Preparation and Properties of the Corner-Shared Double Cube $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ as a Derivative of $[Mo_3S_4(H_2O)_9]^{4+}$ in Aqueous Acidic Solutions

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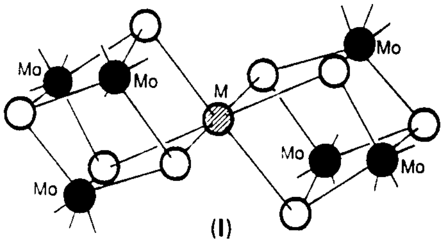
The reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with Bi^{III} in the presence of BH_4^- (rapid), or with Bi metal shot (3−4 days), gives a heterometallic cluster product. The latter has been characterized as the corner-shared double cube $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ by the following procedures. Analyses by ICP-AES confirm the Mo:Bi:S ratio as 6:1:8. Elution from a cation-exchange column by 4 M Hpts (Hpts = *p*-toluenesulfonic acid), but not 2 M Hpts (or 4 M $HClO_4$), is consistent with a high charge. The latter is confirmed as 8+ from the 3:1 stoichiometries observed for the oxidations with $[Co(dipic)_2]^-$ or $[Fe(H_2O)_6]^{3+}$ yielding $[Mo_3S_4(H_2O)_9]^{4+}$ and Bi^{III} as products. Heterometallic clusters $[Mo_6MS_8(H_2O)_{18}]^{8+}$ are now known for M = Hg, In, Tl, Sn, Pb, Sb, and Bi and are a feature of the P-block main group metals. The color of $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ in 2.0 M Hpts (turquoise) is different from that in 2.0 M HCl (green-blue). Kinetic studies (25 °C) for uptake of a single chloride $k_f = 0.80\ M^{-1}\ s^{-1}$, $I = 2.0$ M (Hpts), and the high affinity for Cl^- ($K > 40\ M^{-1}$) exceeds that observed for complexing at Mo. A specific heterometal interaction of the Cl^- not observed in the case of other double cubes is indicated. The Cl^- can be removed by cation-exchange chromatography with retention of the double-cube structure. Kinetic studies with $[Co(dipic)_2]^-$ and hexaaqua−Fe^{III} as oxidants form part of a survey of redox properties of this and other clusters. The Cl^- adduct is more readily oxidized by $[Co(dipic)_2]^-$ (factor of ∼10) and is also more air sensitive.

Introduction

The green trinuclear Mo^{IV}_3 incomplete cuboidal cluster $[Mo_3S_4(H_2O)_9]^{4+}$ has high stability in aqueous acidic solutions, and can be stored in air over long periods (years!).[1,2] It reacts directly with a number of metals giving marked color changes, the unusual reactivity stemming from the presence of three available (facial) μ-sulfido ligands. Different rates of interaction are observed: e.g., Hg, instant; Pb, ∼20 min; Sn ∼1 h); Fe, ∼12 h.[3,4] In the case of Ni a number of days are required, and with Pd it is necessary to use freshly prepared Pd black. With other metals e.g. Cr and Mo, no reactivity has been observed. Other procedures have been described besides direct reaction with the metal,[3−7] and >14 heterometallic M-containing cubes Mo_3MS_4, or related double cubes, have now been reported.

The incorporation of group 12−15 metals M = Hg,[8] In,[9,10] Tl,[11] Sn,[7,12] Pb[13] and Sb[14] into $[Mo_3S_4(H_2O)_9]^{4+}$ has resulted in the identification of corner-shared double cubes as a subgroup type $[Mo_6MS_8(H_2O)_{18}]^{8+}$, with the heterometal atom in a nodal position as illustrated in **I**. The clusters are sometimes referred to as (metal) sandwich compounds.[8,9,12] Structures of the *p*-toluenesulfonate (pts^-) salts of the aqua ions with M = Hg,[8] Sn,[12] Sb,[14] and In (as the oxo−sulfido cluster $[Mo_6InS_6O_2(H_2O)_{18}]^{8+}$),[9] have been determined. In addition the structure of the double cube with M = Mo, $[Mo_7S_8(H_2O)_{18}]^{8+}$, the only example with a transition metal at the nodal position, has been reported.[15] With two main group heterometals only, M = In and Sn, have single cubes been prepared.[7,16] The corner-shared double cubes are unusual in that all seven examples to date have the single stable state of charge 8+. The single cube aqua ions on the other hand (depending on M), have different overall charges which lie in the range 4+ to 6+.[4] In just one case, that of $[Mo_3CuS_4(H_2O)_{10}]^{4+,5+}$, have two oxidation states been identified for the same heterometallic structure.[6] The cubes $[Mo_4S_4(H_2O)_{12}]^{n+}$, n = 4, 5, and 6, provide another example in which different redox states have been obtained.[17] Redox controlled interconversions of e.g. $[Mo_6SnS_8(H_2O)_{18}]^{8+}$ and $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ have been reported.[10] Most heterometallic derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$ are air sensitive and react readily with O_2. Notable exceptions are with M = Pd,[18] and over limited periods M = Ni.[5]



(I)

Studies on bismuth aqueous chemistry are quite rare, but recently the preparation and structure of the aqua ion [Bi-

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$(H_2O)_9]^{3+}$ have been reported.[19] Bismuth(III) also gives hexanuclear bismuthyl ions e.g. $[Bi_6(OH)_{12}]^{6+}$ from $HClO_4$ and HNO_3 solutions.[20,21] Bismuth(V) is a strong oxidant with $E°'$ for Bi^V/Bi^{III} couple in $HClO_4$ reported to be 2.03 V vs nhe.[22] Bismuth- and molybdenum-containing compounds are important as catalysts in the SOHIO alkene oxidation and ammoxidation industrial processes.[23] This has prompted interest in organomolybdenum complexes of bismuth, e.g. $[Et_4N]_2BiMo_4(CO)_{12}(\mu\text{-}OMe)_3]$, which has a cubelike structure.[24] A compound of empirical formula Mo_2BiS has a cluster unit combining three elements involved in the present study.[25] Bismuth citrate preparations (one of the few water-soluble forms) are also used in medicine.[26,27]

To provide further information on Mo−chalcogenide heterometallic clusters we decided to explore the incorporation of bismuth into $[Mo_3S_4(H_2O)_9]^{4+}$ and here report the preparation of $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ and its properties in aqueous solution.

Experimental Section

Preparation of $[Mo_6BiS_8(H_2O)_{18}]^{8+}$. Solutions of $[Mo_3S_4(H_2O)_9]^{4+}$ in 2.0 M HCl were obtained as previously described.[1−2] Conversion to $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ was achieved by syphoning $[Mo_3S_4(H_2O)_9]^{4+}$ (2.5 mM, 50 mL) in 0.50 M HCl onto a 10-fold excess of bismuth(III) citrate ($C_6H_5O_7Bi$) (Sigma Chemicals), under rigorous air-free (N_2) conditions, and warming to ∼40 °C for 5 min to dissolve the solid formed. The solution was then syphoned onto a 100-fold excess of $NaBH_4$ (0.47 g, 0.25 M) in a round-bottomed flask as part of Schlenkware apparatus, when effervescence occurred and some black precipitate formed. A color change from green to dark green-blue was observed. After this was allowed to stand for 30 min, the solution was filtered to remove the black solid and loaded onto Dowex 50W-X2 cation-exchange column, also under N_2. Unreacted $[Mo_3S_4(H_2O)_9]^{4+}$ eluted first with ∼1 M HCl and the green-blue product with ≥2 M HCl. Solutions of concentrations of 3−4 mM were obtained in this way. Anion metathesis from Cl^- to pts^- was accomplished by loading the product in 0.5 M HCl onto a second Dowex column. After the column was washed with Hpts, a turquoise-blue product was eluted with 4 M Hpts. No elution was observed in either 2 M Hpts or 4 M $HClO_4$. Assuming an 8+ product (see below) the equation summarizing reaction is as in (1). Stock solutions of product (1−2 mM) in 4 M Hpts were

$$2Mo_3S_4^{4+} + Bi^{3+} + 3e^- \rightarrow Mo_6BiS_8^{8+} \tag{1}$$

stored one vessel inside another, both under N_2 at 4 °C. Under these conditions negligible oxidation occurs within a week. Solutions in HCl are more air sensitive and are stable for ≤4 days under similar conditions.

The same cluster was obtained by reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ (15 mL; 4−5 mM) in different acids as required with Bi shot (∼5 g) activated by treating with 4M $HClO_4$ prior to use, under N_2 for 3−4 days.

Metal analyses were carried out using inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a sample of the Bi product in 2 M HCl, and gave a Mo:Bi:S ratio of 6.1:1:7.9. For stock solutions in 2 M Hpts, a Mo:Bi ratio of 6.2:1 was obtained. Both results are consistent with a formula Mo_6BiS_8.

UV−Vis and Near-IR Spectra: Spectra of the Bi-containing product $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ in 2.0 M Hpts, peak position λ/nm (ϵ/M^{-1} cm^{-1} per Mo_6) at 366 (9280) and 586 (3125), and in 2.0 M HCl, are shown alongside $[Mo_3S_4(H_2O)_9]^{4+}$ in Figure 1. The absorption coefficients (ϵ) were determined by allowing solutions of $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ to air oxidize when $[Mo_3S_4(H_2O)_9]^{4+}$ is regenerated as the only product with peaks at 248 (8219), 366 (5550), and 603 (362) in both 2.0 M Hpts and $HClO_4$. In 2.0 M HCl, the 366 nm peak shifts to 370 nm, that at 602 nm shifts to 620 nm, and ϵ values decrease by ∼10%.

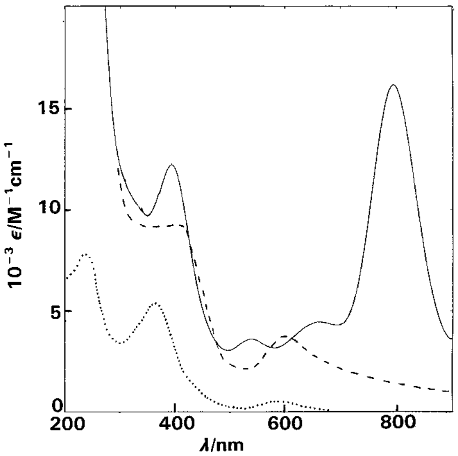

Figure 1. UV−vis spectra (25 °C) of the double cube $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ in 2.0 M Hpts (- - -) and 2.0 M HCl (—) (absorption coefficients ϵ per Mo_6) as compared to $[Mo_3S_4(H_2O)_9]^{4+}$ in 2.0 M $HClO_4$ (···) (ϵ per Mo_3). I = 2.0 M.

Other Reactants. Samples of $NH_4[Co(dipic)_2]\cdot H_2O$ (dipic = pyridine-2,6-dicarboxylate), characterized by the visible absorbance band 510 nm (630) were obtained as previously described.[5] Solutions of $[Fe(H_2O)_6]^{3+}$ were obtained by loading $Fe(ClO_4)_3\cdot 6H_2O$ (Fluka) on a Dowex 50W-X2 cation-exchange column, and after washing with more dilute acid, eluting with 1.0M Hpts. Reduction potentials (vs nhe) are $[Co(dipic)_2]^{-/2-}$ (767 mV) and $[Fe(H_2O)_6]^{3+/2+}$ (770 mV). Other reagents, including HCl, Hpts, and bismuth citrate, were of analytical grade purity and used without further purification. A sample of Li(pts) was prepared by neutralization of Hpts solutions with Li_2CO_3 and recrystallizing.

Stoichiometries for the Oxidation of $[Mo_6BiS_8(H_2O)_{18}]^{8+}$. The stoichiometry of the $[Co(dipic)_2]^-$ oxidation $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ in 2.0 M Hpts was determined by titrating with a ∼20-fold more concentrated solution of $[Co(dipic)_2]^-$ (aliquots added from a Hamilton microsyringe), and monitoring the absorbance decrease at the 586 nm peak ($\epsilon = 3125$ M^{-1} cm^{-1}). The sole Mo containing product was determined as $[Mo_3S_4(H_2O)_9]^{4+}$ from UV−Vis spectrophotometry. From four such determinations a stoichiometry of 2.73 ± 0.14 was obtained consistent with (2) as the dominant process. Bismuth(V) is a strong oxidizing

$$Mo_6BiS_8^{8+} + 3Co^{III} \rightarrow 2Mo_3S_4^{4+} + 3Co^{II} + Bi^{III} \tag{2}$$

agent (E°′ 2.03V) and is not a possible product. Oxidation of $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ with $[Fe(H_2O)_6]^{3+}$ was likewise monitored at 586 nm and from three determinations a stoichiometry of 2.92 ± 0.12 was obtained, (3). Both 3:1 stoichiometries in eqs 2 and 3 require an 8+

$$Mo_6BiS_8^{8+} + 3Fe^{3+} \rightarrow 2Mo_3S_4^{4+} + 3Fe^{2+} + Bi^{III} \tag{3}$$

charge on the bismuth cluster, consistant with the adopted formula $[Mo_6BiS_8(H_2O)_{18}]^{8+}$.

Kinetic Studies. Reactions were carried out at 25 ± 0.1 °C, with ionic strength adjusted to I = 2.00 ± 0.01M (LiCl/Li(pts)) as appropriate, using a Dionex D-110 stopped-flow spectrophotometer, with the oxidant in large ≥20-fold excess over $[Mo_6BiS_8(H_2O)_{18}{}^{8+}]$. Unweighted linear and nonlinear least-squares programs were used in the treatment of data.

Results

Stability of $[Mo_6BiS_8(H_2O)_{18}]^{8+}$. When the concentration of $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ in 2.0M Hpts was varied between 0.04 and 1.0 mM, absorbance readings at the 366 and 586 nm peak positions were found to conform to Beer's law. The same was

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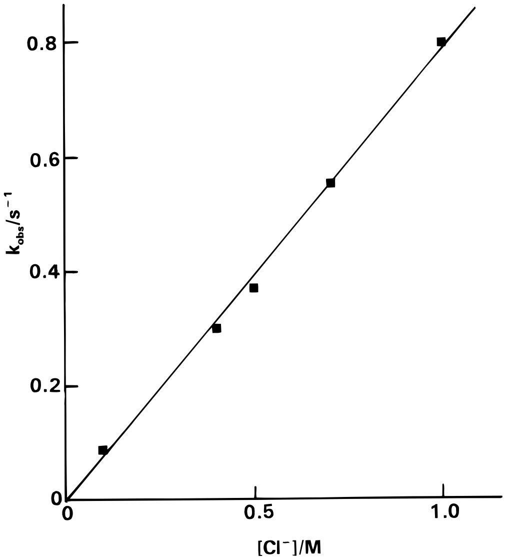


Figure 2. Dependence of first-order rate constants k_{obs}(25 °C) determined at 795 nm for chloride complexing to $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ on $[Cl^-]$. $[H^+] = 2.00$ M; $I = 2.00$ M (Hpts).

found for concentrations (0.09−0.20M) in 2.0 M HCl using the 395 and 795 nm peak positions. There is therefore no evidence from these studies for an equilibrium involving more than one cluster type. On exposure of $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ (3 mM) in a 1 × 1cm optical cell to the atmosphere (with some shaking) oxidation occurs, $t_{1/2}$ for oxidation is ~5 min in 2.0M Hpts, and ~2 min in 2.0 M HCl, (4).

$$4Mo_6BiS_8{}^{8+} + 3O_2 + 12H^+ \rightarrow 8Mo_3S_4{}^{4+} + 4Bi^{3+} + 6H_2O \qquad (4)$$

Complexing with Chloride. Addition of chloride to a solution of $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ in Hpts gives significant changes in the UV−vis spectrum, Figure 1. Spectrophotometric changes with $[Cl^-]$ in the range 0.10−1.00 M (as HCl) were monitored by stopped-flow method at 795 nm. First-order rate constants k_{obs}(25 °C), give a linear dependence on chloride, Figure 2, yielding $k_f = 0.80 \pm 0.03$ M^{-1} s^{-1}, $I = 2.00$ M (Hpts). There was no detectable intercept corresponding to the aquation step (k_{aq}). Studies carried out at lower $[Cl^-]$, in an attempt to define k_{aq}, gave additional complications due to the reaction of $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ with traces of O_2. From those studies it can be concluded that the equilibrium constant for (5), is very favorable and >40 M^{-1}.

$$Mo_6BiS_8{}^{8+} + Cl^- \rightleftarrows Mo_6BiS_8Cl^{7+} \qquad (5)$$

Oxidation of $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ with $[Co(dipic)_2]^-$. First-order rate constants k_{obs}/s^{-1} for the reaction of $[Co(dipic)_2]^-$ (in large excess) with the bismuth cluster, were determined by stopped-flow spectrophotometry at 586 nm. A linear dependence of k_{obs} on $[Co(dipic)_2]^-$ is observed, Figure 3, consistent with the rate law (6).

$$-d[Mo_6BiS_8{}^{8+}]/dt = k_{Co}[Mo_6BiS_8{}^{8+}][Co(dipic)_2{}^-] \qquad (6)$$

No dependence of rate constants on $[H^+]$ is observed in the range 0.50−2.00 M, and from the slope in Figure 3, $k_{Co} = (3.6 \pm 0.1) \times 10^4$ M^{-1} s^{-1} at 25 °C, $I = 2.00$ M (Li(pts)). A possible reaction sequence is shown in (7) and (8), where $Mo_6BiS_8{}^{9+}$ is a transient species for which there is at present no other evidence.

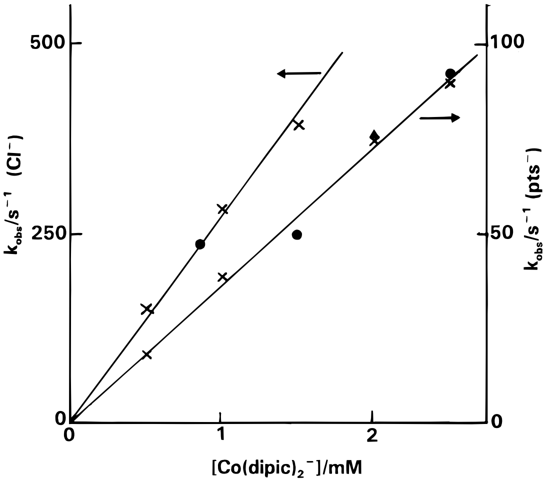


Figure 3. Variation of first-order rate constants k_{obs}(25 °C) for the $[Co(dipic)_2]^-$ (reactant in excess) oxidation of $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ in pts^-, I = 2.00 M (Li(pts)) (right-hand scale), and in Cl^-, I = 2.00 M (LiCl) (left-hand scale). No dependence on $[H^+]$/M = 2.00 (×), 1.00 (●), 0.50 (▲) is observed.

Table 1. Variation of First-Order Rate Constants k_{obs}(25 °C) for the Oxidation of $[Mo_6BiS_8(H_2O)_{18}]^{8+}$, (2.5−5.0) × 10^{-5} M, by Hexaaqua−Fe^{III}, $I = 2.00$ M (Li(pts))

$[H^+]$/M	$[Fe^{III}]$/mM	k_{obs}/s^{-1}
2.00	8.0	4.0
	6.0	3.0
	4.0	1.9
	2.0	1.1
1.50	6.0	3.4
	4.0	2.4
	2.0	1.2
1.00	8.0	6.7
	6.0	5.1
	4.0	3.6
	2.0	1.5
0.75	8.0	7.9
	6.0	6.2
	4.0	4.3
	1.7	1.6
0.50	8.0	10.4
	4.0	5.1
	2.0	2.8

$$Mo_6BiS_8{}^{8+} + Co^{III} \xrightarrow{k_{Co}} Mo_6BiS_8{}^{9+} + Co^{II} \qquad (7)$$

$$Mo_6BiS_8{}^{9+} + 2Co^{III} \xrightarrow{fast} 2Mo_3S_4{}^{4+} + 2Co^{II} + Bi^{3+} \qquad (8)$$

The oxidation of $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ in 2.0 M HCl was also studied at 795 nm. A linear dependence of k_{obs}/s^{-1} on $[Co(dipic)_2]^-$ is observed, Figure 3. There is no dependence on $[H^+]$ in the range 1.00−2.00 M, and $k_{Co} = (2.67 \pm 0.07) \times 10^5$ M^{-1} s^{-1}. The greater reactivity in HCl is consistent with the studies above with O_2.

Oxidation of $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ with Hexaaqua−Fe^{III}. First-order rate constants (k_{obs}) monitored by stopped-flow spectrophotometry at 586 nm for the oxidation of $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ are listed in Table 1. Linear dependencies of k_{obs} on $[Fe^{III}]$ are observed at different $[H^+]$ values in the range 0.50−2.00 M. The rate law given in (9) defines k_{Fe} at each $[H^+]$, Table 2. From the dependence of k_{Fe} on $[H^+]^{-1}$ eq 10

$$-d[Mo_6BiS_8{}^{8+}]/dt = k_{Fe}[Mo_6BiS_8{}^{8+}][Fe(H_2O)_6{}^{3+}] \qquad (9)$$

$$k_{Fe} = k_a + k_b[H^+]^{-1} \qquad (10)$$

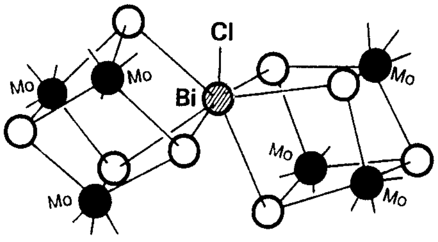
Table 2. Summary of Rate Constants k_{Fe}(25 °C) from the Slopes As Defined in Eq 9, I = 2.00 M (Li(pts))

$[H^+]$/M	$k_{Fe}/M^{-1}\ s^{-1}$	$[H^+]$/M	$k_{Fe}/M^{-1}\ s^{-1}$
2.00	490 ± 10	0.75	1000 ± 30
1.50	570 ± 20	0.50	1290 ± 25
1.00	850 ± 26		

follows, with k_a (245 ± 53 $M^{-1}\ s^{-1}$) assigned to the reactions of $[Fe(H_2O)_6]^{3+}$, and k_b (540 ± 40 s^{-1}) to the reaction of $[Fe(H_2O)_5OH]^{2+}$.

Discussion

A Bi-containing corner-shared double-cube structure, **I**, has been prepared by two procedures. Analysis by ICP-AES give a Mo:Bi:S ratio of 6:1:8, thus ruling out both the single cube and edge-linked double-cube structures which would give Mo:Bi ratios of 3:1. The determination of 3:1 stoichiometries with $[Co(dipic)_2]^-$ and $[Fe(H_2O)_6]^{3+}$ as oxidants, coupled to the cation-exchange elution behavior confirm an 8+ charge cluster of formula $[Mo_6BiS_8(H_2O)_{18}]^{8+}$. This work provides therefore a further example of a P-block main group heterometallic double cube of general formula $[Mo_6MS_8(H_2O)_{18}]^{8+}$ (**I**). A new property in the case of $[Mo_6BiS_8(H_2O)_{18}]^{8+}$ is the reaction with chloride. The change from turquoise (2.0 M Hpts) to green-blue (2.0 M HCl) is clearly detectable by eye. The appearance of a strong peak at 795 nm on addition of Cl^- is noted, Figure 1. The kinetics implicate a single Cl^-, k_f = 0.80 $M^{-1}\ s^{-1}$. By repeating the cation-exchange chromatography and eluting with Hpts, the Cl^- is readily removed with retention of the double-cube structure (ICP-AES analyses). The large absorbance changes observed on addition of chloride suggest that complexing is at the bismuth. In studies on other clusters the complexing of chloride at Mo is much less extensive.[17,28] Previously it has been observed that the addition of chloride to $[Mo_6SnS_8(H_2O)_{18}]^{8+}$ [7] induces conversion to the single cube $[Mo_3(SnCl_3)S_4\ (H_2O)_9]^{3+}$. No similar change is observed with bismuth. It seems unlikely that bismuth is occupying other than the central nodal position. A structure in which a Mo and the Bi are juxtaposed would be expected to complex more Cl^-'s, lead to a higher Bi content, and result in some degree of aggregation at the Bi center. No such properties have been observed with this or any other corner-shared double cube obtained from $[Mo_3S_4(H_2O)_9]^{4+}$. An interesting comparison is with the FeMo cofactor of nitrogenase,[29] where the Mo is known to be in such an outer position of the Fe_7MoS_9 cluster. Complexing of chloride to the Bi, which remains coordinated to six S-atoms, is therefore proposed as in **II**. The change in cube orientations to accommodate the chloride gives rise to the color change, with the 795nm band assigned as a Cl^- dependent charge-transfer process.



(II)

Bismuth generally displays no strong stereo preferences, and coordination numbers up to 9 in $[Bi(H_2O)_9]^{3+}$ are observed, consistent with its atomic radius.[19] Bismuth(III) has a radius of 1.15 Å with no pronounced lone-pair activity,[30] and is similar in size to Nd^{3+} (1.163 Å) and Sm^{3+} (1.132 Å). There is no evidence for any stereochemical influence of the s^2 lone pair in the present chemistry. Lone-pair effects are generally more evident in 3-, 4-, and 5-coordinate metal compounds. In the case of $SbCl_3$ for example a lone pair occupies one of the tetrahedral positions, and in the aniline complex $SbCl_3{\cdot}NH_2Ph$ a square-base pyramidal structure is adopted, with a lone pair occupying the second axial position.[31] Stereochemical activity of the lone pair normally decreases with increasing coordination number and atomic weight e.g. As > Sb > Bi.[32] Many MX_6^{3-} complexes ($X = Cl^-, Br^-$), particularly those with Bi, are close to a regular octahedral structure, despite having an extra pair of valence-shell electrons.[33]

Kinetic studies with $[Co(dipic)_2]^-$ and hexaaqua–Fe^{III} as oxidants provide further information regarding redox properties of heterometallic clusters.[3,34] In the present work outer-sphere $[Co(dipic)_2]^-$ ($3.6 \times 10^4\ M^{-1}\ s^{-1}$) and $[Fe(H_2O)_6]^{3+}$ (245 $M^{-1}\ s^{-1}$) assignments are in accordance with previous studies. The k_b term corresponds to a reaction of $[Fe(H_2O)_5OH]^{2+}$ for which a rate constant (k_b/K_a) of $5.4 \times 10^5\ M^{-1}\ s^{-1}$ is obtained using an acid dissociation constant $K_a = 10^{-3}$ M for $[Fe(H_2O)_6]^{3+}$ at 25 °C, I = 1.0 M (ClO_4^-).[35] The enhancement over the outer-sphere k_a term is consistent with an inner-sphere process. We also note that the second-order rate constant $k_{Co}/M^{-1}\ s^{-1}$, for $[Co(dipic)_2]^-$ oxidation of the cluster in 2.0 M HCl is some 7× larger ($2.7 \times 10^5\ M^{-1}\ s^{-1}$) as compared to the value in 2.0 M Hpts ($3.6 \times 10^4\ M^{-1}\ s^{-1}$). This behavior suggests a change in reduction potential on complexing with Cl^-.

No evidence was obtained for a single cube on addition of less than stoichiometric amounts of $[Co(dipic)_2]^-$ or $[Fe(H_2O)_6]^{3+}$, to $[Mo_6BiS_8(H_2O)_{18}]^{8+}$, and if a single cube is formed decay to $[Mo_3S_4(H_2O)_9]^{4+}$ is rapid. So far only two single cubes containing heterometal main group elements have been prepared (M = In, Sn).[7,16] The colors are quite different from the corresponding double cubes, and intermediate formation of such species is readily observed. Accessibility of different heterometal oxidation states may be a controlling feature with assignments e.g. Sn^{IV} (single cube) and Sn^{II} (double cube) possible.[7] In the case of 6p Tl, Pb, Bi the higher $d^{10}s^0$ oxidation states are more oxidizing, which might account for the difficulty in isolating the single cubes. A Bi^{III} assignment seems likely in $[Mo_6BiS_8(H_2O)_{18}]^{8+}$. Electronic properties of some heterometal cubes have been addressed.[36] From crystallographic dimensions Mo–M metal–metal bonding is not a feature of main group heterometal (M) derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$.[7,8,9,12,16]

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