Preparation and Redox Properties of the Cuboidal Molybdenum(III) Aqua Ion $[Mo_4S_4(H_2O)_{12}]^{4+}$†

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A procedure for the electrochemical preparation of the orange cuboidal Mo^{III} aqua ion $[Mo_4S_4(H_2O)_{12}]^{4+}$ (peak 378 nm; ε = 1 100 M^{-1} cm^{-1} per Mo_4) from $[Mo_4S_4(H_2O)_{12}]^{5+}$ (reduction potential 210 mV) is described. The product is air sensitive and at 25 °C 1 mM solutions are oxidised by O_2 to $Mo_4S_4^{5+}$ within 5 min. With ClO_4^- (2 M $HClO_4$) there is a slow conversion of the aqua ion $Mo_4S_4^{4+}$ to $Mo_4S_4^{5+}$, $t_{\frac{1}{2}}$ *ca.* 12 h at 25 °C. Kinetic studies on the 1 : 1 reductions of seven Co^{III} complexes have been carried out at 25 °C, I = 2.00 M ($LiClO_4$), and are independent of $[H^+]$ in the range 1.0—1.8 M. From linear log–log correlations of rate constants with those for the corresponding $[V(H_2O)_6]^{2+}$ and $[Ru(NH_3)_6]^{2+}$ reductions, it is concluded that the reactions with $[Co^{III}(NH_3)_5X]^{n+}$ (X = H_2O, Cl^-, Br^-, or I^-) as well as $[Co(bipy)_3]^{3+}$ are outer sphere. The rate constant (0.27 s^{-1}) for $[Co(NH_3)_5(O_2CCH_3)]^{2+}$ does not similarly correlate, and this reaction is believed to be inner sphere. The reaction with $[Co(NH_3)_5F]^{2+}$ may also be in some part inner sphere. From the rate constant (460 M^{-1} s^{-1}) with $[Co(bipy)_3]^{3+}$ (370 mV) as oxidant, a self-exchange rate constant for $Mo_4S_4^{4+/5+}$ of 21 M^{-1} s^{-1} is obtained using the Marcus equations.

The preparation of the green cuboidal mixed-valence (average oxidation state +3.25) aqua ion, core structure $Mo_4S_4^{5+}$, by reduction of the di-μ-sulphido Mo^V dimer has been described,[1] and a crystallographic study of $Ca_3[Mo_4S_4(edta)_2]_2 \cdot 28H_2O$ (edta = ethylenediaminetetra-acetate) reported.[2] The aqua ion is remarkably stable in $HClO_4$ over the range $[H^+]$ = 0.01—4.0 M, and in 1 M $HClO_4$ decomposes only slowly in air, $t_{\frac{1}{2}}$ *ca.* 4 d at 50 °C.[3] to give the green (incomplete cuboidal) Mo^{IV} aqua ion, $Mo_3S_4^{4+}$.[1,4–6] Decomposition is somewhat faster in 1 M HCl, with $t_{\frac{1}{2}}$ *ca.* 9.5 h at 50 °C.[3] From cyclic voltammetry we have previously determined a reduction potential of 210 mV‡ for the one-electron reduction to $Mo_4S_4^{4+}$.[3] Here we describe a procedure for the preparation and quantitative solution studies on the orange cuboidal Mo^{III} aqua ion. A crystal structure of the edta complex, $Mg_2[Mo_4S_4(edta)_2] \cdot 22H_2O$, prepared by one-equivalent reduction of $[Mo_4S_4(edta)_2]^{3-}$, has been described,[7] and is the basis for the formulation of the aqua ion as $[Mo_4S_4(H_2O)_{12}]^{4+}$.

Experimental

Oxidants.—The cobalt(III) complexes $[Co(NH_3)_5(O_2CCH_3)]^{2+}$, $[Co(NH_3)_5(H_2O)]^{3+}$, $[Co(NH_3)_5F]^{2+}$, $[Co(NH_3)_5Cl]^{2+}$, $[Co(NH_3)_5Br]^{2+}$, $[Co(NH_3)_5I]^{2+}$, and $[Co(bipy)_3]^{3+}$ (bipy = 2,2′-bipyridine) were prepared by procedures described to give u.v.–visible absorbance spectra (±3%) as reported previously,[8–15] Table 1. Perchlorate salts were obtained by addition of $HClO_4$ to concentrated (acidic) solutions.

Other Reagents.—Lithium perchlorate, $LiClO_4 \cdot 3H_2O$ (Aldrich), was recrystallised twice from water. Perchloric acid (BDH, AnalaR) and sodium thiocyanate (BDH, AnalaR) were used as supplied.

Hexa-ammineruthenium(III) chloride, $[Ru(NH_3)_6]Cl_3$ (Johnson Matthey) (2.5 mM), in 0.010 M HCl, was reduced by passing down a column (25 × 1.5 cm) of amalgamated zinc shot under rigorously air-free conditions (Ar gas). Solutions were standardised using $[(NH_3)_5CoO_2Co(NH_3)_5]^{5+}$ (peak 670 nm; ε = 890 M^{-1} cm^{-1}), which behaves as a 1 : 1 oxidant.[16]

Table 1. Details of U.v.–visible spectra* of cobalt(III) complexes

Complex	$\lambda_{max.}$/nm	ε/$M^{-1}cm^{-1}$	$\lambda_{max.}$/nm	ε/$M^{-1}cm^{-1}$
$[Co(NH_3)_5(O_2CCH_3)]^{2+}$	352	59	502	75
$[Co(NH_3)_5(H_2O)]^{3+}$	345	44	492	47
$[Co(NH_3)_5F]^{2+}$	352	38	511	45
$[Co(NH_3)_5Cl]^{2+}$	362	45	530	47.3
$[Co(NH_3)_5Br]^{2+}$			551	53
$[Co(NH_3)_5I]^{2+}$	388	2 700	580	79
$[Co(bipy)_3]^{3+}$			448	67.9

* See *e.g.* refs. 8—15.

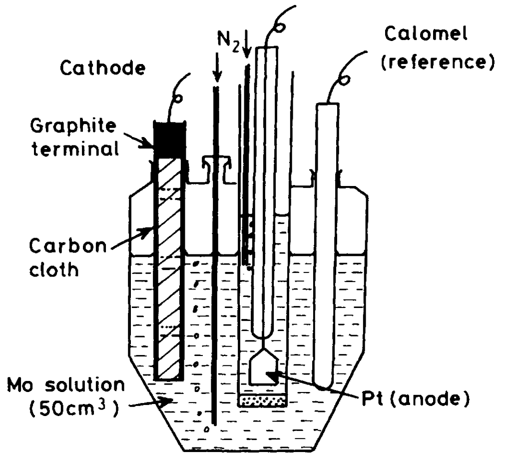

Figure 1. Diagram of electrochemical cell used for the preparation of $[Mo_4S_4(H_2O)_{12}]^{4+}$

Preparation of $Mo_4S_4^{4+}$.—A solution of $Mo_4S_4^{5+}$ (50 cm^3, 1.2 mM)[1] in 1 M *p*-toluenesulphonic acid (Hpts; Sigma Chemicals) was reduced under N_2 at a carbon cloth (RVG 1000; Le Carbonne, Brighton) electrode, at a potential of −120 mV *vs.* s.c.e. for 2 h using the glass cell as in Figure 1. The cathode

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† *Non-S.I. unit employed:* M = mol dm^{-3}.

‡ All reduction potentials quoted are against the normal hydrogen electrode.

consisted of a single layer of carbon cloth wrapped around a glass rod and tied in position using Teflon tape. Electrical contact at the upper end was made by attaching (with epoxide resin) a carbon rod to the glass rod. The carbon cloth covered both these sections and fitted tightly into the glass entry. After reduction was complete the orange solution of $Mo_4S_4^{4+}$ was millipore filtered (8 μm pore size), to remove any small carbon particles, diluted four times with O_2-free H_2O, and loaded onto a short Dowex 50W-X2 cation-exchange column (3 × 1 cm) under rigorous O_2-free conditions. The column was washed with 0.5 M $HClO_4$ (50 cm^3) to remove any pts^-, and the $Mo_4S_4^{4+}$ then eluted (without standing) with 4 M $HClO_4$, and collected in a vessel cooled in ice. When all the $Mo_4S_4^{4+}$ had been eluted the stock was diluted to 2 M $HClO_4$. All these procedures were under O_2-free conditions (N_2 gas). Yields of $Mo_4S_4^{4+}$ were at best 85%. Stock solutions were typically 1.5 mM $Mo_4S_4^{4+}$ in 2 M $HClO_4$. These were stored in ice and used the same day. Decomposition was *ca.* 5% over 8 h.

U.v.–Visible Spectrum.—The spectrum of $Mo_4S_4^{4+}$, Figure 2, peak at 378 nm (ε = 1 100 $M^{-1}cm^{-1}$ per Mo_4), was quantified with reference to the known spectrum of $Mo_4S_4^{5+}$,[1] which is the product generated on air oxidation. It should be noted that $Mo_4S_4^{4+}$ unlike $Mo_4S_4^{5+}$ has no absorbance in the near-i.r. range 800—1 300 nm.

Reaction with O_2.—A sample of $Mo_4S_4^{4+}$ (3 cm^3, 0.86 mM) in 2 M $HClO_4$ was bubbled with O_2 (at a slow rate) for 2 min, the cell stoppered and placed in a spectrophotometer housing at 25 °C. The reaction (1) was complete within a further 3 min.

$$4Mo_4S_4^{4+} + O_2 + 4H^+ \longrightarrow 4Mo_4S_4^{5+} + 2H_2O \quad (1)$$

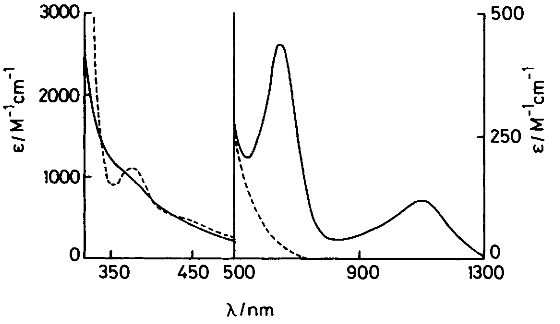

Figure 2. U.v.–visible spectra of green $[Mo_4S_4(H_2O)_{12}]^{5+}$ (——) and orange $[Mo_4S_4(H_2O)_{12}]^{4+}$ (— — —) in 1.0 M $HClO_4$ or Hpts solutions

Table 2. First-order rate constants, $k_{obs.}$(25 °C), for the $Mo_4S_4^{4+}$ reduction of Co^{III} complexes, I = 2.00 M ($LiClO_4$)

Complex	$10^3[Co^{III}]$/M	$10^3[Mo_4S_4^{4+}]$/M	$[H^+]$/M	$k_{obs.}/s^{-1}$
$[Co(NH_3)_5(O_2CCH_3)]^{2+}$	1.5	0.15	1.80	4.2×10^{-4}
	2.5	0.25	1.00	7.1×10^{-4}
	2.5	0.25	1.80	6.7×10^{-4}
	3.0	0.20	1.80	8.1×10^{-4}
	4.0	0.20	1.80	10.8×10^{-4}
	4.5	0.15	1.80	12.1×10^{-4}
$[Co(NH_3)_5(H_2O)]^{3+}$	1.5	0.15	1.80	6.5×10^{-4}
	2.5	0.25	1.80	10.0×10^{-4}
	3.0	0.25	1.80	12.3×10^{-4}
	4.0	0.20	1.00	16.3×10^{-4}
	4.0	0.20	1.40	16.4×10^{-4}
	4.0	0.20	1.80	16.0×10^{-4}
	5.0	0.10	1.80	20.3×10^{-4}
$[Co(NH_3)_5F]^{2+}$	1.5	0.15	1.80	6.1×10^{-4}
	2.5	0.25	1.00	10.3×10^{-4}
	2.5	0.25	1.80	10.3×10^{-4}
	4.0	0.25	1.80	16.1×10^{-4}
	4.8	0.25	1.80	18.9×10^{-4}
$[Co(NH_3)_5Cl]^{2+}$	1.5	0.15	1.80	11.1×10^{-3}
	2.0	0.20	1.00	13.4×10^{-3}
	2.0	0.20	1.80	14.0×10^{-3}
	3.0	0.25	1.00	23.0×10^{-3}
	3.0	0.25	1.80	22.6×10^{-3}
	4.0	0.15	1.80	30.3×10^{-3}
$[Co(NH_3)_5Br]^{2+}$	1.5	0.15	1.80	3.9×10^{-2}
	2.0	0.20	1.80	5.4×10^{-2}
	2.5	0.25	1.00	7.1×10^{-2}
	2.5	0.25	1.80	7.2×10^{-2}
	3.0	0.15	1.80	8.2×10^{-2}
	4.0	0.20	1.80	11.2×10^{-2}
$[Co(NH_3)_5I]^{2+}$	1.5	0.15	1.00	0.31
	1.5	0.15	1.80	0.30
	1.9	0.15	1.00	0.41
	1.9	0.15	1.80	0.40
$[Co(bipy)_3]^{3+}$	1.6	0.15	1.8	0.70
	2.1	0.15	1.8	0.97
	2.6	0.15	1.0	1.18
	2.9	0.20	1.0	1.30
	3.2	0.20	1.8	1.48
	3.7	0.20	1.8	1.67

Table 3. Summary of second-order rate constants, k (25 °C), for the $Mo_4S_4^{4+}$, $[Ru(NH_3)_6]^{2+}$, and $[V(H_2O)_6]^{2+}$ reductions of cobalt(III) complexes, I = 2.0 M ($LiClO_4$)

Complex	$k_{Mo}/M^{-1}\ s^{-1}$	$k_{Ru}{}^{a}/M^{-1}\ s^{-1}$	$k_{V}{}^{b}/M^{-1}\ s^{-1}$
$[Co(NH_3)_5(O_2CCH_3)]^{2+}$	0.26(±0.01)	0.022	1.15
$[Co(NH_3)_5(H_2O)]^{3+}$	0.40(±0.01)	3.0	0.53
$[Co(NH_3)_5F]^{2+}$	0.39(±0.01)	1.1	3.95
$[Co(NH_3)_5Cl]^{2+}$	8.1(±0.4)	2.6×10^2	10.2
$[Co(NH_3)_5Br]^{2+}$	28.9(±1.0)	1.6×10^3	30.0
$[Co(NH_3)_5I]^{2+}$	208(±7)	6.7×10^3	127
$[Co(bipy_3)]^{3+}$	460(±13)	6.9×10^5	1.1×10^3

[a] See for example listing in ref. 17 (Table 6) and refs. therein. The rate constant for $[Co(NH_3)_5F]^{2+}$ was determined in this work, and for $[Co(NH_3)_5(O_2CCH_3)]^{2+}$ is reported in ref. 21. [b] See for example listing in ref. 17 (Table 6), and refs. therein. The rate constant for $[Co(NH_3)_5F]^{2+}$ is from ref. 18, and for $[Co(NH_3)_5(O_2CCH_3)]^{2+}$ is as reported in ref. 8.

Stability to ClO_4^-.—The slow conversion of $Mo_4S_4^{4+}$ (0.25 mM) to $Mo_4S_4^{5+}$ in 2 M $HClO_4$ was monitored at 645 nm. From the initial slopes method a rate constant of $1.5 \times 10^{-5}\ s^{-1}$ ($t_{\frac{1}{2}}$ *ca.* 12 h) was obtained. For a reaction in 1 M $HClO_4$ with 1 M $LiClO_4$ the rate constant was $1.0 \times 10^{-5}\ s^{-1}$ ($t_{\frac{1}{2}}$ *ca.* 19 h), indicating some scatter in data or $[H^+]$ dependence of the reaction. A well defined isosbestic at 366 nm was noted. Solutions in 2 M Hpts showed no similar decay.

Kinetic Studies.—The ionic strength was adjusted to 2.0 M ($LiClO_4$), and the formation of $Mo_4S_4^{5+}$ was monitored at 645 nm. Absorbance changes were in all cases consistent with 1:1 oxidation of $Mo_4S_4^{4+}$ to $Mo_4S_4^{5+}$, equation (2).

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

Reactions with complexes $[Co(NH_3)_5X]^{n+}$ as oxidant were studied by conventional spectrophotometry, X = $CH_3CO_2^-$ (n = 2), H_2O (n = 3), F^- (n = 2), or Cl^- (n = 2), and by the stopped-flow method, X = Br^- or I^- (n = 2) and with $[Co(bipy)_3]^{3+}$. The slopes of first-order plots of absorbance (A) changes $\ln(A_\infty - A_t)$ against time, linear to at least three half-lives, gave first-order rate constants $k_{obs.}$ at 25.0 ± 0.1 °C.

Errors were obtained by unweighted least-squares procedures.

Results

First-order rate constants $k_{obs.}$, Table 2, give linear dependences on [oxidant], equation (3), as illustrated in Figure 3. Values

$$k_{obs.} = k[Co^{III}] \qquad (3)$$

of k are independent of $[H^+]$ in the range 1.0—1.8 M. Second-order rate constants are linked in Table 3, alongside previously determined rate constants with $[Ru(NH_3)_6]^{2+}$ and $[V(H_2O)_6]^{2+}$ as reductants. No rate constant was available for the $[Ru(NH_3)_6]^{2+}$ reduction of $[Co(NH_3)_5F]^{2+}$. Two runs with $[Ru(NH_3)_6{}^{2+}]$ = 1.0 mM, $[Co(NH_3)_5F^{2+}]$ = 10.0 mM, [HCl] = 0.010 M, I = 0.10 M (NaCl), monitored at 511 nm by conventional spectrophotometry gave $k = 1.1 \pm 0.1\ M^{-1}\ s^{-1}$, Table 3.

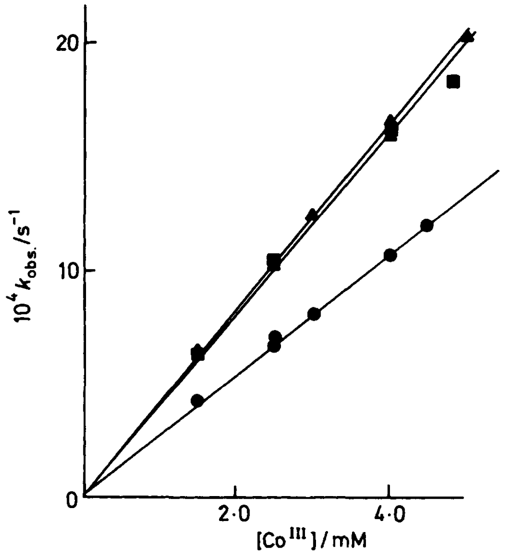

Figure 3. The dependence of first-order rate constants, $k_{obs.}$ (25 °C), on oxidant: $[Co(NH_3)_5(O_2CCH_3)]^{2+}$ (●), $[Co(NH_3)_5(H_2O)]^{3+}$ (▲), $[Co(NH_3)_5F]^{2+}$ (■); $[H^+]$ = 1.0—1.8 M, I = 2.0 M ($LiClO_4$)

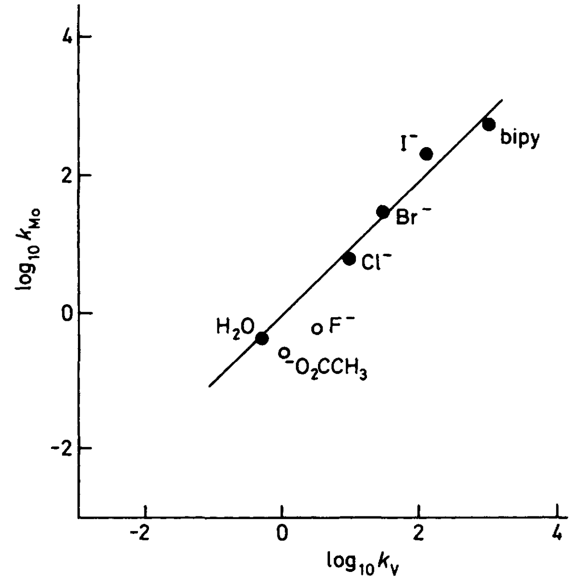

Figure 4. Rate constants (25 °C) for the $[Mo_4S_4(H_2O)_{12}]^{4+}$ (k_{Mo}) and $[V(H_2O)_6]^{2+}$ (k_V) reductions of Co^{III} complexes (full formulae as listed in Tables 1—3). In two cases (○) the $[V(H_2O)_6]^{2+}$ reaction is known to be inner sphere, and these two points do not conform to the linear correlation

Discussion

Rate constants for outer-sphere reductants give linear log–log correlations, and provide a powerful means of distinguishing inner- and outer-sphere reactions.[17–22] The slopes of such plots are often close to 1.0,[18–21] but do vary.[17,22] Here rate constants for five Co^{III} oxidants with $Mo_4S_4^{4+}$ and $[V(H_2O)_6]^{2+}$ as reductants conform to equation (4), with slope close to 1.0,

$$\log_{10}k_{Mo} = (0.97 \pm 0.10)\log_{10}k_V - (0.03 \pm 0.18) \qquad (4)$$

Figure 4. This is consistent with the reactions being of the outer-sphere category. The $[V(H_2O)_6]^{2+}$ reductions of $[Co(NH_3)_5F]^{2+}$ and $[Co(NH_3)_5(O_2CCH_3)]^{2+}$ are known to be inner sphere, and are not included in the correlation.[18,8] The corresponding graph incorporating data for the exclusively outer-sphere reductant $[Ru(NH_3)_6]^{2+}$ is shown in Figure 5.

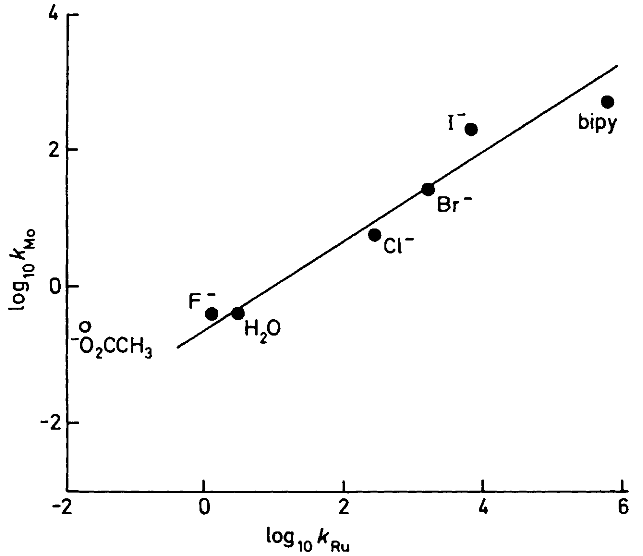

Figure 5. Rate constants (25 °C) for the $[Mo_4S_4(H_2O)_{12}]^{4+}(k_{Mo})$ and $[Ru(NH_3)_6]^{2+}(k_{Ru})$ reductions of Co^{III} complexes (full formulae as listed in Tables 1—3). In the case of $[Co(NH_3)_5(O_2CCH_3)]^{2+}$ (O) the k_{Mo} value can be designated as inner sphere

The line drawn can be expressed by equation (5). A feature of

$$\log_{10}k_{Mo} = (0.59 \pm 0.07)\log_{10}k_{Ru} - (0.47 \pm 0.22) \quad (5)$$

this plot is the rate constant for the $Mo_4S_4^{4+}$ reduction of $[Co(NH_3)_5(O_2CCH_3)]^{2+}$, which is displaced from the line and is *ca.* 10^2 too large to be outer sphere. This reaction can therefore be assigned as inner sphere. Also the point for $[Co(NH_3)_5F]^{2+}$ (although included in the correlation) is such as to leave open the possibility that the reduction with $Mo_4S_4^{4+}$ may be in part inner sphere.

Preliminary stopped-flow studies on the equilibration of NCS^- (10 mM) with $Mo_4S_4^{4+}$ (0.22 mM) in 2.0 M $HClO_4$ gave absorbance changes indicating sequential changes (200 s time base), which did not allow rate constants to be determined. At this time therefore it is not possible to say whether the rate constant for the inner-sphere $[Co(NH_3)_5F]^{2+}$ oxidation of $Mo_4S_4^{4+}$ is electron transfer or substitution-controlled. The value obtained could represent a lower limit for the latter process. This category of reaction is well known in the case of $[V(H_2O)_6]^{2+}$.[18,22]

Because of the ion-exchange chromatographic purification procedure, in which $Mo_4S_4^{4+}$ had to be eluted from Dowex columns,[3] stock solutions were at relatively high $[H^+]$, and this limited the range of $[H^+]$ in kinetic runs. However from studies at $[H^+]$ in the range 1.0—1.8 M, the $[Co(NH_3)_5(H_2O)]^{3+}$ oxidation of $Mo_4S_4^{4+}$ gave no sign of any $[H^+]^{-1}$ dependence consistent with significant $[Co(NH_3)_5(OH)]^{2+}$ participation. Likewise the fact that in all cases investigated no $[H^+]$ dependence is observed argues against involvement of a conjugate-base form of $Mo_4S_4^{4+}$. Previously, in studies on $Mo_4S_4^{5+}$, it has been demonstrated that the pK_a is > 2, and a larger pK_a would normally be expected for the lower charged $Mo_4S_4^{4+}$ ion.

In the case of the $[Co(NH_3)_5X]^{n+}$ (n = 2 or 3) oxidants no reduction potentials or self-exchange rate constants are known. With $[Co(bipy)_3]^{3+}$ however, the reduction potential for the $[Co(bipy)_3]^{3+/2+}$ couple is 370 mV,[23] and from Marcus correlation the self-exchange rate constant has been calculated as 20 M^{-1} s^{-1} (I = 0.10 M).[24] It is possible therefore knowing the rate constant for the $Mo_4S_4^{4+}$ reduction of $[Co(bipy)_3]^{3+}$ (460 M^{-1} s^{-1}), as well as the reduction potential for the $Mo_4S_4^{5+/4+}$ couple (210 mV), to calculate the $Mo_4S_4^{5+/4+}$ self-exchange rate constant.[25] With no work terms included this is 21 M^{-1} s^{-1}. Such a value is of interest compared to the value (760 M^{-1} s^{-1}) calculated from the rate constant for the one-equivalent outer-sphere $[V(H_2O)_6]^{2+}$ (−260 mV) reduction of $Mo_4S_4^{5+}$ (2.5×10^4 M^{-1} s^{-1}).[3] The latter was obtained using the experimentally determined rate constant for the $[V(H_2O)_6]^{2+}$ exchange with $[V(H_2O)_6]^{3+}$ (0.01 M^{-1} s^{-1}).[26] Clearly, in view of the different charge combinations (2+/3+ and 4+/5+ reactions are involved) work terms are not expected to cancel out, and some spread in calculated self-exchange rate constants is expected. A self-exchange rate constant in the range 21—760 M^{-1} s^{-1} for a 4+/5+ reaction indicates a quite favourable electron-transfer process. The one-electron oxidation of $Mo_4S_4^{4+}$ can be summarised as an $Mo^{III}(d^3)$ to $Mo^{IV}(d^2)$ conversion, albeit in a delocalised cuboidal cluster arrangement. This self-exchange process is to be compared therefore with that of $V^{II}(d^3)$ and $V^{III}(d^2)$, which has a much smaller rate constant (0.01 M^{-1} s^{-1}).[26] There are no corresponding values for mononuclear Mo ions to include in this comparison. These observations are of interest in the context of one-electron redox interconversions of cuboidal Fe_4S_4 clusters in the ferredoxins,[27] for which no self-exchange rate constant has been determined. The charge is less in the ferredoxin case, being moderated by the co-ordination of four cysteinyl thiolates.

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