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Electron transfer
120. Reductions of the cuboidal mixed-valence molybdenum/sulfur cluster, $[Mo_4S_4(H_2O)_{12}]^{5+}$

Manik C. Ghosh*, E.S. Gould*

Department of Chemistry, Kent State University, Kent, OH 44242, USA

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Abstract

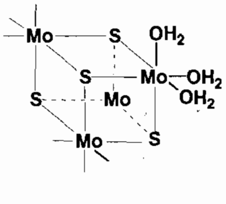
The cuboidal mixed-valence Mo/S cluster, $[Mo_4S_4(H_2O)_{12}]^{5+}$ (I), in which each of the four equivalent Mo atoms assumes a mean oxidation state of 3.25, is reduced to the isostructural Mo(III) tetramer, $[Mo_4S_4(H_2O)_{12}]^{4+}$, by equimolar quantities of Ti(III), Cr(II), Eu(II), V(II), $Ru(NH_3)_6^{2+}$ and Co^{II}(sepulchrate), as well as by radicals derived from flavin-like heterocycles and by dihydro derivatives of these heterocycles. Reaction rates are independent of H^+ (within the range 0.5–2.0 M H^+) for the metal center reductants and for the radicals, but feature prominent $[H^+]^{-1}$-proportional terms for the dihydro compounds. All reactions appear to be outer-sphere. The deprotonated form of the dihydroriboflavin reacts 600 times more rapidly than the corresponding radical, a selectivity similar to that previously observed with an array of Co(III) oxidants. Specific rates for reductions by the metal-ion centers, in conjunction with the treatment of Marcus, lead to a self-exchange rate $10^{3.8 \pm 1.6}$ M^{-1} s^{-1} for the couple $[Mo_4S_4]^{5+/4+}$. The latter lies very close to that recorded for the truncated cuboidal trinuclear OH-bridged system, $Mo^{IV,III,III}/(Mo^{III})_3$. It is possible that the observed correspondence in rates reflects a similarity in net valence change in the absence of major alterations in bond connectivities or in molecular geometry.

Keywords: Kinetics and mechanism; Electron transfer; Molybdenum complexes; Sulfur complexes; Mixed valence complexes; Cluster complexes

1. Introduction

Polynuclear transition metal ions held together by μ-(–S–) linkages have received much attention as analogs of the active sites in several metalloenzymes [1]. Although particular emphasis has been on cubane-type Fe_4S_4 and $MoFe_3S_4$ clusters as synthetic models of such sites in ferredoxins [2] and the MoFe protein in nitrogenases [3], aqua complexes of such centers apparently have not yet been described, and exploration of the aqueous chemistry of water-soluble Fe_4S_4 complexes has been limited by the ease with which these solutions undergo decomposition [4,5].

However, aqua derivatives of the closely related Mo_4S_4 cluster have been recently prepared and found to exhibit considerable stability in aqueous acid [6]. Probably the most notable species of the latter type is the pentapositive cation, $[Mo_4S_4(H_2O)_{12}]^{5+}$ (I), which persists for weeks in 2 M H^+ if protected from oxygen. In this complex, each of the four equivalent Mo atoms has assumed a mean oxidation state of 3.25.



$[Mo_4S_4(H_2O)_{12}]^{5+}$

I

In the present study we have examined the reactions of this mixed-valence cluster with a variety of metal ion centers and non-metallic and dihydro derivatives of several flavin-like heterocycles. These aromatics are included because of the importance of flavins as oxidation coenzymes, reflecting their ability to participate in both one- and two-unit oxidative transactions and, hence, their capacity to mediate between electron transfer processes and the even-electron changes charac-

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*Corresponding authors.

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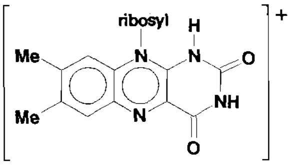
terizing metabolic conversions [7]. The most familiar of these is riboflavin (**II**), but both *N*-methylphenazinium (**III**) and 1-deazariboflavin (**IV**), despite structural alterations, retain the same pyrazine ring system associated with redox versatility. (The indicated protonated forms of **II** and **IV** predominate in the acidic media used.)



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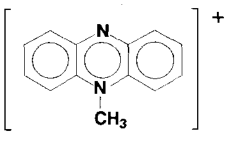

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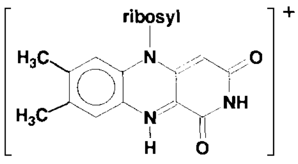

IV

2. Experimental

2.1. Materials

Sodium di-μ-sulfido-bis[(cysteinato)oxomolybdate(V)] tetrahydrate, $Na_2[Mo_2O_2(cys)_2]\cdot 4H_2O$, was prepared from sodium molybdate as described by Shibahara et al. [8] and characterized by its electronic spectrum. After recrystallization, it was converted to the mixed-valence cluster, $[Mo_4S_4(H_2O)_{12}]^{5+}$, using a modification of the method of these authors, by dissolving 1.13 g of the tetrahydrate in 50 ml of 1 M HCl, cooling to 0 °C, and then slowly adding 1.38 g of sodium borohydride with continuous stirring. The color changed from orange–red to brown. After slow addition of 2.5 ml of conc. HCl, the solution was heated on a water bath for 30 min while sparged with air. The resulting red preparation was cooled to 25 °C and then filtered. The filtrate was subjected to column chromatography using Sephadex G-10 (column 25 cm long, diameter 2.5 cm). Elution with 1 M HCl yielded first an orange fraction (which was discarded), then the desired green cation, $[Mo_4S_4(H_2O)_{12}]^{5+}$ (λ_{max} 642 nm), which was, however, contaminated with the green trinuclear cation, $[Mo_3O_2S_2(aq)]^{4+}$ (λ_{max} 580 nm). Slower moving fractions were rejected. Further fractionation of the green eluate was carried out by diluting fivefold with water and absorbing on cation exchange resin (Dowex 50W-X2-200). Washing the resin with 1 M HCl removed the tetrapositive Mo_3 cation, after which the column was washed with 1 M $HClO_4$ or with 0.5 M*p*-toluenesulfonic acid (HPTS) to remove Cl^-. The desired mixed-valence cation **I** was then eluted, either with 4 M $HClO_4$ or 2 M HPTS, under N_2; λ_{max} 643 ($HClO_4$), 642 (HPTS) nm; reported [8b] 643. The concentration of $[Mo_4S_4(H_2O)_{12}]^{5+}$ was calculated from the reported [7,8] molar absorbances (ϵ^{643}_{max} 445 M^{-1} cm^{-1} per Mo_4). Reduction of this complex with zinc amalgam in 1 M HPTS or 1 M $HClO_4$ under N_2 yielded a golden-yellow species, the spectrum of which ($\epsilon^{375}_{max} = 1140$ M^{-1} cm^{-1}) corresponds to that of the reduction product, $[Mo_4S_4(H_2O)_{12}]^{4+}$ ($\epsilon^{378}_{max} = 1100$) prepared electrolytically from the mixed-valence complex **I** by Li et al. [6f].

Solutions of Cr^{2+}, V^{2+} and Eu^{2+} were prepared by reduction of upper oxidation states with zinc amalgam [9], and $Ru(NH_3)_6{}^{2+}$ was prepared by reducing $Ru(NH_3)_6{}^{3+}$ with Eu^{2+} under argon [9]. Solutions of Ti(III) in HPTS were prepared as described by Martin and Gould [10]. Solutions of the riboflavin radical [11a] and dihydroriboflavin [11b] were prepared as described by Singh et al. The *N*-methylphenazine radical was prepared by adding V^{2+} to a fivefold excess of phenazine methosulfate in 1 M $HClO_4$, whereas the preparations of *N*-methyldihydrophenazine [11c] and dihydro-1-deazariboflavin [11c] required slightly more than 2 equiv. of V^{2+} per mole of parent heterocycle, as indicated by complete disappearance of the color of the radical intermediate. Cobalt(II) sepulchrate and $Ru(NH_3)_6(triflate)_3$ were prepared as described by Ghosh and Gould [12], and solutions of Cu^+ as described by Shaw and Espenson [13].

2.2. Stoichiometric studies

Stoichiometries of the reactions of mixed valence complex $[Mo_4S_4]^{5+}$ with several metal-center reductants were determined spectrophotometrically at 643 nm. Measured deficient quantities of the reductant were added to a known excess of the molybdenum complex in 1.0 M $HClO_4$. After net reaction had ceased (generally 15 s), decreases in absorbance were measured. These changes were then compared to those resulting from an excess of the reductant. Results are summarized in Table 1.

2.3. Kinetic measurements

Rates of reaction of $[Mo_4S_4]^{5+}$ with metal-center reductants were estimated from absorbance changes at 643 nm (λ_{max} for the oxidant), whereas reductions by heterocyclic radicals or dihydro derivatives were monitored at λ_{max} for the radicals. Except for the (relatively slow) reductions with Ti(III), which were observed on a Beckman 5260 spectrophotometer, reactions were followed using a Durrum-Gibson stopped-flow spectrophotometer interfaced with an OLIS computer sys-

Table 1. Stoichiometries of the reductions of $[Mo_4S_4(H_2O)_{12}]^{5+}$ [a]

Reductant	$[Mo_4S_4{}^{5+}]$ $(M \times 10^4)$	$10^4[Red]$	$\Delta[Mo_4S_4{}^{5+}]$ $(M \times 10^4)$	$\Delta[Mo_4S_4{}^{5+}]/\Delta[Red]$
Eu^{2+}	4.0	1.0	0.88	0.88
		2.0	1.81	0.90
		3.0	2.74	0.91
		4.0	3.7	0.93
$Ru(NH_3)_6{}^{2+}$	4.0	1.0	1.09	1.09
		2.0	1.95	0.98
		3.0	2.64	0.88
$Co^{II}(sep)$	4.0	1.0	1.03	1.03
		2.0	1.96	0.98
		3.0	2.81	0.94
Ti(III)[b]	3.6	1.0	0.98	0.98
		2.0	1.96	0.98
		3.0	2.84	0.95

[a] Reactions in 1.0 M $HClO_4$ at 25 °C; $\lambda = 643$ nm; waiting period 15 s.

[b] Reaction in 1.0 M HPTS; waiting period 10 min.

tem. Ionic strength was maintained at 2.0 M by addition of $HClO_4/NaClO_4$, $HPTS/Na^+PTS^-$ or triflic acid/Na^+-triflate$^-$. Most experiments were carried out under pseudo-first-order conditions with no more than 10% of the reagent in excess consumed during a run, but reductions with $Ru(NH_3)_6{}^{2+}$ and Co^{II}(sepulchrate) were so rapid that meaningful profiles could be obtained only under second-order conditions at the lowest observable concentration levels [$(5–10) \times 10^{-5}$ M in each reagent]. Rate constants, both for exponential and second-order curves, were obtained by OLIS programs. Pseudo-first-order rate constants greater than 50 s^{-1} were adjusted upward to accommodate the mixing rate associated with our stopped-flow instrument as described by Dickson and Margerum [14]. Values obtained from replicate experiments agreed to within 3% for exponential runs and to within 9% for runs under second-order conditions.

The reaction of the dihydro derivative of 1-deazariboflavin, (2×10^{-5} M) with 1×10^{-4} M $Mo_4S_4{}^{5+}$, when monitored at 665 nm, featured a very rapid rise in absorbance ($t_{1/2} \sim 0.5$ ms), reflecting the generation of the corresponding radical ($\epsilon = 2 \times 10^3$), followed by a much slower decrease, resulting from further oxidation of the radical to the parent heterocycle (**IV**). Rates for the second step could be measured, but only an upper limit for the first could be estimated. At 341 nm (where both the dihydro compound and the radical absorb significantly) a very fast drop in absorbance was followed by a much slower decrease, with the latter exhibiting the same $t_{1/2}$ as that noted at 665 nm.

2.4. Additional observations

Neither Sn^{2+} (0.025 M) nor V^{3+} (0.05 M) reacts at a measurable rate with $[Mo_4S_4]^{5+}$. Reaction with the *N*-methylphenazinium radical is too slow to compete with decomposition of this radical.

The reaction of $[Mo_4S_4]^{5+}$ with Cu^+ is too rapid ($t_{1/2} < 1$ s at $[Cu^I] = 10^{-3}$ M) to measure by conventional mixing. If this oxidation is taken to be more than 90% complete within a mixing time of 6 s in the presence of 10^{-3} M Cu^+, we may estimate a lower limit for *k* of 3×10^2 M^{-1} s^{-1}. Since $CuClO_4$ solutions undergo rapid disproportionation to Cu^{2+} and elemental copper upon touching metal surfaces, this reaction could not be examined using our stopped-flow equipment in which reactant solutions come into contact with stainless steel valve parts.

When $[Mo_4S_4(H_2O)_{12}]^{5+}$ solutions were reduced with a 20% excess of Eu^{2+} or $Ru(NH_3)_6{}^{2+}$ in 2 M $HClO_4$, the spectrum of the resulting solution ($\epsilon_{max}^{375} = 1120$ per Mo_4) corresponded closely to that of the $[Mo_4S_4]^{4+}$ cation prepared here by reduction, using Zn/Hg, of the mixed valence cation and also generated cathodically by Li et al. [6f].

3. Results and discussion

The approach to 1:1 stoichiometry observed for the reactions of $[Mo_4S_4(H_2O)_{12}]^{5+}$ with metal-center reductants (Table 1), in conjunction with the spectrum of the reduction product, indicates that we are dealing with single electron transactions, which may be represented schematically as Eq. (1).

$$[Mo_4S_4]^{5+} + M^{II} \longrightarrow [Mo_4S_4]^{4+} + M^{III} \tag{1}$$

The slight departures from 1:1 stoichiometry observed for reductions by Eu(II) probably reflect partial consumption of this reductant by traces of O_2 during transfer.

The colored radicals formed from reduction of the protonated forms of the flavin-related species, riboflavin (**II**), *N*-methylphenazine (**III**) and 1-deazariboflavin (**IV**) also function as 1*e* reagents, for they are readily oxidized, under the conditions used, to their parent cations [11]. Moreover, the dihydro derivatives of these heterocycles, although generated via $2e^-$ reductions, have been shown to react with $1e^-$ oxidants in single-electron steps, i.e. through their respective radicals [11].

Representative kinetic data appear in Table 2. Reductions by Eu^{2+} are seen to be independent of $[H^+]$ within the (relatively narrow) acidity range examined, but reductions by both dihydro species are accelerated by increases in pH. Rates with *N*-methyldihydrophenazine are very nearly proportional to $[H^+]^{-1}$, whereas oxidations of dihydroriboflavin conform to rate law (2).

$$\text{rate} = [Mo_4S_4{}^{5+}][Red](k_0 + k'/[H^+]) \tag{2}$$

Treatment of data for the latter system yields $k_0 = (6.3 \pm 0.3) \times 10^6$ M^{-1} s^{-1} and $k' = (2.0 \pm 0.4) \times 10^6$

Table 2
Representative kinetic data for reductions of $[Mo_4S_4(H_2O)_{12}]^{5+}$ (25 °C, $\mu = 2.0$ M)

Reductions with Eu(II)[a]			Reductions with dihydroriboflavin[b]			Reductions with *N*-methyldihydrophenazine[c]		
[Red] ($M \times 10^3$)	$[H^+]$	k (s^{-1})	[Ox] ($M \times 10^5$)	$[H^+]$	$10^{-2}k$ (s^{-1})	[Ox] ($M \times 10^5$)	$[H^+]$	$10^{-2}k$ (s^{-1})
1.00	2.0	3.6	2.50	2.0	1.74 (1.82)	4.5	2.0	0.84 (0.92)
2.0	2.0	7.8	3.75	2.0	2.8 (2.7)	5.5	2.0	1.10 (1.12)
3.5	2.0	12.4	5.0	2.0	3.9 (3.6)	7.2	2.0	1.33 (1.47)
5.0	2.0	19.6	6.0	2.0	4.6 (4.4)	9.0	2.0	1.80 (1.83)
5.0	1.50	19.1	2.50	1.50	1.82 (1.90)	4.5	1.5	1.13 (1.22)
5.0	1.10	19.0	2.50	1.20	1.88 (1.98)	4.5	1.0	1.93 (1.83)
			2.50	0.90	2.1 (2.1)	4.5	0.75	2.8 (2.4)
			2.50	0.60	2.5 (2.4)	4.5	0.60	3.9 (3.1)

[a] Reactions monitored at 643 nm; $[Mo_4S_4^{5+}] = 1.15 \times 10^{-5}$ M throughout.
[b] 495 nm; $[Red] = (5.0–8.0) \times 10^{-6}$ M.
[c] 443 nm; $[Red] = 9.0 \times 10^{-6}$ M throughout.
[d] Parenthetical values calculated using rate laws and parameters in Table 3.

s^{-1} (25 °C, $\mu = 2.0$ M). Rates calculated using Eq. (2) are compared to observed values in Table 2.

Prominent inverse-acid terms are found to be characteristic of reductions of metal-center oxidants by substituted dihydropyrazines of the type considered here [11c]. Such terms are best taken to reflect predominant reaction through the deprotonated form of the reductant. From earlier studies dealing with the reductions of a variety of Co(III) complexes [11b,c] (which react exclusively through deprotonated paths), K_A values of 0.13 and 0.10 M (25 °C, $\mu = 1.30$ M) have been estimated for dihydroriboflavin and *N*-methyldihydrophenazine. These lie well below the range of acidities examined in the present work, and kinetic saturation effects due to substantial conversion to the deprotonated reductant are therefore not detectable. Note that inverse-acid dependencies are generally not observed for reductions by the corresponding heterocyclic radicals [11a,c].

Rate laws and kinetic parameters pertaining to reactions of the mixed-valence cation, $Mo_4S_4^{5+}$, with the reductants at hand are summarized in Table 3. The value observed here for reduction by Cr^{2+} in perchlorate media is in agreement with that reported by Ooi et al. [6e], but this reaction is seen to be accelerated by a factor of 2.5 on being transferred to *p*-toluenesulfonate solutions. This modest enhancement may be related to the greater degree of association by the organic supporting anion toward the tetrapositive oxidant, a difference which is in accord with the reported ion-exchange elution behavior of the cation in the presence of solutions containing these counterions [6e].

The substitution-inert character of two of the metal-center reductants, $Ru(NH_3)_6^{2+}$ and Co^{II}(sepulchrate), dictate reaction via outer-sphere paths. A similar conclusion applies in the present case to reduction by V^{2+}, which exhibits a rate far in excess of the limit (near 10^2 M^{-1} s^{-1}) on inner-sphere reductions imposed by slow substitution on this center [15]. Moreover the pattern of relative reactivities observed here, $k_V : k_{Eu} : k_{Cr} = 40/7/1$, corresponds closely to that found for this trio of dipositive reductants [9] toward oxidants devoid of bridging groups, pointing to outer-sphere routes for Cr(II) and Eu(II) as well, an assignment which is consistent also with the high rate ratio ($>10^4$) found for reductions with $Ru(NH_3)_6^{2+}$ and Cr^{2+}.

In earlier work, radicals and dihydro species obtained from $1e^-$ and $2e^-$ reductions of flavin-related heterocycles were allowed to react with a variety of metal-center oxidants [11]. These studies supported the view that species of both types act as outer-sphere reductants, even when the available oxidant features one or more ligands that may serve as unusually effective bridging groups in reactions between metal ion centers. Given similar conditions, reductions with dihydroriboflavin, an even-electron molecule, proceed 10^2–10^3 times as rapidly as those by the related radical. Bimolecular rate constants for reductions by the deprotonated dihydro compounds in Table 3 may be calculated by dividing the inverse-$[H^+]$ parameter k' by the acidity constant (K_A) for the reductant. The resulting quotient for dihydroriboflavin, 1.5×10^7 M^{-1} s^{-1} (6×10^2 $k_{radical}$), fits the earlier pattern, and it is likely that the same mechanistic picture applies here as well.

Ooi et al. [6e] have taken the observed rate constant for the $Mo_4S_4^{5+}$–V^{2+} reaction, in conjunction with the model of Marcus [16], to estimate a self-exchange rate for the couple $[Mo_4S_4(H_2O)_{12}]^{5+/4+}$. Data from the present study allow a reevaluation of this parameter applicable to a wider variety of systems. Moreover, the high charge of the oxidant and the range of ΔG_0 values for our reactions justify a more detailed treatment. We have used Eq. (3), in which the rate constant, k_{12}, of

Table 3
Rate laws and kinetic parameters for reductions of $[Mo_4S_4(H_2O)_{12}]^{5+}$ [a]

Reductant (Red)	λ (nm)	Rate law	Parameters[b]
Ti(III)	643	$k[Ox][Red]$	$k=49\pm5$ [c]
Cr(II)	643	$k[Ox][Red]$	$k=(6.0\pm0.3)\times10^2$
			6.1×10^2 [d]
			$k=(1.50\pm0.05)\times10^3$ [c]
Eu(II)	643	$k[Ox][Red]$	$k=(3.7\pm0.2)\times10^3$
V(II)	643	$k[Ox][Red]$	$k=2.5\times10^4$ [d]
$Ru(NH_3)_6^{2+}$	643	$k[Ox][Red]$	$k=(9.5\pm0.9)\times10^6$ [e]
Co^{II}(sepulchrate)	643	$k[Ox][Red]$	$k=(6.6\pm0.4)\times10^6$
Riboflavin radical	495	$k[Ox][Red]$	$k=(2.4\pm0.4)\times10^4$
1-Deazariboflavin radical	341	$k[Ox][Red]$	$k=(1.07\pm0.05)\times10^5$
	665		$k=(1.18\pm0.07)\times10^5$
Dihydro-1-deazariboflavin	665		$k\geqslant6\times10^7$ in 2 M $HClO_4$
Dihydroriboflavin	495	$[Ox][Red](k_0+k'/[H^+])$	$k_0=(6.3\pm0.3)\times10^6$
			$k'=(2.0\pm0.4)\times10^6\ s^{-1}$
N-Methyldihydrophenazine	443	$k'[Ox][Red][H^+]^{-1}$	$k'=(4.1\pm0.2)\times10^6\ s^{-1}$

[a] Reactions were carried out at 25 °C; $\mu=2.0$ M (ClO_4^- medium) unless otherwise indicated.
[b] Rate constants are in $M^{-1}\ s^{-1}$ unless otherwise specified.
[c] *p*-Toluenesulfonate medium.
[d] Ref. [6e].
[e] $\mu=1.50$ M (ClO_4^- + triflate).

an outer-sphere electron transfer reaction is taken as the sum of three terms [17]

$$\ln k_{12}=1/2\left[\ln(k_{11}k_{22}K_{12})+\frac{[\ln K_{12}+(w_{12}-w_{21})/RT]^2}{4\left[\ln\frac{k_{11}k_{22}}{Z^2}+\frac{(w_{11}+w_{22})}{RT}\right]}\right]+\frac{w_{11}+w_{22}-w_{12}-w_{21}}{2RT} \tag{3}$$

where k_{11} and k_{22} are the self-exchange rates for the oxidant and reductant, K_{12} is the equilibrium constant for the redox reaction, Z is the collision frequency, $10^{11}\ M^{-1}\ s^{-1}$, and the w are electrostatic work contributions from the reactants, the products, and the two self-exchanging systems, terms which were neglected by Ooi et al. [6e]. Each w term is, in turn, calculated by Eq. (4)

$$w_{cd}=4.23\ z_cz_d/a_{cd}\ (1+0.33a_{cd}\mu^{1/2}) \tag{4}$$

where z are the ionic charges on interacting species c and d, μ is the ionic strength of the medium, and a_{cd} is the distance of closest approach, as estimated from the presumed geometry of the encounter and reported atomic and ionic radii.

Among the reductants to be considered are the radical and the dihydro derivative formed by reductions of riboflavin. Since electron self-exchange rates pertaining to oxidations of these species appear not to have been documented, these rates are here estimated from the reported [11a] rate constants (8×10^4 and $4\times10^4\ M^{-1}\ s^{-1}$; 21 °C, $\mu=0.2$ M) for generation of these reductants via the necessarily outer-sphere [15a] reactions of V^{2+} (Table 4).

Estimated terms contributing to the reductions of $[Mo_4S_4(H_2O)_{12}]^{5+}$ are listed in Table 5. Experimental values of the observed rate constants, k_{12}, in combination with Eq. (3), lead to a calculated self exchange rate of $10^{3.8\pm1.6}\ M^{-1}\ s^{-1}$ for $[Mo_4S_4]^{5+/4+}$. The indicated deviation, which arises mainly from the unusually high rate constant for $Ru(NH_3)_6^{2+}$, is substantial but is comparable to those associated with other treatments of this type [24]. Considering this uncertainty, agreement with the value recorded by Ooi et al. (log $k_{11}=10^{2.9}$ [6e]) may be considered satisfactory.

The calculated self-exchange rate lies remarkably close to that reported for the system $Mo^{IV,III,III}/(Mo^{III})_3$, ($10^{4.2\pm0.6}\ M^{-1}\ s^{-1}$), estimated from oxidation studies involving the $(Mo^{III})_3$ cluster [25]. Both systems include a polynuclear oxidant in which molybdenum has assumed a net oxidation state between 3+ and 4+ (i.e. both oxidants are $1e^-$ removed from clusters containing only Mo^{III}), and both are, in effect, derived from Mo–chalcogen cubes. The Mo_3 cluster, however, is an incomplete cube (one metal atom missing) and, in addition, features μ-OH, rather than μ-S–, bridges. The high rate for the Mo_3 system was taken as evidence that major changes in bond connectivity or molecular geometry were not associated with the act of electron transfer, a condition which is almost certainly fulfilled

Table 4
Estimated electron self-exchange rates for systems derived from riboflavin (RbF); $RbFH^+/RbFH^{\cdot}$ and $RbFH_2^{\cdot+}/RbFH_2$ (25 °C, $\mu = 2.0$ M)[a]

Oxidant (Ox)	$E°_{Ox}$ (V)	log K_{12}[b]	log w_{12}[c]	log f_{12}[d]	k_{12}[e]	log k_{11}[f]
$RbFH^+$	0.22[g]	8.1	0.24	−0.94	2.2×10^5	5.2
$RbFH_2^{\cdot+}$	0.15[g]	6.9	0.24	−0.61	1.1×10^5	5.4

[a] Reductant in both cases was V^{2+}(aq), $E° = 0.255$ V; log $k_{22} = -2.0$ (Ref. [17]).
[b] log K_{12} for the cross reaction, evaluated as $(E°_{Ox} - E°_{Red})/0.059$.
[c] Sum of electrostatic work terms, evaluated from Eq. (4) in text.
[d] Second term in Eq. (3)/2.3.
[e] Values obtained by adjustment of reported rates (Ref. [11a]) to 25 °C and $\mu = 2.0$. See, for example, Ref. [18].
[f] Self-exchange rates for riboflavin-related systems, evaluated from Eq. (3) in text.
[g] Ref. [11a].

Table 5
Calculated self-exchange rates and contributing parameters for reductions of $[Mo_4S_4(H_2O)_{12}]^{5+}$ (25 °C, $\mu = 2.0$ M)

Reductant (Red)	$E°_{Red}$ (V)	log k_{22}[a]	log K_{12}[a]	log w_{12}[a]	log f_{12}[a]	k_{12} (M^{-1} s^{-1})	log k_{11}[b]
Eu(II)	−0.38[c]	−4.5[d]	10.04	0.23	−1.13	3.7×10^3	2.3
Ti(III)	0.10[c]	−2.0[e]	1.87	0.056	−0.04	45	2.5
V(II)	−0.255[c]	−2.0[e]	7.92	0.25	−0.87	2.5×10^4[k]	3.3
Co^{II}(sep)	−0.30[f]	0.71[g]	8.70	0.47	−1.31	6.6×10^6	4.6
Cr(II)	−0.40[e]	< −4.7[e]	10.40	0.25	⩾ −1.13	6.0×10^2	> 0.5
$Ru(NH_3)_6^{2+}$	0.067[h]	4.30[d]	2.44	0.44	−0.14	9.5×10^6	6.5
$RbFH^{\cdot}$	0.22[i]	5.2[j]	−0.17	0.97	−0.02	2.4×10^4	2.0
$RbFH_2$	0.15[i]	5.4[j]	1.04	0.98	−0.01	6.3×10^6	5.2

[a] Parameters are defined in Table 4 and in the text. $E°_{Ox} = 0.21$ V (Ref. [6e]).
[b] Self-exchange rate for $[Mo_4S_4(H_2O)_{12}]^{5+/4+}$, evaluated from Eq. (3) in text.
[c] Ref. [19].
[d] Ref. [20].
[e] Ref. [17].
[f] Ref. [21].
[g] Ref. [22].
[h] Ref. [23].
[i] Ref. [11a].
[j] Table 4.
[k] Ref. [6e].

by the present Mo_4 couple. The marked similarity in self-exchange rates for the two systems appears to add credence to this view.

The non-utilization of inner-sphere routes in reduction of $Mo_4S_4^{5+}$ is not unexpected. Sulfur atoms bound to two electron-withdrawing positive metal centers, in contrast to those bound to just one [26], should be much less effective redox bridges, and Toppen and Linck [27] have shown that metal-bound aqua ligands (as opposed to hydroxo groups) do not partake in bridging. At greater pHs, where partial deprotonation of peripheral H_2O molecules will occur, an inner-sphere contribution may enter the picture, but whether it could be detected in competition with the increasingly pronounced decomposition of the oxidant [6e] is doubtful.

The reduction by Cu^+ in this series ($k > 3\times10^2$ M^{-1} s^{-1}) may be expectional in this respect, for the estimated lower limit is more than 10^2 time the rate calculated for an outer-sphere transfer from this d^{10} center ($E^0 = 0.15$ V, log $k_{Cu(I,II)} = -5.0$ [17]). Some bridging action involving this unusually soft reductant and the μ-S group is conceivable.

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