe^{III} \rightarrow 2Mo_3S_4^{\ 4+} + 2Fe^{II} + Hg^{II} \qquad (16)$$

$$Mo_6HgS_8^{\ 8+} + Hg^{II} \rightarrow 2Mo_3S_4^{\ 4+} + Hg^I_{\ 2} \qquad (17)$$

$$2Mo_6HgS_8^{\ 8+} + 2Fe^{III} \rightarrow 4Mo_3S_4^{\ 4+} + 2Fe^{II} + Hg^I_{\ 2} \qquad (18)$$

Kinetic studies (25 °C) with $[Fe(H_2O)_6]^{3+}$ (770 mV) in the range 4.6−10.0 mM in >10-fold excess, $I = 2.00$ (Lipts), gave plots linear to 50−70% and rate constants ∼0.4 M$^{-1}$ s$^{-1}$ in 2.0 M Hpts. Reactions were faster at lower $[H^+]$, suggesting an $[H^+]^{-1}$ dependence as in other studies with heterometallic cubes.

**Oxidation of $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ with $[Co(dipic)_2]^-$.** Conditions explored were $[Mo_6HgS_8(H_2O)_{18}]^{8+} \geq 0.065$ mM, with the $Co^{III}$ oxidant (362 mV) in >10-fold excess, range 2−6 mM, $I = 2.00$ (Lipts). Reactions monitored over ∼5 min gave first-order plots linear to 50−70% completion. On varying the $[Co^{III}]$ a second-order rate constant of ∼1.2(2) M$^{-1}$ s$^{-1}$ was obtained. There was no dependence on $[H^+]$. Relevant equations are as for the $[Fe(H_2O)_6]^{3+}$ oxidation, eqs 16−18.

## Discussion

Equilibration of $[Mo_3S_4(H_2O)_9]^{4+}$ in 2.0 M HCl, Hpts (or $HClO_4$) with Hg metal or $Hg^I_2$ gives the corner-shared double cube $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ (or related with some anion com-

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plexing), which has an intense purple color. The absorbance which develops at 560 nm is dependent on $[Mo_3S_4(H_2O)_9{}^{4+}]^2$ with $K = 265\ M^{-1}$ (2.0 M Hpts) and $K \sim 600\ M^{-1}$ (2.0 M HCl). From dilution studies Beer's law does not apply, and there is evidence for the decay of $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ with formation of 2 mol of $[Mo_3S_4(H_2O)_9]^{4+}$. From kinetic studies, however, the rate-determining step exhibits a first-order dependence on $[Mo_3S_4(H_2O)_9{}^{4+}]$, with no evidence for buildup of the single cube. The order of events envisaged is therefore interaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with Hg to give a single cube, followed by rapid conversion to the double cube. With $Hg^{I}{}_2$ as the reactant, disproportionation provides an alternative source of $Hg^0$. The Se analogue $[Mo_6HgSe_8(H_2O)_{18}]^{8+}$, although less studied, exhibits similar behavior.

This work has established that corner-shared mercury heteroatom derivatives of $[M_3Q_4(H_2O)_9]^{4+}$ (M = Mo, W; Q = S, Se) (**1**, **2**) can be prepared, the exception being with $[W_3S_4(H_2O)_9]^{4+}$. In previous work,[23,31] $[W_3S_4(H_2O)_9]^{4+}$ heteroatom derivatives were obtained with Mo, Rh, Ni, Pt, Cu, In, Ge, and Sn but are not observed with Fe, Co, Pd, Pb, As, Sb, Bi, and now Hg (8 out of 16), whereas all 16 derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$ have been prepared. The greater reluctance of $[W_3S_4(H_2O)_9]^{4+}$ to form heterometallic derivatives has been discussed.[23] The structures of $[Mo_6HgQ_8Cl_4(H_2O)_{14}](C_{36}H_{36}N_{24}O_{12})Cl_4 \cdot 14H_2O$ (M = Mo, W; Q = S, Se) (**1**−**3**), with four chlorides coordinated to the double cube, have been determined as supramolecular assemblies with cucurbituril ($C_{36}H_{36}N_{24}O_{12}$). At $[Cl^-]$ levels as high as 4 M only substitution at the Mo atoms of $[Mo_6HgQ_8(H_2O)_{18}]^{8+}$ occurs, indicating low affinity of the core Hg for $Cl^-$.

X-ray crystallographic evidence for the association of $M_3Q_4{}^{4+}$ (M = W, Mo; Q = S, Se) to give dimers with short-range Q···Q interactions (3.6−3.7 Å) has been obtained. These are particularly prevalent for Q = Se forms and have been observed for $[W_3Se_4(NCS)_9]^{5-}$ and $[W_3Se_4(CN)_9]$,[5−32,33] as well as for $[W_3Q_4(H_2O)_9]^{4+}$ (Q = S, Se)$pts^-$ salts,[23] and for cucurbituril adducts of chloro complexes of $[W_3Se_4(H_2O)_9]^{4+}$ and $[Mo_3S_4(H_2O)_9]^{4+}$.[4,27] In binary $MQ_2$ chalcogenide compounds of early transition metals the chalcogen atoms of the neighboring layers interact with each other in the same way, and metal atoms and small molecules can intercalate between these layers.[33] The structures **1**−**3** and the dimer structures of the trinuclear incomplete cubes are formally related as those of a matrix and an intercalate.[4] From kinetic studies the first-order dependencies on $[Mo_3Q_4(H_2O)_9]^{4+}$ rule out a solution process in which Hg intercalates between two associated $[Mo_3Q_4(H_2O)_9]^{4+}$ (Q = S, Se) ions. Instead the reaction steps 19, 20

$$Mo_3Q_4{}^{4+} + Hg^0 \rightleftharpoons Mo_3HgQ_4{}^{4+} \tag{19}$$

$$Mo_3HgQ_4{}^{4+} + Mo_3Q_4{}^{4+} \xrightleftharpoons{\text{fast}} Mo_6HgQ_8{}^{8+} \tag{20}$$

are proposed, with the forward reaction in eq 19 rate determining. From the studies carried out it is not clear whether $[Hg^0]$ (which is constant) is determined by the surface area of the Hg or its concentration in solution.

The most likely core composition for the single cube is $Mo_3HgS_4{}^{4+}$, which differs from $Mo_6HgS_8{}^{8+}$ by $Mo_3S_4{}^{4+}$. The same heterometal oxidation state applies in both cases therefore using the formalism $(Mo_3S_4{}^{4+})Hg^0$ and $(Mo_3S_4{}^{4+})_2Hg^0$. Different oxidation states apply for all other post-transition heteroatoms, where the single and double cubes are, e.g., $Mo_3InS_4{}^{5+}/Mo_6InS_8{}^{8+}$ (group 13)[35,36] and $Mo_3SnS_4{}^{6+}/Mo_6SnS_8{}^{8+}$ (group 14),[29,37] and the two can only be interconverted with the involvement of redox changes. To better illustrate this the indium cubes can be written as $(Mo_3S_4{}^{4+})In^+$ and $(Mo_3S_4{}^{4+})_2In^0$, and the tin cubes as $(Mo_3S_4{}^{4+})Sn^{2+}$ and $(Mo_3S_4{}^{4+})_2Sn^0$. In common with other group 13−15 corner-shared double cubes,[3] the Mo−Mo (but not Mo−M′ heteroatom) bonds are short, indicating metal−metal bonding.

The $Hg^0$ formalism helps explain the reaction with $Hg^{II}$. Thus direct attack of $Hg^{II}$ on the $Hg^0$ of the double cube gives $Hg^{I}{}_2$ and $[Mo_3S_4H_2O)_9]^{4+}$. In the redox studies with $[Fe(H_2O)_6]^{3+}$, $[Co(dipic)_2]^-$ (and $O_2$) as oxidants, the $Hg^{II}$ released reacts further with the $Hg^0$ of a second double cube. Although conditions were chosen to maximize the main reaction, kinetic plots are linear to only ∼50% due to the competing reaction with $Hg^{II}$. The ratio of $k_{Co}/k_{Fe}$ values in 2 M Hpts is close to 3, in reasonable agreement with ∼10 reported for other heterometallic cubes.[38]

To summarize, thermodynamic studies on the overall reaction in the presence of $Hg^0$ metal give equilibrium constants $K$ defined as $[Mo_6HgS_8{}^{8+}]/[Mo_3S_4{}^{4+}]^2 = 265\ M^{-1}$ in 2.0 M Hpts, and $\sim 600\ M^{-1}$ in 2.0 M HCl. Similar behavior is apparent with $[M_3Se_4(H_2O)_9]^{4+}$ (M = Mo, W). Two reaction steps involving the formation of single and then double cubes (eqs 19, 20) are proposed. Kinetic studies on the formation of the double cubes indicate first-order dependences on the concentration of $[Mo_3Q_4(H_2O)_9]^{4+}$(Q = S, Se), consistent with rate-determining formation of the single cubes $[Mo_3HgQ_4(H_2O)_x]^{4+}$. The long Hg−S bonds in **1**−**3** help to explain the properties of the double cube, and the ease with which equilibration steps take place. Unlike other single and double cubes of group 13−15 heteroatoms the Hg containing single and double cubes have similar $Hg^0$ components, and interconversion is achieved without an accompanying redox change. Oxidation of the double cubes releases $Hg^{II}$, which is itself an oxidant for the double cube.

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**Supporting Information Available:** X-ray crystallographic data in CIF format for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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