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Behavioral Patterns of Heterometallic Cuboidal Derivatives of $[M_3Q_4(H_2O)_9]^{4+}$ (M = Mo, W; Q = S, Se)

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ABSTRACT

This Account reports recent progress in the study of some ~20 heterometal derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$ with reference also to W and Se analogues. Single cubes (3:1) and corner-shared double cubes (6:1), as well as dimers of the 3:1 single cubes, are considered. A classification of the heterometals as subtypes A, B, and C is introduced.

Introduction

Recent studies on metal−chalcogenide cluster complexes have provided exciting new developments which relate to solid-state chemistry, catalysis, and metalloprotein systems.[1−4] In the latter, Fe_4S_4 was the first cuboidal cluster to be identified, and Fe−S clusters are a major component of biological electron-transport chains.[5] The structure and reactivity of synthetic analogues have been successfully investigated,[1] but in aqueous solution these have limited stability. In the case of nitrogenase, not only is the larger Fe, S, and Mo (or V) eight-metal cluster Fe_7MoS_9 difficult to synthesize, but further mechanistic understanding is required.[6]

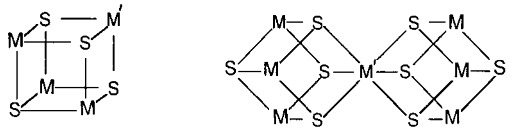
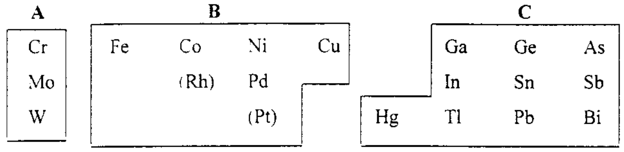


FIGURE 1. Single $M_3M'S_4$ and double $M_6M'S_8$ heterometal cube core structures (M = Mo, W).



A	B					C		
Cr	Fe	Co	Ni	Cu		Ga	Ge	As
Mo		(Rh)	Pd			In	Sn	Sb
W			(Pt)		Hg	Tl	Pb	Bi

FIGURE 2. Elements for which heterometallic derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$ can be prepared.

It is remarkable that alongside Fe only molybdenum and, to a lesser extent, tungsten provide a similar range of cuboidal clusters. The $M_4Q_4^{n+}$ (M = Mo, W; Q = S, Se, Te) cubes have all been prepared, although those containing Te remain comparatively rare.[7] Both Mo and W are octahedrally coordinated, and the aqueous chemistry is accessible as long as acid conditions (pH < 1) are maintained to avoid conjugate-base ($H_2O \rightarrow OH^-$) ligand effects. The $[Mo_4Q_4(H_2O)_{12}]^{5+}$ (Q = S, Se) state is most readily prepared, with the 4+ and 6+ cubes readily accessed by electrochemical or chemical means.[8] On mild oxidation, one of the molybdenums is lost to give the Mo^{IV}_3 incomplete cube $[Mo_3Q_4(H_2O)_9]^{4+}$. The latter can incorporate ~20 different transition and post-transition metals M′ to give single ($Mo_3M'S_4$) and/or double cubes ($Mo_6M'S_8$), which together provide the main focus of this Account (Figure 1). Early examples are described in ref 3. One of the most fascinating aspects is that zero oxidation state heteroatoms can be used as the source of M′. Thus, with $[Mo_3S_4(H_2O)_9]^{4+}$, direct incorporation of 14 heteroatoms, Fe, Co, Ni, Cu, Pd, Hg, Ga, In, Tl, Ge, Sn, Pb, Sb, and Bi, has been achieved.[2−4] The existence of tungsten analogues of $[W_3Q_4(H_2O)_9]^{4+}$ (Q = S, Se) has been demonstrated, but there is less tendency to incorporate heteroatoms, and to date only ~7 have been identified.[9]

Classification of Heterometallic Derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$

In 1986, a report[10] that $[Mo_3S_4(H_2O)_9]^{4+}$ reacts with metallic iron to give the 3:1 heterometallic cube $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ led to an intense search for similar reactions. The extent of the chemistry of 3:1 and 6:1 adducts is summarized with reference to the Periodic Table (Figure 2). Three subtypes of $Mo_3S_4^{4+}$ derivatives, A, B, and C, are defined, and distinctive properties of each are now considered.

In type A with Group 6 metals, the Mo_3CrS_4, Mo_4S_4, Mo_3WS_4 and W_3MoS_4 cores are formed. The metal atoms are all octahedral and have variable oxidation states, $[Mo_4S_4(H_2O)_{12}]^{n+}$, $[Mo_3WS_4(H_2O)_{12}]^{n+}$, and $[W_3MoS_4$-

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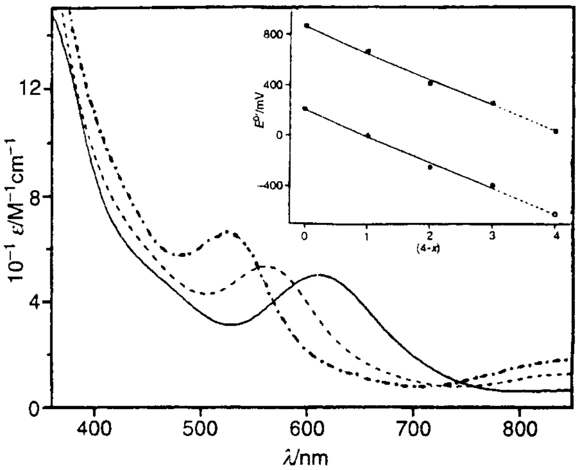
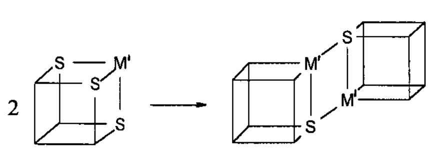


FIGURE 3. UV–vis spectra of $[Mo_3WS_4(H_2O)_{12}]^{5+}$ (——), $[Mo_2W_2S_4(H_2O)_{12}]^{5+}$ (- - -) and $[MoW_3S_4(H_2O)_{12}]^{5+}$ (···) in 2 M Hpts. The inset gives reduction potentials ($E°'$) for $[Mo_xW_{4-x}S_4(H_2O)_{12}]^{6+/5+}$ and $[Mo_4W_{4-x}S_4(H_2O)_{12}]^{5+/4+}$ couples.[11]

$(H_2O)_{12}]^{n+}$ ($n = 4$, 5, and 6),[8,11] with $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ an exception.[12] Reduction potentials (vs NHE) for the 6+/5+ and 5+/4+ couples of $[Mo_4S_4(H_2O)_{12}]^{n+}$ are 860 and 210 mV. Although $[W_4S_4(CN)_{12}]^{6-/7-}$ have been prepared,[7] $[W_4S_4(H_2O)_{12}]^{n+}$ cubes have not, so far, been obtained. Details of the UV–vis spectrum ($n = 5$) can be predicted (Figure 3). Also, by extrapolation of data for $[Mo_xW_{4-x}S_4(H_2O)_{12}]^{n+}$ ($x = 1-4$), reduction potentials of 39 and −627 mV, respectively, are obtained (inset, Figure 3),[11] which are 821 and 833 mV more reducing than those for the corresponding Mo_4S_4 couples. The 6:1 corner-shared double cube $[Mo_7S_8(H_2O)_{18}]^{8+}$ is the only example with a transition metal at the nodal position.[13]

For type B with Groups 8–11, 3:1 single cubes are obtained.[3] Of these, only the Cu cube exhibits more than one oxidation state, $Mo_3CuS_4^{4+}$ and $Mo_3CuS_4^{5+}$.[14] The latter is a derivative formed by addition of Cu^I (d^{10}) in a process similar to that of In^I or Sn^{II}.[15,16] The single cubes incorporating Fe, Co, Ni, Pd, and Cu (4+ products) have tetrahedrally coordinated heteroatoms, which for M′ = Co, Pd, and Cu give edge-linked double cubes, $[\{Mo_3M'S_4(H_2O)_9\}_2]^{8+}$, (1), confirmed by X-ray crystallography.[2–4] The two μ_4-S-to-M′ bridges formed give a rhombic M'_2S_2 arrangement. These are particularly well characterized in the Pd case, which is air stable (Figure 4).[17] No edge-linked forms have been detected for $[Mo_3M'S_4(H_2O)_{10}]^{4+}$ (M′ = Fe, Ni), but they are observed with $[Mo_xW_{3-x}NiS_4(H_2O)_{10}]^{4+}$ ($x = 0$, 1).[18] The Ni of $Mo_3NiS_4^{4+}$ is also capable of expanding its coordination to give $[Mo_3(NiL)S_4(H_2O)_9]^{4+}$ with the tridentate ligand L = 1,4,7-triazacyclononane.[19] In the case M′ = Co, the high air-sensitivity of the edge-linked double cube has made it difficult to confirm the existence of the single cube.[20] With M′ = Rh or Pt, the heteroatom is inert, and for Rh at least octahedral coordination seems likely.[2,21]



(1)

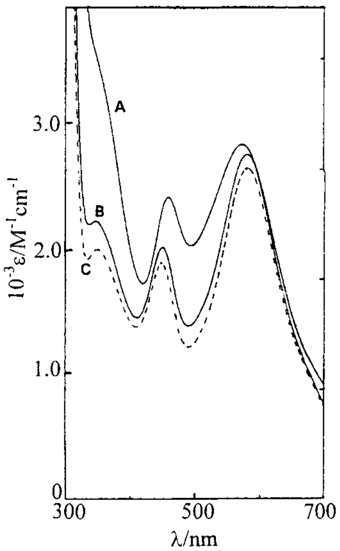


FIGURE 4. UV–vis spectra ε's per Mo_3: (A) purple $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$, (B) blue single cube $[Mo_3(PdCl)S_4(H_2O)_9]^{4+}$ on addition of a 10-fold excess of Cl^-, and (C) on addition of 1 M Cl^-.[32]

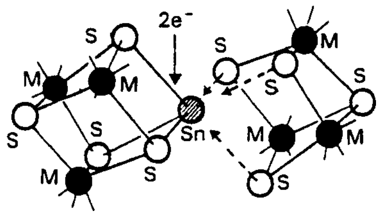
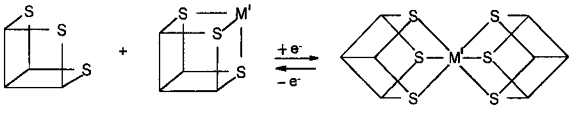


FIGURE 5. Conversion of a single cube $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ to the corresponding double cube by reductive addition.

Finally, for type C (Groups 12–15), single cubes are formed by direct addition of Ga^I, In^I, Ge^{II}, and Sn^{II} to $[Mo_3S_4(H_2O)_9]^{4+}$, where the heteroatom is octahedral and products have 5+ or 6+ charges. Corner-shared 6:1 double cubes are obtained with Hg, In, Tl, Ge, Sn, Pb, As, Sb, and Bi (but not Ga!), all of which are 8+ in charge.[22] A redox-induced interconversion of single and double cubes is observed, (2), with double-cube formation occurring in a reductive addition step (Figure 5). The above studies have been extended to include $[Mo_4Se_4(H_2O)_{12}]^{n+}$, the incomplete cube $[Mo_3Se_4(H_2O)_9]^{4+}$, and derivatives of the latter.[8,23] Whereas $[Mo_3S_4(H_2O)_9]^{4+}$ is extremely stable, with $[Mo_3Se_4(H_2O)_9]^{4+}$ there is a tendency for Se to deposit within days as a result of air oxidation, $Se^{2-} \rightarrow Se$.



(2)

Preparation and Properties

The driving force for the incorporation of heteroatoms into $M_3Q_4^{4+}$ cores (Q = S, Se) stems from two sources. Affinity of the heterometal M′ for μ_2-chalcogen atoms (chalcophilicity) is required. The heterometal must also serve as an electron donor, which is why incorporation requires either M'^0 or a low oxidation state. Nonreducing Pb^{II}, Tl^{I}, and Bi^{III} are not incorporated, despite their chalcophilicity. The $Mo_3PbS_4^{6+}$ and $Mo_3BiS_4^{7+}$ cubes have been prepared in nonaqueous solutions, with negatively charged thiophosphate ester ligands.[24] The reactivity of the host cluster is also important: $[W_3S_4(H_2O)_9]^{4+}$ is the most inert and does not incorporate Hg, but $[Mo_3S_4(H_2O)_9]^{4+}$, $[Mo_3Se_4(H_2O)_9]^{4+}$, and $[W_3Se_4(H_2O)_9]^{4+}$ give 6:1 products.[25] The reactivity of the heterometal in its elementary form is not always very high, and reactions can take several hours or even days for completion. With M'^{II} transition metals (M' = V, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pd, Pt), or with post-transition metals in their higher oxidation states, e.g., Ga^{III}, In^{III}, Ge^{IV}, and Sn^{IV}, no heterometallic cube formation is observed. However, the $Mo_3M'S_4^{4+}$ clusters are obtained on addition of heterometal cations to $[Mo_3S_4(H_2O)_9]^{4+}$ in the presence of BH_4^-. This method is effective in the preparation of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ in 2 M HCl (3)[19] and complete within a few minutes, as compared to ~7 days with the metal.

$$Mo_3S_4^{4+} + Ni^{II} + 2e^- \rightarrow Mo_3NiS_4^{4+} \qquad (3)$$

Other, more specific preparative details are now considered. Purification is by O_2-free (N_2) Dowex cation-exchange chromatography, at which stage different acids can be introduced. In HCl solution, heterometallic single cubes from $[M_3Q_4(H_2O)_9]^{4+}$ (M = Mo, W; Q = S, Se) undergo Cl^- complexing, M' generally $>$M. The less complexing perchloric acid and *p*-toluenesulfonic acid (Hpts) can be used, but no elution of 8+ double cubes occurs with $HClO_4$. With 4 M Hpts, the pts^- complexes at a low level, elution occurs, and an H-bonded $H^+/H_2O/pts^-$ network induces crystallization of the aqua ions.

Type A. In the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with $[Cr(H_2O)_6]^{2+}$, the Cr^{II} is able to reduce $Mo_3S_4^{4+}$ with Cr^{II} uptake (4).[12] Similarly, by using $K_4[Mo_2Cl_8]$ as a source of Mo^{II},

$$Mo_3S_4^{4+} + 3Cr^{II} \rightarrow Mo_3CrS_4^{4+} + 2Cr^{III} \qquad (4)$$

reaction with $[W_3S_4(H_2O)_9]^{4+}$, $[W_3Se_4(H_2O)_9]^{4+}$, $[Mo_2WS_4(H_2O)_9]^{4+}$, and $[MoW_2S_4(H_2O)_9]^{4+}$ occurs, with Mo^{III} a product (5).[11] Again, an excess of reducing agent is

$$W_3S_4^{4+} + 3Mo^{II} \rightarrow W_3MoS_4^{4+} + 2[Mo^{III}] \qquad (5)$$

required to give prior reduction of the trinuclear species. In some cases with $[Mo_3S_4(H_2O)_9]^{4+}$ and V, Mg, Al, or H_3PO_2 as reductant, fragmentation occurs with reassembly into $[Mo_4S_4(H_2O)_{12}]^{5+}$ and $[Mo_7S_8(H_2O)_{18}]^{8+}$. The yields of these two products with H_3PO_2 are $>$30% and ~20%, respectively, after 3 days at 20 °C.[13]

Type B. Direct reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with Fe, Co, Ni, Cu, or Pd (as Pd black)[2,3] takes place in 2 M HCl solutions. The metals are incorporated formally as tetrahedral M^0, leading to $Mo_3M'S_4^{4+}$ and edge-linked products.[22] In the Cu case, Dowex chromatography gives $Mo_3CuS_4^{4+}$ as product.[14] An interesting exception is the incorporation of nonreducing Rh(III) by reaction of Cp^*RhCl_2 (Cp^* is η^5-C_5Me_5) with $[Mo_3S_4(H_2O)_9]^{4+}$.[21] Adducts are also formed with $[PtCl_4]^{2-}$ (in 2 M HCl) in the presence of H_3PO_2, and on heating with $RhCl_3$ in 4 M HCl for 3 h. Analyses have confirmed 3:1 metal ratios, but more extensive characterization has proved difficult.[2] In the case of M' = Ni, Pd water-soluble products incorporating $M'(CO)$,[26] $Ni(C_2H_4)$,[18] and Pd(*t*-BuNC),[17] have been prepared.

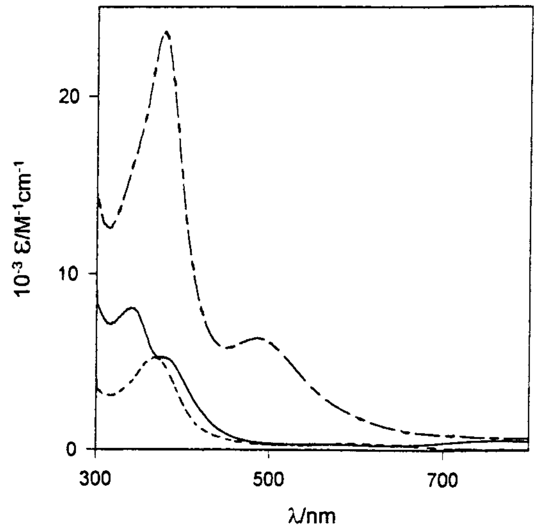


FIGURE 6. UV–vis spectra of $[Mo_3S_4(H_2O)_9]^{4+}$ (- - -), $[Mo_3InS_4(H_2O)_{12}]^{5+}$ (——) (ε's per Mo_3), and $[Mo_6InS_8(H_2O)_{18}]^{8+}$ (-··-) (ε's per Mo_6) in 2 M HCl.[15]

With $[W_3S_4(H_2O)_9]^{4+}$, both Cu^I and Cu metal give $W_3CuS_4^{5+}$ (6), and the 4+ analogue has not, so far, been

$$W_3S_4^{4+} + Cu^{I} \rightarrow W_3CuS_4^{5+} \qquad (6)$$

prepared.[28] This illustrates the difficulty in preparing W_3 cubes in the more reduced 4+ state. Similarly, W_6 corner-shared double cubes are more difficult to prepare than their Mo_6 analogues.

It remains to be seen whether Re, Ru, Os, Ir, or indeed Ag, Au, and Zn can be incorporated into $[M_3Q_4(H_2O)_9]^{4+}$.

Type C. The reaction of $Mo_3S_4^{4+}$ with In^I, or $In^{III} + BH_4^-$, to give the single cube $Mo_3InS_4^{5+}$ suggests direct addition. Metallic In or Ga also incorporates as Ga^+ or In^+ to form $[Mo_3M'S_4(H_2O)_{12}]^{5+}$,[15] where the presence of M^+ cations on the metal surface is possible. There is no evidence for $[Mo_3InS_4(H_2O)_{12}]^{4+}$, and In metal reacts with $[Mo_3S_4(H_2O)_9]^{4+}$ in 0.1 M Hpts to give the corner-shared product $[Mo_6InS_8(H_2O)_{18}]^{8+}$ (Figure 6). Similarly, from $[Mo_3S_3O(H_2O)_9]^{4+}$, the product $[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$ has been obtained, which is a comparatively rare example of oxo-sulfido trinuclear participation. Incorporation of Hg, Tl, Sn, and Sb metals into the nodal position of double cube $[Mo_6M'S_8(H_2O)_{18}]^{8+}$ is also observed,[2,3,29] but $[W_3S_4(H_2O)_9]^{4+}$ reacts with Sn only, and the single-cube product $[W_3(SnCl_3)S_4(H_2O)_9]^{3+}$ is formed in HCl.[30] The heteroatoms of single cubes react with complexing anions, e.g., Cl^- (Figure 7).

With In^{III}, Tl^{I}, Pb^{II}, and Bi^{III} in the presence of BH_4^-, the double cubes $[Mo_6M'S_8(H_2O)_{18}]^{8+}$ (M' = In, Tl, Pb, Bi) are formed. However, with Ga^{III} under similar conditions, only the single cube $[Mo_3GaS_4(H_2O)_{12}]^{5+}$ is obtained,[15] and no double cube has been identified, which is unique for

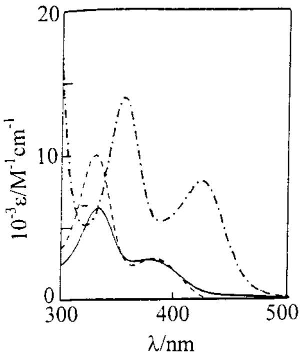


FIGURE 7. UV−vis spectra of [Mo$_3$SnS$_4$(H$_2$O)$_{12}$]$^{6+}$ (ε's per Mo$_3$) in 2.0 M acids Hpts (——), HClO$_4$ (- - -), Hand Cl (-••-).[16]

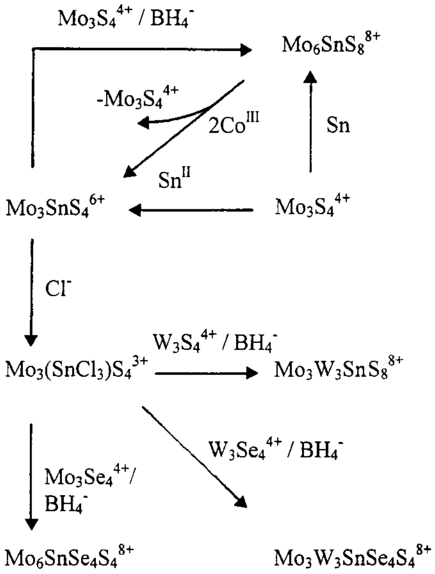


FIGURE 8. Summary of reactions of [Mo$_3$S$_4$(H$_2$O)$_9$]$^{4+}$ and Sn heterometallic products.[23]

type C heteroatoms. A procedure involving conversion of single (In, Ge, Sn) to double cubes in the presence of BH$_4^-$ (M = Mo, W) (7) is used as the only route to prepare [W$_6$SnS$_8$(H$_2$O)$_{18}$]$^{8+}$ and gives approaching quantitative yields.

$$[M_3SnS_4(H_2O)_{12}]^{6+} + [M_3S_4(H_2O)_9]^{4+} + 2e^- \rightarrow [M_6SnS_8(H_2O)_{18}]^{8+} \quad (7)$$

Similarly, [W$_6$GeS$_8$(H$_2$O)$_{18}$]$^{8+}$ and [Mo$_6$SnSe$_8$(H$_2$O)$_{18}$]$^{8+}$ have been prepared, and the synthesis of mixed-metal [Mo$_3$W$_3$SnS$_8$(H$_2$O)$_{18}$]$^{8+}$ and mixed-chalcogen [Mo$_6$SnS$_4$Se$_4$(H$_2$O)$_{18}$]$^{8+}$ products has also been achieved.[9] It should, however, be noted that (7) occurs much less readily with W than with Mo. A summary of the chemistry of [Mo$_3$S$_4$(H$_2$O)$_9$]$^{4+}$ with Sn is given in Figure 8.

One drawback to using BH$_4^-$ is the fast decomposition with H$^+$ (pH ≤ 1), leading to a loss of BH$_4^-$, initially in ~100-fold excess. Vigorous H$_2$ gas evolution and heating effects are difficult to control, and the heterometal is sometimes precipitated as, e.g., metal boride. The use of hypophosphorous acid instead of BH$_4^-$ gives better results, since H$_3$PO$_2$ is stable in acidic conditions. The reduction potential for the reaction of H$_3$PO$_2$ is a large negative value, but kinetically the reactions are slower. It has been used in many cases, notably to prepare [Mo$_6$AsS$_8$(H$_2$O)$_{18}$]$^{8+}$ with NaAsO$_2$ or Na$_3$AsO$_4$ as the As source.[22] In the case of In^{III}, formation of [Mo$_3$InS$_4$(H$_2$O)$_{12}$]$^{5+}$ precedes [Mo$_6$InS$_8$(H$_2$O)$_{18}$]$^{8+}$ (8, 9).[15]

$$In^{3+} + Mo_3S_4^{4+} + 2e^- \rightarrow Mo_3InS_4^{5+} \quad (8)$$

$$Mo_3InS_4^{5+} + Mo_3S_4^{4+} + 1e^- \rightarrow Mo_6InS_8^{8+} \quad (9)$$

Several attempts have been made to incorporate early transition metals such as Ti and V as well as lanthanoids and actinoids (e.g., the strongly reducing Eu^{2+} and U^{3+}), so far without success.[2,13] This appears to corroborate the need for some heterometal chalcogen affinity to stabilize to the heterometallic product, especially in water.

Molecular and Electronic Structures

Simple principles help to rationalize the cluster types considered herein. The structures are based on single cubes with an M$_3$M′Q$_4$ core. The M$_3$Q$_4$ unit retains features present in the incomplete cube. Indeed, in most oxidation and heteroatom transfer processes, re-formation of M$_3$Q$_4^{4+}$ is observed. The tendency of both components to retain their initial coordination[30] is illustrated in (10). When M′ is type C, both M′ and M have octahedral coordination, but M′ has a preference for Cl$^-$ over H$_2$O, and products, e.g., [W$_3$(SnCl$_3$)S$_4$(H$_2$O)$_9$]$^{3+}$, are obtained with [Cl$^-$] ≥ 0.05 M.

$$M_3Q_4(NCS)_9^{5-} + SnCl_3^- \rightarrow [M_3(SnCl_3)Q_4(NCS)_9]^{6-} \quad (10)$$

Hence, it is easy to replace the three ligands to M′ by three chalcogen atoms of a second M$_3$Q$_4$, as in (7). In the case of Group 12, the single and double cubes Mo$_3$HgS$_4^{4+}$ and Mo$_6$HgS$_8^{8+}$ should interconvert in the presence of Mo$_3$S$_4^{4+}$ without any need for redox. The single cube Mo$_3$HgS$_4^{4+}$ has not so far been identified, but is very likely the initial product from the reaction of Mo$_3$S$_4^{4+}$ with Hg^0.

The tetrahedral B heteroatoms Co, Ni, Pd, and Cu have affinity for the softer ligands. When no such ligands are present, dimerization occurs by interaction of the heterometal with a μ_3-Q of a second cube, and edge-linked double cubes result. An interesting consequence of dimerization is the close contact, giving M′−M′ bonding. In the Co case, the Co−Co distance is 2.498 Å.[3] The corresponding M′−M′ distances in the Cu and Pd edge-linked double cubes are 2.426 Å (Cu)[3] and 2.790 Å (Pd).[17] For [Mo$_x$W$_{3-x}$NiS$_4$(H$_2$O)$_{10}$]$^{4+}$, distances are 2.549 Å (x = 1) and 2.560 Å (x = 0).[18]

Many heterometal cubes have Mo−Mo distances close to the 2.732 Å value of [Mo$_3$S$_4$(H$_2$O)$_9$](pts)$_4$·9H$_2$O,[8] which is diamagnetic and has a triangular arrangement of three metal−metal bonded Mo^{IV} (d^2) atoms. The type C [Mo$_6$M′S$_8$(H$_2$O)$_{18}$]$^{8+}$ cubes have an 8+ charge *in all cases*, which suggests that two Mo$_3$S$_4^{4+}$ units are retained as a common feature and are bridged by M^0. The Mo−M′ separations are ~1 Å longer than Mo−Mo, and no Mo−M′ metal−metal bonding is apparent.[22] Formally, the double cubes can be written as (Mo$_3$S$_4^{4+}$)$_2$M′^{0} and the single cubes (also with long Mo−M′) as Mo$_3$S$_4^{4+}$M′$^+$ (M′ = Ga, In) and

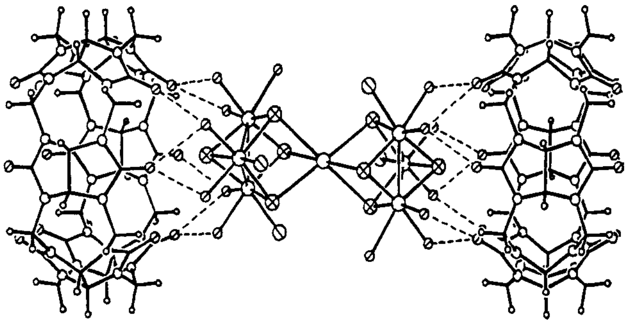


FIGURE 9. Interaction of two cucurbituril $C_{36}H_{36}N_{24}O_{12}$ molecules with the double cube $[Mo_6HgSe_8(H_2O)_{14}Cl_4]^{4+}$ in a supramolecular assembly.[25]

$Mo_3S_4^{4+}M'^{2+}$ (M′ = Ge, Sn). Furthermore, when M′ is a transition metal (e.g., Cr, Fe, Co, Ni, Cu, or Pd),[22] single cubes of 4+ charge are obtained, and the heteroatom M′ can be designated M'^0. The short Mo−M′ bond lengths for type A and type B cubes provide evidence for Mo−M′ bonding. Quantum chemical calculations provide an explanation of this sharp division.[31] The energy level of the d electrons of the transition metal is close to the LUMO of the M_3Q_4 fragment. This makes formation of covalent M′−M bonds possible. In contrast, the post-transition metals have only high-energy s or p orbitals available, and instead of M′−M bonding the electron density is transferred to the M_3Q_4 core.

In the case of $[Mo_7S_8(H_2O)_{18}]^{8+}$, each cube has three short Mo−Mo (2.770 Å) and three long (3.046A) Mo−Mo′ (nodal) separations.[3] Here the Mo−Mo′ bond appears less strong. A structure approximating to $(Mo_3S_4^{4+})_2Mo^0$, with adjacent Mo's assigned as Mo^{IV} and Mo^0, is clearly less satisfactory, and an intermediate oxidation state may apply.

Characterization of the cubes by X-ray crystallography is not always possible, and in many cases crystallization has only been achieved as pts^- salts of the aqua ions $[Mo_6M'S_8(H_2O)_{18}](pts)_8{\cdot}xH_2O$.[3,22] Recently, however, crystals of cucurbituril adducts have been prepared. Cucurbituril ($C_{36}H_{36}N_{24}O_{12}$) is a macrocyclic cavitand molecule of D_{6h} symmetry, having two identical carbonyl-fringed portals. These can H-bond with coordinated water molecules to give supramolecular aggregates. Crystals of $[M_6HgQ_8(H_2O)_{14}Cl_4](C_{36}H_{36}N_{24}O_{12})Cl_4{\cdot}14H_2O$ (M = Mo, W; Q = S, Se) have been prepared by reaction of $[M_3Q_4(H_2O)_9]^{4+}$ with metallic Hg in 4 M hydrochloric acid and crystallization in the presence of cucurbituril.[25] These have cluster cations $[M_6HgQ_8(H_2O)_{14}Cl_4]^{4+}$ (with Cl^- replacing H_2O ligands) sandwiched between two cucurbituril units (Figure 9). The Hg−S distances are unusually long, with two at 2.768(2) Å and four longer at 2.903(2) Å, in good agreement with the value of 2.84(12) Å reported for $[Mo_6HgS_8(H_2O)_{18}](pts)_8{\cdot}20H_2O$.[3] The complex $[Hg([9]\text{-}aneS_3)_2]^{2+}$ is the closest structural analogue, with six Hg−S bonds varying between 2.638(3) and 2.728(3) Å, which seems to be the upper limit for Hg^{II}−S bonds. It is concluded[25] that, in the double cube, Hg retains a large part of its formal Hg^0 oxidation state.

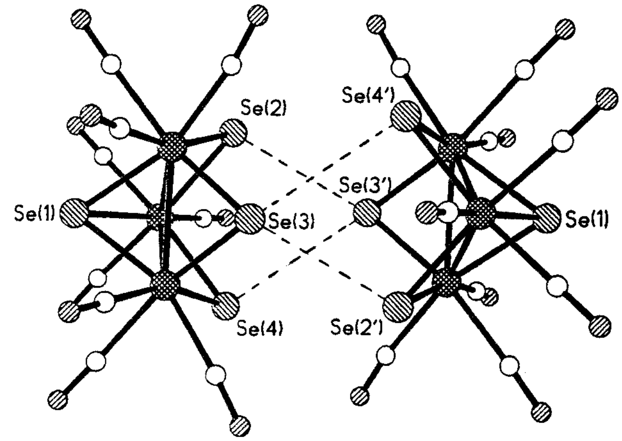


FIGURE 10. Structure of $[W_3Se_4(CN)_9]^{5-}$ anions showing Se- - -Se interactions between two adjacent clusters.[31]

One of the most striking features of the cucurbituril structures is that they are isostructural with assemblies incorporating a dimeric trinuclear unit $[W_3Se_4(H_2O)_8Cl]_2(C_{36}H_{36}N_{24}O_{12})Cl_6{\cdot}12H_2O$.[25] Here, two W_3Se_4 units are held together by Se···Se interactions (3.617−3.740 Å) and are embedded between the cucurbituril molecules (O···O, 2.719−2.779 Å) in exactly the same way as the heterometallic double cubes. Similar dimeric aggregates have been reported previously for $[W_3Se_4(NCS)_9]^{5-}$ and $[W_3Se_4(CN)_9]^{5-}$ (Figure 10), as well as for other M_3Q_4 (M = Mo, W; Q = S, Se) derivatives.[32] Moreover, in binary MQ_2 chalcogenides of the early transition metals, the chalcogen atoms of the neighboring layers interact with each other in the same way. Metal atoms and small molecules can intercalate between these layers. Thus, the structures are formally related to those of a matrix and of an intercalate. This means that the two W_3Se_4 trinuclear units, sandwiched between two cucurbituril molecules, mimic rather closely two neighboring layers QMQ···QMQ in solid MQ_2 (with the M_3 units as building blocks). These results show that solid-state chemistry is related to the chemistry of small molecular clusters in a more intimate way than might have been suspected.

Stability in Air

Single and double cubes are, in almost all cases, O_2 sensitive, and rigorous air-free techniques are required. With O_2, the cubes re-form the trinuclear incomplete cube. However, both the single $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ and double $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ cubes are air stable over long periods. Also, $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ is one of the more stable cubes in air and shows no decay over periods of ∼1 h. Heterometallic cubes from $[W_3Q_4(H_2O)_9]^{4+}$ (Q = S, Se) are less stable in air. The more tungsten atoms included, the more air-sensitive the cluster becomes. Thus, for the cubes $[Mo_xW_{4-x}S_4(H_2O)_{12}]^{5+}$,[11] with $[Fe(H_2O)_6]^{3+}$ (or O_2) as oxidant, the 6+ cube is first obtained, which fragments with loss of W exclusively as a high oxidation state product (11).

$$MoW_3S_4^{5+} + Fe^{III} \rightarrow MoW_2S_4^{4+} + Fe^{II} + [W^{VI}] \qquad (11)$$

Heteroatom-Transfer Reactions

Transfer[22] of Sn^{II} is observed in the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$, $[W_3SnSe_4(H_2O)_{12}]^{6+}$, and $[W_3SnS_4(H_2O)_{12}]^{6+}$, and the reactions can be written as in (12). No corresponding reactions of $[W_3S_4(H_2O)_9]^{4+}$ with $[W_3SnSe_4(H_2O)_{12}]^{6+}$ or of $[W_3S_4(H_2O)_9]^{4+}$ and $[W_3Se_4(H_2O)_9]^{4+}$ with $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$ are observed. The reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with $[Mo_3SnSe_4(H_2O)_{12}]^{6+}$ gives an equilibrium mix,[23] with $K = 4.0(9)$ for (13). Affinities of the different aqua ions for Sn^{II} are $Mo_3S_4^{4+} > Mo_3Se_4^{4+} > W_3Se_4^{4+} > W_3S_4^{4+}$.

$$Mo_3S_4^{\ 4+} + W_3SnSe_4^{\ 6+} \rightleftharpoons Mo_3SnS_4^{\ 6+} + W_3Se_4^{\ 4+} \quad (12)$$

$$Mo_3SnSe_4^{\ 6+} + Mo_3S_4^{\ 4+} \rightleftharpoons Mo_3Se_4^{\ 4+} + Mo_3SnS_4^{\ 6+} \quad (13)$$

Displacement of the heteroion In^I by Sn^{II} occurs, and the affinity $Sn^{II} > In^I$ for $M_3Q_4^{4+}$ (M = Mo, W; Q = S, Se) has been established (14). Reactions occur by re-equilibration (15) and redistribution of In^I between the trinuclear species.

$$W_3InS_4^{\ 5+} + Sn^{II} \rightarrow W_3SnS_4^{\ 6+} + In^I \quad (14)$$

$$W_3InS_4^{\ 5+} \rightleftharpoons W_3S_4^{\ 4+} + In^I \quad (15)$$

The above mechanism holds for post-transition elements. No reaction between $[Ni(H_2O)_6]^{2+}$ and $Mo_3FeS_4^{4+}$, or $[Fe(H_2O)_6]^{2+}$ and $Mo_3NiS_4^{4+}$, is observed, and there is no evidence for equilibria as in (15). However, Cu^{2+} gives a net displacement of heteroatoms from $Mo_3FeS_4^{4+}$ and $Mo_3NiS_4^{4+}$, which has been explained by a redox mechanism involving intermediate formation of small amounts of Cu^+ (16), followed by (17).

$$Mo_3MS_4^{\ 4+} + 2Cu^{2+} \rightleftharpoons Mo_3S_4^{\ 4+} + M^{2+} + 2Cu^+ \quad (M = Fe, Ni) \quad (16)$$

$$Mo_3S_4^{\ 4+} + Cu^+ \rightleftharpoons Mo_3CuS_4^{\ 5+} \quad (17)$$

Reactions with H^+

Group 13 (Ga, In, Tl) heterometallic cube[15] derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$ are oxidized by H^+ in HCl, giving H_2, which can be determined by gas chromatography. The reaction is unique to Group 13 derivatives. Thus, the Tl-containing double cube $[Mo_6TlS_8(H_2O)_{18}]^{8+}$ reacts with H^+ according to (18). However, the In-containing double cubes $[Mo_6InS_8(H_2O)_{18}]^{8+}$ and $[Mo_6InO_2S_6\,(H_2O)_{18}]^{8+}$ react with H^+ with formation of the single cube, e.g., (19). The reaction of $Mo_3InS_4^{5+}$ (and $Mo_3GaS_4^{5+}$) with 2 M HCl is slow, and no H_2 was detected by GC after 2 d. However, in 4 M HCl, reaction according to (20) is observed. No H_2 was detected in 2 M Hpts. Chloride coordination to the heterometal may catalyze the oxidation by H^+. Kinetic studies (25 °C) on the reactions of H^+ with $[Mo_6InO_2S_6\,(H_2O)_{18}]^{8+}$ and $[Mo_6TlS_8(H_2O)_{18}]^{8+}$ give second-order rate constants $k_H = 4.9 \times 10^{-3}$ (In) and $0.25 \times 10^{-3}\ M^{-1}\ s^{-1}$ (Tl),[15] $I = 2.00$ M (pts^-).

$$Mo_6TlS_8^{\ 8+} + H^+ \rightarrow 2Mo_3S_4^{\ 4+} + Tl^I + {}^1/_2H_2 \quad (18)$$

$$Mo_6InS_8^{\ 8+} + H^+ \rightarrow Mo_3InS_4^{\ 5+} + Mo_3S_4^{\ 4+} + {}^1/_2H_2 \quad (19)$$

$$Mo_3MS_4^{\ 5+} + 2H^+ \rightarrow Mo_3S_4^{\ 4+} + M^{III} + H_2 \quad (20)$$

Substitution at Heteroatoms

Reactions involving the substitution of H_2O by L at the Ni of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ have been studied.[19] Formation rate constants for L = Cl^-, Br^-, I^-, and NCS^- lie in the narrow range 9.4–44 $M^{-1}\ s^{-1}$. Such behavior is interpreted in terms of a dissociative interchange I_d mechanism (21). Inclusion of two water-soluble phosphines, 1,3,5-triaza-7-phosphaadamantane (PTA) and tris(3-sulfonatophenyl)phosphine ($P(C_6H_4SO_3)_3^{3-}$), requires a 3-fold extension of this range, but for CO k_f is 10 times smaller. It is possible to explain these results while retaining essential features of an I_d process.[19] Rate constants are ca. 10^3 times smaller than those for water exchange on $[Ni(H_2O)_6]^{2+}$, with an even bigger factor for tetrahedral Ni^{II}. Rate constants for substitution on tetrahedral $[Ni(CO)_4]$ ($2.0 \times 10^{-2}\ M^{-1}\ s^{-1}$ in toluene) are smaller, and the behavior observed is therefore in the Ni^0 to Ni^{II} range, with Ni^0 the more likely if the three μ_3-S ligands bring about a labilizing effect.

$$Mo_3(NiH_2O)S_4^{\ 4+} + L \rightarrow Mo_3(NiL)S_4^{\ 4+} + H_2O \quad (21)$$

The conversion[32] of edge-linked $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ to $[Mo_3(PdL)S_4(H_2O)_9]^{4+}$ is induced by L = CO, the phosphines PTA and $P(C_6H_4SO_3)_3^{3-}$, Cl^-, Br^-, and NCS^-, all of which complex at the tetrahedral Pd (22). Cleavage of an intercube Pd–μ_3-S bond occurs in the rate-determining step involving one L. Rate constants $k_f/M^{-1}\ s^{-1}$ are CO, 1.11×10^5; PTA, 27.8×10^5; and $P(C_6H_4SO_3)_3^{3-}$, 9.6×10^5, where the products have strong colors. The reactions are independent of $[H^+] = 0.30-2.0$ M. The first stages with L = Cl^-, Br^-, and NCS^- are too fast to monitor, but equilibrium formation constants K/M^{-1} are Cl^-, 490; Br^-, 8040; and NCS^-, 630. The results indicate a preference for L as compared to H_2O, which is unable to retain the single-cube structure. Subsequent steps have been assigned to substitution at the Mo's, and a $[NCS^-]$-independent step has been assigned to the isomerization Pd–NCS → Pd–SCN.[32]

$$\{Mo_3PdS_4\}_2^{\ 8+} + 2L \rightarrow 2Mo_3(PdL)S_4^{\ 4+} \quad (22)$$

Aqueous solution reactions of CO with $[Mo_3M'S_4(H_2O)_{10}]^{4+}$ (M′ = Co, Ni, Pd) have been compared (23).[26] Electron counts are 15 for the single cube Mo_3Co and 16 for Mo_3Ni and Mo_3Pd. On bubbling N_2 through the solutions, no reverse reaction is detected. Similar reactions are observed for $[Mo_3NiSe_4(H_2O)_{10}]^{4+}$ and $[W_3NiS_4(H_2O)_{10}]^{4+}$. No reaction is observed for $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ (14 electrons) and $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ (17 electrons). However, the

$$Mo_3(M'H_2O)S_4^{\ 4+} + CO \rightarrow Mo_3(M'CO)S_4^{\ 4+} \quad (23)$$

higher oxidation state cube $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ (16 electrons) reacts with CO. The reaction is different from (23) in that $[Mo_3S_4(H_2O)_9]^{4+}$ and $Cu(CO)^+$ are formed (24). On

$$Mo_3CuS_4^{5+} + CO \rightarrow Mo_3S_4^{4+} + Cu(CO)^+ \tag{24}$$

bubbling of N_2 through the solutions, the $Cu(CO)^+$ decomposes with release of CO (25), and the Cu^+ recombines with $[Mo_3S_4(H_2O)_9]^{4+}$ (26).

$$Cu(CO)^+ \rightarrow Cu^+ + CO \tag{25}$$

$$Cu^+ + Mo_3S_4^{4+} \rightarrow Mo_3CuS_4^{5+} \tag{26}$$

Uptake of ethylene by $[M_3NiS_4(H_2O)_{10}]^{4+}$ ($M_3 = Mo_2W$, MoW_2, W_3) in aqueous or organic solvents to give olefin π-complexes $[Mo_3(NiC_2H_4)S_4(H_2O)_9]^{4+}$ has been reported and is as expected for Ni^0.[18] The equilibration of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ with ethylene is not as extensive as for the tungsten cluster, and in solvent H_2O (for CH_2Cl_2) the reaction is readily reversible.

Substitution of H_2O by NCS^- at the Cr of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ gives a rate law $k[Mo_3CrS_4^{4+}][NCS^-]$, with k(25 °C) $= 37\ M^{-1}\ s^{-1}$ in 2.00 M Hpts.[12] The magnitude of k suggests a Cr^{III} rather than Cr^{II} assignment, with the three μ_3-S ligands to Cr^{III} having a labilizing effect. The dependence of k on $[H^+]^{-1}$ indicates a conjugate-base pathway. For such a mechanism, the Cr requires at least two H_2O ligands; hence, a six-coordinate Cr and the formula $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ are proposed.

At 25 °C, the formation constant K for 1:1 Cl^- complexing to $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ ($K = 3500\ M^{-1}$) compares with a value ($K = 500\ M^{-1}$) for the complexing of Cl^- to Cu^+.[14] The reaction of Cl^- with $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ is assigned as rapid substitution at the tetrahedral Cu. Similarly, the 1:1 reactions (25 °C) of Cl^- with $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ ($K = 106\ M^{-1}$) and $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ ($K = 560\ M^{-1}$) are fast and in the stopped-flow range. However, in the case of $[Mo_4S_4(H_2O)_{12}]^{4+}$, 1:1 complexing is much less favorable ($K = 1.98\ M^{-1}$), and a substantially smaller rate constant of $9.7 \times 10^{-3}\ M^{-1}\ s^{-1}$ is observed.[8]

The only example of kinetic studies on the uptake of a heteroatom is for the reactions of Cu^I with $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$.[27]

Redox Reactions

Studies on the oxidation of single and double cubes with the 2,6-dicarboxylatopyridine (dipicolinate) Co^{III} complex $[Co(dipic)_2]^-$ ($E^{\circ\prime}$ for Co^{III}/Co^{II}, 362 mV) or hexaaquairon(III) ($E^{\circ\prime} \approx 770$ mV), stoichiometries (27, 28),

$$Mo_3SnS_4^{6+} + 2Co^{III} \rightarrow Mo_3S_4^{4+} + Sn^{IV} + 2Co^{II} \tag{27}$$

$$Mo_6SnS_4^{8+} + 4Co^{III} \rightarrow 2Mo_3S_4^{4+} + Sn^{IV} + 4Co^{II} \tag{28}$$

have been carried out. Rate laws first-order in oxidant and cube indicate a rate-controlling first stage followed by fast steps. The reactions of $[Co(dipic)_2]^-$ are independent of $[H^+]$ in the range 0.5–2.0 M and are assigned as outer-sphere electron transfer. In the case of the corner-shared double cubes, intermediate formation of the single cubes can be observed. With stoichiometric amounts of oxidant, the single cube can be isolated in high yield for M′ = In, Sn, and Ge.[15,16] Relevant stoichiometries for Sn and Ge are as in (29), where the single cube reacts with two further

$$Mo_6M'S_8^{8+} + 2Co^{III} \rightarrow Mo_3M'S_4^{6+} + Mo_3S_4^{4+} + 2Co^{II} \tag{29}$$

Co^{III} to give $[Mo_3S_4(H_2O)_9]^{4+}$. Oxidation of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ with $[Co(dipic)_2]^-$ has two stages with intermediate formation of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ (30, 31).[14]

$$Mo_3CuS_4^{4+} + Co^{III} \rightarrow Mo_3CuS_4^{5+} + Co^{II} \tag{30}$$

$$Mo_3CuS_4^{5+} + Co^{III} \rightarrow Mo_3S_4^{4+} + Cu^{II} + Co^{II} \tag{31}$$

The 5+ oxidation state has recently been confirmed by X-ray crystallography.[33] In pts^- solution, disproportionation of the 5+ ion to give $Mo_3CuS_4^{4+}$, $MO_3S_4^{4+}$, and Cu^{II} is observed. No similar process is observed with $W_3CuS_4^{5+}$.[27]

Virtually all heteroatom derivatives of $[M_3Q_4(H_2O)_9]^{4+}$ react with O_2. In the absence of electrochemical information on reduction potentials, and considering the difficulty in carrying out mechanistic studies with O_2, rate constants for the oxidation with $[Co(dipic)_2]^-$ (k_{Co}) and $[Fe(H_2O)_6]^{3+}$ (k_{Fe}) can be informative. There is little or no $[Co(dipic)_2]^-$ oxidation of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ and$[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$, which are least reactive with O_2. Linear free energy plots of log k_{Co} vs log k_{Fe}, where k_{Fe} is for the $[H^+]$-independent reaction of $[Fe(H_2O)_6]^{3+}$, have been reported.[20]

Future Trends

At present, the formation of heteroatom cubes of $M_3Q_4^{4+}$ with Group 6 metals, but nonparticipation of other early transition metals, is quite striking. Cyclopentadienyl (Cp) $[M'_4S_4(Cp)_4]$ cubes have been prepared (M′ = Ti, V, Cr, Mo),[34,35] and incorporation of other M′(Cp) into $[M_3Q_4(H_2O)_9]^{4+}$ may be possible.[21] The self-assembly of trinuclear $\{M_3Q_7Br_7\}_x$ polymers by heating together the elements, and ready access to $[M_3Q_4(H_2O)_9]^{4+}$ (M = Mo, W; Q = S, Se),[8,31] may prove to be a route to other clusters with N, P, As, etc. instead of the chalcogenides. A niobium cluster $[Nb_4(\mu_4\text{-}O)(\mu_3\text{-}Te)_4(CN)_{12}]^{6-}$ has recently been prepared with the oxo anion at the center of the cube.[36] Determining the synthesis and structure of larger nitrogenase-like clusters remains a challenge. In the lanthanoid area, the face-sharing double cube $[Yb_6S_6(SPh)_6(py)_{10}]$ represents a new type of structure.[37]

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