Inorg. Chem. **1992**, *31*, 3011-3017

Kinetics of 1:1 Thiocyanate (and Chloride) Substitution at Molybdenum on the Cuboidal Clusters $[Mo_4S_4(H_2O)_{12}]^{4+}$ and $[Mo_4S_4(H_2O)_{12}]^{5+}$ in Aqueous Solution

Yue-Jin Li, Mohamed Nasreldin, M. Humanes, and A. Geoffrey Sykes*

Department of Chemistry, The University, Newcastle upon Tyne NE1 7RU, U.K.

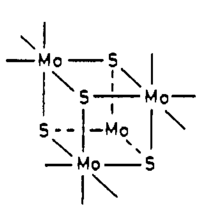
Received September 19, 1991

Substitution studies at 25 °C, $I = 2.00$ M ($LiClO_4$), on the title cuboidal Mo/S aqua ions are reported for the first time. Two consecutive reaction steps with large and small absorbance changes, respectively, are identified for the NCS^- substitution on the $Mo^{III}{}_4$ ion $[Mo_4S_4(H_2O)_{12}]^{4+}$. With thiocyanate in large >10-fold excess the first step corresponds to equilibrium kinetics, $k_{eq} = k_f([NCS^-]/4) + k_b$, and the second (independent of $[NCS^-]$) is assigned as isomerization, $k_{isom} = 3.6 \times 10^{-5}\ s^{-1}$. Rate constants for the first stage with cube in excess differ from those with NCS^- in excess by a statistical factor of 4, corresponding to the number of equivalent Mo's, and forward and back rate constants are $k_f = 1.95\ M^{-1}\ s^{-1}$ and $k_b = 1.44 \times 10^{-3}\ s^{-1}$, respectively. Two concurrent $[NCS^-]$-dependent reactions are observed in the overall slower substitution on $[Mo_4S_4(H_2O)_{12}]^{5+}$. For the first a statistical factor of 3 applies, and the rate constant $k_{1f} = 0.116\ M^{-1}\ s^{-1}$ is assigned to substitution at each of three Mo(III)'s. For the second there is no statistical factor, and $k_{2f} = 0.0166\ M^{-1}\ s^{-1}$ is assigned to substitution at the single Mo(IV). No isomerization step was detected for $[Mo_4S_4(H_2O)_{12}]^{5+}$. Kinetic studies therefore provide the first evidence that the electron distribution approximates to $Mo^{III}{}_3Mo^{IV}$ in the case of $[Mo_4S_4(H_2O)_{12}]^{5+}$. The magnitude of the various rate constants is considered. For both the 4+ and 5+ cubes no variation of rate constants with $[H^+]$ was observed over the range 0.40–2.00 M. Whereas no absorbance changes were observed for $[Mo_4S_4(H_2O)_{12}]^{4+}$ with Cl^- up to 1.5 M, small absorbance changes for the Cl^- anation of $[Mo_4S_4(H_2O)_{12}]^{5+}$ gave a single detectable rate constant ($9.7 \times 10^{-3}\ M^{-1}\ s^{-1}$) and a ratio k_{NCS}/k_{Cl} consistent with an I_d mechanism. The formation constant for the reaction with Cl^- ($1.9\ M^{-1}$) is $\sim 10^3$ less than that with NCS^-.

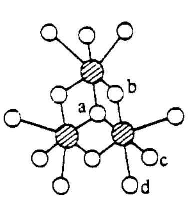
Introduction

Although the preparation[1] and properties[2,3] of the cuboidal aqua ions $[Mo_4S_4(H_2O)_{12}]^{4+}$ (orange) and $[Mo_4S_4(H_2O)_{12}]^{5+}$ (green), average oxidation states 3.0 and 3.25, respectively, have been described previously, no substitution studies have appeared. X-ray crystal structures of $[Mo_4S_4(NH_3)_{12}]Cl_4{\cdot}7H_2O$ and $Mg_2[Mo_4S_4(edta)_2]{\cdot}22H_2O$ (both derivatives of the 4+ ion)[4,5] and of $[Mo_4S_4(H_2O)_{12}](pts)_5{\cdot}14H_2O$ and $Ca_{1.5}[Mo_4S_4(edta)_2]{\cdot}13H_2O$ (derivatives of the 5+ ion)[6,7] (edta = ethylenediaminetetraacetate; pts = *p*-toluenesulfonic acid) have been reported. Relevant reduction potentials of the aqua ions in 2.0 M Hpts are for the $Mo_4S_4{}^{5+/4+}$ couple 0.21 V and for the $Mo_4S_4{}^{6+/5+}$ couple 0.86 V (both vs NHE).[3] The 5+ ion is the most accessible and easy to handle, but over a number of days it decays to $[Mo_3S_4(H_2O)_9]^{4+}$ (also green), a reaction which is made use of in the preparation of the latter (heating for 1–2 h at 90 °C).[1] The 4+ ion on the other hand is very air-sensitive, and rigorous air-free techniques are required to avoid oxidation to the 5+ ion.[2] Also, in the presence of NCS^- the 5+ ion is air-sensitive and gives a 6+ state product, as first demonstrated by Cotton and colleagues.[8]

The above complications combined with the slowness of the reactions have made it more difficult to carry out substitution studies (replacement of H_2O) on the cubes. For example preliminary observations in the Experimental Section of an earlier paper on $[Mo_4S_4(H_2O)_{12}]^{5+}$ (absorption changes in the stopped-flow range on mixing with NCS^-) are now clearly attributable to traces of $[Mo_3S_4(H_2O)_9]^{4+}$.[3] Studies on the substitution reactions of the trinuclear $Mo^{IV}{}_3$ incomplete cuboidal complexes $[Mo_3S_4(H_2O)_9]^{4+}$,[9] $[Mo_3O_4(H_2O)_9]^{4+}$,[10] and three other oxo/sulfido complexes $[Mo_3O_{4-x}S_x(H_2O)_9]^{4+}$ have been reported and provide a sharp contrast in behavior.[11] Important structural features in the case of e.g. $[Mo_3O_4(H_2O)_9]^{4+}$ and $[Mo_3S_4(H_2O)_9]^{4+}$ are the existence of (three) μ_2- and (one) μ_3-oxo/sulfido core ligands, the result of which is a nonequivalence of the three H_2O's attached to each Mo.[12-14] Thus in one description often used there are two d-H_2O's trans to the μ_2-sulfido groups and one c-H_2O trans to the μ_3-sulfido on each Mo as illustrated. The electron-rich μ_2 ligands labilize the trans H_2O's.



$[Mo_4S_4(H_2O)_{12}]^{5+/4+}$



$[Mo_3S_4(H_2O)_9]^{4+}$

The situation is simpler in the case of the cubes since all four core

---

(1) Martinez, M.; Ooi, B.-L.; Sykes, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 4615.
(2) Sharp, C.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1988**, 2579.
(3) Ooi, B.-L.; Sharp, C.; Sykes, A. G. *J. Am. Chem. Soc.* **1989**, *111*, 125.
(4) Shibahara, T.; Kawano, E.; Okano, M.; Nishi, M.; Kuroya, H. *Chem. Lett.* **1986**, 827.
(5) Shibahara, T.; Kuroya, H.; Matsumoto, K.; Ooi, S. *Inorg. Chim. Acta* **1986**, *116*, L25.
(6) Akashi, H.; Shibahara, T.; Narabara, T.; Tsuru, H.; Kuroya, H. *Chem. Lett.* **1989**, 129.
(7) Shibahara, T.; Kuroya, H.; Matsumoto, K.; Ooi, S. *J. Am. Chem. Soc.* **1984**, *106*, 789.
(8) Cotton, F. A.; Diebold, M. P.; Dori, Z.; Llusar, R.; Schwotzer, W. *J. Am. Chem. Soc.* **1985**, *107*, 6735.
(9) Ooi, B.-L.; Sykes, A. G. *Inorg. Chem.* **1989**, *28*, 3799.
(10) Ooi, B.-L.; Sykes, A. G. *Inorg. Chem.* **1988**, *27*, 310.
(11) Ooi, B.-L.; Martinez, M.; Sykes, A. G. *J. Chem. Soc., Chem. Commun.* **1988**, 1324.
(12) (a) Shibahara, T.; Kuroya, H. *Polyhedron* **1986**, *5*, 357. (b) Akashi, H.; Shibahara, T.; Kuroya, H. To be published.
(13) (a) Rogers, K. R.; Murmann, R. K.; Schlemper, E. O.; Shelton, M. E. *Inorg. Chem.* **1985**, *24*, 1313. (b) Hinch, G. D.; Wycoff, D. E.; Murmann, R. K. *Polyhedron* **1986**, *5*, 487.
(14) Richens, D. T.; Helm, L.; Pittet, P.-A.; Merbach, A. E.; Nicolo, F.; Chapins, G. *Inorg. Chem.* **1989**, *28*, 1394.

0020-1669/92/1331-3011$03.00/0

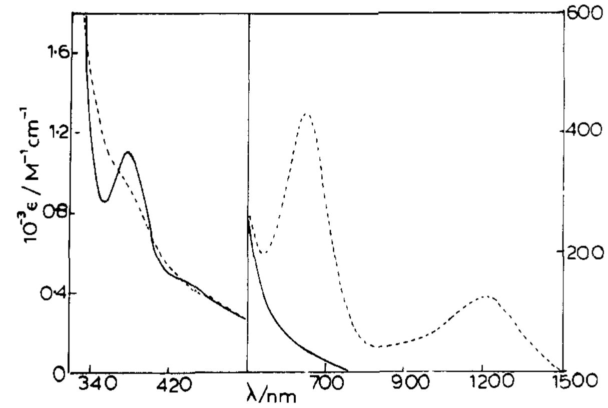


Figure 1. UV–vis spectra of the $[Mo_4S_4(H_2O)_{12}]^{5+}$ (- - -) and $[Mo_4S_4(H_2O)_{12}]^{4+}$ (—) complexes in 2 M $HClO_4$.

sulfido ligands are of the μ_3-type. As a result, the H_2O's are understandably more inert. Interestingly, for the 5+ mixed-valence cube, we find that the four Mo's do not behave in an equivalent manner. Also, in the case of the 4+ cube, isomerization is observed for the first time in studies on the NCS^- substitution of Mo/S clusters. The 6+ aqua ion exhibits a number of properties different from those of the 5+ and 4+ ions[3] and will be the subject of a separate study.

Experimental Section

Preparation of $[Mo_4S_4(H_2O)_{12}]^{5+}$. Solutions of the bis(cysteinato)-bis(μ-sulfido)dimolybdenum(V) complex $Na_2[Mo_2O_2S_2(cys)_2]\cdot 4H_2O$ were reduced with $NaBH_4$ and then treated with HCl in the presence of O_2 to give the green cuboidal aqua ion $[Mo_4S_4(H_2O)_{12}]^{5+}$, as previously described.[12a] Purification was carried out by Dowex 50W-X2 cation-exchange chromatography. Lower charge products, mainly $[Mo_3OS_3(H_2O)_9]^{4+}$, were eluted with 1 M HCl. The more tightly held $[Mo_4S_4(H_2O)_{12}]^{5+}$ was eluted with 2 M HCl and further purified on a second column. Solutions of $[Mo_4S_4(H_2O)_{12}]^{5+}$ in HCl were diluted to 0.5 M HCl, reloaded onto a Dowex column, washed with 0.5 M followed by 1.0 M Hpts, and then eluted with 4 M Hpts under N_2. The latter was kept as stock and stored under N_2 at 4 °C. Solutions in $HClO_4$ were obtained by loading on a short (4-cm length × 1.2-cm diameter) column. After washing with 1 M $HClO_4$, the aqua ion was eluted with 4 M $HClO_4$. Solutions were again stored at 4 °C and standardized spectrophotometrically at the 645-nm peak (ϵ = 435 M^{-1} cm^{-1}/cube) (Figure 1).

Preparation of $[Mo_4S_4(H_2O)_{12}]^{4+}$. Electrolytic reduction of $[Mo_4S_4(H_2O)_{12}]^{5+}$ in 2 M $HClO_4$ at a carbon-cloth electrode (RVG 1000; Le Carbonne, Brighton, U.K.) at a potential of −120 mV (vs SCE) for 2 h under N_2 was carried out as previously described.[2] After reduction the orange $[Mo_4S_4(H_2O)_{12}]^{4+}$ solution was Millepore filtered (8-μm pore size), to remove any carbon particles, and used the same day. Standardization was carried out by using the 378-nm peak (ϵ = 1100 M^{-1} cm^{-1}/cube) (Figure 1).

Other Reagents. Sodium thiocyanate and perchloric acid (both BDH, Analar) were used without further purification. Lithium perchlorate (Aldrich, reagent grade) was recrystallized twice from water. Stock sodium thiocyanate solutions were standardized by titration against Ag(I) (BDH, Convol) with Fe(III) as indicator. The $[H^+]$ of stock $[Mo_4S_4(H_2O)_{12}]^{5+}$ solutions was determined by exchanging the 5+ cube for H^+ on an Amberlite 1R(H)120 resin and titrating the total H^+ against NaOH (BDH, Convol).

Kinetics. Runs with NCS^-, under rigorous air-free conditions, were monitored at 400 nm (4+) and 450 nm (5+) by conventional spectrophotometry. Concentrations of NCS^- used were such as to restrict reaction to 1:1 substitution at each Mo. Plots of absorbance (A) changes ln ($A_\infty - A_t$) against time for the 4+ cube indicate biphasic kinetics. Rate constants for the second phase (k_{isom}) were obtained from slopes of the linear portion, which also gave the intercept x ($t = 0$). To obtain rate constants for the first phase, a standard consecutive treatment involving plotting ln ($A_\infty - A_t - xe^{-k_{isom}t}$) against time was carried out.[15] A similar treatment was used for the reaction of the 5+ ion. Contributions from two phases are indicated in the plot shown in Figure 2.

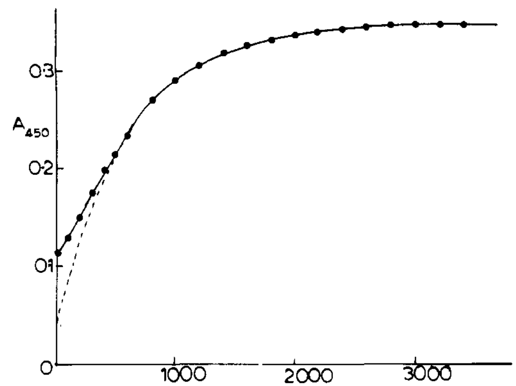


Figure 2. Absorbance changes at 450 nm for the reaction (25 °C) of $[Mo_4S_4(H_2O)_{12}]^{5+}$ (1.29 × 10^{-4} M) with NCS^- (1.53 × 10^{-3} M) in 2.0 M $HClO_4$ indicating the two-phase nature of the reaction. The broken line is an extrapolation of the second phase to t = 0.

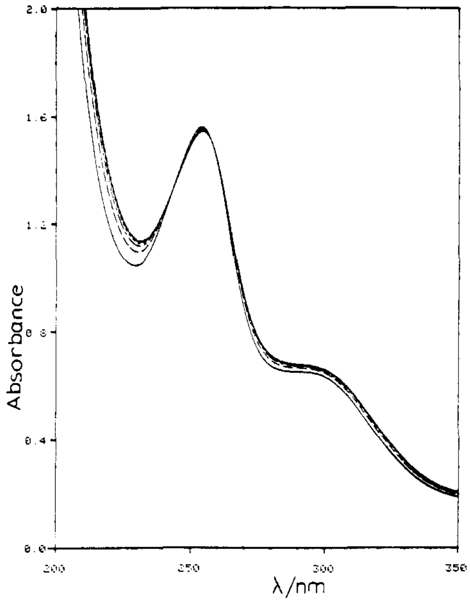


Figure 3. Scan spectra recorded every 2 min for the reaction (25 °C) of $[Mo_4S_4(H_2O)_{12}]^{5+}$ (1.53 × 10^{-2} M) with Cl^- (0.13 M) where $[H^+]$ = 2.00 M and I = 2.00 M ($HClO_4$).

No UV–vis absorbance changes were observed on reacting Cl^- with $[Mo_4S_4(H_2O)_{12}]^{4+}$. Also with the 5+ complex large concentrations of Cl^- up to 1.0 M were required, and even then absorbance changes were substantially less than for the NCS^- reaction. Isosbestic points were also noted at 243 and 258 nm (Figure 3). Only a single reaction stage was observed, and in this respect the reaction differs from the NCS^- studies. This may of course be related to the smallness of absorbance changes. A 1-cm (split) optical cell, with a partition to divide solutions prior to mixing, enabled absorbance changes to be monitored. No changes consistent with a fast initial stage were detected, and this was confirmed in stopped-flow mixing experiments. The reaction was monitored at 220 nm. Plots of ln ($A_\infty - A_t$) against time were linear to 80–90% completing.

Ion-Exchange Separation of Products of the Reaction of $[Mo_4S_4(H_2O)_{12}]^{5+}$ with NCS^-. A reaction solution (30 mL) with $[NCS^-]$ = 6.5 × 10^{-3} M, $[Mo_4S_4^{5+}]$ = 1.5 × 10^{-3} M, and [Hpts] = 0.3 M (ionic strength not adjusted) was thermostated at 25 °C for 3 h. Ion-exchange separation of the products was carried out on an air-free, ice-cooled Dowex 50W-X2 column (16-cm length × 1.2-cm diameter). After the column was loaded, elution was commenced with 0.5 M $HClO_4$. Six bands in all were obtained with colors ranging from yellow-brown to green. The first band was not held by the column. Bands five and six required 2 M $HClO_4$ for elution. Band six was from its spectrum characterized as $[Mo_4S_4(H_2O)_{12}]^{5+}$, and band five is a 4+ product. The important point here is the number of bonds, where some are probably spurious products (see Discussion).

---

[15] See e.g.: (a) Frost, A. A.; Pearson, R. G. In *Kinetics and Mechanisms*, 2nd ed.; J. Wiley: New York, 1961; p 160. (b) Espenson, J. H. In *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; p 69.

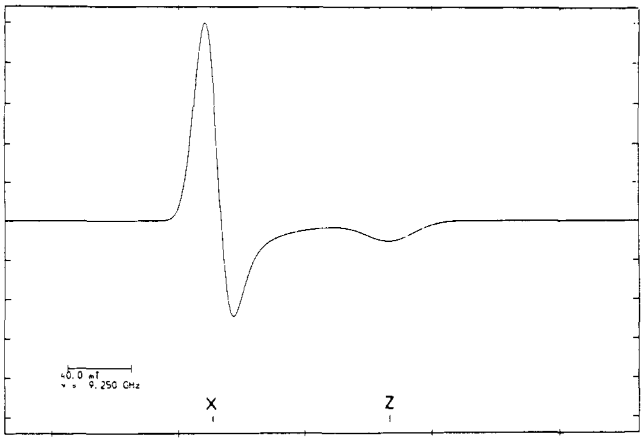


Figure 4. EPR spectrum of $[Mo_4S_4(H_2O)_{12}]^{5+}$ (2 mM) in 2.0 M Hpts, at 3.8 K, with microwave frequency 925 GHz, power 20 mW, and gain 1.25×10^3.

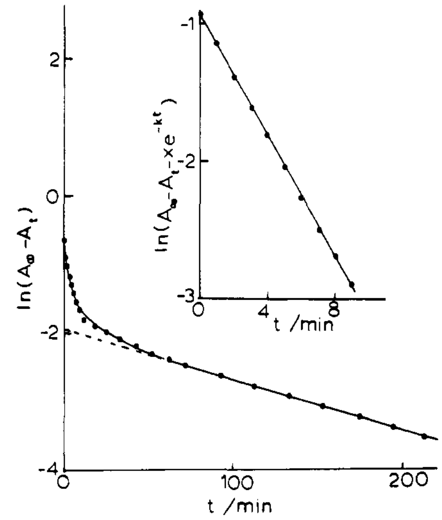


Figure 5. Kinetic plots for the reaction of $[Mo_4S_4(H_2O)_{12}]^{4+}$ (1.25×10^{-4} M) with NCS^- (4.96×10^{-3} M) at 25 °C, in 2.00 M $HClO_4$, illustrating the biphasic nature of the reaction. Consecutive equilibration rate constants k_{isom} and k_{eq} (inset) are obtained from the slopes.

EPR Spectrum. Solutions of $[Mo_4S_4(H_2O)_{12}]^{5+}$ (2 mM) in 2.0 M Hpts were loaded into an EPR tube and frozen in liquid He. Spectra were run on a Varian E-112 instrument at a low temperature (3.8 K) obtained by using an Oxford Instruments EPR9 continuous-flow cryostat coupled to a Harwell DT temperature controller. A net spin of one electron per cube with $g_{\parallel} = 1.77$ and $g_{\perp} = 2.47$ was observed (Figure 4). The $g_{\parallel}$ value is very different from the one reported for the edta derivative $[Mo_4S_4(edta)_2]^{3-}$ (2.31), while the $g_{\perp}$ values are approximately similar for both complexes (2.52 for the edta derivative). No sign of any hyperfine structure was detected, but the individual lines are very broad possibly due to unresolved structure. On the change of the temperature from 3.8 to 100 K, no significant change was observed in the spectrum. Accordingly no firm decision can be made regarding the possibility of one Mo of one kind and three of another. We thank Dr. F. E. Mabbs for help with experiments carried out at the University of Manchester.

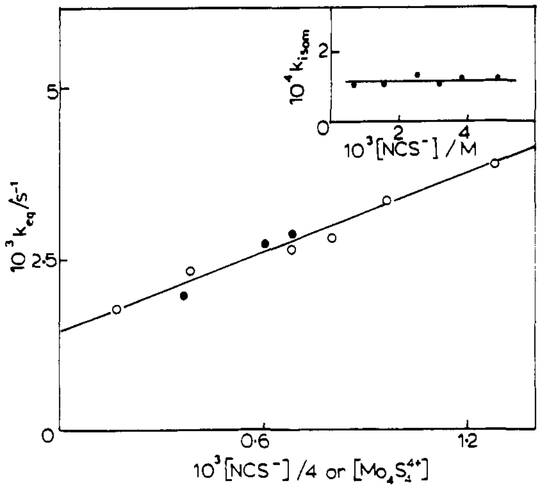


Figure 6. Substitution of NCS^- on $[Mo_4S_4(H_2O)_{12}]^{4+}$, showing dependence of rate constants k_{eq} (25 °C) on $[NCS^-]/4$ (○) and $[Mo_4S_4^{4+}]$ (●) in 2.0 M $HClO_4$, with $I = 2.00$ M. The inset illustrates the absence of a dependence of k_{isom} on $[NCS^-]$.

Table I. Equilibrium Rate Constants (25 °C) k_{1eq} and k_{2eq} for the Reaction of NCS^- with $[Mo_4S_4(H_2O)_{12}]^{4+}$ with (A) I = 2.00 M ($H/LiClO_4$) and (B) I = 2.00 M (Hpts)

$10^3[NCS^-]$/M	$10^4[Mo_4S_4^{4+}]$/M	$[H^+]$/M	$10^3k_{eq}/s^{-1}$	$10^4k_{isom}/s^{-1}$
		A		
0.062	3.6	2.00	1.95	
0.128	6.0	2.00	2.72	
0.062	6.8	2.00	2.89	
0.64	0.52	2.00	1.77	1.04
1.54	0.71	2.00	2.32	1.09
2.56	1.31	0.44	2.57	1.06
2.56	1.31	1.00	2.70	1.15
2.56	1.31	1.50	2.80	1.36
2.56	1.31	2.00	2.63	1.32
3.20	1.14	2.00	2.80	1.10
3.84	1.31	2.00	3.35	1.25
4.96	1.25	2.00	3.88	1.25
		B		
1.06	1.04	2.00	1.49	3.68
2.55	1.23	2.00	2.58	3.66
3.21	1.23	2.00	2.98	3.55
4.95	1.23	2.00	3.94	3.54

Results

Reaction of $[Mo_4S_4(H_2O)_{12}]^{4+}$ with NCS^-. For runs with $[NCS^-]$ in excess, two stages were observed (Figure 5). Equilibration rate constants, k_{eq} followed by k_{isom}, are obtained from a consecutive treatment and are as listed in Table I. With $[Mo_4S_4(H_2O)_{12}]^{4+}$ in large excess the substantially smaller absorbance changes give only k_{eq}. Rate constants for the first stage with NCS^- in excess correspond to those obtained with $[Mo_4S_4(H_2O)_{12}]^{4+}$ in excess only if a statistical factor of 4 is allowed for (Figure 6).[16] Thus, for the runs with $[NCS^-]$ in excess, $[NCS^-]/4$ values have to be used, and the dependence is as in (1),whereas with $[Mo_4S_4(H_2O)_{12}]^{4+}$ in excess (2) applies.

$$k_{eq} = k_f[NCS^-]/4 + k_b \qquad (1)$$

$$k_{eq} = k_f[Mo_4S_4^{4+}] + k_b \qquad (2)$$

The combined plot is shown in Figure 6. From an unweighted least-squares fit $k_f = 1.95 \pm 0.15$ M^{-1} s^{-1} and $k_b = (1.44 \pm 0.10) \times 10^{-3}$ s^{-1}.

The second stage, clearly defined in runs with NCS^- in large excess, gives rate constants which are independent of $[NCS^-]$ (Figure 6 inset). Experiments on the complexing of $[Mo_4S_4(H_2O)_{12}]^{4+}$ with NCS^- in 2.00 M Hpts also indicate two stages (Table I). However, rate constants for the second stage are greater in 2.00 M $HClO_4$ (11.7×10^{-5} s^{-1}) than in 2.00 M Hpts (3.61×10^{-5} s^{-1}). The difference corresponds to some $HClO_4$ oxidation of 4+ to 5+ cube, a process observed in separate experiments in 2.00 M $HClO_4$ with no NCS^- present. Negligible conversion is obtained in 2.00 M Hpts. The second stage is

---

(16) (a) Kathirgamanathan, P.; Soares, A. B.; Richens, D. T.; Sykes, A. G. *Inorg. Chem.* **1985**, *24*, 2950. (b) Li, Y.-J.; Routledge, C. A.; Sykes, A. G. Paper in preparation.

Table II. Equilibration Rate Constants (25 °C) for the Reaction of NCS^- with $[Mo_4S_4(H_2O)_{12}]^{5+}$ ($[H^+] = 0.4$–2.0 M, $I = 2.0$ M ($LiClO_4$))[a]

$10^3[NCS^-]/M$	$10^3[Mo_4S_4^{5+}]/M$	$10^5k_{1eq}/s^{-1}$	$10^5k_{2eq}/s^{-1}$
0.10	1.04	16.7	3.14
0.14	0.37	7.81	1.78
0.14	0.59	11.2	1.98
1.53	0.13	9.27	2.80
1.65	0.13	10.5	3.07
1.92[b]	0.13	12.8	3.88
2.20	0.13	13.8	4.09
2.31	0.13	13.7	4.08
2.61	0.13	15.4	4.88
2.94	0.13	16.4	5.98
3.42[b]	0.18	16.5	6.60
3.87	0.13	18.4	7.15
4.10	0.13	18.9	7.05
5.17	0.13	23.3	9.07
5.47	0.16	24.5	9.50
5.50	0.13	27.6	9.50
6.27	0.13	30.2	10.2
7.33	0.13	33.6	13.1
7.52	0.26	31.3	13.8

[a] Two stages corresponding to substitution at the three Mo(III) ions (k_{1eq}) and the Mo(IV) ion (k_{2eq}) are indicated. [b] $[H^+] = 0.4$ M.

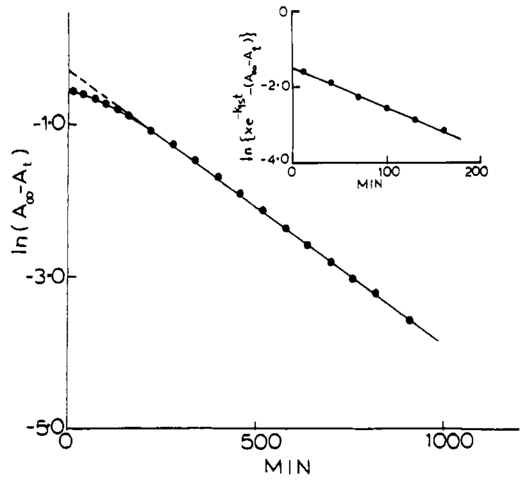


Figure 7. Kinetic plots for the reaction of $[Mo_4S_4(H_2O)_{12}]^{5+}$ (1.3×10^{-4} M) with NCS^- (2.9×10^{-3} M) at 25 °C, in 2.00 M $HClO_4$, illustrating two concurrent stages. Equilibrium rate constants k_{1eq} and k_{2eq} (inset) are obtained from the slopes.

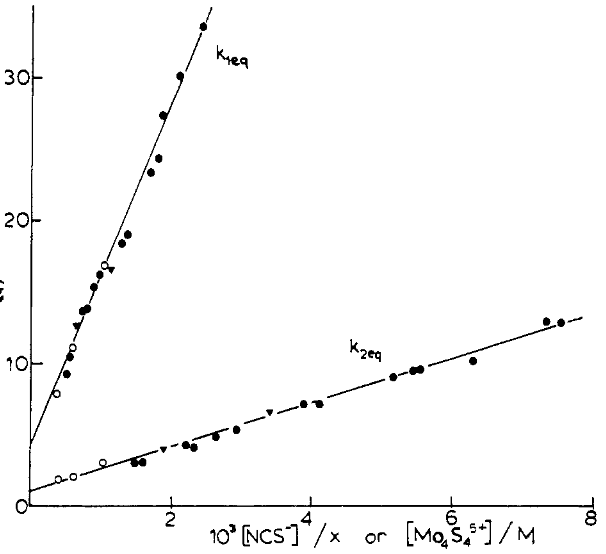


Figure 8. First and second stages for the reaction of NCS^- with $[Mo_4S_4(H_2O)_{12}]^{5+}$ and involvement of the statistical factor x. The dependence of rate constants k_{1eq} ($x = 3$) and k_{2eq} ($x = 1$) on $[NCS^-]/x$ (●) or $[Mo_4S_4^{5+}]$ (○) for reaction in 2.00 M $HClO_4$ is indicated. Rate constants (▼) in 0.40 M $HClO_4$, I = 2.00 M ($LiClO_4$), are also shown.

Table III. First-Order Equilibration Rate Constants k_{eq} (25 °C) for the Reaction of $[Mo_4S_4(H_2O)_{12}]^{5+}$ (1.1×10^{-4} M) with Cl^- (in Excess) ($[H^+] = 2.00$ M (Except As Stated), $I = 2.0$ M ($LiClO_4$))

$[Cl^-]/M$	$10^3k_{eq}/s^{-1}$	$[Cl^-]/M$	$10^3k_{eq}/s^{-1}$
0.013	4.9	0.50	10.5[a]
0.05	5.2	0.50	10.5[b]
0.10	5.8	0.53	10.2
0.13	5.8	0.60	10.8
0.20	7.0	0.67	11.3
0.27	7.8	0.70	11.6
0.30	8.0	0.78	12.5
0.33	8.3	0.90	13.6
0.40	9.0	1.00	14.3
0.50	9.9		

[a] $[H^+] = 1.00$ M. [b] $[H^+] = 0.75$ M.

therefore partially ($HClO_4$) or completely (Hpts) assigned to isomerization, with the latter giving $k_{isom} = 3.6 \times 10^{-5}\ s^{-1}$. Ion-exchange product isolation did not provide a satisfactory route in the further characterization of this process.

No variation of k_{eq} or k_{isom} with $[H^+]$ was observed (investigated $[H^+]$ range = 0.44–2.00 M, $I = 2.00$ M ($LiClO_4$); Table I).

Reaction of $[Mo_4S_4(H_2O)_{12}]^{5+}$ with NCS^-. Two equilibrium steps, defined as k_{1eq} and k_{2eq}, are observed for runs with $[Mo_4S_4(H_2O)_{12}]^{5+}$ present in large excess (Table II). Two stages are observed also for runs with NCS^- the reactant in large excess (Figure 7). Both give a first-order dependence on $[NCS^-]$. The rate law dependencies are as in (3) and (4), where a statistical

$$k_{1eq} = k_{1f}[Mo_4S_4^{5+}] + k_{1b} \qquad (3)$$

$$k_{1eq} = k_{1f}[NCS^-]/3 + k_{1b} \qquad (4)$$

factor of 3 is required in (4) for the two sets of data to fall on the same line. From the slope and intercept, respectively (Figure 8), rate constants $k_{1f} = 0.116 \pm 0.004\ M^{-1}\ s^{-1}$ and $k_{1b} = (4.3 \pm 0.6) \times 10^{-5}\ s^{-1}$ are obtained. For k_{2eq} however the rate law dependencies are as in (5) and (6), no statistical factor is required,

$$k_{2eq} = k_{2f}[Mo_4S_4^{5+}] + k_{2b} \qquad (5)$$

$$k_{2eq} = k_{2f}[NCS^-] + k_{2b} \qquad (6)$$

and $k_{2f} = (1.66 \pm 0.05) \times 10^{-2}\ M^{-1}\ s^{-1}$ and $k_{2b} = (5.0 \pm 2.0) \times 10^{-6}\ s^{-1}$. Unlike the $[Mo_4S_4(H_2O)_{12}]^{4+}$ reaction where consecutive processes (k_{eq} and k_{isom}) are observed, concurrent steps involving the three Mo(III) centers (k_{1eq}) and the Mo(IV) center (k_{2eq}) are assigned. No variation of rate constants with $[H^+]$ in the range 0.40–2.00 M was observed.

Reaction of $[Mo_4S_4(H_2O)_{12}]^{5+}$ with Cl^-. Only a single stage was observed. Rate constants k_{eq} (Table III) gave a linear dependence on $[Cl^-]$ which was varied over the range 0.01–1.00 M (eq 7). Absorbance changes were not large enough to monitor

$$k_{eq} = k_f[Cl^-] + k_b \qquad (7)$$

with the cube in excess, and it was not possible therefore to determine the statistical factor. From an unweighted least-squares fit to Figure 9, $k_f = (9.7 \pm 0.2) \times 10^{-3}\ M^{-1}\ s^{-1}$ and $k_b = (4.9 \pm 0.1) \times 10^{-3}\ s^{-1}$. There was no change in k_{eq} when $[H^+]$ was varied within the range 0.75–2.00 M (Table I). The equilibrium constant (k_f/k_b) is 1.98 (±0.08) M^{-1}.

No absorbance changes were observed on mixing Cl^- (1.5 M) with $[Mo_4S_4(H_2O)_{12}]^{4+}$ (2.9×10^{-4} M).

Discussion

The relatively straightforward substitution behavior of $[Mo_4S_4(H_2O)_{12}]^{4+}$ is considered first. A novel aspect is that for

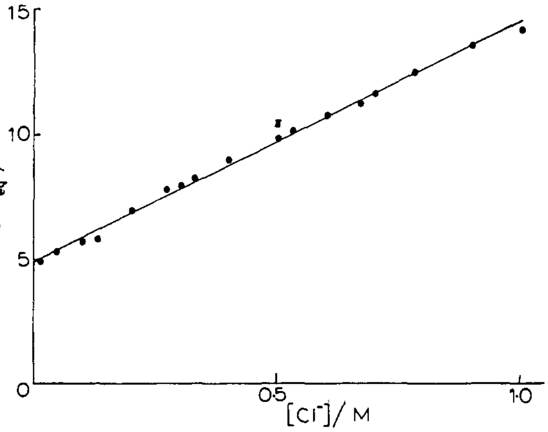
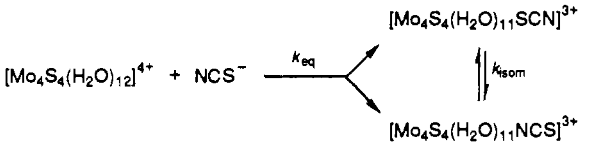


Figure 9. Dependence of rate constants k_{eq} (25 °C) for the equilibration of Cl$^-$ with $[Mo_4S_4(H_2O)_{12}]^{5+}$ on [Cl$^-$], I = 2.00 M ($LiClO_4$), with [H$^+$] = 2.00 (●), 1.00 (▼), and 0.75 M (▲).

the first time in NCS$^-$ substitution studies on Mo ions a process corresponding to isomerization has been observed. Previously the kinetics of the reactions of the Mo^{II}_2, Mo^{III}, Mo^{IV}_3, and Mo^{V}_2 aqua ions $[Mo_2(H_2O)_8]^{4+}$,[17] $[Mo(H_2O)_6]^{3+}$,[18] $[Mo_3O_4(H_2O)_9]^{4+}$,[10] and $[Mo_2O_4(H_2O)_6]^{2+}$,[19] respectively, and Mo^{IV}_3 clusters in which sulfido replaces the oxo ligands to give $[Mo_3O_xS_{4-x}(H_2O)_9]^{4+}$ [11] have been studied. No isomerization steps were detected. Now in the case of cuboidal $[Mo_4S_4(H_2O)_{12}]^{4+}$ evidence is obtained for a reaction scheme as in (8). The existence of crystal structures



(8)

of N-bonded thiocyanato complexes of Mo in oxidation states II–V, e.g. $K_3[Mo(NCS)_6]\cdot MeCO_2H\cdot H_2O$,[20] $(NMe_4)_4[Mo_3O_4(NCS)_8(H_2O)]\cdot 3H_2O$,[21] $(pyH)_5[Mo_3O_2S_2(NCS)_9]\cdot 2H_2O$,[22] $(NH_4)_6[Mo_4S_4(NCS)_{12}]\cdot 10H_2O$,[8] $(pyH)_4[Mo_2O_4(NCS)_6]$,[23] and $(pyH)_3[Mo_2O_4(HCO_2)(NCS)_4]\cdot H_2O$,[24] with no examples of S-bonded forms, strongly suggests that the N-bonded isomers are the more stable. Although in (7) we indicate an equilibration process for k_{isom}, it is possible that isomerization from Mo–SCN to Mo–NCS only is effective.

In recent studies on the IV state trinuclear $[W_3S_4(H_2O)_9]^{4+}$, but not $[Mo_3S_4(H_2O)_9]^{4+}$, a process corresponding to isomerization has likewise been detected.[16b] It is possible to explain the behavior observed by hard–soft (or class a/b) acid–base theory.[25,26] Thus, the third transition-series element W is expected to be softer than the second series congener Mo. Also Mo of $[Mo_4S_4(H_2O)_{12}]^{4+}$ with an average oxidation state of 3.0 should be softer than that for the incomplete cuboidal Mo^{IV}_3 trinuclear ion $[Mo_3S_4(H_2O)_9]^{4+}$ and could well give larger amounts of the S-bonded NCS$^-$ complex. Because of their similar composition there are grounds for supposing that isomerization should be observed also in the case of $[Mo_4S_4(H_2O)_{12}]^{5+}$. However for this reaction two [NCS$^-$]-dependent stages are observed, and we have not been able to detect the relatively small changes which isomerization might be expected to give. Other examples, notably with Co(III), have been reported in which there is isomerization of S- to N-bonded thiocyanate.[27,28] By a comparison of behavior in 2.00 M $HClO_4$ and 2.00 M Hpts, it has been possible to detect small contributions to the second stage from the ClO_4^- oxidation of $[Mo_4S_4(H_2O)_{12}]^{5+/4+}$. The reduction potential of the $[Mo_4S_4(H_2O)_{12}]^{4+}$ couple of 0.21 V [3] is consistent with such reducing properties. The rate constant (25 °C) for isomerization is 3.6×10^{-5} s^{-1} from experiments in 2.00 M Hpts.

Table IV. Summary of Kinetics and Thermodynamic Data for Substitution Reactions of NCS$^-$ and Cl$^-$ at 25 °C (I = 2.00 M ($LiClO_4$))[a]

reactant	rate consts	equilibrium const
$[Mo_4S_4(H_2O)_{12}]^{4+}$ + NCS$^-$	$k_f = 1.95$ M^{-1} s^{-1} $k_b = 1.44 \times 10^{-3}$ s^{-1} $k_{isom} = 1.17 \times 10^{-4}$ s^{-1}	1.3×10^3 M^{-1} at Mo(III)
$[Mo_4S_4(H_2O)_{12}]^{5+}$ + NCS$^-$	$k_{1f} = 0.116$ M^{-1} s^{-1} $k_{1b} = 4.3 \times 10^{-5}$ s^{-1}	2.7×10^3 M^{-1} at Mo(III)
	$k_{2f} = 1.66 \times 10^{-2}$ M^{-1} s^{-1} $k_{2b} = 5.0 \times 10^{-6}$ s^{-1}	3.3×10^{-3} M^{-1} at Mo(IV)
$[Mo_4S_4(H_2O)_{12}]^{5+}$ + Cl$^-$	$k_{1f} = 9.7 \times 10^{-3}$ M^{-1} s^{-1} $k_{1b} = 4.9 \times 10^{-3}$ s^{-1}	1.98 M^{-1} [b]

[a] No [H$^+$] dependencies were observed over the range 0.40–2.00 M explored. [b] Most likely assignment is substitution at Mo(IV); see text.

The nonidentical behavior of the Mo's of the mixed-valence (average oxidation state 3.25) $[Mo_4S_4(H_2O)_{12}]^{5+}$ cube is an observation of considerable importance. In the case of $[Mo_4S_4(H_2O)_{12}]^{4+}$ the single [NCS$^-$]-dependent step requires a statistical factor of 4, consistent with four identical Mo(III)'s. Two [NCS$^-$]-dependent steps are observed with $[Mo_4S_4(H_2O)_{12}]^{5+}$. The one requiring a statistical factor of 3 is assigned as substitution at three identical Mo's in oxidation state approximating to III. The rate constant k_{1eq} corresponds to substitution at each of these Mo's. The second k_{2eq} with no statistical factor is assigned as substitution at Mo in oxidation state IV. From an X-ray crystallographic study on the edta complex of the $Mo_4S_4^{5+}$ cluster $Ca_{1.5}[Mo_4S_4(edta)_2]\cdot 13H_2O$ there are four short (2.780 [19] Å) and two long (2.863 [25] Å) Mo–Mo bonds.[7,29] However, no similar differences have been reported for $[Mo_4S_4(H_2O)_{12}](pts)_5\cdot 14H_2O$ (2.802 [18] Å),[6] and there is no crystallographic evidence to suggest that one of the Mo's is different from the other three. This can of course be explained by random crystal packing of the cubes, the averaging effect giving four apparently identical Mo's.

The kinetic and thermodynamic results obtained are summarized in Table IV. Rate constants for NCS$^-$ substitution on $[Mo_4S_4(H_2O)_{12}]^{5+}$ are 0.116 M^{-1} s^{-1} for reaction at each of three Mo(III)'s and 0.0166 M^{-1} s^{-1} for reaction at Mo(IV). The former is 18 times less than for substitution at each of four Mo(III)'s on $[Mo_4S_4(H_2O)_{12}]^{4+}$. One explanation is that there is some electron delocalization giving mobility of oxidation state and some Mo(IV) character at each Mo(III) in the case of $[Mo_4S_4(H_2O)_{12}]^{5+}$. The faster substitution observed for studies on the $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ and $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ clusters is believed to result from substitution occurring at the heterometal centers, which from crystallography are tetrahedral.[30,31] The EPR spectrum of $[Mo_4S_4(H_2O)_{12}]^{5+}$ at 3.8 K gives no evidence for hyperfine splitting in support of a $Mo^{III}_3Mo^{IV}$

---

(17) Finholt, J. E.; Leupin, P.; Sykes, A. G. *Inorg. Chem.* **1983**, *22*, 3315.

(18) Sasaki, Y.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 1048.

(19) Sasaki, Y.; Taylor, R. S.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 396.

(20) Knox, J. R.; Eriks, K. *Inorg. Chem.* **1968**, *7*, 84.

(21) Schlemper, E. O.; Hussain, M. S.; Murmann, R. K. *Cryst. Struct. Commun.* **1982**, *11*, 89.

(22) Shibahara, T.; Yamada, T.; Kuroya, H.; Hills, E. F.; Kathirgamanathan, P.; Sykes, A. G. *Inorg. Chim. Acta* **1986**, *113*, L19.

(23) Referred to in: Cayley, G. R.; Sykes, A. G. *Inorg. Chem.* **1976**, *15*, 2882.

(24) Glowiak, T.; Rudolf, M. F.; Sabat, M.; Jezowska-Trzebiatowska, B. In *Proceedings of the Second International Conference on the Chemistry and Uses of Molybdenum*; Mitchell, P. C. H., Seaman, A., Eds.; Climax Molybdenum Co.: Climax, MI, 1976; p 17. Also published in *J. Less-Common Met.*

(25) Pearson, R. G. *Inorg. Chem.* **1988**, *27*, 734 and references therein.

(26) Ahrland, S.; Chatt, J.; Davis, N. R. *Q. Rev.* **1958**, *12*, 265.

(27) Buckingham, D. A.; Creaser, I. I.; Sargeson, A. M. *Inorg. Chem.* **1970**, *9*, 655.

(28) Jackson, W. G.; Jurisson, S. S.; McGregor, B. C. *Inorg. Chem.* **1985**, *24*, 1788.

(29) Shibahara, T. *Adv. Inorg. Chem.* **1991**, *37*, 143–173. Personal communication from Professor Shibahara.

(30) Dimmock, P. W.; Dickson, D. P. E.; Sykes, A. G. *Inorg. Chem.* **1990**, *29*, 5920.

structure. On heating of solutions to 45 °C, a 4% decrease in absorbance at 645 nm was observed which is reversible. This is however comparable to a similar 5% effect observed for the trinuclear Mo^{IV}_3 ion $[Mo_3S_4(H_2O)_9]^{4+}$ and does not therefore seem relevant in the present context.

The existence of a band at 1100 nm for the mixed-valent $[Mo_4S_4(H_2O)_{12}]^{5+}$ complex, and its disappearance on reduction to Mo^{III}_4 in $[Mo_4S_4(HO)_{12}]^{4+}$, suggests that this is an intervalence band. Robin and Day[32] proposed a classification of mixed-valence systems according to the degree of coupling. Three classes were suggested, class I for systems with no coupling interaction, class II for metal centers showing weak coupling, and class III for systems with strong delocalization. Hush has studied the properties of intervalence transitions in mixed-valent species and developed an equation (eq 9) for class II systems.[33,34] The

$$\Delta\nu_{1/2} = (2310\nu_{max})^{1/2}\ \mathrm{cm}^{-1} \qquad (9)$$

bandwidth at half-height ($\Delta\nu_{1/2}$) can be calculated by using (9), where ν_{max} is the energy of the intervalence band. Equation 9 has been applied to mixed-valent binuclear systems and enables these compounds to be assigned according to the Robin and Day classification. Application of (9) to the $[Mo_4S_4(H_2O)_{12}]^{5+}$ band at 1100 nm indicates that the measured bandwidth at half-height (2080 cm^{-1}) is significantly less than the calculated value (4580 cm^{-1}). This suggests that there is strong delocalization and class III behavior.

On the other hand studies on Fe/S clusters have indicated valence localization effects. Thus Fe_2S_2 proteins in the reduced state have been shown to have Fe^{2+} and Fe^{3+} centers.[35] Mixed-valence pairs appear to be present also in $Fe_4S_4^{2+}$ (2.5 oxidation state) clusters.[36] Interestingly $Fe_3S_4^0$ has been assigned one localized Fe^{3+} site and a delocalized Fe^{2+}–Fe^{3+} pair. This behavior suggests that some valence localization on $Mo_4S_4^{5+}$ is perfectly reasonable. The $Mo_4S_4^{5+}$ cluster has 11 d-electrons and is 1 electron short of the 12 required to provide six Mo–Mo bonds. In the present context a key factor is the rapidity of what amounts to "electron-hole hopping" as compared to the lifetime of NCS^- in an ion-pair prior to complexation.

Not only is the equilibrium constant for Cl^- complexing to $[Mo_4S_4(H_2O)_{12}]^{5+}$ ($K = 1.98$ M^{-1}) much less than those observed for NCS^- (2700 and 3320 M^{-1}), but absorbance changes are much less, and only one stage is detected. An assignment as to which process is being monitored can be made by indirect means only. At all the UV–vis wavelengths investigated in the reaction of NCS^- with $[Mo_4S_4(H_2O)_{12}]^{5+}$ (e.g. 350, 400, 450, and 500 nm), the larger absorbance change (ratio 6:1 at 450 nm) is for substitution at Mo(IV). On this basis, reaction at Mo(IV) is favored for the single-phase reaction with Cl^-. In order to assign the mechanism of substitution on $[Mo_4S_4(H_2O)_{12}]^{5+}$, one approach which has been used is to determine the ratio of rate constants k_{NCS}/k_{Cl}. For an associative interchange mechanism (I_a) this ratio is generally substantially >10, but for a dissociative interchange (I_d) it is close to unity.[18] Thus in the case of $[Mo(H_2O)_6]^{3+}$ (ratio 59), an I_a assignment has been made, which has been further substantiated by determining the volume of activation with NCS^-.[37]

Since rate constants (k_1) for substitution at Mo(IV) on $[Mo_4S_4(H_2O)_{12}]^{5+}$ are $k_{NCS} = 16.6 \times 10^{-3}$ M^{-1} s^{-1} and $k_{Cl} = 9.7 \times 10^{-3}$ M^{-1} s^{-1}, the ratio k_{NCS}/k_{Cl} is 1.7. Therefore a dissociative interchange I_d process can be assigned, which is in sharp contrast to the I_a assignment for $[Mo(H_2O)_6]^{3+}$.[18] If in fact the Cl^- kinetics correspond to substitution at Mo(III), then the relevant ratio k_{NCS}/k_{Cl} is 3.9 (including a statistical factor of 3 for both reactions), and an I_d mechanism can likewise be assigned. Associative processes are a feature of reactions of metal ions with low d-electron populations (particularly those ≤ 3).[18] Here the μ_3-S core ligands presumably modify the electronic structure on the d^2 Mo(IV) sufficiently for this to be no longer true. No absorbance changes were detected on mixing Cl^- with the Mo^{III}_4 cube $[Mo_4S_4(H_2O)_{12}]^{4+}$, which supports the assignment of Cl^- substitution on $[Mo_4S_4(H_2O)_{12}]^{5+}$ as substitution at Mo(IV) rather than Mo(III). The similarity of rate constants (25 °C) for the substitution of NCS^- on $[Mo_4S_4(H_2O)_{12}]^{4+}$ (1.95 M^{-1} s^{-1}) and on $[Mo(H_2O)_6]^{3+}$ (0.28 M^{-1} s^{-1} at $I = 1.00$ M (Lipts)) is noted in spite of the different mechanistic assignments.

Rate constants for aquation of thiocyanate on $[Mo_4S_4(H_2O)_{12}]^{5+}$ have been determined and are more favorable for Mo(III) than Mo(IV), $k_{1b} > k_{2b}$, again as might be expected. There is also a significant difference in the behavior of Mo(III) centers in the 4+ and 5+ cubes, with aquation on the 4+ cube 33 times faster. Equilibrium constants K (Table III), obtained from the ratio of forward and back rate constants, indicate values of similar magnitude for Mo(III) on the two cubes and for Mo(IV) on $[Mo_4S_4(H_2O)_{12}]^{5+}$.

Product analyses carried out by ion-exchange chromatography on equilibrated $[Mo_4S_4(H_2O)_{12}]^{5+}$ (1.5×10^{-3} M) and NCS^- (6.5×10^{-3} M) in [Hpts] = 0.3 M are notable for the separation of at least six bands. Air-free techniques were used, but experiments are of long duration, and we cannot exclude the possibility that some extra bands may result from air oxidation to the 6+ state. The faster moving bands most likely correspond to the products from substitution on the 5+ ion and originate therefore from concurrent substitution at the three Mo(III)'s, as well as Mo(IV). These experiments, although not allowing a quantitative approach, support the various assignments made.

Studies of NCS^- substitution on five Mo(IV) incomplete cuboidal complexes $[Mo_3O_{4-x}S_x(H_2O)_9]^{4+}$ have been carried out previously.[11] The behavior observed for $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_3O_4(H_2O)_9]^{4+}$ are relevant here. Both have nonidentical H_2O's, the one type trans to a μ_2 core atom (two d-H_2O's on each Mo) and the other trans to the μ_3 core atom (one c-H_2O on each Mo). The μ_2-sulfido core ligands have been shown to be $\sim 10^2$ more trans labilizing than μ_2-oxo, and substitution at the c-H_2O's is $\sim 10^5$ times less favorable than at d-H_2O, at least in the case of $[Mo_3O_4(H_2O)_9]^{4+}$.[14] Furthermore, the two d-H_2O's on $[Mo_3O_4(H_2O)_9]^{4+}$ are more acidic (K_a = 0.2–0.4 M) than the c-H_2O's, a pattern which is expected to repeat itself with $[Mo_3S_4(H_2O)_9]^{4+}$.[9,10] At any one Mo the conjugate base of a d-H_2O labilizes the second d-H_2O for substitution, which is the only reaction path detected.[14] Substitution of the first d-H_2O on $[Mo_3S_4(H_2O)_9]^{4+}$ proceeds via the aqua ion alongside the conjugate base pathway.

Studies on $[Mo_4S_4(H_2O)_{12}]^{4+}$ and $[Mo_4S_4(H_2O)_{12}]^{5+}$ have revealed substantially slower substitution rates than for $[Mo_3S_4(H_2O)_9]^{4+}$ (which is in the stopped-flow range), with no $[H^+]$ dependence in the range 0.4–2.0 M investigated. The cubes have no electron-rich μ_2-sulfido ligands, and since H_2O's trans to μ_3-sulfido ligands do not have high acid dissociation constants, no inverse $[H^+]$-dependent terms implying conjugate-base participation are observed. The rate constant for substitution at the c-H_2O's on $[Mo_3S_4(H_2O)_9]^{4+}$ has not as yet been determined, but would be expected to be comparable to that of the two cubes.

The studies here described provided an understanding of essential substitution properties of the $[Mo_4S_4(H_2O)_{12}]^{4+}$ and

---

[31] Dimmock, P. W.; Lamprecht, G. J.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1991**, 955.

[32] Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391; *Electrochim. Acta* **1968**, *13*, 1005.

[33] Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

[34] (a) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247. (b) Cannon, R. D. In *Electron-Transfer Reactions*; Butterworth: London, 1982; p 270.

[35] Dugad, L. B.; La Mar, G. N.; Banci, L.; Bertini, I. *Biochemistry* **1990**, *29*, 2263.

[36] Noodleman, L.; Case, D. A. *Adv. Inorg. Chem.* **1992**, *38*, 464.

[37] Richens, D. T.; Ducommun, Y.; Merbach, A. E. *J. Am. Chem. Soc.* **1987**, *109*, 603.

$[Mo_4S_4(H_2O)_{12}]^{5+}$ cuboidal complexes and complement previous studies on the incomplete cubes e.g. $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_3O_4(H_2O)_9]^{4+}$. We note that the μ_3-sulfido-containing complexes $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_3SO_3(H_2O)_9]^{4+}$ are more stable to oxidation than $[Mo_3O_4(H_2O)_9]^{4+}$. The existence of Mo_4S_4 cubes in the 4+, 5+, or 6+ states, but no corresponding Mo_4O_4 analogues, also indicates a stabilizing influence of μ_3-sulfido ligands.

Acknowledgment. We thank the Royal Society for a Royal Fellowship, the SERC for postdoctoral support (to Y.-J.L.), the University of Lisbon for leave of absence, and the INIC for financial support (to M.H.).

Registry No. $[Mo_4S_4(H_2O)_{12}]^{4+}$, 104843-16-5; $[Mo_4S_4(H_2O)_{12}]^{5+}$, 99145-05-8; NCS^-, 71048-69-6; Cl^-, 16887-00-6.