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Electron transfer reactivity of cuboidal heterometallic Mo_3MS_4 clusters in aqueous acidic solutions

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Abstract

Rate constants (25 °C) are reported for the first time for the oxidation of the cuboidal heterometallic Mo_3CoS_4 cluster, which in 2 M $ClO_4^-/HClO_4$ solutions exists predominantly as the edge-linked double cube $[\{Mo_3CoS_4(H_2O)_9\}_2]^{8+}$. Reactions with one-equivalent oxidants, the outer-sphere reagent $[Co(dipic)_2]^-$ ($E°' = 0.75$ V) (dipic = pyridine-2,6-dicarboxalate) and hexaaqua Fe(III) ($E°' = 0.77$ V), have been studied, $I = 2.00$ M ($LiClO_4$). Comparisons are made with rate constants already reported for the same two oxidants with $[Mo_4S_4(H_2O)_{12}]^{4+}$, and heterometallic cuboidal clusters $[Mo_3CrS_4(H_2O)_{12}]^{4+}$, $[Mo_3FeS_4(H_2O)_{10}]^{4+}$, $[Mo_3NiS_4(H_2O)_{10}]^{4+}$, edge-linked $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$, $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ and $[Mo_3CuS_4(H_2O)_{10}]^{5+}$, all of which are derivatives of the trinuclear incomplete cuboidal $Mo(IV)_3$ cluster $[Mo_3S_4(H_2O)_9]^{4+}$. Rate constants for the reactions of $[Co(dipic)_2]^-$ (k_{Co}) are independent of $[H^+]$ in the range 0.50–2.00 M. In the case of the Fe(III) oxidations (k_{Fe}), the dependence $k_{Fe} = k_a + k_b[H^+]^{-1}$ is observed for all the clusters except $[Mo_4S_4(H_2O)_{12}]^{4+}$. The term k_a is assigned as an outer-sphere reaction of $[Fe(H_2O)_6]^{3+}$, and k_b as an inner-sphere reaction of $[Fe(H_2O)_5OH]^{2+}$. Linear correlations of log k_{Co} versus log k_a, and of log k_{Co} versus log k_b, have slopes close to 1.0. Exceptions are the edge-linked $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$, and to a lesser extent the k_b term for $[\{Mo_3CoS_4(H_2O)_9\}_2]^{8+}$. The correlation of log k_{Co} versus log k_b values is unexpected since k_b is for an inner-sphere process. It can be concluded that electron transfer following OH^- bridging of the Fe(III) to the heterometal atom is rate determining. Rate constants k_{Co} and k_{Fe} for $[W_3CuS_4(H_2O)_{10}]^{5+}$, the first heterometallic cluster obtained from $[W_3S_4(H_2O)_9]^{4+}$, also conform to the same two correlations.

Keywords: Kinetics and mechanism; Oxidation; Electron transfer; Molybdenum complexes; Transition metal complexes; Sulfur complexes; Cuboidal complexes; Cluster complexes

Introduction

The preparation and properties of cuboidal cluster complexes $[Mo_4S_4(H_2O)_{12}]^{n+}$ ($n = 4,5,6$), which have high stability in aqueous acidic solutions, have already been reported [1–4]. The related trinuclear $Mo(IV)_3$ incomplete cuboidal cluster $[Mo_3S_4(H_2O)_9]^{4+}$ is also well characterised [5], and is of interest not least because it yields heterometallic cuboidal complexes of the type Mo_3MS_4, seven of which are considered in the present paper. As far as the heterometallic atoms are concerned early transition metals are octahedrally coordinated $[Mo_3MS_4(H_2O)_{12}]^{4+}$ (M = Cr, Mo) [6], while later transition metals are tetrahedral giving $[Mo_3MS_4(H_2O)_{10}]^{4+/5+}$ structures (M = Fe [7], Co [8], Ni [9], Pd [10], Cu [11]), Fig. 1. In the case of the Co, Pd and Cu(4+) cubes X-ray crystal structures [8,10,11] have illustrated the tendency to form double cubes, which in the Co and Pd cases are also believed to be present in weakly complexing aqueous acidic $HClO_4$ and Hpts (pts^- = *p*-toluenesulfonate) solutions, Fig. 1.

In the present paper mechanistic aspects of electron transfer (ET) reactions of the cubes are considered. Redox studies with one-equivalent oxidants having virtually identical reduction potentials $[Co(dipic)_2]^-$ ($E°' = 0.75$ V), and hexaaqua Fe(III) ($E°' = 0.77$ V), are the prime focus of attention. New data for the reactions of $[\{Mo_3CoS_4(H_2O)_9\}_2]^{8+}$ are presented, and comparisons are made for the first time with data reported elsewhere for the Mo_3MS_4 cubes, M = Cr [6], Mo [6], Fe [12], Ni [13], Pd [14] and Cu [15]. Rate constants for the heterometallic derivative $[W_3CuS_4(H_2O)_{10}]^{5+}$ obtained by reacting the trinuclear $[W_3S_4(H_2O)_9]^{4+}$ cluster with Cu^+ [16], are also included.

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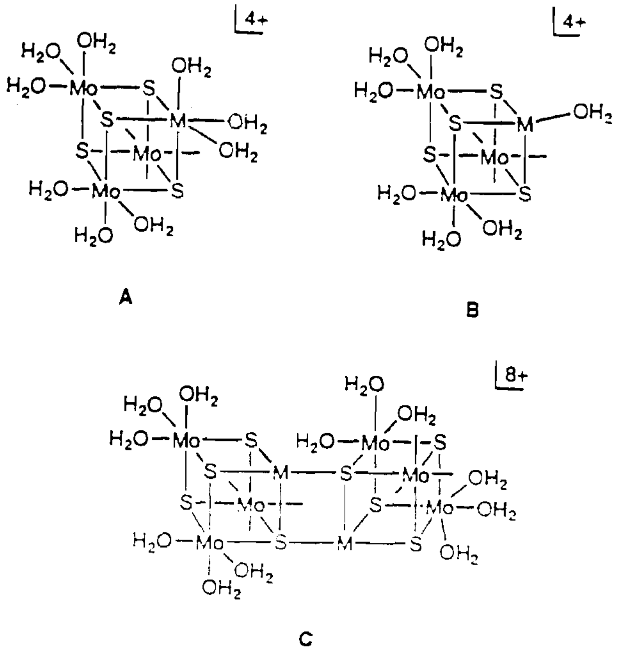

Fig. 1. Structures of (A) single cubes $[Mo_3MS_4(H_2O)_{12}]^{4+}$ with an octahedral fourth metal atom (M = Cr, Mo), (B) single cubes $[Mo_3MS_4(H_2O)_{10}]^{n+}$ ($n = 4$ or 5) with a tetrahedral heterometal atom (M = Fe, Ni, Cu), and (C) double cubes which are edge-linked, $[\{Mo_3MS_4(H_2O)_9\}_2]^{8+}$ (M = Co, Pd).

The crystal structure of a $W_3CuS_4^{5+}$ cube has already been reported [17]. The cube gives 1:1 stoichiometries with both oxidants as in the case of $[Mo_3CuS_4(H_2O)_{10}]^{5+}$.

2. Experimental

2.1. Preparation of $[\{Mo_3CoS_4(H_2O)_9\}_2]^{8+}$

The product is air-sensitive and rigorous O_2-free conditions are required throughout. The method used involves addition of cobalt granules (~5 g; Aldrich) to a solution of column purified $[Mo_3S_4(H_2O)_9]^{4+}$ (10 ml of 5 mM) in 2.0 M $HClO_4$ [18]. The reaction vessel was sealed under N_2, which was stored in a second vessel also under N_2, and allowed to react for 1–3 days. The grey–black cobalt granules were pretreated first with 12 M $HClO_4$ to clean and activate the surface, and then washed with 2 M $HClO_4$ to remove any Co(II) formed by the action of the concentrated acid. The product was used without further purification. It is not possible to elute the cube from Dowex 50W-X2 columns using up to 4 M $HClO_4$, consistent with the existence of an edge-linked double cube structure $[\{Mo_3CoS_4(H_2O)_9\}_2]^{8+}$. The UV–Vis spectrum of 2 M $HClO_4$ solutions of the double cube gives peaks λ (nm) (ϵ (M^{-1} cm^{-1} per single cube)) at 244 (17 900), 365 (12 400) and 795 (4400) with a shoulder at 445 (6200), which compares with the spectrum obtained for $[Mo_3S_4(H_2O)_9]^{4+}$, 248 (8200), 367 (5550) and 602 (362).

2.2. Other reagents

The complex $NH_4[Co(dipic)_2]\cdot 2H_2O$, where dipic is the dipicolinate ligand pyridine-2,6-dicarboxylate, absorption peak at 510 nm ($\epsilon = 630$ M^{-1} cm^{-1}), was prepared as previously described [19]. Solutions of $[Fe(H_2O)_6]^{3+}$ were obtained by Dowex 50W-X2 cation-exchange column purification of $Fe(ClO_4)_3\cdot 6H_2O$ (Fluka), where the final elution was with 1.0 M $HClO_4$. Acids used were HCl and $HClO_4$ (both BDH Analar), and $LiClO_4$ (Aldrich) was recrystallized three times from water.

2.3. Stability of $[\{Mo_3CoS_4(H_2O)_9\}_2]^{8+}$

On exposure of solutions to air immediate changes in the UV–Vis absorbance spectrum are observed, Eq. (1).

$$(Mo_3CoS_4)_2^{8+} + O_2 + 4H^+ \longrightarrow 2Mo_3S_4^{4+} + 2Co^{2+} + 2H_2O \qquad (1)$$

The half-life for the reaction with O_2 in excess over the cube is typically ~5 min. The high ϵ values for the Mo_3CoS_4 chromophore allow concentrations of $\sim 10^{-5}$ M to be used. On varying the concentration within the range 0–0.5 mM (365 nm) and 0–1.0 mM (795 nm) in 2.0 M $HClO_4$, and using narrow path-length cells, absorbance readings at 795 (±5%) and 365 (±8%) nm were found to conform to Beer's Law.

2.4. Stoichiometries

Stoichiometries for the reactions of $[\{Mo_3CoS_4(H_2O)_9\}_2]^{8+}$ with $[Co(dipic)_2]^-$ and $[Fe(H_2O)_6]^{3+}$ were determined by UV–Vis spectrophotometry using a Perkin-Elmer Lambda 9 instrument. Aliquots of oxidant were added to a solution of $[\{Mo_3CoS_4(H_2O)_9\}_2]^{8+}$ in an optical cell using a Hamilton micro-syringe, and the decrease in absorbance at 795 nm ($\epsilon = 4400$ M^{-1} cm^{-1} per single cube) monitored. Stoichiometries expressed as moles of oxidant per double cube (each an average of nine experiments) were determined as 3.85:1 for $[Fe(H_2O)_6]^{3+}$ and 3.92:1 for $[Co(dipic)_2]^-$.

Other stoichiometries relevant to this paper can be summarised as follows, where R(III) represents the oxidant Co(III) or Fe(III). The cube $[Mo_4S_4(H_2O)_{12}]^{4+}$ behaves in a unique manner giving $[Mo_4S_4(H_2O)_{12}]^{5+}$ as final product in a 1:1 reaction (Eq. (2)) [6].

$$Mo_4S_4^{4+} + R(III) \longrightarrow Mo_4S_4^{5+} + R(II) \qquad (2)$$

All other reactions give cube products which fragment yielding trinuclear $[Mo_3S_4(H_2O)_9]^{4+}$. Thus with $[Mo_3MS_4(H_2O)_{10}]^{4+}$ (M = Fe [12], Ni [13]) 2:1 stoichiometries are observed and the final products are as given in Eq. (3).

$$\mathrm{Mo_3MS_4}^{4+} + 2\mathrm{R(III)} \longrightarrow \mathrm{Mo_3S_4}^{4+} + \mathrm{M(II)} + 2\mathrm{R(II)} \quad (3)$$

The same 2:1 reaction is observed with $[\mathrm{Mo_3CuS_4(H_2O)_{10}}]^{4+}$, but biphasic kinetics are observed, where the rate constant for the second stage is reproduced in separate studies with $[\mathrm{Mo_3CuS_4(H_2O)_{10}}]^{5+}$ [15]. The $[\mathrm{Mo_3CrS_4(H_2O)_{12}}]^{4+}$ cube gives a 3:1 stoichiometry, Eq. (4) [6]

$$\mathrm{Mo_3CrS_4}^{4+} + 3\mathrm{R(III)} \longrightarrow \mathrm{Mo_3S_4}^{4+} + \mathrm{Cr(III)} + 3\mathrm{R(II)} \quad (4)$$

and the double cube (M = Pd), as with M = Co, gives a 4:1 stoichiometry as in Eq. (5) [14]

$$(\mathrm{Mo_3PdS_4})_2{}^{8+} + 4\mathrm{R(III)} \longrightarrow 2\mathrm{Mo_3S_4}^{4+} + 2\mathrm{Pd(II)} + 4\mathrm{R(II)} \quad (5)$$

In all cases the first stage is rate determining, and rate laws are of the simplest possible kind, Eq. (6)

$$\mathrm{Rate} = k_{\mathrm{R}}[\mathrm{Mo_3MS_4}][\mathrm{R(III)}] \quad (6)$$

where k_{R} is for $[\mathrm{Co(dipic)_2}]^-$ (k_{Co}) and hexaaqua Fe(III) (k_{Fe}).

2.5 *Kinetic studies*

The reactions of $[\{\mathrm{Mo_3CoS_4(H_2O)_9}\}_2]^{8+}$ with $[\mathrm{Co(dipic)_2}]^-$ and $[\mathrm{Fe(H_2O)_6}]^{3+}$, the oxidant in > tenfold excess, were studied using a Dionex D-110 stopped-flow spectrophotometer. Reactions were monitored at 795 nm. First-order rate constants were obtained using fitting routines from OLIS, (Bogart, GA, USA).

2.6. *Treatment of data*

Unweighted least-squares fits of all data were carried out.

3. Results and discussion

In the case of three heterometallic cubes $\mathrm{Mo_3MS_4}$ (M = Co, Pd, Cu) the structures as determined by X-ray crystallography have indicated the existence of edge-linked double cubes $[\{\mathrm{Mo_3CoS_4(H_2O)_9}\}_2](\mathrm{pts})_8 \cdot 18\mathrm{H_2O}$ [8], $[\{\mathrm{Mo_3PdS_4(H_2O)_9}\}_2](\mathrm{pts})_8 \cdot 24\mathrm{H_2O}$ [10] and $[\{\mathrm{Mo_3CuS_4(H_2O)_9}\}_2](\mathrm{pts})_8 \cdot 20\mathrm{H_2O}$ [11]. All three are strongly held on Dowex 50W-X2 cation-exchange columns consistent with the presence of 8+ species. Although eluted by HCl and Hpts, which coordinate and/or induce single cube formation, they are not eluted by $\mathrm{HClO_4}$ upto 4 M. Solutions of 4 M Hpts are required to elute the purple Pd double cube from Dowex columns consistent with a high overall charge. Different colours are observed for $[\{\mathrm{Mo_3PdS_4(H_2O)_9}\}_2]^{8+}$ (purple in Hpts, on Dowex columns, and in crystals), and dark blue for $[\mathrm{Mo_3PdS_4(H_2O)_{10}}]^{4+}$, or more precisely $[\mathrm{Mo_3PdS_4(H_2O)_9Cl}]^{3+}$, on addition of as little as 0.01 M $\mathrm{Cl^-}$.

Elution of the Co containing cube from Dowex columns, with HCl or Hpts, occurs after $[\mathrm{Mo_3S_4(H_2O)_9}]^{4+}$ consistent with the presence of a double cube. EPR studies provide support for a predominance of the double cube in Hpts (and $\mathrm{HClO_4}$) solutions, and an additional species (most likely the single cube) in HCl [20]. As yet however no clearcut differences in UV–Vis spectra for the single and double cubes have been identified as observed for $\mathrm{Mo_3PdS_4}$. All other $\mathrm{Mo_3MS_4}^{4+}$ cubes, including $\mathrm{Mo_3CuS_4}^{4+}$, elute before $[\mathrm{Mo_3S_4(H_2O)_9}]^{4+}$, thus providing evidence in the case of M = Cu for the single cube $[\mathrm{Mo_3CuS_4(H_2O)_{10}}]^{4+}$. The $[\mathrm{Mo_3CuS_4(H_2O)_{10}}]^{5+}$ and $[\mathrm{W_3CuS_4(H_2O)_{10}}]^{5+}$ cubes elute after $[\mathrm{Mo_3S_4(H_2O)_9}]^{4+}$.

Rate constants for the oxidation of $[\{\mathrm{Mo_3CoS_4(H_2O)_9}\}_2]^{8+}$ with $[\mathrm{Co(dipic)_2}]^-$ (k_{Co}) and hexaaqua Fe(III) (k_{Fe}) are listed in Tables 1 and 2, respectively. As in previous studies $[\mathrm{H^+}]$ was varied. No $[\mathrm{H^+}]$-dependence is observed for the $[\mathrm{Co(dipic)_2}]^-$ reaction, and at 25 °C $k_{\mathrm{Co}} = (6.7 \pm 0.1) \times 10^3\ \mathrm{M^{-1}\ s^{-1}}$, $I = 2.00$ M ($\mathrm{LiClO_4}$). However in the case of k_{Fe} Eq. (7) applies

$$k_{\mathrm{Fe}} = k_{\mathrm{a}} + k_{\mathrm{b}}[\mathrm{H^+}]^{-1} \quad (7)$$

and for the same conditions, $k_{\mathrm{a}} = 56 \pm 2\ \mathrm{M^{-1}\ s^{-1}}$ and $k_{\mathrm{b}} = 21.0 \pm 1.6\ \mathrm{s^{-1}}$.

Values of k_{Co}, k_{a} and k_{b} for $\mathrm{Mo_3CoS_4}$ are listed alongside data for other heterometal cubes in Table 3. No $[\mathrm{H^+}]^{-1}$ dependencies are observed for any of the $[\mathrm{Co(dipic)_2}]^-$ reactions, consistent with an outer-sphere assignment. Since no acid dissociation process

Table 1
First-order rate constants, k_{obs} (25 °C), for the $[\mathrm{Co(dipic)_2}]^-$ oxidation of $[\{\mathrm{Mo_3CoS_4(H_2O)_9}\}_2]^{8+}$ (0.10 mM), showing a dependence on the concentration of oxidant but not $[\mathrm{H^+}]$, $I = 2.00$ M ($\mathrm{LiClO_4}$)

$[\mathrm{H^+}]$ (M)	10^3[Co(III)] (M)	k_{obs} ($\mathrm{s^{-1}}$)
1.80	5.0	32.5(2)
	3.75	25.4
	2.5	16.0
	1.5	10.9
	1.0	6.3(2)
1.00	5.0	34.0
	3.75	25.5
	2.5	16.4
	1.0	6.7
0.50	5.0	34.1
	2.5	16.4
	1.0	6.2

Table 2
The variation of second-order rate constants, k_{Fe} (25 °C), for the hexaaqua Fe(III) oxidation of $[\{Mo_3CoS_4(H_2O)_9\}_2]^{8+}$ (0.21–0.10 mM) with $[H^+]$, $I=2.00$ M ($LiClO_4$)

$[H^+]$ (M)	[Fe(III)] (M)	k_{Fe} (M^{-1} s^{-1})
1.80	20.0	69
	10.0	64
	5.0	68
1.40	20.0	71
	10.0	73
	5.0	70
1.00	20.0	75(2)
	20.0	75
	20.0	78
	15.0	63
	10.0	82
	5.0	74
0.70	20.0	85
	10.0	85
	5.0	88
0.50	20.0	100(2)
	10.0	102(2)
	5.0	96

has been detected for any of the cubes in the range $[H^+]=0.5$–2.0 M investigated, the k_b term observed with hexaaqua Fe(III) is assigned to the reaction of $[Fe(H_2O)_5(OH)]^{2+}$. Second-order rate constants k_b' ($=k_b/K_a$) can be obtained, where K_a is the acid dissociation constant, Eq. (8).

$$[Fe(H_2O)_6]^{3+} \rightleftharpoons [Fe(H_2O)_5(OH)]^{2+} + H^+ \qquad (8)$$

At 25 °C and $I=2.0$ M ($NaClO_4$), $K_a=1.0\times10^{-3}$ M [21]. Enhancement factors k_b'/k_a of ~10^3 [22] indicate inner- and outer-sphere assignments to k_b' and k_a, respectively.

For outer-sphere reactions logarithmic correlations of rate constants are observed for the reaction of two redox partners with a series of reagents. Thus for outer-sphere $[Cr(H_2O)_6]^{2+}$ and $[V(H_2O)_6]^{2+}$ reductions of a wide range of oxidants [23] and of Co(III) complexes [24], a linear correlation of log k_{Cr} versus log k_v has been observed, and a similar relationship holds for outer-sphere $[V(H_2O)_6]^{2+}$ and $[Ru(NH_3)_6]^{2+}$ reductions [25]. The slope of such plots is close to 1.0. Here we report a linear plot of log k_{Co} versus log k_a, Fig. 2. From a least-squares treatment this gives the relationship (9), with standard deviations given in brackets.

$$\log k_a = 0.98(0.10) \log k_{Co} - 1.40\ (0.36) \qquad (9)$$

The slope is close to 1.0. Therefore k_{Co} and k_a are assigned as outer-sphere oxidations. Surprisingly when the corresponding log k_{Co} versus log k_b plot is carried out, Fig. 3, this also gives a good linear correlation, Eq. (10).

$$\log k_b = 1.06\ (0.07) \log k_{Co} - 1.45\ (0.25) \qquad (10)$$

The latter clearly requires further discussion in view of the inner-sphere assignments made for k_b.

It is unlikely that the following processes can be rate determining for k_b in view of the behaviour observed in Eq. (10): (a) $[Fe(H_2O)_5(OH)]^{2+}$ substitution into or addition to the heterometal coordination sphere, and (b) substitution into the $[Fe(H_2O)_5(OH)]^{2+}$ coordination sphere. Instead, since k_b behaves like k_a, it is concluded that the redox driving force for reaction is rate determining. An important observation is that there is no k_b term for the Fe(III) oxidation of $[Mo_4S_4(H_2O)_{12}]^{4+}$. For this more inert $Mo(III)_4$ cube [3], substitution of $[Fe(H_2O)_5(OH)]^{2+}$ into the Mo(III) coordination sphere is too slow to be effective. A mechanism involving $[Fe(H_2O)_5(OH)]^{2+}$ substitution (or addition) to the heterometal atoms is believed to occur with the subsequent ET process rate determining.

Table 3
Summary of rate constants for the oxidation of different cubes with $[Co(dipic)_2]^-$ (k_{Co}) and hexaaqua Fe(III) as $Fe(H_2O)_6{}^{3+}$ (k_a) and $[Fe(H_2O)_5OH]^{2+}$ (k_b)

Cube complex	k_{Co} (M^{-1} s^{-1})	k_a (M^{-1} s^{-1})	k_b[a] (s^{-1})	Ref.
$[Mo_4S_4(H_2O)_{12}]^{4+}$	3.7×10^5	4.5×10^4		[6]
$[Mo_3CuS_4(H_2O)_{10}]^{4+}$	5.9×10^4	1.33×10^3	5.1×10^3	[15]
$[Mo_3CuS_4(H_2O)_{10}]^{5+}$	3.0×10^4	0.72×10^3	2.38×10^3	[15]
$[W_3CuS_4(H_2O)_{10}]^{5+}$	1.77×10^4	2.68×10^2	5.0×10^2	[16]
$[\{Mo_3CoS_4(H_2O)_9\}_2]^{8+}$	6.7×10^3	56	21	this work
$[Mo_3FeS_4(H_2O)_{10}]^{4+}$	87	4.8	4.0	[12]
$[Mo_3CrS_4(H_2O)_{12}]^{4+}$	16.3	3.9	2.3	[6]
$[Mo_3NiS_4(H_2O)_{10}]^{4+}$	0.35	5.4×10^{-3} [b]	5.4×10^{-3} [b]	[13]
$[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$	4.5×10^{-2}	[c]		[14]

[a] Second-order rate constants k_b' are obtained from k_b/K_a, where $K_a=1.0\times10^{-3}$ M^{-1}, Ref. [21].

[b] Rate constants (k_{Fe}) reported in Ref. [13] were in error by an order of magnitude.

[c] Rate constant for reaction in 2.0 M Hpts is $<2\times10^{-5}$ M^{-1} s^{-1}.

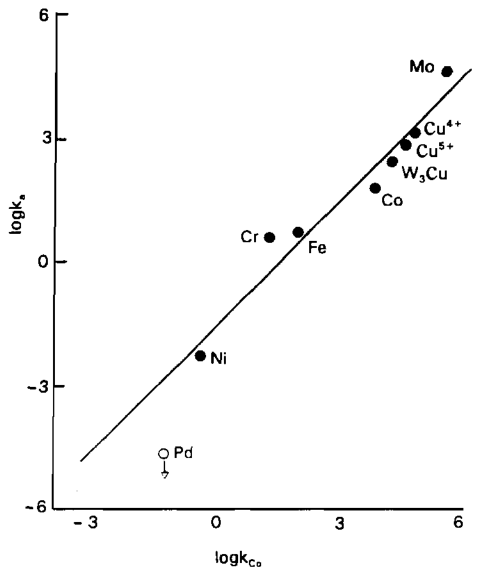

Fig. 2. Correlation of rate constants (25 °C) for the $[Co(dipic)_2]^-$ (k_{Co}) and $[Fe(H_2O)_6]^{3+}$ (k_a) oxidations of $[Mo_4S_4(H_2O)_{12}]^{4+}$ (Mo), and heterometal cubes $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ (Cr), $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ (Fe), $[\{Mo_3CoS_4(H_2O)_9\}_2]^{8+}$ (Co), $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ (Ni), $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ (Pd), $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ (Cu^{4+}), $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ (Cu^{5+}) and $[W_3CuS_4(H_2O)_{10}]^{5+}$ (W_3Cu), $I = 2.00$ M ($LiClO_4$) in all cases except for Cr, Pd and Cu^{5+}, when $I = 2.00$ M (Lipts). Solid points only were used in the least-squares fit.

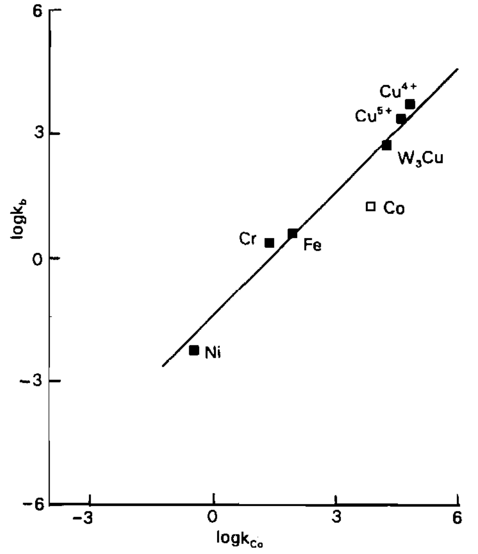

Fig. 3. Correlation of rate constants (25 °C) for the $[Co(dipic)_2]^-$ (k_{Co}) and conjugate-base $[Fe(H_2O)_5OH]^{2+}$ (k_b) oxidations of $[Mo_4S_4(H_2O)_{12}]^{4+}$ and heterometal cubes, key as for Fig. 2.

As a result the rate constants in Fig. 3 are of the same order as in Fig. 2. Bridging by H_2O is not a strong possibility in ET processes between two metal centres, and coordination of the OH^- of $[Fe(H_2O)_5(OH)]^{2+}$ to the heteroatom to give an activated complex $[Mo_3S_4MOHFe(H_2O)_5]^{6+}$ is therefore proposed for k_b.

No absorbance changes were detected for the hexa-aqua Fe(III) oxidation of $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ during an overnight period (> 15 h), and it is concluded that the rate constant k_{Fe} (or indeed k_a) has an upper limit of 2×10^{-5} M^{-1} s^{-1}. The point for $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ in Fig. 2 lies well away from the line and has not therefore been included in the least-squares treatment. The most likely explanation is the unfavourable 8+ and 3+ charge interaction, and vice versa for $[Co(dipic)_2]^-$. The point for $[\{Mo_3CoS_4(H_2O)_9\}_2]^{8+}$ has been included in the least-squares for Fig. 2, but excluded from Fig. 3. The less favourable k_b term may be due to the difficulty $[Fe(H_2O)_5(OH)]^{2+}$ has in accessing the Co heteroatom of the double cube structure to give an inner-sphere activated complex. We note that the $Mo_3CuS_4{}^{4+}$ point correlates well in both Figs. 2 and 3, thus supporting the assignment of a single cube structure. In the case of $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ the point has been made previously [6] that the rate constant k_b' may be too large for FeOH substitution into the Cr coordination sphere to occur, and in this instance substitution into the Fe(III) coordination sphere may be relevant. The reactions of Mo_3Cr, Mo_3Pd and Mo_3Cu were studied in 2.0 M pts^- rather than $ClO_4{}^-$ solutions. Previous studies suggest that rate constants may differ by factors of ~2 as a result of such changes [26].

In further work we plan to test whether corner-shared double cubes [27,28] conform to the two rate constant correlations reported in this paper.

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