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Rate Constants for Electron-transfer Reactions of Cuboidal $[Mo_4S_4(edta)_2]^{4-, 3-, 2-}$ Cluster Complexes

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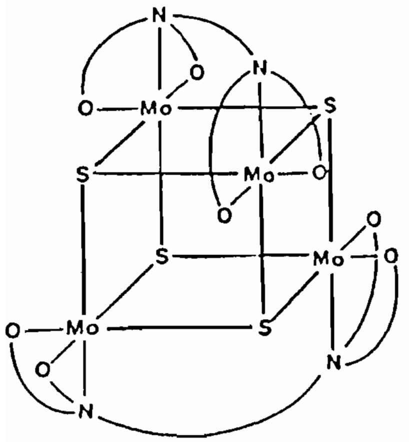
The question of ease of electron transfer in reactions involving cuboidal clusters is of current interest, not the least because it relates to biological electron transfer of Fe/S clusters in proteins [1]. There is at present a lack of information on self-exchange rate constants for Fe/S proteins [2]**. Estimates based on experimental cross reactions involving different redox partners and the use of Marcus Theory have been made [3, 4]†, but at this stage must be viewed cautiously because of variations with the identity of the redox partner used. The recent preparation and stability of $Mo_4S_4^{n+}$ clusters ($n = 4$, 5 and 6) [5] makes it possible to address this question further. The interconversion of the aqua ions $[Mo_4S_4(H_2O)_{12}]^{4+}$ and $[Mo_4S_4(H_2O)_{12}]^{5+}$ has been studied previously at $[H^+]$ in the range 0.5–2.0 M [6, 7]. There are, however, difficulties in working with the corresponding 6+ aqua ion [7]. An advantage in using the bis-*N,N,N′,N′*-ethylenediaminetetraacetate (edta) complexes of $Mo_4S_4^{n+}$ is that interconversion involving all three states can be explored. All three complexes have been characterised by X-ray crystallography [8, 9]. A feature of the structures is the very similar core sizes, Mo–Mo distances 2.783, 2.807 and 2.826 Å as the oxidation state increases, with Mo–S invariant at 2.355 Å [10]. In this work studies were at pH > 3.



$[Mo_4S_4(edta)_2]^{n+}$

Experimental

Green $[Mo_4S_4(edta)_2]^{3-}$ is obtained by reduction of the di-μ-sulfido Mo(V) dimer, $[Mo_2O_2S_2(edta)]^{2-}$ [10], with $NaBH_4$ by a procedure already described [5]. In the reduction process the cyclic Mo_2S_2 unit dimerises to give cuboidal Mo_4S_4. Electrochemical reduction (−0.50 V versus SCE) of $[Mo_4S_4(edta)_2]^{3-}$ under O_2-free conditions yields the 4− analogue, and oxidation (+0.50 V) the 2− product (eqn. (1)).

$$\underset{\text{(orange)}}{[Mo_4S_4(edta)_2]^{4-}} \underset{-0.046\ \text{V}}{\rightleftharpoons} \underset{\text{(green)}}{[Mo_4S_4(edta)_2]^{3-}} \underset{0.65\ \text{V}}{\rightleftharpoons} \underset{\text{(red)}}{[Mo_4S_4(edta)_2]^{2-}} \qquad (1)$$

Average oxidation states for the 4−, 3−, 2− ions are 3.0, 3.25 and 3.5 respectively. The orange and red forms are diamagnetic and the green form is one-electron paramagnetic ($g = 2.45$ from the EPR of aqueous solutions at 10 K). Reduction potentials in 1 M $LiClO_4$ (versus NHE) are indicated in eqn. (1).

Results and Discussion

Rate constants for cross reactions (Table 1) were obtained by stopped-flow and in one case conventional spectrophotometry. To obtain self-exchange rate constants the Marcus equations (eqns. (2) and (3)) [11] were used relating the rate constant (k_{12}) and

$$k_{12}^2 = k_{11}k_{22}K_{12}f \qquad (2)$$

$$\log f = (\log K_{12})^2/4 \log(k_{11}k_{22}/Z^2) \qquad (3)$$

equilibrium constant (K_{12}) for the cross reaction, to the self-exchange rate constants (k_{11} and k_{22}) for the two redox couples with a value for the collision frequency Z of 10^{11} M^{-1} s^{-1}. A self-exchange rate constant for $[Co(edta)]^{2-/-}$ (0.37 V) [12] of 3.8×10^{-7} M^{-1} s^{-1} was obtained by extrapolation of data determined by two methods using isotopic labelling

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**Recently a self-exchange rate constant for *Chromatium vinosum* $Fe_4S_4^{2+/3+}$ (Hipip) of 1.7×10^4 M^{-1} s^{-1} has been reported [2].

†Ref. 3 gives variable $Fe_2S_2^{+/2+}$ calculated self-exchange rate constants for spinach [2Fe–2S] ferredoxin from 1.7×10^{-3} M^{-1} s^{-1}. The rate constant for the $[Co(edta)]^-$ oxidation of *Clostridium pasteurianum* 2[4Fe–4S] ferredoxin of 1.1×10^4 M^{-1} s^{-1} in ref. 4 gives a calculated protein self-exchange rate constant of 920 M^{-1} s^{-1} using eqns. (2) and (3).

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TABLE 1. Summary of self-exchange and comproportionation rate constants (25 °C) (results in this work at $I = 1.0$ M ($LiClO_4$), neutral pH)

Reaction	k_{12} (M^{-1} s^{-1})	K_{12}[a] (M^{-1} s^{-1})	k_{11}[b] (M^{-1} s^{-1})	k_{22}[c] (M^{-1} s^{-1})
$[Fe(edta)]^{2-}$ + $[Co(edta)]^{-}$	4.4[d]	1.73×10^{4}	4.5×10^{3}[e]	3.8×10^{-7}[f]
$[Mo_4S_4(edta)_2]^{4-}$ + $[Co(edta)]^{-}$	5.4×10^{3}[d]	1.12×10^{7}	2.6×10^{7}[e]	3.8×10^{-7}[f]
$[Mo_4S_4(edta)_2]^{4-}$ + $[Fe(edta)]^{-}$	2.4×10^{6}[d]	651	3.0×10^{6}[e]	4.5×10^{3}[g]
$[Mo_4S_4(edta)_2]^{3-}$ + $[Co(dipic)_2]^{-}$	17.8[d]	44.1	7.7×10^{5}[e]	1.0×10^{-5}[h]
$[Mo_4S_4(edta)_2]^{4-}$ + $[Mo_4S_4(edta)_2]^{2-}$	2.4×10^{10}[e]	6.3×10^{11}	1.5×10^{7}[i]	7.7×10^{5}[g]

[a] Calculated from reduction potentials (using the Nernst equation). [b] Self-exchange rate constant for reductant. [c] Self-exchange rate constant for oxidant. [d] Experimental result, this work. [e] Calculated using eqns. (2) and (3). [f] From direct measurement, see refs. 13 and 14 and extrapolation of data to 25 °C in ref. 19. [g] Calculated value; entry under k_{11} in this Table. [h] Ref. 16. [i] Average of entries above 2.6×10^{7} and 3.0×10^{6} M^{-1} s^{-1}.

[13], and optical isomers at higher temperatures [14]. Corresponding values for $[Fe(edta)]^{2-/-}$ (0.12 V) ranging from 10^{3}–10^{4} M^{-1} s^{-1} [15]*, and for $[Co(dipic)_2]^{2-/-}$ (0.747 V) of 1.0×10^{-5} M^{-1} s^{-1} [16], have been reported from studies of cross reactions. As a part of this investigation the rate constant for the $[Fe(edta)]^{2-}$ reduction of $[Co(edta)]^{-}$ was determined, and the self-exchange rate constant for $[Fe(edta)]^{2-/-}$ calculated as 4.5×10^{3} M^{-1} s^{-1}. Calculated self-exchange k_{11} values for $[Mo_4S_4(edta)_2]^{4-/3-}$ of 2.6×10^{7} M^{-1} s^{-1} ($[Co(edta)]^{-}$ reaction) and 3.0×10^{6} M^{-1} s^{-1} ($[Fe(edta)]^{-}$ reaction) give an average value of 1.5×10^{7} M^{-1} s^{-1}. Similarly a self-exchange rate constant of 7.7×10^{5} M^{-1} s^{-1} is obtained for the $[Mo_4S_4(edta)_2]^{3-/2-}$ couple from the study with $[Co(dipic)_2]^{-}$.

In separate experiments the comproportionation reaction (eqn. (4)) was found to be too fast to study

$$[Mo_4S_4(edta)_2]^{4-} + [Mo_4S_4(edta)_2]^{2-} \longrightarrow 2[Mo_4S_4(edta)_2]^{3-} \qquad (4)$$

by the stopped-flow method. From the self-exchange rate constants for $[Mo_4S_4(edta)_2]^{4-/3-}$ (1.5×10^{7} M^{-1} s^{-1}) and $[Mo_4S_4(edta)_2]^{3-/2-}$ (7.7×10^{5} M^{-1} s^{-1}) a comproportionation rate constant of 2.4×10^{10} M^{-1} s^{-1} was obtained using eqns. (2) and (3). From relevant crystallographic information [10] the distance from the centre of an Mo_4S_4 cube to the outer carboxylate O atom, plus the van der Waals radius (1.4 Å) [17] for the O atom, is ~7.4 Å**. Because of the size of the two reactants, the collision frequency will be correspondingly bigger. Clearly, electron transfer is very efficient and the comproportionation rate constant is at or near the diffusion-controlled limit. Interestingly for $[Mo_4S_4(H_2O)_{12}]^{4+/5+}$, the self-exchange rate constant is somewhat smaller (values of 26 M^{-1} s^{-1} and 3.8×10^{3} M^{-1} s^{-1} are obtained after allowing for f) from studies on the cross reactions with $[V(H_2O)_6]^{2+}$ (reductant) and $[Co(bipy)_3]^{3+}$ (oxidant) respectively [6, 7]. A significant beneficial effect of edta as opposed to H_2O ligands is noted.

Holm and colleagues [18] have also obtained rate constants in the range 10^{6}–10^{7} M^{-1} s^{-1} from NMR studies on the self-exchange reactions $Fe_4S_4(SR)_4]^{2-/3-}$ ($R = CH_2Ph$, p-C_6H_4Me) in acetonitrile solvent. The results obtained here firmly establish electron self-exchange processes between cuboidal clusters as favourable and amongst the fastest studied. On present evidence, protein self-exchange processes appear to be somewhat slower, presumably due to the restrictions/control imposed by the protein structure.

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*Although the formula is here written as $[Fe(edta)]^{-}$, an H_2O is coordinated and the situation is different from that of substitution inert $[Co(edta)]^{-}$.

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