Concurrent NCS^- Substitution at Non-equivalent Molybdenum(IV) Centres of the Incomplete Cuboidal Aqua Ion $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9]^{4+}$ †

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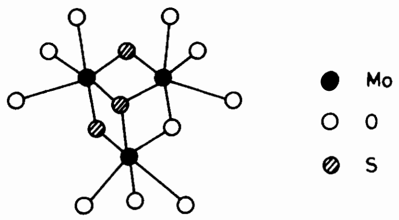
The kinetics of NCS^- substitution on the unsymmetrical (crystallographically defined) molybdenum(IV) aqua ion, $Mo_3SOS_2^{4+}$, have been studied, under conditions in which substitution is confined to 1 : 1 reaction at each Mo^{IV}. Biphasic behaviour was observed with first $Mo_3SOS_2^{4+}$ (>10-fold) and then NCS^- (>10-fold) in excess, and two equilibration rate constants were obtained. These correspond to concurrent substitution at the molybdenum(IV) centres, two of one kind and one of another. A statistical factor of 2 applies to the slower process, which is therefore assigned to substitution at the two μ-oxo co-ordinated molybdenum(IV) centres. Formation rate constants are 82 and 23 $M^{-1}\,s^{-1}$ respectively at 25 °C in 2 M $HClO_4$.

The synthesis of incomplete cuboidal (one Mo depleted) oxosulphidomolybdenum(IV) aqua ions, $Mo_3O_xS_{4-x}^{4+}$, has recently been described.[1] The procedure, involving reduction of the di-μ-sulphido-molybdenum(V) dimer, $Mo_2O_2S_2^{2+}$, as the aqua ion or cysteinato complex, yields $Mo_3OS_3^{4+}$ as one of the major products. This ion has been characterised by *X*-ray crystallography on $Ba[Mo_3OS_3(ida)_3]\cdot 7H_2O$ (ida = iminodiacetate) which has indicated an unsymmetrical $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9]^{4+}$ structure,[2] hereafter referred to as $Mo_3SOS_2^{4+}$. As work in this area has progressed, with extensive crystallographic work on the various $Mo_3O_xS_{4-x}^{4+}$ types,[2–7] it has become clear that the μ_3-sulphido structures ($x < 4$) prevail, presumably because of the size and bonding characteristics of sulphide as compared to oxide. The core clusters $Mo_3O_3S^{4+}$,[3] $Mo_3SO_2S^{4+}$,[4] $Mo_3SOS_2^{4+}$,[2] and $Mo_3S_4^{4+}$,[5–7] as well as $Mo_3O_4^{4+}$,[8–10] are now well established. Two of these, $Mo_3SO_2S^{4+}$ and $Mo_3SOS_2^{4+}$, are unsymmetrical, with two molybdenum(IV) centres of one type and one of another. Here we report a study on the kinetics of substitution of one of these, full formula $[Mo_3SOS_2(H_2O)_9]^{4+}$, (I).

The involvement of a statistical factor in the equilibration of NCS^- with $Mo_3O_4^{4+}$,[11] and the high acidity of H_2O ligands, are questions that have been previously addressed.[11,12] Reactant concentration ranges adopted here were such as to confine reaction to 1:1 complexing at each molybdenum(IV) centre.



(I)

Experimental

Preparation of $[Mo_3SOS_2(H_2O)_9]^{4+}$.—This was obtained in aqueous 2 M *p*-toluenesulphonic acid (Hpts, Sigma Chemicals) by reduction of the di-μ-sulphido-molybdenum(V) dimer $Mo_2O_2S_2^{2+}$ as previously described.[1] At an early stage in this work the aqua ion was also obtained by aquating solid $Ba[Mo_3SOS_2(ida)_3]\cdot 7H_2O$ as used in the crystal structure determination.[2] In a typical procedure 0.3 g of the latter were left to stand in 2—3 M HCl at room temperature for 2 d. After dilution to $[H^+] \approx 0.3$ M the product was separated by Dowex 50W-X2 cation-exchange chromatography (25 × 1.5 cm column). All bands were eluted with 2 M HCl after first washing with 0.3 M HCl, and left overnight for further aquation. Solutions in Hpts were obtained by using a second Dowex 50W-X2 column. After loading and washing with 0.5 and 1 M Hpts the $Mo^{IV}{}_3$ aqua ion was eluted with 2 M Hpts. Solutions of $Mo_3SOS_2^{4+}$ could also be eluted in 2 M $HClO_4$. The spectrum has been reported previously.[1,2] Spectrophotometric standardisation of solutions was at 588 nm (ε 263 $M^{-1}\,cm^{-1}$ per mole of trimer) in 2 M Hpts. We have noted a small shift to 590 nm in 2 M $HClO_4$ with the ε remaining unchanged (±2%). Kinetic runs on the NCS^- reaction with solutions of $Mo_3SOS_2^{4+}$ in 2 M Hpts prepared directly,[1] and from the crystalline sample (four runs in each case) were in good agreement (±4%). This point having been established we chose subsequently to work in 2 M $HClO_4$ to establish further the kinetics. The μ-sulphido substituted $Mo^{IV}{}_3$ ions are unusually stable in 2 M $HClO_4$ compared with $Mo_3O_4^{4+}$, which (under N_2) is known to become oxidised overnight.

Other Reagents.—Sodium thiocyanate and perchloric acid (both AnalaR) were used as supplied. Lithium perchlorate, $LiClO_4\cdot 3H_2O$ (Aldrich), was recrystallised twice from water. Thiocyanate solutions were standardised by titration against silver(I) (BDH, Convol), with Fe^{III} as indicator. The $[H^+]$ of stock $Mo_3SOS_2^{4+}$ solutions was determined by ion exchange onto Amberlite IR(H) 120 resin, and titration for the H^+ released.

Kinetic Studies.—Absorbance increases on treating $Mo_3SOS_2^{4+}$ with NCS^- were monitored at 450 nm on a Dionex D-110 stopped-flow spectrophotometer, and in some cases by conventional spectrophotometry using a Hi-Tech SFA 11 rapid-mixing accessory. Runs were carried out with $[NCS^-]$

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

Table. Equilibration rate constants, k_{1eq} and k_{2eq}, for the reaction (25 °C) of NCS^- with $[Mo_3SOS_2(H_2O)_9]^{4+}$ in 2.0 M $HClO_4$

$10^3[NCS^-]$	$10^3[Mo_3SOS_2{}^{4+}]$	10^2k_{1eq}*	10^2k_{2eq}*
M		s^{-1}	
0.050	0.50	2.7	6.8
0.100	0.80	3.2	8.8
0.100	1.00	3.6	10.5
1.2	0.04	2.7	12.1
1.6	0.05	3.3	15.3
2.0	0.05	3.6	19.0
2.4	0.05	4.2	22.1
2.8	0.05	4.6	25.0
3.0	0.05	4.9	27.4

* Each entry is an average of at least two determinations.

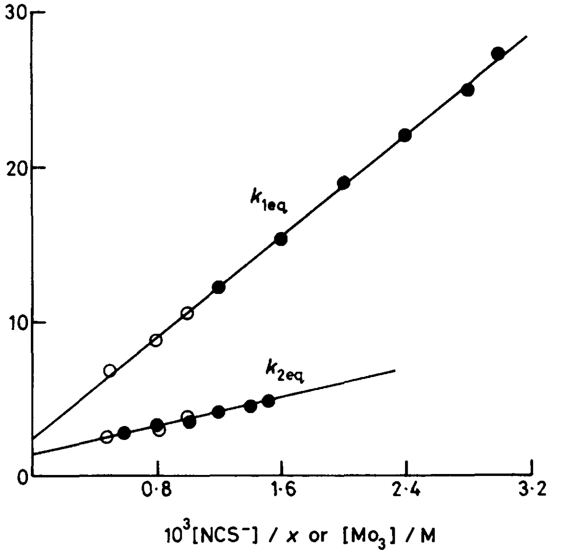

Figure. The dependence of equilibration rate constants k_{1eq} and k_{2eq} on the concentration of the reactant in excess: NCS^- (●) and $Mo_3SOS_2{}^{4+}$ (○). A statistical factor is required and has been applied ($x = 2$) to $[NCS]^-$ values for k_{2eq}

in excess (> 10-fold) over the $[Mo^{IV}]$ expressed as monomer, and $[Mo_3SOS_2{}^{4+}]$ (> 10-fold) in excess over $[NCS^-]$. Concentrations of NCS^- were limited to $< 4 \times 10^{-3}$ M. All traces were biphasic and a concurrent reaction treatment (which is the same as for consecutive reactions) was applied.[13] Thus the slower equilibration rate constant was first obtained from a plot of absorbance (A) changes, $\ln(A_\infty - A_t)$, against time (the slope of the linear portion gives k_{2eq}). By allowing for this slower process the equilibration rate constant (k_{1eq}) for the faster stage could be determined.

Results

Rate constants k_{1eq} and k_{2eq} are listed in the Table. For the slower process (k_{2eq}) it was found that rate constants determined with $[NCS^-]$ in excess only agree with those with $[Mo_3SOS_2{}^{4+}]$ in excess if a statistical factor is allowed for. Thus for the runs with $[NCS^-]$ in excess, Figure, $[NCS^-]/2$ values have to be used. This stage can therefore be assigned to substitution at the (two) equivalent molybdenum(IV) sites. No similar statistical factor is required for k_{1eq} values in the Figure. The slopes and intercepts give $k_1 = 82 \pm 1$ M^{-1} s^{-1}, $k_{-1} = (2.4 \pm 0.2) \times 10^{-2}$ s^{-1}, $k_2 = 23 \pm 1.1$ M^{-1} s^{-1}, $k_{-2} = (1.4 \pm 0.1) \times 10^{-1}$ s^{-1}, at 25 °C and $I = 2.0$ M ($HClO_4$). From additional runs in which the $[H^+]$ was decreased, $I = 2.0$ M ($LiClO_4$), it was found that rate constants increased, indicating contributions from conjugate-base pathways. Results illustrating this behaviour in full for $Mo_3O_4{}^{4+}$ have already been presented.[12]

Discussion

The X-ray crystal structure of $Ba[Mo_3SOS_2(ida)_3]\cdot 7H_2O$ has clearly demonstrated that the μ-oxo ligand of the $Mo_3SOS_2{}^{4+}$ cluster is in a μ and not μ_3 position, implicating non-equivalent molybdenum(IV) centres as illustrated in (I).[2] This is supported by two kinetic stages for runs with $Mo_3SOS_2{}^{4+}$ in excess, both dependent on $[Mo_3SOS_2{}^{4+}]$. The correspondence of rate constants for runs with first $Mo_3SOS_2{}^{4+}$ and then NCS^- in 10-fold excess rules out the possibility of appreciable bis complex formation in the latter case. An interesting feature is the need for inclusion of the statistical factor of two for the slower process (k_{2eq}), when $[NCS^-]$ is in excess, thus clearly indicating that this process corresponds to substitution (23 M^{-1} s^{-1}) at the equivalent μ-oxo bonded molybdenum(IV) sites. The more rapid H_2O replacement (82 M^{-1} s^{-1}) is therefore at the Mo^{IV} which is co-ordinated to three μ-sulphido ligands. Both processes are more rapid than NCS^- substitution observed on $Mo_3O_4{}^{4+}$ ($k_1 = 2.13$ M^{-1} s^{-1} at 25 °C in 2.0 M $HClO_4$),[11] indicating a pattern of increasing lability of H_2O ligands as more sulphido groups are substituted into the core.[14]

Acknowledgements

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References

1 M. Martinez, B-L.-Ooi, and A. G. Sykes, *J. Am. Chem. Soc.*, 1987, **109**, 4615.
2 T. Shibahara, H. Miyake, K. Kobayashi, and H. Kuroya, *Chem. Lett.*, 1986, 139.
3 T. Shibahara, H. Hattori, and H. Kuroya, *J. Am. Chem. Soc.*, 1984, **106**, 2710.
4 T. Shibahara, T. Yamada, H. Kuroya, E. F. Hills, P. Kathirgamanathan, and A. G. Sykes, *Inorg. Chim. Acta*, 1986, **113**, L19.
5 A. Bino, F. A. Cotton, and Z. Dori, *J. Am. Chem. Soc.*, 1978, **100**, 5252.
6 F. A. Cotton, Z. Dori, R. Llusar, and W. Schwotzer, *J. Am. Chem. Soc.*, 1985, **107**, 6734.
7 T. Shibahara and H. Kuroya, *Polyhedron*, 1986, **5**, 357.
8 A. Bino, F. A. Cotton, and Z. Dori, *J. Am. Chem. Soc.*, 1978, **100**, 5252.
9 E. O. Schlemper, M. S. Hussain, and R. K. Murmann, *Cryst. Struct. Commun.*, 1982, **11**, 89.
10 K. R. Rodgers, R. K. Murmann, E. O. Schlemper, and M. E. Shelton, *Inorg. Chem.*, 1985, **24**, 1313.
11 P. Kathirgamanathan, A. B. Soares, D. T. Richens, and A. G. Sykes, *Inorg. Chem.*, 1985, **24**, 2950.
12 B-L. Ooi and A. G. Sykes, *Inorg. Chem.*, 1988, **27**, 310.
13 J. H. Espenson, in 'Chemical Kinetics and Reaction Mechanisms,' Series in Advanced Chemistry, McGraw-Hill, 1981, p. 55.
14 F. A. Armstrong, T. Shibahara, and A. G. Sykes, *Inorg. Chem.*, 1978, **17**, 189.

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