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Redox Interconversions and Aqueous Solution Properties of the Cuboidal Complexes $[Mo_4S_4(edta)_2]^{m-}$ (m = 4, 3, 2)

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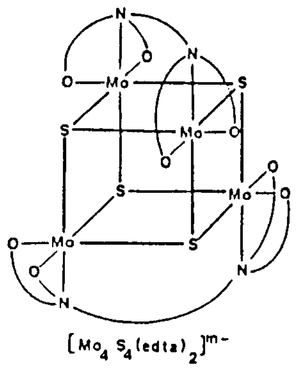
Received July 5, 1989

Redox interconversions of the recently prepared Mo_4S_4 complexes present in the 4+, 5+, and 6+ states, and in this case with *N,N,N′,N′*-ethylenediaminetetraacetate (edta) as ligand, $[Mo_4S_4(edta)_2]^{m-}$ (m = 4, 3, and 2, respectively), have been studied at 25 °C, I = 1.00 M ($LiClO_4$). The most readily obtained complex is green $[Mo_4S_4(edta)_2]^{3-}$, the EPR spectrum of which (in H_2O at 10 K) confirms one unpaired electron, g_{av} value 2.48. From cyclic voltammetry in 0.5 M $LiClO_4$, reduction potentials (vs NHE) are $[Mo_4S_4(edta)_2]^{3-/4-}$ (−0.046 V) and $[Mo_4S_4(edta)_2]^{2-/3-}$ (0.65 V). The $[Mo_4S_4(edta)_2]^{4-}$ ion is air-sensitive, and in the presence of H^+ and ClO_4^- is oxidized to $[Mo_4S_4(edta)_2]^{3-}$. Reactions studied were at pH >3 to limit also dechelation of the edta, except in the case of the fast $[Fe(H_2O)_6]^{3+}$ oxidation of $[Mo_4S_4(edta)_2]^{3-}$, when it was necessary to work at higher $[H^+]$ in the range 0.075–0.30 M. The kinetics of the 1:1 cross-reactions with $[Co(edta)]^-$ (0.37 V; 5.4×10^3 M^{-1} s^{-1}) and $[Fe(edta)]^-$ (0.12 V; 2.4×10^6 M^{-1} s^{-1}) as oxidants for $[Mo_4S_4(edta)_2]^{4-}$ give a self-exchange rate constant for the $[Mo_4S_4(edta)_2]^{4-/3-}$ couple of 1.5×10^7 M^{-1} s^{-1}. Similarly with $[Co(dipic)_2]^-$ (0.747 V; 17.8 M^{-1} s^{-1}) as the oxidant, 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. The reaction with $[Fe(H_2O)_6]^{3+}$ as oxidant (0.77 V; 6.7×10^4 M^{-1} s^{-1} at 10 °C) gives no dependence on $[H^+]$ and is too fast to be other than outer-sphere. Both self-exchange reactions are clearly very favorable processes. The comproportionation reaction of $[Mo_4S_4(edta)_2]^{4-}$ with $[Mo_4S_4(edta)_2]^{2-}$ is too fast to measure directly by stopped-flow UV–vis spectrophotometry. A rate constant of 2.4×10^{10} M^{-1} s^{-1} calculated from the self-exchange values is close to or at the diffusion-controlled limit for reactants of radius ~7.4 Å. The two-electron oxidant $[PtCl_6]^{2-}$ (0.726 V) oxidizes $[Mo_4S_4(edta)_2]^{4-}$ in one-electron steps. Interestingly, the self-exchange rate constant for $[Mo_4S_4(edta)_2]^{4-/3-}$ is ~10^4 times more favorable than that for the $[Mo_4S_4(H_2O)_{12}]^{4+/5+}$ exchange.

Introduction

The preparation and properties of cuboidal aqua ions $[Mo_4S_4(H_2O)_{12}]^{n+}$ (n = 4, 5, 6) have been the subject of recent reports.[1-3] Of these the green mixed-valence (3.25) 5+ ion is the most readily prepared,[1] and it can be converted into the air-sensitive 4+ ion by electrochemical reduction.[2] A particular problem in obtaining the 6+ state is that electrochemical oxidation cannot be used, and likewise in chemical procedures care is required to avoid further oxidation with breakdown of the cube. Furthermore, even in 1–3 M acid the "6+ state" ion is present as a lower charged (~4+) species due possibly to acid dissociation and/or anation processes.[3] There are no similar problems with the edta complex, and the readily accessed complexes $[Mo_4S_4(edta)_2]^{m-}$ (m = 4, 3, and 2, respectively), are the subject of the present study. X-ray crystal structures of all three forms as $Mg_2[Mo_4S_4(edta)_2]\cdot 22H_2O$, $Ca_3[Mo_4S_4(edta)_2]_2\cdot 28H_2O$, and $Na_2[Mo_4S_4(edta)_2]\cdot 6.5H_2O$ have been determined,[4,5] and shown to have the same basic structure:



$[Mo_4S_4(edta)_2]^{m-}$

There are small differences only in bond lengths, and from the information in Table I we note that the average Mo–Mo distance increases with oxidation state. In contrast the Mo–O bond distances decrease, while those for Mo–S and Mo–N remain very nearly the same.

Table I. Average Oxidation States, Core Charges, and Bond Lengths for $[Mo_4S_4(edta)_2]^{m-}$ (m = 4, 3, 2) Cuboidal Ions[a]

	formula		
	$[Mo_4S_4(edta)_2]^{4-}$	$[Mo_4S_4(edta)_2]^{3-}$	$[Mo_4S_4(edta)_2]^{2-}$
oxidn state of Mo's	3.00	3.25	3.50
Mo_4S_4 charge	4+	5+	6+
	Bond Distances (Å)		
Mo–Mo	2.783	2.807	2.826
Mo–S	2.355	2.356	2.355
Mo–N	2.28	2.29	2.27
Mo–O	2.18	2.14	2.09

[a] Crystallographic data from ref. 5.

The present studies are of interest because of the novelty of cuboidal ions in aqueous solution and, in this case, availability of three adjacent oxidation states. The approach has been to investigate a number of cross-reactions in order to calculate, by using the Marcus equation, rate constants for the $[Mo_4S_4(edta)_2]^{4-/3-}$ and $[Mo_4S_4(edta)_2]^{3-/2-}$ self-exchange processes. Also of interest are rate constants for the related comproportionation and disproportionation reactions and whether single-stage 2-equiv redox interconversions of the 4− and 2− ions can occur. In spite of the importance in biology of Fe/S cuboidal active sites and the existence of a range of synthetic analogues, the Fe/S clusters are not sufficiently stable in protic media to allow corresponding aqueous solution studies to be carried out.[6]

Experimental Section

Preparation of $[Mo_4S_4(edta)_2]^{3-}$. The bis(μ-sulfido)dimolybdenum(V) dimer $Na_2[Mo_2O_2S_2(edta)_2]\cdot 2H_2O$ was first prepared.[7] In order to bring about the cyclic Mo_2S_2 to cuboidal Mo_4S_4 conversion, the dimer (2 g) in 0.03 M HCl (200 mL) was reduced by addition to sodium borohydride, $NaBH_4$ (1 g), all under N_2.[4] The resultant solution was left to stand overnight at ~4 °C under N_2, after which it was heated in air to 90 °C on a steam bath for ~24 h. The solution changed from an initial dark brown to dark green. Any brown solid was filtered off, and the filtrate was subjected to Sephadex G-10 column purification, the elution

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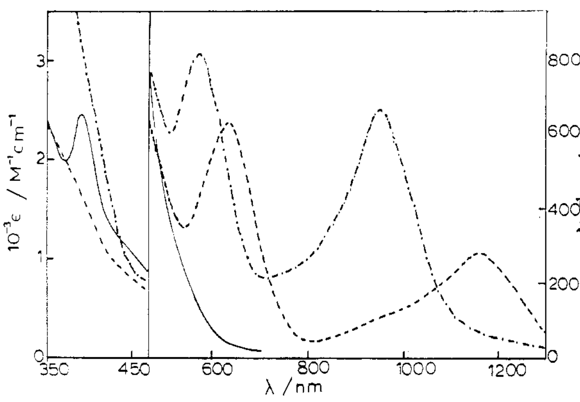

Figure 1. UV-vis-near-IR spectra of cuboidal $[Mo_4S_4(edta)_2]^{4-}$ (—), $[Mo_4S_4(edta)_2]^{3-}$ (- - -), and $[Mo_4S_4(edta)_2]^{2-}$ (···) in 0.5 M $LiClO_4$, ϵ values per cube.

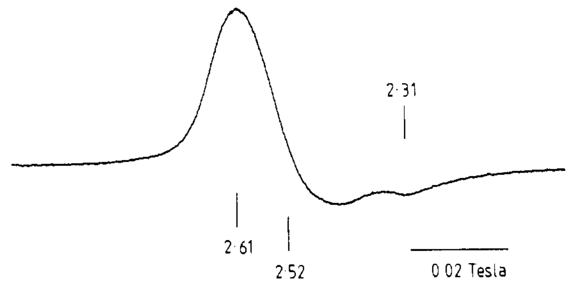

Figure 2. Electron paramagnetic resonance (EPR) spectrum of $[Mo_4S_4(edta)_2]^{3-}$ (1 mM) in water, $T = 10$ K, microwave frequency 944 GHz, power 2.4 mV, modulation intensity 1 mT, and gain 6.3 × 10^4.

Table II. Reduction Potentials for $[Mo_4S_4(edta)]^{3-/4-}$, $[Mo_4S_4(edta)_2]^{2-/3-}$, and Oxidants As Used in These Studies

couple	$E°$/V (vs NHE)	ref
$[Mo_4S_4(edta)_2]^{3-/4-}$	-0.046	this work
$[Mo_4S_4(edta)_2]^{2-/3-}$	0.653	this work
$[PtCl_6]^{2-}/[PtCl_4]^{2-}$	0.726[a]	16
$[Fe(H_2O)_6]^{3+/2+}$	0.771	16
$[Co(dipic)_2]^{-/2-}$	0.747	17
$[Co(edta)]^{-/2-}$	0.37	18
$[Fe(edta)]^{-/2-}$	0.12	9

[a] Two-electron change, Cl^- dependent.

being with H_2O. Final purification was on a QAE-Sephadex anion-exchange column (25 × 1.5 cm diameter) equilibrated with 0.1 M $LiClO_4$. Sufficient 1 M $LiClO_4$ was added to the green solution to give ~0.1 M $LiClO_4$ (50 mL) followed by 0.25 M $LiClO_4$ until two green bands separate. The less tightly held band of $[Mo_4S_4(edta)_2]^{3-}$ was eluted with 0.25 M $LiClO_4$. A more tightly held band eluted with 1 M $LiClO_4$ has not yet been characterized. The UV-vis-near-IR spectrum of $[Mo_4S_4(edta)_2]^{3-}$ in 0.5 M $LiClO_4$ (Figure 1) gives peaks/nm (ϵ/M^{-1} cm^{-1} per cube) at 636 (635) and 1145 (280), with shoulders at 300 (7500) and 450 (750). Stock solutions, typically ~4 mM in 0.5 M $LiClO_4$, were stable in air. Solutions were standardized for $[Li^+]$ by loading onto an Amberlite IR(H)120 cation-exchange column and titrating for $[H^+]$ released.

Preparation of $[Mo_4S_4(edta)_2]^{4-}$. A solution of $[Mo_4S_4(edta)_2]^{3-}$ (2-4 mM, 20 mL) in 0.5 M $LiClO_4$ was reduced under N_2 at a high surface area carbon-cloth electrode (RVG 100 cloth, Le Carbonne, Brighton, U.K.) as previously described[2] by using a constant potential of -0.50 V (vs SCE) for ~2 h. The cathode consisted of a layer of cloth wrapped around a glass rod and tied in position with Teflon tape. Electrical contact was at a carbon rod attached (with epoxide resin) to the upper end of the glass rod. The carbon cloth covered both these sections and fitted tightly into the glass entry of the cell. After reduction was complete the orange solution of $[Mo_4S_4(edta)_2]^{4-}$ was millipore-filtered (8-μm pore size) to remove any small carbon particles. This operation was performed under N_2 in a glovebag. Spectrophotometric standardization was carried out at the 390-nm peak (ϵ = 2445 M^{-1} cm^{-1} per cube) (Figure 1) and checked by allowing it to air-oxidize to $[Mo_4S_4(edta)_2]^{3-}$. Stock solutions were stored under N_2 at 0 °C and used the same day for kinetic runs.

Preparation of $[Mo_4S_4(edta)_2]^{2-}$. The same electrochemical cell was used to prepare brown-red $[Mo_4S_4(edta)_2]^{2-}$ by controlled-potential oxidation of $[Mo_4S_4(edta)_2]^{3-}$ (2-4 mM in 0.5 M $LiClO_4$) at +0.50 V (vs SCE). Oxidation was complete in ~2 h and the solution millipore-filtered before use. The UV-vis-near-IR spectrum [nm (ϵ/M^{-1} cm^{-1} per cube)] has two peaks at 572 (825) and 945 (665) (Figure 1).

Oxidants. Sodium (*N,N,N′,N′*-ethylenediaminetetraacetato)cobaltate(III) tetrahydrate, $Na[Co(edta)]\cdot 4H_2O$, absorbance peak at 535 nm (ϵ = 320 M^{-1} cm^{-1}), was prepared by the procedure described.[8] Sodium aqua(*N,N,N′,N′*-ethylenediaminetetraacetato)ferrate(III), $Na[Fe(edta)(H_2O)]$ (Sigma Chemicals), was used as supplied. Although H_2O is coordinated,[9] the couple is here represented as $[Fe(edta)]^{-/2-}$. Samples of ammonium bis(pyridine-2,6-dicarboxylato)cobaltate(III), $(NH_4)[Co(dipic)_2]$, peak at 510 nm (ϵ = 630 M^{-1} cm^{-1}), was prepared as described.[10] Solutions of $[Fe(H_2O)_6]^{3+}$ in perchloric acid were obtained from ferric perchlorate hydrate, $Fe(ClO_4)_3\cdot xH_2O$ (G. F. Smith). Stock solutions were obtained by elution from a Dowex 50W-X2 cation-exchange column and standardized spectrophotometrically after reduction with hydroxylamine hydrochloride (Aldrich) and addition of an excess of 1,10-phenanthroline hydrate (Aldrich) at pH 3.5 (sodium acetate) to give $[Fe(phen)_3]^{2+}$, peak at 510 nm (ϵ = 10900 M^{-1} cm^{-1}).[11] Ammonium hexachloroplatinate(IV), $(NH_4)_2[PtCl_6]$ (Johnson-Matthey) was used, peaks at 262 nm (ϵ = 2.45 × 10^4 M^{-1} cm^{-1}) and 454 (ϵ = 48 M^{-1} cm^{-1}).[12] Solutions of $[PtCl_6]^{2-}$ were transferred with Teflon needles (not stainless steel) and were protected from direct sunlight (Al foil) to avoid photochemical reactions.[13]

Reductant. The $[Fe(edta)]^{2-}$ reactant was prepared by electrochemical reduction of $[Fe(edta)]^-$, pH 3 ($HClO_4$), at -0.5 V vs SCE for 2 h, with use of the same cell as for the preparation of $[Mo_4S_4(edta)_2]^{4-}$. A 20% excess of free edta (disodium salt) was added. The $[Fe(edta)]^{2-}$ concentration was determined by spectrophotometric titration using $[Fe(CN)_6]^{3-}$.

Stability. Solutions of green $[Mo_4S_4(edta)_2]^{3-}$ and brown-red $[Mo_4S_4(edta)_2]^{2-}$ in 0.50 M $LiClO_4$ are stable for several days when stored at ~4 °C. Storage of $[Mo_4S_4(edta)_2]^{4-}$ presented more of a problem, because of the extreme air sensitivity and oxidation to $[Mo_4S_4(edta)_2]^{3-}$ with H^+/ClO_4^-, which in 2 M ClO_4^- is rapid (76 M^{-1} s^{-1} at 25 °C).[14] No similar reaction is observed for the 3- and 2- analogues. The tendency of edta to protonate and dechelate from $[Mo_4S_4(edta)_2]^{3-}$ was investigated briefly in 0.5 M $HClO_4$ + 0.5 M $LiClO_4$ at 25 °C. Spectrophotometric changes at 636 nm were monitored for ~4 h, over which time, assuming a reaction to give $[Mo_4S_4(H_2O)_{12}]^{5+}$, <5% conversion occurs. We have no reason for believing that the corresponding reaction of $[Mo_4S_4(edta)_2]^{2-}$ is any faster.

Electron Paramagnetic Resonance Spectrum. A sample of $[Mo_4S_4(edta)_2]^{3-}$ (1 mM in H_2O) was frozen in a quartz EPR tube (internal diameter 3 mm) by immersion in a freezing mixture of isopentane/hexane (5:1) cooled with a liquid N_2 cold finger. The EPR spectrum at 10 K was recorded on a Bruker ER 200D spectrometer fitted with an Oxford Instruments cryostat. The spectrum gave a net spin of one unpaired electron per complex with a g_{av} value of 2.48. The spectrum sharpened (Figure 2) on diluting to 0.2 mM possibly by minimizing dipole-dipole interactions. We are grateful to Dr. J. Ingledew at St. Andrews for these measurements. Solid crystalline material has previously been shown to give a room-temperature magnetic moment of 2.0 μ_B, and $S = {}^1/_2$ from the measurement of the temperature dependence of the magnetic susceptibility.[4,15] All these measurements are consistent with the $[Mo_4S_4(edta)_2]^{3-}$ formulation. In spite of some difference in Mo-Mo bond lengths as noted in Table I, for present purposes the complex can be regarded as having an average Mo oxidation state of 3.25. The $[Mo_4S_4(edta)_2]^{m-}$ (m = 4, 2) complexes are both diamagnetic, consistent with average Mo oxidation states of 3.0 and 3.5, respectively.

Cyclic Voltammograms. These were recorded on a Princeton Applied Research PAR 173 potentiostat interfaced with an Apple II Europlus microcomputer using a PAR 276 unit. The working electrode was a glassy-carbon disk (Metrohm, 2.5-mm diameter), Pt wire was used as a secondary electrode, and a saturated calomel electrode was used as a

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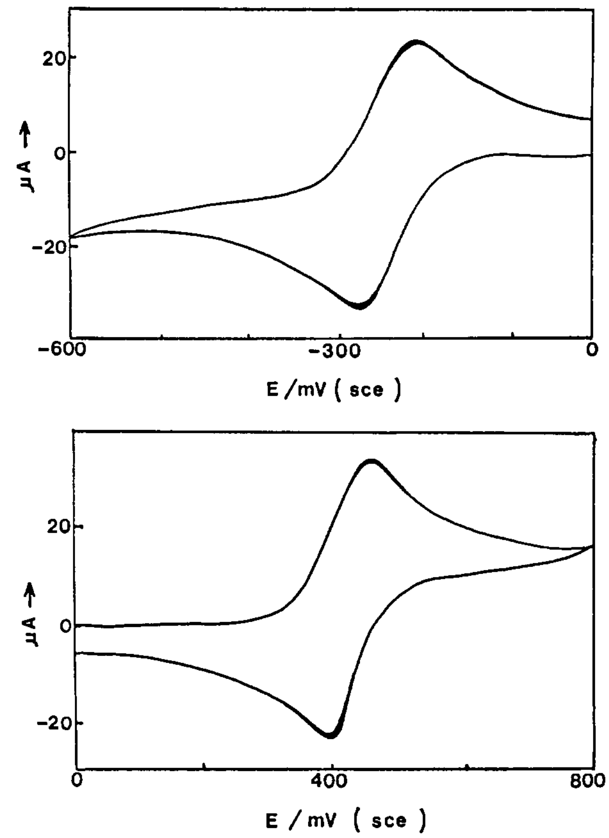

Figure 3. Cyclic voltammograms (20 °C) of $[Mo_4S_4(edta)_2]^{3-}$ (2 mM) in 0.5 M $LiClO_4$, scan rate 100 mV s^{-1}, corresponding to redox changes for the 5+/4+ and 6+/5+ states, respectively.

reference. The concentration of $[Mo_4S_4(edta)_2]^{3-}$ was 2 mM in 0.50 M $LiClO_4$, and the scan rate 100 mV/s. The cyclic voltammograms show quasi-reversible one-electron reduction and oxidation (Figure 3). Reduction potentials from Figure 3 (vs SCE) are converted to the values indicated in (1) and (2) (vs NHE) by adding 0.241 V.

$$[Mo_4S_4(edta)_2]^{3-} + e^- \rightleftharpoons [Mo_4S_4(edta)_2]^{4-} \quad (-0.046\ V) \qquad (1)$$

$$[Mo_4S_4(edta)_2]^{2-} + e^- \rightleftharpoons [Mo_4S_4(edta)_2]^{3-} \quad (0.65\ V) \qquad (2)$$

Reduction Potentials and Stoichiometries. Reduction potentials[9,16-18] are listed in Table II. From spectrophotometric changes (Figure 1), all the oxidants give one-equivalent redox changes on the Mo_4S_4 reactant. The product of the reaction of the 2-equiv oxidant $[PtCl_6]^{2-}$ is square-planar $[PtCl_4]^{2-}$.

Kinetic Studies. These were carried out on a Dionex D-110 stopped-flow spectrophotometer, except for the $[PtCl_6]^{2-}$ oxidation of $[Mo_4S_4(edta)_2]^{3-}$ and the $[Co(edta)]^-$ oxidation of $[Fe(edta)]^{2-}$, which were studied by conventional spectrophotometry. Rigorous air-free conditions were observed throughout for studies on $[Mo_4S_4(edta)_2]^{4-}$. Kinetic runs were with the oxidants in >10-fold excess over the Mo_4S_4 complexes. The slope of plots of absorbance (A) changes ln ($A_\infty - A_t$) against time (t) gave first-order rate constants k_{obs} for runs monitored by conventional spectrophotometry. The $[Fe(edta)]^-$ oxidation of $[Mo_4S_4(edta)]^{4-}$ was too fast to study with the oxidant in 10-fold excess, and 1:1 amounts of the two reactants were used. The $[Fe(H_2O)_6]^{3+}$ oxidation of $[Mo_4S_4(edta)]^{3-}$ was investigated at 10 °C because of the rapidity of the reaction at 25 °C. All the other reactions were studied at 25 °C, and ionic strengths were adjusted to I = 1.00 M ($LiClO_4$). Stopped-flow first-order rate constants, k_{obs}, were evaluated by successive integration fits using programs from OLIS (Jefferson, GA). Second-order rate constants were obtained from the dependence of k_{obs} on the reactant in excess by an unweighted standard linear-least-squares treatment.

Table III. Rate Constants (25 °C) for the 1:1 $[Co(edta)]^-$ Oxidation of $[Fe(edta)]^{2-}$ at pH 3 ($HClO_4$), I = 1.00 M ($LiClO_4$), Monitored at 535 nm

$10^3[[Fe(edta)]^{2-}]$, M	$10^4[[Co(edta)]^-]$, M	10^3k_{obs}, s^{-1}
1.32	1.25	4.9
1.99	1.25	7.8
2.65	1.25	10.9
2.65	2.52	10.3
3.31	1.25	14.6

Table IV. Rate Constants (25 °C) for the 1-equiv $[Co(edta)]^-$ and $[Fe(edta)]^-$ Oxidations of $[Mo_4S_4(edta)_2]^{4-}$, I = 1.00 M ($LiClO_4$), Monitored at 636 nm

$10^3[[Mo_4S_4(edta)_2]^{4-}]$, M	10^3[oxidant], M	k_{obs}, s^{-1}	k, M^{-1} s^{-1}
Oxidant $[Co(edta)]^-$; No $[H^+]$ Added (Neutral pH)			
0.2	1.96	12.9	
0.2	3.9	25.1	
0.2	5.9	32.2	
Oxidant $[Fe(edta)]^-$; $[HClO_4] = 1.0 \times 10^{-3}$ M			
1.2	1.2		2.8
0.6	0.6		2.4
0.3	0.3		2.0
1.2	1.2		2.9[a]

[a] $[HClO_4] = 1.0 \times 10^{-4}$ M.

Table V. First-Order Rate Constants for the 1-equiv Oxidations of $[Mo_4S_4(edta)_2]^{3-}$ with $[Co(dipic)_2]^-$ (25 °C; No H^+ Added, Neutral pH) and $[Fe(H_2O)_6]^{3+}$ (10 °C; $[H^+]$ = 0.075–0.30 M), with the Oxidant in >10-fold Excess, I = 1.00 M ($LiClO_4$)

10^3[oxidant], M	$10^3[[Mo_4S_4(edta)_2]^{3-}]$, M	$[H^+]$, M	k_{obs}, s^{-1}
	$[Co(dipic)_2]^-$ as Oxidant[a]		
1.43	0.14		0.025
2.44	0.14		0.044
3.46	0.30		0.063
4.47	0.30		0.079
5.32	0.30		0.094
6.10	0.30		0.108
7.17	0.30		0.128
	$[Fe(H_2O)_6]^{3+}$ as Oxidant		
1.10	0.11	0.075	81
1.25	0.11	0.15	87
1.82	0.11	0.30	126
2.24	0.11	0.075	154
2.77	0.26	0.15	191
3.23	0.26	0.075	220
3.63	0.26	0.15	250
4.27	0.26	0.075	294
4.27	0.26	0.15	300
5.77	0.26	0.15	382

[a] No H^+ was added.

Results

$[Co(edta)]^-$ Oxidation of $[Fe(edta)]^{2-}$. This study enabled the self-exchange rate constant of 10^3–10^4 M^{-1} s^{-1} for $[Fe(edta)]^{2-/-}$ to be further refined.[17] The reaction was monitored by conventional time-range spectrophotometry at the $[Co(edta)]^-$ absorption peak at 535 nm (ϵ = 330 M^{-1} cm^{-1}), with the reductant $[Fe(edta)]^{2-}$ in large >10-fold excess. First-order rate constants k_{obs} (Table III) give a second-order rate constant $k = 4.4 \pm 0.2$ M^{-1} s^{-1}.

$[Co(edta)]^-$ and $[Fe(edta)]^-$ Oxidations of $[Mo_4S_4(edta)_2]^{4-}$. Both reactions were monitored at 630 nm. First-order rate constants k_{obs} were determined for the $[Co(edta)]^-$ reaction (the oxidant was in large excess), and second-order rate constants k (Table III) were obtained from these. The $[Fe(edta)]^-$ reaction was investigated with equal amounts of the two reactants, and second-order rate constants (Table III) were determined directly. Studies were at pH 3 ($HClO_4$) to avoid acid dissociation of the aqua ligand (see comments in Experimental Section) and associated dimerization. A 20% excess of free edta was also present.

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Table VI. First-Order Rate Constants (25 °C) for the Oxidation of $[Mo_4S_4(edta)_2]^{3-}$ to $[Mo_4S_4(edta)_2]^{2-}$ with $[PtCl_6]^{2-}$ (No $[H^+]$ Added, Neutral pH), I = 1.00 M ($LiClO_4$)

$10^3[[PtCl_6]^{2-}]$, M	$10^3[[Mo_4S_4(edta)_2]^{3-}]$, M	10^3k_{obs}, s^{-1}
1.51	0.15	0.60
2.20	0.20	0.88
3.02	0.30	1.12
4.00	0.30	1.54
5.03	0.30	1.89

Second-order rate constants in Table IV give (5.4 ± 0.5) × 10^3 M^{-1} s^{-1} ($[Co(edta)]^-$ reaction) and (2.4 ± 0.4) × 10^6 M^{-1} s^{-1} ($[Fe(edta)]^-$ reaction). The $[Fe(edta)]^-$ reaction is independent of pH in the range 3–4.

$[Co(dipic)_2]^-$ and $[Fe(H_2O)_6]^{3+}$ Oxidations of $[Mo_4S_4(edta)_2]^{3-}$. The formation of $[Mo_4S_4(edta)_2]^{2-}$ was monitored in both cases at 850 nm, with the oxidant in >10-fold excess. From a plot of k_{obs} (Table V) against $[Co(dipic)_2^-]$ the second-order rate constant k = 17.8 ± 0.1 M^{-1} s^{-1} was obtained. Because the $[Fe(H_2O)_6]^{3+}$ oxidation is very fast and at the limit of the stopped-flow range at 25 °C, this reaction was studied at 10 °C. No dependence of k_{obs} on $[H^+]$ in the range 0.075–0.30 M was observed, and from the $[Fe(H_2O)_6{}^{3+}]$ dependence k = (6.7 ± 0.1) × 10^4 M^{-1} s^{-1}. The absence of an $[H^+]$ dependence indicates no enhancement in rate from the conjugate-base $[Fe(H_2O)_5OH]^{2+}$ and is consistent therefore with an outer-sphere mechanism. Reactions of both oxidants with $[Mo_4S_4(edta)_2]^{4-}$ gave fast first stages followed by the slower (measurable) oxidation of $[Mo_4S_4(edta)_2]^{3-}$.

Comproportionation Reaction of $[Mo_4S_4(edta)_2]^{4-}$ and $[Mo_4S_4(edta)_2]^{2-}$. The comproportionation reaction, the forward reaction in (3), was too fast to follow by stopped-flow spectrophotometry (reactants both 0.25 mM).

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

With 1.0 mM oxidant and 0.1 mM reductant the reaction is complete in less than 5 ms, and the rate constant is therefore >10^6 M^{-1} s^{-1}. The driving force is 0.70 V (Table II), which gives an equilibrium constant for (3) of 6.3 × 10^{11}.

$[PtCl_6]^{2-}$ Oxidation of $[Mo_4S_4(edta)_2]^{4-}$. In an experiment (25 °C) with $[Mo_4S_4(edta)_2]^{4-}$ (0.4 mM) and $[PtCl_6]^{2-}$ (0.2 mM), I = 1.00 M ($LiClO_4$), instant quantitative conversion of orange $[Mo_4S_4(edta)_2]^{4-}$ to green $[Mo_4S_4(edta)_2]^{3-}$ was observed. With 1:1 mole amounts of the reactants no evidence was obtained for initial rapid formation of $[Mo_4S_4(edta)_2]^{2-}$ at 945 nm. At this wavelength $[Mo_4S_4(edta)_2]^{2-}$ is the only absorbing species. The rapid formation of $[Mo_4S_4(edta)_2]^{3-}$ is followed by a slower stage in which $[Mo_4S_4(edta)_2]^{3-}$ is oxidized to $[Mo_4S_4(edta)_2]^{2-}$. A separate study of this reaction was made with $[PtCl_6]^{2-}$ in >10-fold excess. Rate constants k_{obs} (Table VI) gave a first-order dependence on $[PtCl_6{}^{2-}]$ from which k = 0.38 ± 0.01 M^{-1} s^{-1} (Figure 4).

Calculation of Self-Exchange Rate Constants. Second-order rate constants obtained in this work are summarized in Table VII, alongside existing self-exchange rate constants.[10,20-23] The Marcus equations (4) and (5),[24] relating the rate constant (k_{12}) and

$$k_{12}{}^2 = k_{11}k_{22}K_{12}f \quad (4)$$

$$\log f = (\log K_{12})^2/4 \log (k_{11}k_{22}/Z^2) \quad (5)$$

equilibrium constant (K_{12}) for a cross-reaction to the self-exchange rate constants k_{11} and k_{22} for the two redox couples, were used. From the rate constant for the $[Fe(edta)]^{2-}$ reduction of $[Co(edta)]^-$ (4.4 M^{-1} s^{-1}), the self-exchange rate constant for $[Fe(edta)]^{2-/-}$ was calculated to be 4.5 × 10^3 M^{-1} s^{-1}. This is consistent with a previous calculated value in the range 10^3–10^4 M^{-1} s^{-1}.[19] From these k_{22} values and k_{12} for the corresponding oxidations of $[Mo_4S_4(edta)_2]^{4-}$, k_{11} values for the $[Mo_4S_4(edta)_2]^{4-/3-}$ self-exchange are calculated to be 2.6 × 10^7 M^{-1} s^{-1} (reaction with $[Co(edta)]^-$) and 3.0 × 10^6 M^{-1} s^{-1} (reaction with $[Fe(edta)]^-$), which give an average of 1.5 × 10^7 M^{-1} s^{-1}. Similarly from the k_{12} values for the oxidation of $[Mo_4S_4(edta)_2]^{3-}$, k_{11} self-exchange rate constants for the $[Mo_4S_4(edta)_2]^{3-/2-}$ reaction are calculated to be 7.7 × 10^5 M^{-1} s^{-1} ($[Co(dipic)_2]^-$) and 1.2 × 10^7 M^{-1} s^{-1} ($[Fe(H_2O)_6]^{3+}$). In the latter case the k_{12} value used was determined at 10 °C.

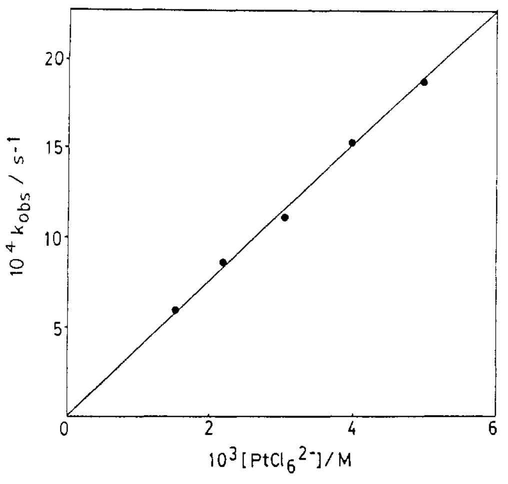

Figure 4. Dependence of first-order rate constants k_{obs}(25 °C) on oxidant concentration for the reaction of $[Mo_4S_4(edta)_2]^{3-}$ with $[PtCl_6]^{2-}$, I = 1.00 M ($LiClO_4$).

Discussion

The reactions reported here in Table VII can all be assigned as outer-sphere electron-transfer processes. In the case of the $[Fe(H_2O)_6]^{3+}$ oxidation the absence of an $[H^+]^{-1}$ dependence[25] and a measured k_{12} rate constant (6.7 × 10^4 M^{-1} s^{-1} at 10 °C) in excess of substitution on $[Fe(H_2O)_6]^{3+}$ (1.6 × 10^2 M^{-1} s^{-1} at 25 °C)[26] are criteria for an outer-sphere reaction. Although ionic strengths in the present work have been made up to I = 1.00 ($LiClO_4$), some of the literature rate constants used were with I as low as 0.10 M. The effect on rate constants (factors of 2–3) is not expected to influence significantly the outcome in terms of calculated self-exchange rate constants (where the order of magnitude is of prime importance) or the related discussion.

The self-exchange rate constant for $[Mo_4S_4(edta)_2]^{4-/3-}$, calculated from the cross-reactions with $[Co(edta)]^-$ (2.6 × 10^7 M^{-1} s^{-1}) and $[Fe(edta)]^-$ (3.0 × 10^6 M^{-1} s^{-1}) as oxidants, give an average value of 1.5 × 10^7 M^{-1} s^{-1}. In the case of the $[Mo_4S_4(edta)_2]^{3-/2-}$ reaction we favor the self-exchange rate constant (7.7 × 10^5 M^{-1} s^{-1}) obtained from the $[Co(dipic)_2]^-$ study. This is not only because the value from the corresponding $[Fe(H_2O)_6]^{3+}$ oxidation (1.2 × 10^7 M^{-1} s^{-1}) was at 10 °C but because work terms for the 3+,3− charge combination on the reactants are different, and no allowance has been made for such contributions. Both self-exchange rate constants lie close to or within the 10^6–10^7 M^{-1} s^{-1} range.

From direct experiment the comproportionation rate constant k_c for the reaction of $[Mo_4S_4(edta)_2]^{4-}$ with $[Mo_4S_4(edta)_2]^{2-}$ (eq 3) is rapid, >10^6 M^{-1} s^{-1}. From the two self-exchange rate constants (1.5 × 10^7 M^{-1} s^{-1} and 7.7 × 10^{-5} M^{-1} s^{-1}) and eqs 4 and 5, k_c = 2.4 × 10^{10} M^{-1} s^{-1}. A value of this magnitude is of considerable interest, reflecting not only the favorable nature of electron transfer but the size of both reactants. From structural information,[5] the distances from the center of each cube to the outer carboxylate O atoms are, with the inclusion of the van der

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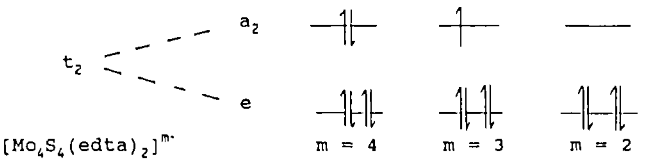
Table VII. Summary of Self-Exchange and Comproportionation Rate Constants (25 °C)[a]

reacn	k_{12}, M^{-1} s^{-1}	K_{12}[b]	k_{11},[c] M^{-1} s^{-1}	k_{22},[d] M^{-1} s^{-1}
$[Fe(edta)]^{2-}$ + $[Co(edta)]^-$	4.4[e]	1.73×10^4	4.5×10^3[f]	3.8×10^{-7}[g]
$[Mo_4S_4(edta)_2]^{4-}$ + $[Co(edta)]^-$	5.4×10^3[e]	1.12×10^7	2.6×10^7[f]	3.8×10^{-7}[g]
$[Mo_4S_4(edta)_2]^{4-}$ + $[Fe(edta)]^-$	2.4×10^6[e]	651	3.0×10^6[f]	4.5×10^3[h]
$[Mo_4S_4(edta)_2]^{3-}$ + $[Co(dipic)_2]^-$	17.8[e]	44.1	7.7×10^5[f]	1.0×10^{-5}[i]
$[Mo_4S_4(edta)_2]^{3-}$ + $[Fe(H_2O)_6]^{3+}$	6.7×10^4[j]	108	1.2×10^7[f,k]	4[l]
$[Mo_4S_4(edta)_2]^{3-}$ + $[PtCl_6]^{2-}$	0.38			
$[Mo_4S_4(edta)_2]^{4-}$ + $[Mo_4S_4(edta)_2]^{2-}$	2.4×10^{10}[f]	6.3×10^{11}	1.5×10^7[f,m]	7.7×10^5[f,h]

[a] Results in this work at I = 1.0 M ($LiClO_4$), pH >3, except as indicated for $[Fe(H_2O)_6]^{3+}$. [b] Calculated from reduction potentials (by using the Nernst equation). [c] Self-exchange rate constant for reductant. [d] Self-exchange rate constant for oxidant. [e] Experimental results, this work. [f] Calculated by using eq 2 and 3. [g] From direct studies at 74–100 °C[20,21] and extrapolation of data to 25 °C (see ref 22). [h] As in footnote *f*, previous entry. [i] Reference 10. [j] $[H^+]$ = 0.075–0.30 M; 10 °C. [k] Corrections are required here for work terms. [l] Reference 22. [m] Average of entries above (2.6×10^7 and 3.0×10^6 M^{-1} s^{-1}).

Waals radius for O^{2-} (1.4 Å),[27] the same and are ~7.4 Å. The charge on each reactant is therefore fairly diffuse. From a consideration of the comproportionation rate constant k_c, and equilibrium constant K for (3), the rate constant for disproportionation of $[Mo_4S_4(edta)_2]^{3-}$ is 0.038 M^{-1} s^{-1}. No change in absorbance at 945 nm attributable to the formation of $[Mo_4S_4(edta)_2]^{2-}$ was observed for a 6 mM solution of $[Mo_4S_4(edta)_2]^{3-}$, consistent with the K value. The concentration of $[Mo_4S_4(edta)_2]^{3-}$ would have to be much higher for a significant amount of $[Mo_4S_4(edta)_2]^{2-}$ to be generated in this way.

The similar magnitude of the rate constants for the $[Mo_4S_4(edta)_2]^{4-/3-}$ and $[Mo_4S_4(edta)_2]^{3-/2-}$ couples is of interest in the context of electron population of the t_2 bonding orbitals of such clusters. For C_{3v} symmetry these are as shown:



Of the two exchange processes it might have been expected that the 3−/2− reaction would have been energetically the more favorable (no spin-pairing factor) than the 4−/3− reaction. Charge repulsion is also greater in the latter instance.

In view of the very favorable nature of electron transfer in the Mo_4S_4 exchange processes, we thought it also of interest to see whether it was possible to oxidize $[Mo_4S_4(edta)_2]^{4-}$ in a two-electron process. The two-electron oxidant $[PtCl_6]^{2-}$ that was selected reacts rapidly with $[Mo_4S_4(edta)_2]^{4-}$ with quantitative formation of $[Mo_4S_4(edta)_2]^{3-}$. It is not immediately clear whether this rules out a two-electron change in view of the rapidity of the comproportionation of the 4− and 2− cubes. It is unlikely that a rapid two-electron change (eq 6) occurs in the first stage, because

$$[Mo_4S_4(edta)_2]^{4-} + Pt(IV) \rightarrow [Mo_4S_4(edta)_2]^{2-} + Pt(II) \quad (6)$$

(a) the driving force $[Mo_4S_4(edta)_2]^{2-/4-}$ (0.70 V) and Pt(IV)/Pt(II) (0.726 V) is not sufficiently favorable, (b) there is a large accompanying structural change of $[PtCl_6]^{2-}$ to square-planar $[PtCl_4]^{2-}$, and (c) the reaction has difficulty in proceeding by an inner-sphere mechanism (which is preferred for two-electron processes) unless there is an increase in coordination. There is moreover no evidence for the reaction proceeding via $[Mo_4S_4(edta)_2]^{2-}$ when the reaction is monitored at 945 nm. It is concluded therefore that the rapid $[Mo_4S_4(edta)_2]^{4-}$ to $[Mo_4S_4(edta)_2]^{3-}$ change occurs with stepwise reduction of Pt(IV) → Pt(III) → Pt(II). From the second-order kinetics observed for the slower one-electron oxidation of $[Mo_4S_4(edta)_2]^{3-}$, it can be concluded that the reaction sequence is (7) and (8), with (7) rate determining.

$$[Mo_4S_4(edta)_2]^{3-} + Pt(IV) \rightarrow [Mo_4S_4(edta)_2]^{2-} + Pt(III) \quad (7)$$

$$[Mo_4S_4(edta)_2]^{3-} + Pt(III) \xrightarrow{\text{fast}} [Mo_4S_4(edta)_2]^{2-} + Pt(II) \quad (8)$$

The rate constant of 1.5×10^7 M^{-1} s^{-1} for the self-exchange reaction $[Mo_4S_4(edta)_2]^{4-/3-}$ is of considerable interest alongside values obtained previously for the $[Mo_4S_4(H_2O)_{12}]^{4+/5+}$ exchange from (a) the $[V(H_2O)_6]^{2+}$ reduction of $[Mo_4S_4(H_2O)_{12}]^{5+}$ (760 M^{-1} s^{-1}),[3] and (b) the $[Co(bpy)_3]^{3+}$ oxidation of $[Mo_4S_4(H_2O)_{12}]^{4+}$ (21 M^{-1} s^{-1}).[2] The latter have been refined by inclusion of the f term, eqs 4 and 5, to give 3.8×10^3 M^{-1} s^{-1} and 26 M^{-1} s^{-1}, respectively. The edta ligands would appear to provide an environment more conducive to electron transfer than the H_2O ligands. Whether this is due to some (minor) distortion of the Mo octrahedral angles in the edta case or different electron-transfer properties in the presence of the edta is not clear.

In the only other study of the kind reported herein, rate constants for electron self-exchange of Fe_4S_4 analogues $[Fe_4S_4(SR)_4]^{2-/3-}$ (R = CH_2Ph, *p*-C_6H_4Me) have been obtained directly by ^1H NMR line broadening in acetonitrile solution.[28] The reactions are first-order in oxidized (2−) and reduced (3−) clusters in each case, and ambient temperature rate constants are in the range 10^6–10^7 M^{-1} s^{-1}. In spite of the different electron populations (Fe as opposed to Mo) and different coordination geometries (Fe is high-spin tetrahedral), the similarity in rate constants is striking. In both cases the favorable rate constants obtained suggest low reorganization energy requirements. Certainly in the case of the $[Mo_4S_4(edta)_2]$ electron-exchange processes the bond length differences are small (Table I). Activation parameters determined for the exchange $[Fe_4S_4(S\text{-}p\text{-}C_6H_4Me)_4]^{2-/3-}$ are $\Delta H^\ddagger$ = 3.6 kcal mol^{-1} and $\Delta S^\ddagger$ = −17 cal K^{-1} mol^{-1}.

The self-exchange rate constants determined in this paper, alongside the Fe_4S_4 study just referred to,[28] are consistent with the favorable electron-transfer properties of metal/sulfide clusters in biological redox processes.[29] In nitrogenase, metals such as Mo and V that exhibit coordination numbers of 6 are present alongside tetrahedral Fe in mixed metal/sulfide clusters.[30]

Acknowledgment. P.W.D. acknowledges the award of a U.K. SERC studentship, and B.-L.O. the award of a Ridley Fellowship from the University of Newcastle upon Tyne.

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