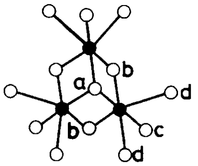
Kinetics of 1 : 1 NCS^- for H_2O Substitution on W^{IV} of $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]^{4+}$ and $[W_3(\mu_3\text{-}S)(\mu\text{-}O)_3(H_2O)_9]^{4+}$: The Effect of replacing Core Oxo by Sulphido Ligands and Comparisons with $Mo^{IV}{}_3$†

Mohamed Nasreldin, Ade Olatunji, Paul W. Dimmock, and A. Geoffrey Sykes*
Department of Chemistry, The University, Newcastle upon Tyne NE1 7RU

The kinetics (25 °C) of 1 : 1 complexing of NCS^- for H_2O at W on the incomplete cuboidal $W^{IV}{}_3$ clusters $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]^{4+}$ and $[W_3(\mu_3\text{-}S)(\mu\text{-}O)_3(H_2O)_9]^{4+}$ has been investigated, and together with previous data for $[W_3(\mu_3\text{-}O)(\mu\text{-}O)_3(H_2O)_9]^{4+}$, indicate the reactivity pattern for the $[W_3O_xS_{4-x}(H_2O)_9]^{4+}$ (here abbreviated to $W_3O_xS_{4-x}{}^{4+}$) series of µ-oxo/µ-sulphido aqua ions. Formation rate constants (k_f/M^{-1} s^{-1}) in 2.00 M $HClO_4$, I = 2.00 M are 38.4 for $W_3S_4{}^{4+}$, 0.008 0 for $W_3O_3S^{4+}$, and 0.11 for $W_3O_4{}^{4+}$, exhibiting an identical trend to that of the corresponding $Mo^{IV}{}_3$ aqua ions, which react an order of magnitude faster. Reactions are faster at lower [H^+] values indicating an involvement of conjugate-base forms of the $W^{IV}{}_3$ reactant. From a full study on the $W_3S_4{}^{4+}$ reaction the acid-dissociation constant is K_a = 0.35 M, and rate constants are k_1 = 11.9 M^{-1} s^{-1} for the aqua ion, and k_2 = 192 M^{-1} s^{-1} for the conjugate base. This contrasts with $W_3O_4{}^{4+}$, which as far as could be ascertained proceeds exclusively by the conjugate-base route, k_2 = 1.2 M^{-1} s^{-1}. Again the behaviour observed is very similar to that for the $[Mo_3O_xS_{4-x}(H_2O)_9]^{4+}$ series of complexes.

Substitution of H_2O by NCS^- on five µ-oxo/µ-sulphido incomplete cuboidal $Mo^{IV}{}_3$ cluster ions, $[Mo_3O_xS_{4-x}(H_2O)_9]^{4+}$, has been studied previously,[1-5] and the kinetic effect of replacing core oxo by sulphido ligands determined.[5] Thus from investigations at I = [$HClO_4$] = 2.0 M a 570-fold spread in rate constants (25 °C) is observed for 1 : 1 NCS^- substitution at Mo, with replacement of core μ_3-O by μ_3-S decreasing (factor of 10), and further replacement of three µ-O by µ-S leading to a stepwise (factor of 570 total) increase in rate constants for substitution.[5] Differences are observed in the behaviour of H_2O (c) *trans* to the μ_3 core atom and (d) *trans* to the µ core atoms, with substitution at the latter the dominant process occurring.[6-9] Acid dissociation constants (K_a) are in the range 0.2—0.5 M.[1,9] From ^{17}O n.m.r. studies on $Mo_3O_4{}^{4+}$ only the d-H_2O ligands give detectable acid dissociation over the [H^+] range 0.1—0.9 M.[9] Whereas the substitution of $Mo_3S_4{}^{4+}$ involves the aqua ion as well as the conjugate base,[3] the other $Mo_3O_xS_{4-x}{}^{4+}$ ions so far studied appear to react predominantly *via* the conjugate base.[5] The ions $Mo_3O_4{}^{4+}$, $Mo_3O_3S^{4+}$, and $Mo_3S_4{}^{4+}$ are symmetrical, and each has only one type of Mo to consider therefore, whereas $Mo_3O_2S_2{}^{4+}$ and $Mo_3OS_3{}^{4+}$ have non-identical Mo atoms displaying different reactivities.[4] The $Mo_3O_xS_{4-x}{}^{4+}$ complexes (x = 3, 2, or 1), with the μ_3 position occupied by oxo, are not obtained in significant amounts by existing preparative procedures. A statistical factor of three for $Mo_3O_4{}^{4+}$ is well documented,[1,2] being apparent when rate constants are obtained with first NCS^- and then $Mo^{IV}{}_3$ present in large >10-fold excess. This behaviour contrasts with that observed for $Mo_3OS_3{}^{4+}$, when the two different molybdenum sites require statistical factors of 2 and 1 respectively.[4]



We now turn to the corresponding $W^{IV}{}_3$ reactions, to establish the reactivity pattern, and whether there are any strikingly different aspects in behaviour as compared to $Mo^{IV}{}_3$. It has already been demonstrated that NCS^- reacts *ca.* 10 times slower with $W_3O_4{}^{4+}$ than $Mo_3O_4{}^{4+}$.[10] Otherwise the substitution properties are very similar. We have selected the two other symmetrical clusters $W_3S_4{}^{4+}$ and $W_3O_3S^{4+}$, which in the most direct way should enable us to comment on the overall behaviour of the $W^{IV}{}_3$ complexes. Both the $W_3S_4{}^{4+}$ and $W_3O_3S^{4+}$ ions have been prepared previously, and characterised by X-ray crystallography.[11,12]

Experimental

Preparation of $W_3S_4{}^{4+}$.—The procedure involves reduction of $[NH_4]_2[WS_4]$, the preparation of which has been described,[13] with sodium tetrahydroborate, $Na[BH_4]$, in the presence of HCl.[11] More HCl was added to the resultant brown solution and air passed through for 12 h at 80 °C. The dark brown solution obtained was left to stand overnight at room temperature. After filtration Sephadex G-10 or Dowex 50W-X2 chromatography was applied (1 M HCl), when two bands were obtained. The first purple band, peak at 570 nm in 1 M HCl, was purified using a Dowex 50W-X2 cation exchanger, eluting with 2 M HCl. The resultant solution was loaded into a second column (20 × 1.5 cm diameter), washed with 0.5 M p-toluenesulphonic acid (Hpts, Sigma Chemicals), and $W_3S_4{}^{4+}$ eluted as a single purple band with 2 M Hpts. The second band (red-purple) was identified as the μ_3-sulphido cluster $W_3OS_3{}^{4+}$.[14] Solutions in perchloric acid were obtained by reloading on a 3 cm long column; the $W_3S_4{}^{4+}$ moved to the bottom of the column with 1 M $HClO_4$ during which process Hpts was washed off, and final elution was with 2 M $HClO_4$. The $W_3S_4{}^{4+}$ solution has two peaks at 314 (ε 6 350) and 557 nm (ε 446 M^{-1} cm^{-1} per

---

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

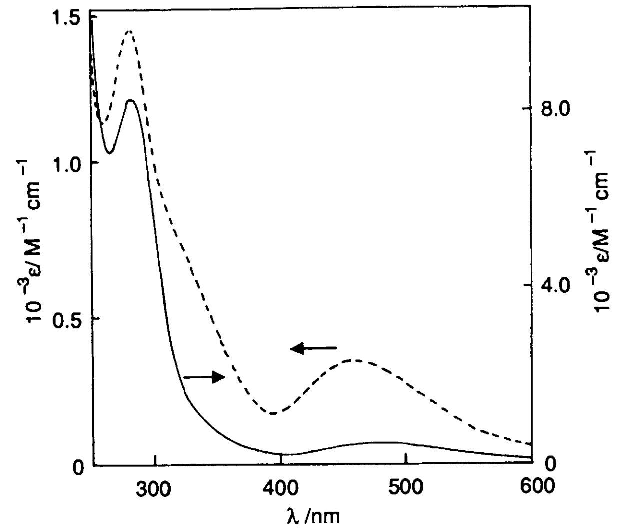


Figure 1. U.v.-visible absorption spectra for $W_3O_3S^{4+}$ (– – –) and $[W_3O_3S(NCS)]^{3+}$ (——) in aqueous acidic solution (ε per trimer), I = 2.00 M ($LiClO_4$)

trimer).[11] Solutions in 2 M Hpts under N_2 were stable over periods of months, and in 2 M $HClO_4$ under air showed <4% decay within 1 week.

Preparation of $W_3O_3S^{4+}$.—The procedure used was that of Cotton *et al.*[12] Amounts of the red precipitate, obtained after refluxing hexacarbonyltungsten (1 g, Aldrich) with anhydrous Na_2S (0.8 g, BDH, Analar) in acetate anhydride (100 cm^3) for 12 h under N_2, were increased by evaporation (Rotavap) treatment to give a significantly higher yield. The product was then dissolved in 2 M Hpts. After dilution to 0.3 M Hpts this was loaded onto a Dowex 50W-X2 cation-exchange column (20 × 1.5 cm diameter). On elution with 0.5 followed by 1.0 M Hpts the main orange band was eluted with 2 M Hpts. A similar procedure to that used for $W_3S_4^{4+}$ was employed to exchange the acid for 2 M $HClO_4$. Solutions in 2 M Hpts could be stored for periods of months. In 2 M $HClO_4$ in air only 10% decay is observed within a week. Solutions have absorption maxima at 280 and 458 nm. Using inductively coupled plasma atomic emission spectroscopy to determine W, u.v.–visible absorption peak positions λ/nm (ε/M^{-1} cm^{-1} per trimer) were at 458 (349 *cf.* 361 in ref. 11) and 280 (1.48 × 10^3), Figure 1.

Other Reagents.—Sodium thiocyanate (BDH, Analar) was recrystallised once from ethanol, and lithium perchlorate (Aldrich, Reagent Grade) twice from water. Tungstic acid (Aldrich, Reagent Grade), *p*-toluenesulphonic acid (Sigma), perchloric acid (BDH, Analar), and sodium tetrahydroborate were used without further purification.

Standardisation of Reagents.—Sodium thiocyanate solutions were standardised by titration against Ag^I (BDH, Convol) with Fe^{III} (aq) as indicator. The $[H^+]$ of stock $W^{IV}{}_3$ solutions was determined by exchanging the $W^{IV}{}_3$ for H^+ on an Amberlite IR(H) 120 resin, and titrating the total H^+ released against NaOH (BDH, Convol).

Products from the Reactions with NCS^-.—For the reaction of $W_3S_4^{4+}$ (0.75 × 10^{-3} M) with NCS^- (0.27 M) in 0.5 M $HClO_4$, the equilibrated products from an ice-cooled Dowex 50W-X2 column were, in order of elution with 0.5 M $HClO_4$, $[W_3S_4(NCS)_2]^{2+}$, $[W_3S_4(NCS)]^{3+}$, and $W_3S_4^{4+}$. The $[W_3S_4(NCS)]^{3+}$ product aquated during elution and we were unable to determine a precise spectrum. In a similar experiment on $W_3O_3S^{4+}$ (6.5 × 10^{-4} M) with NCS^- (2 × 10^{-3} M) in 0.5 M $HClO_4$ (36 h) the product $[W_3O_3S(NCS)]^{3+}$ was isolated and gave peaks at 475 (430) and 282 nm (8.35 × 10^3 M^{-1} cm^{-1}), Figure 1. The latter value was checked by allowing aquation to the known $W_3O_3S^{4+}$ spectrum to occur.

Kinetic Studies.—The $W_3S_4^{4+}$ reaction was monitored by Dionex D-110 stopped-flow spectrophotometry at 314 (NCS^- in excess) and 370 nm ($W_3S_4^{4+}$ in excess). First-order equilibration rate constants k_{eq} were obtained from absorbance (A) plots of $\ln(A - A_t)$ against time. Rate constants with NCS^- in >10-fold excess were one-third those with $W_3S_4^{4+}$ in large excess, and to allow for this $[NCS^-]$ values were divided by three (the statistical factor) to obtain rate constants k_f (formation) and k_{aq} (aquation). The $[NCS^-]$ was restricted to <2.5 × 10^{-3} M to avoid greater than 1:1 NCS^- complexing at each W. Small contributions from a second stage were noted.

Reactions were very much slower in the case of $W_3O_3S^{4+}$ and conventional spectrophotometry was required. From the spectrum of $[W_3O_3S(NCS)]^{3+}$ (Figure 1), a wavelength of 280 nm was selected to monitor the reaction. Thiocyanate concentrations up to 3.0 × 10^{-3} M were used. Final (equilibrium) absorbance values were in excess of those predicted from the spectrum of $[W_3O_3S(NCS)]^{3+}$, consistent with substitution occurring at each W and a statistical factor of three applying. Because runs required 4—5 d to reach equilibrium, and over this period there were absorbance changes due to NCS^- decay in 2.0 M $HClO_4$ (separate experiments), Guggenheim plots,[15] giving rate constants some 10—20% lower than those from $\ln(A - A_t)$ against time plots, were used. From half-lives rate constants *ca.* 20% smaller than the Guggenheim values were obtained, and a more generous allowance for errors is probably appropriate in this study.

The temperature of all runs was 25.0 ± 0.1 °C. The ionic strength was adjusted to 2.00 ± 0.02 M using amounts of $HClO_4$ and $LiClO_4$ as required.

Treatment of Data.—Unweighted non-linear regression and linear least-squares fitting procedures were used.

Results

Reaction of $W_3S_4^{4+}$.—First-order equilibration rate constants k_{eq}, Table 1, with $[NCS^-]$ in large excess, are dependent on $[NCS^-]$ at fixed $[H^+]$ in the range 0.30—2.00 M. With the inclusion of the statistical factor (see above), the dependence (1)

$$k_{eq} = k_f[NCS^-]/3 + k_{aq} \qquad (1)$$

holds, Figure 2. In the presence of excess of $W_3S_4^{4+}$ only $[W_3S_4(NCS)]^{3+}$ is formed, and k_{eq} conforms to equation (2). Values of k_f and k_{eq} are listed in Table 2.

$$k_{eq} = k_f[W_3S_4^{4+}] + k_{aq} \qquad (2)$$

A plot of k_f against $[H^+]^{-1}$ is curved (Figure 3), and gives a positive intercept on the *y*-axis. The latter indicates that the aqua ion $W_3S_4^{4+}$ as well as the conjugate base is contributing to the kinetics. The reaction sequence (3)—(6) with $W_3S_4^{4+}$ here written as W_3^{4+} gives a satisfactory fit to the

$$W_3^{4+} \overset{K_a}{\rightleftharpoons} W_3(OH)^{3+} + H^+ \qquad (3)$$

$$W_3^{4+} + NCS^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} W_3(NCS)^{3+} \qquad (4)$$

$$W_3(OH)^{3+} + NCS^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} W_3(OH)(NCS)^{2+} \qquad (5)$$

Table 1. First-order equilibration rate constants, k_{eq} (25 °C), for the reaction of $W_3S_4^{4+}$ (4.0×10^{-5} M) with NCS^-, I = 2.00 M ($LiClO_4$)

$[H^+]$/M	$10^3[NCS^-]$/M	$10^2k_{eq}/s^{-1}$
2.00	2.33	5.5
	2.17	5.3
	1.98	5.1
	1.69	4.8
	1.34	4.3
	0.99	3.85
	0.69	3.47
	0.38	3.01
	0.03	5.3^{a}
	0.03	4.6^{b}
	0.03	3.50^{c}
1.50	2.33	6.5
	1.69	5.6
	0.99	4.6
	0.40	3.59^{d}
	0.03	3.63
1.00	2.33	8.1
	2.17	7.7
	1.98	7.5
	1.69	6.8
	1.34	6.3
	0.99	5.4
	0.69	5.0
	0.40	4.4
	0.03	6.9
	0.03	5.3^{c}
	0.03	4.5^{e}
0.75	1.98	8.6
	1.69	7.9
	1.34	7.2
	0.89	6.3
	0.69	5.5
	0.60	5.5
	0.40	5.1
0.50	1.98	10.7
	1.69	9.7
	1.34	8.9
	0.99	7.9
	0.69	7.0
	0.40	6.1
0.40	1.69	11.2
	1.34	10.4
	0.99	9.0
	0.69	8.1
	0.40	7.1
0.30	1.34	11.9
	0.99	10.4
	0.69	9.6
	0.40	8.4

[a] $[W_3S_4^{4+}] = 0.75 \times 10^{-3}$ M. [b] $[W_3S_4^{4+}] = 0.55 \times 10^{-3}$ M. [c] $[W_3S_4^{4+}] = 0.31 \times 10^{-3}$ M. [d] $[W_3S_4^{4+}] = 0.17 \times 10^{-3}$ M. [e] $[W_3S_4^{4+}] = 0.19 \times 10^{-3}$ M.

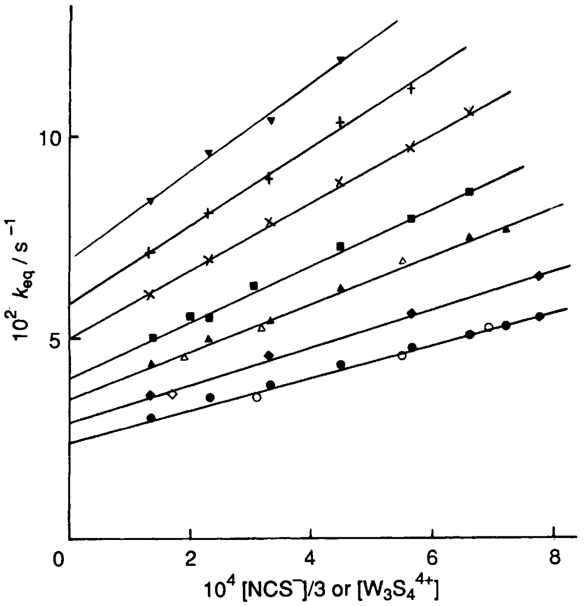


Figure 2. The variation of equilibration rate constants, k_{eq}(25 °C), with $[NCS^-]$ or $[W_3S_4^{4+}]$ (reactant present in large excess) at different $[H^+]$ values, for the NCS^- substitution of H_2O at W on the incomplete cuboidal ion $W_3S_4^{4+}$, I = 2.0 M ($LiClO_4$). The statistical factor of 3 has to be allowed for in the case of runs with NCS^- in excess (solid points). Runs with $W_3S_4^{4+}$ in excess are indicated by open points. $[H^+]$ = 0.3 (▼), 0.4 (+), 0.5 (×), 0.75 (■), 1.0 (▲, △), 1.5 (◆, ◇), or 2.0 M (●, ○)

$$W_3(NCS)^{3+} \overset{K_a'}{\rightleftharpoons} W_3(OH)(NCS)^{2+} + H^+ \qquad (6)$$

data. Thus the forward reaction can be expressed as in equation (7). Using a non-linear regression program of the general form

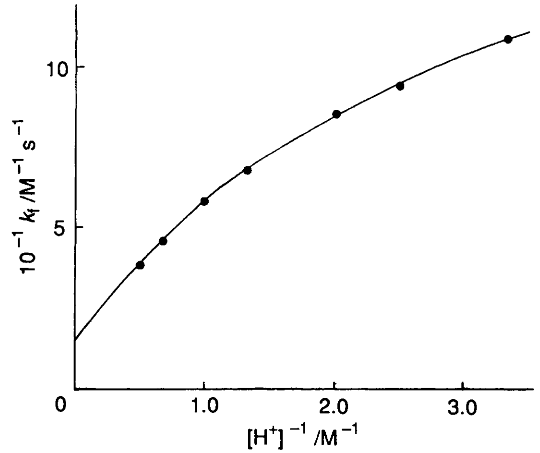


Figure 3. The non-linear dependence on $[H^+]^{-1}$ of formation rate constants k_f at 25 °C (slopes in Figure 2), for the NCS^- substitution of H_2O on $W_3S_4^{4+}$, I = 2.00 M ($LiClO_4$)

$$k_f = \frac{k_1[H^+] + k_2K_a}{[H^+] + K_a} \qquad (7)$$

of (7), $K_a = 0.35 \pm 0.01$ M, $k_1 = 11.9 \pm 0.5$ M^{-1} s^{-1}, and $k_2 = 192 \pm 6$ M^{-1} s^{-1}.

The corresponding plot of k_{aq} against $[H^+]^{-1}$ is only slightly curved, and from reactions (3)—(5) k_{aq} can be expressed as in equation (8). A similar treatment of the data gives K_a' =

$$k_{aq} = \frac{k_{-1}[H^+] + k_{-2}K_a'}{[H^+] + K_a'} \qquad (8)$$

0.1 ± 0.02 M, $k_{-1} = (1.50 \pm 0.05) \times 10^{-2}$ s^{-1}, and $k_{-2} = 0.244 \pm 0.032$ s^{-1}.

Table 2. Formation (k_f) and aquation (k_{aq}) rate constants (25 °C) for the equilibration of $W_3S_4^{4+}$ with NCS^- from equation (2), I = 2.00 M ($LiClO_4$)

$[H^+]$/M	$10^{-1}k_f/M^{-1}\ s^{-1}$	$10^2k_{aq}/s^{-1}$
2.00	3.84 ±0.14	2.53 ±0.08
1.50	4.6 ±0.2	2.96 ±0.08
1.00	5.9 ±0.1	3.54 ±0.07
0.75	6.8 ±0.3	4.1 ±0.1
0.50	8.6 ±0.2	5.0 ±0.1
0.40	9.5 ±0.4	5.9 ±0.1
0.30	10.9 ±0.8	7.0 ±0.2

Table 3. Rate constants, k_{eq}, for NCS^- complexing with $W_3O_3S^{4+}$ (1.0 × 10^{-4} M except as stated) in 2.0 M $HClO_4$ obtained using the Guggenheim method, at 25 °C, I = 2.00 M

$10^3[NCS^-]$/M	$10^5k_{eq}/s^{-1}$
0.75	0.77
1.00	0.79
1.00	0.86
1.50	0.96
1.75	1.11
2.00	0.97
2.00	1.03
2.00[a]	0.96
2.00[b]	0.98
2.50	1.24
3.00	1.38
3.00	1.29

[a] $[W_3O_3S^{4+}]$ = 0.5 × 10^{-4} M. [b] $[W_3O_3S^{4+}]$ = 0.75 × 10^{-4} M.

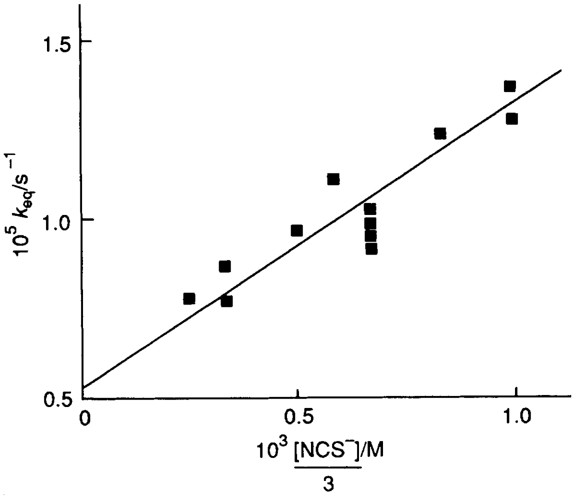


Figure 4. The variation of rate constants k_{eq} (25 °C) for the NCS^- substitution of H_2O at W on the incomplete cuboidal ion $W_3O_3S^{4+}$ in 2 M $HClO_4$, I = 2.0 M

Table 4. Summary of rate constants $k_f/M^{-1}\ s^{-1}$ for the 1 : 1 complexing of NCS^- with $W_3S_4^{4+}$, $W_3O_3S^{4+}$ (this work), and $W_3O_4^{4+}$ (ref. 10) in 2.00 M $HClO_4$ I = 2.00 M. A comparison of k_f values in 2.0 M $HClO_4$ for the corresponding $Mo_3O_xS_{4-x}^{4+}$ series of complexes is also made (from ref. 5). The ratio of rate constants is indicated in parentheses.

	$k_f/M^{-1}\ s^{-1}$	
	M = W	M = Mo
$M_3S_4^{4+}$	38.4 (4 880)	212 (570)
$M_3O_3S^{4+}$	0.0080 (1)	0.37 (1)
$M_3O_4^{4+}$	0.11 (13.8)	2.13 (5.8)

Reaction of $W_3O_3S^{4+}$.—Guggenheim plots gave k_{eq} values as listed in Table 3. A statistical factor of three was assumed, and Figure 4 is a plot of k_{eq} (25 °C) *vs.* $[NCS^-]/3$ from which k_1 is (8.0 ± 1.0) × 10^{-3} $M^{-1}\ s^{-1}$ and k_{aq} = (5.4 ± 0.6) × $10^{-6}\ s^{-1}$ at $[H^+]$ = 2.00 M, I = 2.00 M. Much more scatter is observed in this set of data. As in other related studies the reaction is faster at lower $[H^+]$, but this effect was not investigated further.

Discussion

It is now clear that similar oxo clusters, $M_3O_4^{4+}$ for the IV state and $M_2O_4^{2+}$ for the V state, are a feature of molybdenum and tungsten chemistry, and that the structures are unique to these elements and not (as yet) observed elsewhere in the Periodic Table. The similar chemistry is attributable to the virtually identical radii of Mo and W resulting from the lanthanide contraction. However strikingly different redox behaviour is observed, with the $W_3O_4^{4+}$ and $W_2O_4^{2+}$ ions some *ca.* 10^6 times more reactive than the molybdenum analogues.[10,16] As far as substitution of terminal H_2O ligands is concerned, W has been shown to be *ca.* 10 times less reactive.[10,17] Here we explore the substitution chemistry of μ-oxo/μ-sulphido cluster complexes $W_3O_xS_{4-x}^{4+}$, and make comparisons with the previously studied molybdenum analogues.

The $W_3S_4^{4+}$ ion is resistant to oxidation by O_2 (<4% reaction in 1 week), whereas studies with $W_3O_4^{4+}$ required air-free techniques.[10] Both can be studied in the presence of ClO_4^- although in the case of $W_3O_4^{4+}$ greater care is required and solutions had to be used within a few hours of preparation. Similar trends are observed with the molybdenum analogues.[3] Thus, overnight (under N_2), $Mo_3O_4^{4+}$ undergoes virtually complete oxidation by 2 M ClO_4^-, and in 2 M pts^- 10% by air, whereas $Mo_3S_4^{4+}$ is stable indefinitely to both ClO_4^- and O_2 at pH < 1. The observation that the $[IrCl_6]^{2-}$ oxidation of $W_3O_4^{4+}$ occurs *ca.* 10^6 times more rapidly than for $Mo_3O_4^{4+}$ makes clear the greater reducing power of W over Mo.[10] The clusters $W_3S_4^{4+}$ and $Mo_3S_4^{4+}$ exhibit such a marked increase in stability as to make comparisons difficult. With strong oxidants such as $[IrCl_6]^{2-}$ oxidation of S^{2-} can also occur.

A marked increase in stability is observed in going from $W_3O_4^{4+}$ to $W_3O_3S^{4+}$. For example $W_3O_3S^{4+}$ is stable indefinitely to O_2 in 2 M Hpts, and shows only slow 10% decay in 2 M $HClO_4$ in air within 1 week. Similar behaviour is observed for the molybdenum analogues and replacement of the μ_3-oxo by μ_3-sulphido appears to be a stabilising influence.

Rate constants for 1:1 NCS^- substitution of H_2O at W on three $W_3O_xS_{4-x}$ ions are summarised in Table 4. The values for W are approximately an order of magnitude smaller as compared to the corresponding values for Mo, with a greater overall spread in the case of W. From the entries for $W_3O_3S^{4+}$ and $W_3O_4^{4+}$, replacement of μ_3-oxo by sulphide produces a decrease in reactivity as for the molybdenum counterparts. Similarly incorporation of μ-oxo ligands increases the rate constants for substitution. The general pattern therefore repeats fairly closely that observed for the molybdenum analogues, Table 4. Two complexes $Mo_3O_2S_2^{4+}$ and $Mo_3OS_3^{4+}$ with non-identical molybdenum sites have also been studied, when biphasic kinetics are observed. Otherwise the same pattern of behaviour is noted.[4,5] As in the case of the μ-oxo ligands of $Mo_3O_4^{4+}$,[9] the greater electron density on μ-sulphido ligands is expected to labilise the d-H_2O as opposed to c-H_2O positions.

From the hydrogen-ion dependence of the $W_3S_4^{4+}$ reaction with NCS^-, and acid-dissociation constant K_a = 0.35 M has been obtained [equation (3)]. This is similar to the kinetically determined value for $Mo_3S_4^{4+}$ ($K_a = 0.22$ M). Unlike $Mo_3O_4^{4+}$ there are no significant spectrophotometric changes with range [H^+] 0.1—2.0 M. Also of interest are the K_a values for $W_3O_4^{4+}$ (0.22 M) and $Mo_3O_4^{4+}$ (values in range 0.24—0.42 M from three methods). From crystallography the separation of the metal atoms is virtually identical for the oxo complexes $W_3O_4^{4+}$ (2.52Å)[18,19] and $Mo_3O_4^{4+}$ (2.49Å),[20,21] and sulphido complexes $W_3S_4^{4+}$ (2.77Å)[11] and $Mo_3SO_4^{4+}$ (2.76Å).[22,23] The variation in metal–metal distance and invariance of K_a values argues against an interaction of OH^- and H_2O to give an $H_3O_2^-$ bridge.

The equilibrium constant K(25 °C) in 2 M $HClO_4$ defined by the ratio k_f/k_{aq} is 1 520 M^{-1} for $W_3S_4^{4+}$ and 1 480 M^{-1} for $W_3O_3S^{4+}$. The corresponding value for $W_3O_4^{4+}$ is 3 140 M^{-1}.[10] Corresponding values for the $Mo_3O_xS_{4-x}^{4+}$ ions have been obtained,[5] and are in the range 968—3 420 M^{-1}.

Acknowledgements

We are grateful to the Association of Commonwealth Universities for a Staff Fellowship (to A. O.), and the S.E.R.C. for a Studentship (to P. W. D.). We also thank Ian Ridley for assistance with some of the preparative work.

References

1 B-L. Ooi and A. G. Sykes, *Inorg. Chem.*, 1988, **27**, 310.
2 P. Kathirgamanathan, A. B. Soares, D. T. Richens, and A. G. Sykes, *Inorg. Chem.*, 1985, **24**, 2950.
3 B-L. Ooi and A. G. Sykes, *Inorg. Chem.*, 1989, **28**, 3799.
4 B-L. Ooi, M. Martinez, T. Shibahara, and A. G. Sykes, *J. Chem. Soc., Dalton Trans*, 1988, 2239.
5 B-L. Ooi, M. Martinez, and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, 1988, 1324.
6 K. R. Rodgers, R. K. Murmann, E. O. Schlemper, and M. E. Shelton, *Inorg. Chem.*, 1985, **24**, 1313.
7 G. D. Hinch, D. E. Wycott, and R. K. Murmann, *Polyhedron*, 1986, **5**, 487.
8 D. T. Richens, L. Helm, P-A. Pittet, and A. E. Merbach, *Inorg. Chim. Acta*, 1987, **132**, 85.
9 D. T. Richens, L. Helm, P-A. Pittet, A. E. Merbach, F. Nicolo, and G. Chapius, *Inorg. Chem.*, 1989, **28**, 1394.
10 B-L. Ooi, A. L. Petrou, and A. G. Sykes, *Inorg. Chem.*, 1988, **27**, 3626.
11 T. Shibahara, H. Kohda, A. Ohtsuji, K. Yasuda, and H. Kuroya, *J. Am. Chem. Soc.*, 1986, **108**, 2757.
12 F. A. Cotton, Z. Dori, R. Llusar, and W. Schwotzer, *Polyhedron*, 1986, **5**, 907.
13 J. W. McDonald, G. D. Frieson, L. D. Rosenhein, and W. E. Newton, *Inorg. Chim. Acta*, 1983, **72**, 205.
14 T. Shibahara, A. Taksuchi, and H. Kuroya, *Inorg. Chim. Acta*, 1987, **127**, 239.
15 E. S. Swinbourne, in 'Analysis of Kinetic Data,' Nelson, 1971, p. 55; A. A. Frost and R. G. Pearson, in 'Kinetics and Mechanism,' 2nd edn., Wiley, New York, 1961.
16 C. Sharp and A. G. Sykes, *Inorg. Chem.*, 1988, **27**, 501.
17 C. Sharp, E. F. Hills, and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 1987, 2293.
18 M. Segawa and Y. Sasaki, *J. Am. Chem. Soc.*, 1985, **107**, 5565.
19 R. Mattes and K. Mannemann, *Z. Anorg. Allg. Chem.*, 1977, **437**, 175.
20 A. Bino, F. A. Cotton, and Z. Dori, *J. Am. Chem. Soc.*, 1978, **100**, 5252.
21 S. F. Gheller, T. W. Hambley, R. T. C. Brownlee, M. J. O'Connor, M. R. Snow, and A. G. Wedd, *J. Am. Chem. Soc.*, 1983, **105**, 1527.
22 T. Shibahara and H. Kuroya, *Polyhedron*, 1986, **5**, 357.
23 N. C. Howlader, G. P. Haight, T. W. Hambley, G. A. Lawrence, G. A. Rahmoller, and M. R. Snow, *Aust. J. Chem.*, 1983, **22**, 3104.

Received 30th *June* 1989
Revised manuscript received 23rd *November* 1989
Paper 9/02788B