Rate Constants for Thiocyanate Substitution at Mo and W on the Trinuclear Incomplete-cuboidal Clusters $[Mo_2WS_4(H_2O)_9]^{4+}$ and $[MoW_2S_4(H_2O)_9]^{4+}$ †

Jane E. Varey and A. Geoffrey Sykes *

Department of Chemistry, University of Newcastle, Newcastle upon Tyne NE1 7RU, UK

Rate constants (25 °C) have been determined for two kinetic stages, both in the stopped-flow range, for substitution by NCS^- on the trinuclear clusters $[Mo_2WS_4(H_2O)_9]^{4+}$ and $[MoW_2S_4(H_2O)_9]^{4+}$, $I = 2.00$ M ($LiClO_4$). All the metal atoms are in oxidation state IV. Both steps are dependent on $[NCS^-]$ and statistical factors for the first stages, 2 in the case of the Mo_2W and 1 in the case of the MoW_2 complex, are consistent with substitution at the Mo. Variations in $[H^+]$ were carried out in the case of the Mo_2W complex and indicate contributions from conjugate-base pathways for both the first and second stages. That for the second stage is consistent with an assignment of substitution at the W, and not the second d-H_2O on each Mo. From a comparison of rate constants in 2.00 M $HClO_4$ it is clear that substitution at the Mo and W of the Mo_2W and MoW_2 complexes is little changed and within 50% of values for the homonuclear trinuclear clusters $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$ respectively. As previously, the substitution at Mo^{IV} is ≈10 times faster than at W^{IV}.

The aim of this study was to explore whether molybdenum(IV) and tungsten(IV) ions in heterometallic incomplete-cuboidal trinuclear clusters of the type $[M_2M'S_4(H_2O)_9]^{4+}$ display the same or different substitution properties to those of the homonuclear $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$ clusters.[1,2] Previously, in studies on the series of mixed oxo–sulfido core complexes $[Mo_3O_xS_{4-x}(H_2O)_9]^{4+}$ (ref. 3) and $[W_3O_xS_{4-x}(H_2O)_9]^{4+}$ (refs. 4 and 5) it has been demonstrated that there are remote influences of core O^{2-} and S^{2-} ions on substitution at metals (in the same core) to which they are not directly bonded. These have been summarised in a recent paper,[6] in which core Se^{2-} ions have also been considered. Whether different metal identities in the same cluster might likewise have an influence one on the other was therefore of interest.

The heterometallic trinuclear complexes $[Mo_2WS_4(H_2O)_9]^{4+}$ and $[MoW_2S_4(H_2O)_9]^{4+}$, containing metal atoms in oxidation state IV have been prepared and X-ray crystallographically characterised by Shibahara and Yamasaki.[7] To some extent studies were influenced by the availability (6:1 or greater) of $[Mo_2WS_4(H_2O)_9]^{4+}$ as compared to $[MoW_2S_4(H_2O)_9]^{4+}$. A full study of the former was therefore carried out, and sufficient detail was obtained for the latter to leave the outcome in no doubt. The Mo and W atoms are disordered in the crystal structure of the toluene-*p*-sulfonate (pts^-) salts of $[Mo_2WS_4(H_2O)_9]^{4+}$ and $[MoW_2S_4(H_2O)_9]^{4+}$ with M–M distances 2.728(6) Å and 2.723(6) Å respectively.[7] These are very similar to the M–M distances in $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$ which are 2.735(8) and 2.724(17) Å respectively.[8]

Experimental

Preparation of the Mo_2W *and* MoW_2 *Clusters.*—The procedure used was as described.[7] Small portions of sodium tetrahydroborate (Aldrich) (3.0 g in 20 cm³ water) and 6 M HCl (20 cm³) were added to an aqueous solution (50 cm³) containing ammonium tetrasulfidotungstate(VI), $[NH_4]_2[WS_4]$ (1.0 g, 2.87 mmol)[9] and sodium di-μ-sulfido-bis[cysteinatooxomolybdate(V)], $Na_2[Mo_2O_2S_2(cys)_2]\cdot 4H_2O$ (cys = cysteinate here refers to the doubly deprotonated 2− form of cysteine) (1.85 g, 2.87 mmol).[10] Hydrochloric acid (6 M, 80 cm³) was then added and the solution in a conical flask was heated for 5 h on a steam-bath (≈90 °C) in air. After cooling, the green-brown solution was filtered and loaded onto a G10 Sephadex column (90 × 4 cm) and eluted with 1.0 M HCl (> 500 cm³). The sixth and seventh bands which separated (grey MoW_2 and green Mo_2W complex respectively) were purified (and concentrated) by loading onto a Dowex 50W-X2 column and eluting with 2.0 M $HClO_4$; UV/VIS spectra are shown in Fig. 1. Metal analyses were by inductively coupled plasma (ICP) atomic emission spectroscopy on a Thermo Electron Instrument at Albright & Wilson's, Whitehaven, Cumbria. For the green trinuclear ion the ratio of Mo:W obtained was 2.08:1.0 consistent with the formula $[Mo_2WS_4(H_2O)_9]^{4+}$, and for the more dilute solutions of the grey product 1:1.75 consistent with the formula $[MoW_2S_4(H_2O)_9]^{4+}$. Stock solutions of $[Mo_2WS_4(H_2O)_9]^{4+}$ obtained were typically ≈20 cm³ of the trinuclear ion (≈0.5 mM). Yields of $[MoW_2S_4(H_2O)_9]^{4+}$ were on the other hand much smaller (and variable). Both solutions in 2.0 M $HClO_4$ were stable in air over periods of at least 1 week at 4 °C.

Other Reagents.—Lithium perchlorate (Aldrich) was recrystallised twice from water, and concentrations of stock

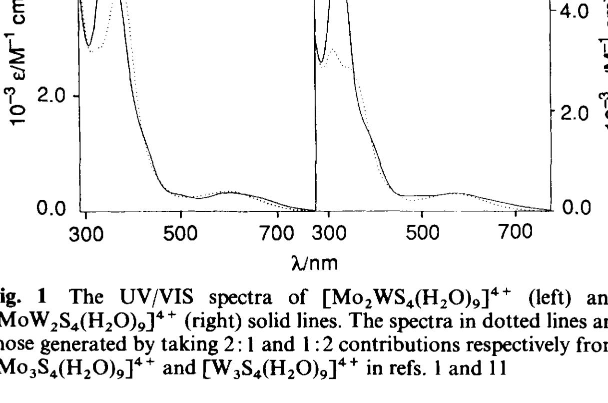

Fig. 1 The UV/VIS spectra of $[Mo_2WS_4(H_2O)_9]^{4+}$ (left) and $[MoW_2S_4(H_2O)_9]^{4+}$ (right) solid lines. The spectra in dotted lines are those generated by taking 2:1 and 1:2 contributions respectively from $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$ in refs. 1 and 11

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† *Non-SI unit employed*: M = mol dm⁻³.

Table 1 Details of the UV/VIS spectra, λ/nm (ε/M^{-1} cm^{-1} per M$_3$), of trinuclear complexes of general formula $[M_3S_4(H_2O)_9]^{4+}$ (M = Mo or W) in aqueous 2.00 M $HClO_4$

$Mo_3S_4^{4+}$	$Mo_2WS_4^{4+}$	$MoW_2S_4^{4+}$	$W_3S_4^{4+}$
363 (5550)[a]	340 (4390)	325 (5420)	314 (6350)[b]
	490 (298)[c]	490 (320)[c]	
602 (362)[a]	590 (322)[c]	570 (363)[c]	557 (446)[b]

[a] Ref. 1. [b] Refs. 2 and 11. [c] Ref. 7.

solutions were determined by titration of H$^+$, following the exchange of Li$^+$ by H$^+$ using an Amberlite IR-120(H) cation-exchange column. Perchloric acid (70%, Fisons) was diluted as required. Sodium thiocyanate (BDH, Analar) was used as supplied. Concentrations of stock solutions $\approx$0.10 M in water were determined by titration against 0.10 M silver nitrate with aqueous Fe^{III} as indicator.

UV/VIS Spectra.—Peak positions and absorption coefficients (ε) for the Mo_2W and MoW_2 complexes obtained from crystalline material (Table 1) were used in this study.[7] We attempted to generate the Mo_2W and MoW_2 spectra by taking appropriate contributions (one-third and two-thirds) of known spectra of the homonuclear ions $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$.[1,11] Although the main features are present in such spectra there are some differences, Fig. 1. The same holds for the spectrum of $[Mo_2WO_4(H_2O)_9]^{4+}$ and that obtained from a consideration of $[Mo_3O_4(H_2O)_9]^{4+}$ and $[W_3O_4(H_2O)_9]^{4+}$.[12]

Kinetic Studies.—At 25.0 ± 0.1 °C two stopped-flow stages were monitored for each of the trinuclear clusters with NCS$^-$ (reactant in > 30-fold excess). The Mo_2W reaction was followed at 335 nm, and the MoW_2 reaction at 325 nm. The Mo_2W reaction was also monitored at 490 nm, but at this wavelength no second stage was observed presumably because the $\Delta\varepsilon$ was too small. Ionic strengths were adjusted to I = 2.00 M with $LiClO_4$. The effect of [H$^+$] variations was explored for the Mo_2W but not the MoW_2 reaction. Runs were also carried out with the trinuclear complex in large (> 10-fold) excess of NCS$^-$ to determine the statistical factors applying.

Treatment of Data.—Stopped-flow traces were analysed using OLIS (Bogart, GA, USA) programs. Unweighted least-squares treatments were used to determine errors.

Other Reaction Steps.—The UV/VIS scan spectra were recorded between 300 and 550 nm on a Philips Unicam 8700 spectrophotometer (Philips analytical). The reaction of the Mo_2W complex (0.18 mM) with NCS$^-$ (5.9 mM) gave absorbance increases (up to 30%) over 60 min further to the stopped-flow changes. An initial cross-over point at 357 nm was not retained, consistent with more than one stage. For the corresponding reaction of the MoW_2 complex (0.084 mM) with NCS$^-$ (5.9 mM) similar observations were made, but in this case a cross-over point at 349 nm was retained as a well defined isosbestic.

Results

Kinetics of Mo_2W *Complex with* NCS$^-$.—Equilibration rate constants k_{1eq} and k_{2eq} are listed in Table 2. The dependence on [NCS$^-$] (reactant in > 10-fold excess) at each [H$^+$] is indicated in Fig. 2. At [H$^+$] = 2.00 M it was possible to carry out three runs with the Mo_2W complex in > 10-fold excess which define the rate equation (1), where k_{1f} and k_{1aq} are for complex formation and aquation respectively in the reversible process observed. Only by including a statistical factor of 2 for the runs with NCS$^-$ in excess, equation (2), is there a correspondence of

$$k_{1eq} = k_{1f}[Mo_2W] + k_{1aq} \qquad (1)$$

$$k_{1eq} = (k_{1f}[NCS^-]/2) + k_{1aq} \qquad (2)$$

k_{1f} and k_{1aq}. As in previous studies[6] the absorbance changes

Table 2 Equilibration rate constants (25 °C) for the first (k_{1eq}) and second (k_{2eq}) phases of the reaction of $[Mo_2WS_4(H_2O)_9]^{4+}$ with NCS$^-$, I = 2.00 M ($LiClO_4$)

[H$^+$]/M	[Mo_2W]/mM	[NCS$^-$]/mM	$10k_{1eq}$/s^{-1}	10^2k_{2eq}/s^{-1}
2.00	0.02	0.60	1.91	3.8
	0.04	1.20	2.79	4.9
	0.04	1.50	3.3	6.0
	0.04	1.80	3.7	6.6
	0.15	0.015	1.36	
	0.25	0.015	1.84	
	0.50	0.015	2.58	
1.50	0.02	0.60	2.10	4.3
		0.90	2.65	4.7
	0.04	1.20	3.2	5.4
		1.50	3.5	6.2
		1.80	4.1	7.2
1.00	0.02	0.60	2.4	4.7
		0.90	3.2	5.6
	0.04	1.20	3.5	6.5
		1.50	4.3	7.2
		1.80	4.7	8.3
0.75	0.02	0.60	2.82	*
		0.90	3.4	6.6
	0.04	1.20	3.8	7.8
		1.50	4.5	8.7
		1.80	5.2	9.5
0.50	0.02	0.60	3.1	*
		0.90	3.8	7.7
	0.04	1.20	4.4	8.8
		1.80	5.8	11.3
0.25	0.02	0.60	4.3	*
		0.90	5.5	10.1
	0.04	1.20	6.1	11.4
		1.50	67.1	12.6
		1.80	7.8	14.1

* Small absorbance change. No self-consistent data obtained.

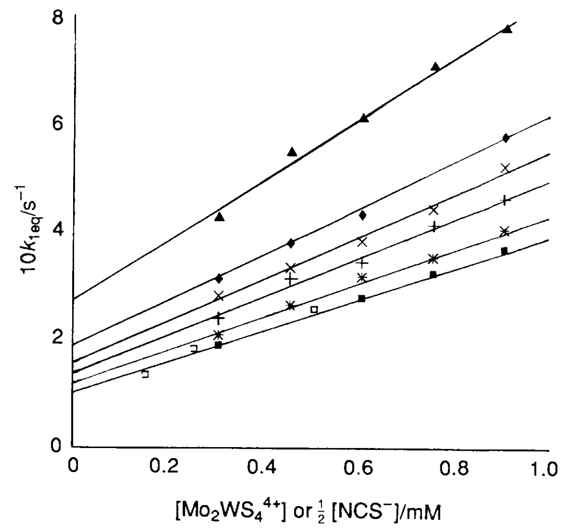


Fig. 2 Dependence of equilibration rate constants k_{1eq} (25 °C) on complex concentration for the first (stopped-flow) stage of the reaction of NCS$^-$ (> 10-fold excess) with $[Mo_2WS_4(H_2O)_9]^{4+}$ at [H$^+$]/M 2.00 (■), 1.5 (✱), 1.00 (+), 0.75 (×) 0.50 (◆), and 0.25 (▲), I = 2.00 M ($LiClO_4$). Runs at [H$^+$] = 2.00 M with $[Mo_2WS_4(H_2O)_9]^{4+}$ the reactant in > 10-fold excess are indicated (□)

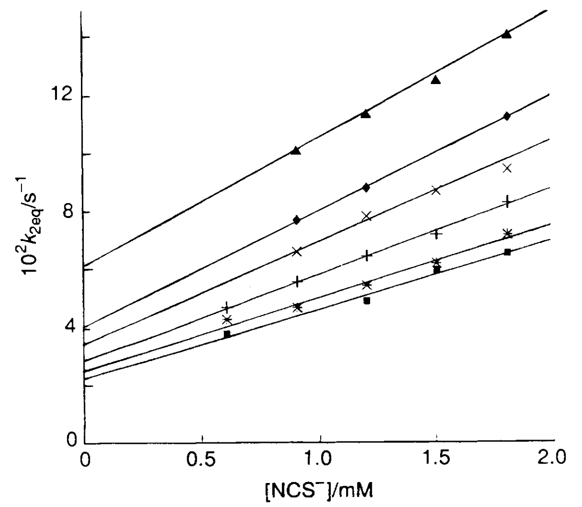


Fig. 3 Dependence of equilibration rate constants $k_{2\mathrm{eq}}$ (25°C) on [NCS$^-$] for the second (stopped-flow) stage of reaction of NCS$^-$ (> 10-fold excess) with $[\mathrm{Mo_2WS_4(H_2O)_9}]^{4+}$ at [H$^+$]/M 2.00 (■), 1.5 (✱), 1.00 (+), 0.75 (×), 0.50 (◆) and 0.25 (▲), I = 2.00 M (LiClO$_4$)

with the Mo$_2$W complex in excess are not sufficiently large to define the second stage. For runs with NCS$^-$ in > 10-fold excess, rate constants $k_{2\mathrm{eq}}$ are plotted against [NCS$^-$], Fig. 3, on the assumption that a statistical factor of 1 applies, equation (3), where $k_{2\mathrm{f}}$ and $k_{2\mathrm{af}}$ are the corresponding terms to those defined above.

$$k_{2\mathrm{eq}} = k_{2\mathrm{f}}[\mathrm{NCS}^-] + k_{2\mathrm{aq}} \tag{3}$$

Values of $k_{1\mathrm{f}}$, $k_{1\mathrm{aq}}$, $k_{2\mathrm{f}}$ and $k_{2\mathrm{aq}}$ at different [H$^+$] are listed in Table 3. The absorbance changes are smaller and the errors much larger for the second stage. The dependence on [H$^+$] was investigated over the range 0.25–2.00 M. For the first stage the variation of $k_{1\mathrm{f}}$ with [H$^+$] is non-linear, Fig. 4. The reaction sequence (4)–(7) is proposed, where the conjugate base in (4) is

$$\mathrm{Mo_2W^{4+}} \underset{}{\overset{K_{1a}}{\rightleftharpoons}} \mathrm{Mo_2W(OH)^{3+}} + \mathrm{H^+} \tag{4}$$

$$\mathrm{Mo_2W^{4+}} + \mathrm{NCS^-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Mo_2W(NCS)^{3+}} \tag{5}$$

$$\mathrm{Mo_2W(OH)^{4+}} + \mathrm{NCS^-} \underset{k'_{-1}}{\overset{k'_1}{\rightleftharpoons}} \mathrm{Mo_2W(OH)(NCS)^{2+}} \tag{6}$$

$$\mathrm{Mo_2W(NCS)^{3+}} \overset{K'_{1a}}{\rightleftharpoons} \mathrm{Mo_2W(OH)(NCS)^{3+}} + \mathrm{H^+} \tag{7}$$

assigned to the Mo at which substitution is occurring, and the presence of Mo$_2$W(OH)$^{3+}$ brings about a labilisation effect.

From this sequence $k_{1\mathrm{f}}$ can be expressed as in equation (8).[1]

$$k_{1\mathrm{f}} = \frac{k_1[\mathrm{H^+}] + k'_1K_\mathrm{a}}{[\mathrm{H^+}] + K_\mathrm{a}} \tag{8}$$

From a fit of data k_1 = 219 ± 14 M^{-1} s^{-1}, k'_1 = 890 ± 60 M^{-1} s^{-1} and $K_{1\mathrm{a}}$ = 0.27 ± 0.02 M (substitution at Mo). The corresponding expression for k_2 (where $K_{2\mathrm{a}}$ is for acid dissociation at the W) generates k_2 = 15.3 ± 1.4 M^{-1} s^{-1}, k'_2 = 63 ± 6 M^{-1} s^{-1} and $K_{2\mathrm{a}}$ = 0.45 ± 0.04 M (substitution at W). For the back reaction involving aquation of the thiocyanate a plot of $k_{1\mathrm{aq}}$ against [H$^+$]$^{-1}$ is linear, Fig. 5, and gives k_{-1} = (8.6 ± 0.5) × 10^{-1} s^{-1} and $k'_{-1}K'_{1\mathrm{a}}$ = (4.8 ± 0.2) × 10^{-2} M s^{-1} (for Mo). Similarly a plot of $k_{2\mathrm{aq}}$ against [H$^+$]$^{-1}$ gives k_{-2} = (1.57 ± 0.14) × 10^{-2} s^{-1} and $k'_{-2}K'_{2\mathrm{a}}$ = (1.67 ± 0.21) × 10^{-2} M s^{-1} (for W). The constants $K'_{1\mathrm{a}}$ and $K'_{2\mathrm{a}}$ are both $\ll$[H$^+$].

Table 3 Summary of k_f and k_aq values (25 °C) for the two phases of the reaction of $[\mathrm{Mo_2WS_4(H_2O)_9}]^{4+}$ with NCS$^-$, I = 2.00 M (LiClO$_4$)

[H$^+$]/M	k_f/M^{-1} s^{-1}	10^3k_aq/s^{-1}
First phase ($k_{1\mathrm{f}}$ and $k_{1\mathrm{aq}}$)		
2.00	300(10)	100(5)
1.50	320(10)	117(8)
1.00	370(20)	137(15)
0.75	400(20)	156(14)
0.50	440(20)	188(25)
0.25	570(31)	274(20)
Second phase ($k_{2\mathrm{f}}$ and $k_{2\mathrm{aq}}$)		
2.00	24(2)	23(3)
1.50	25(2)	26(3)
1.00	30(1)	29(1)
0.75	35(3)	35(4)
0.50	40(1)	41(1)
0.25	44(2)	62(3)

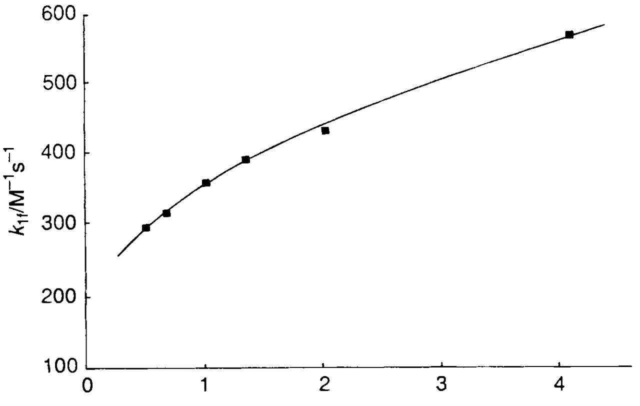


Fig. 4 Non-linear dependence of rate constants $k_{1\mathrm{f}}$ (25 °C) on [H$^+$]$^{-1}$ for the first stage of the complexing of NCS$^-$ (formation step) to $[\mathrm{Mo_2WS_4(H_2O)_9}]^{4+}$, I = 2.00 M (LiClO$_4$)

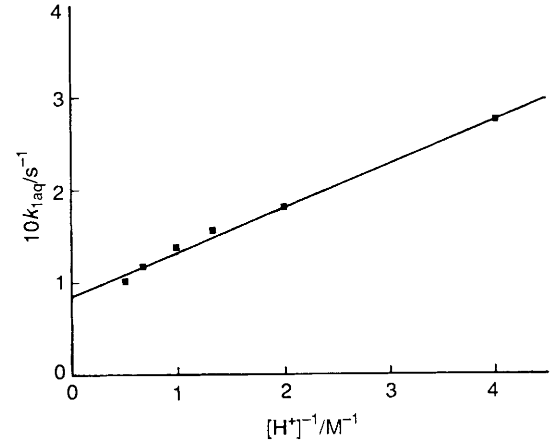


Fig. 5 Linear dependence of rate constants $k_{1\mathrm{aq}}$ (25 °C) on [H$^+$]$^{-1}$ for the first (aquation) step in equilibration studies of NCS$^-$ with $[\mathrm{Mo_2WS_4(H_2O)_9}]^{4+}$, I = 2.00 M (LiClO$_4$)

Kinetics of MoW$_2$ *Complex with* NCS$^-$.—Having confirmed the pattern of behaviour for the Mo$_2$W complex less-extensive studies were called for with the MoW$_2$ complex. Equilibration rate constants for the first two stages in 2.00 M HClO$_4$, $k_{3\mathrm{eq}}$ and $k_{4\mathrm{eq}}$, are listed in Table 4. The dependence of $k_{3\mathrm{eq}}$ on [MoW$_2$] and [NCS$^-$], Fig. 6, defines a statistical factor of unity. The slope and intercept give $k_{3\mathrm{f}}$ = 171 ± 6 M^{-1} s^{-1} and $k_{3\mathrm{aq}}$ =

Table 4 Equilibration rate constants (25 °C) for the first ($k_{3_{eq}}$) and second ($k_{4_{eq}}$) phases of the reaction of $[MoW_2S_4(H_2O)_9]^{4+}$ with NCS^-, $[H^+] = 2.00$ M, $I = 2.00$ M ($HClO_4$)

$[MoW_2]$/mM	$[NCS^-]$/mM	$10k_{3_{eq}}/s^{-1}$	$10^2k_{4_{eq}}/s^{-1}$
0.02	0.60	1.43	3.1
0.04	1.20	2.29	4.4
0.04	1.50	2.94	4.9
0.04	1.80	3.5	5.4
0.13	0.015	0.60	

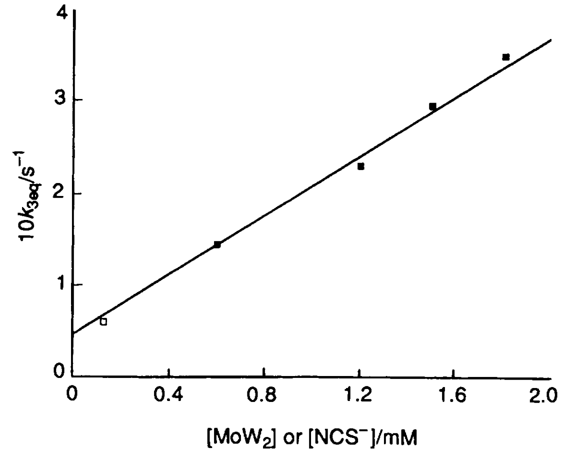


Fig. 6 Dependence of equilibration rate constants $k_{3_{eq}}$ (25 °C) on complex concentration for the first (stopped-flow) stage of the reaction of NCS^- (> 10-fold excess) with $[MoW_2S_4(H_2O)_9]^{4+}$ at $[H^+] = 2.00$ M, $I = 2.00$ M. (□) Run with the $[MoW_2S_4(H_2O)_9]^{4+}$ in 10-fold excess

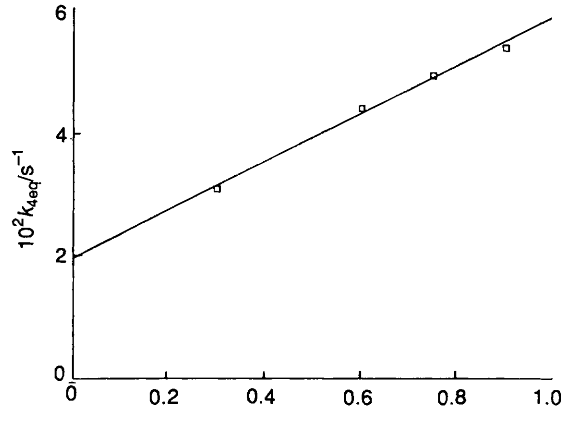


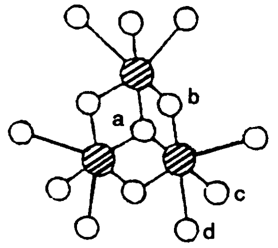
Fig. 7 Dependence of equilibration rate constants $k_{4_{eq}}$ (25 °C) on thiocyanate concentration for the second (stopped-flow) stage of the reaction of NCS^- (>10-fold excess) with $[MoW_2S_4(H_2O)_9]^{4+}$ at $[H^+] = 2.00$ M, $I = 2.00$ M. A statistical factor of 2 is assumed for this stage since the factor is demonstrated as equal to 1 for $k_{3_{eq}}$ in Fig. 6

0.036 ± 0.007 s^{-1}. A statistical factor of 2 is assumed for the second stage of reaction, Fig. 7, giving $k_{4f} = 39 \pm 2.3$ M^{-1} s^{-1} and $k_{4_{aq}} = (1.98 \pm 0.16) \times 10^{-2}$ s^{-1}, also in 2.00 M $HClO_4$.

Table 5 Summary of rate constants (25 °C) for the substitution of H_2O by NCS^- at Mo and W in the trinuclear complexes $[M_3S_4(H_2O)_9]^{4+}$, $[H^+] = 2.00$ M, $I = 2.00$ M ($HClO_4$)

	k_f/M^{-1} s^{-1}		k_{aq}/s^{-1}		K/M^{-1}	
Complex	Mo	W	Mo	W	Mo	W
$[Mo_3S_4(H_2O)_9]^{4+}$	212[a]		0.092[a]		2300	
$[W_3S_4(H_2O)_9]^{4+}$		38		0.025		1520
$[Mo_2WS_4(H_2O)_9]^{4+}$	300		0.10		3000	
		23.7[b]		0.023[b]		1040
$[MoW_2S_4(H_2O)_9]^{4+}$	171		0.036		4750	
		39		0.020		1950

[a] $[NCS^-]$-Dependent and $[H^+]$-independent second stage assigned as substitution of second d-H_2O, $k_f = 1.24$ M^{-1} s^{-1} and $k_{aq} = 5.8 \times 10^{-4}$ s^{-1}, ref. 13. [b] $[NCS^-]$-independent second stage assigned as isomerisation of co-ordinated NCS^-, $k_1 = 1.0 \times 10^{-4}$ s^{-1}, ref. 13.



Discussion

An appraisal of the present results is dependent on an understanding of the reactivity of the homonuclear $[M_3S_4(H_2O)_9]^{4+}$ clusters (M = Mo or W). In all incomplete cuboidal clusters the H_2O molecules are of two types c and d depending on whether they are *trans* to core μ_3-S or μ-S ligands. Previous kinetic studies on the substitution of $[Mo_3S_4(H_2O)_9]^{4+}$ by NCS^- have indicated three stages. These are assigned as the (stopped-flow) reaction at the first d-H_2O,[1] a process which is more favourable if the other d-H_2O on the same Mo is present in the Mo–OH conjugate-base form (effect of $[H^+]$). Reaction at the second d-H_2O can be monitored in conventional ($t_{\frac{1}{2}} > 1$ min) time-range experiments. No conjugate-base pathway is observed since the other d position is already occupied by NCS^-.[13] The c-H_2Os do not exhibit any comparable acid dissociation.[14] A third slower stage detected in $H_2{}^{17}O$ exchange studies on $[Mo_3S_4(H_2O)_9]^{4+}$ is assigned to the $\approx 10^5$ times slower substitution at the c-H_2O.[14] For the first stage a statistical factor of 3 has established that reaction is occurring concurrently at all three Mo atoms when NCS^- is present in excess. No $[NCS^-]$-independent step, which has been assigned to the isomerisation of co-ordinated NCS^-, has been detected in the case of $[Mo_3S_4(H_2O)_9]^{4+}$.

With $[W_3S_4(H_2O)_9]^{4+}$ again two kinetic stages are observed, but the $[NCS^-]$-independent second stage, is assigned as isomerisation,[13] most likely W–SCN ⟶ W–NCS. While it is reasonable that substitution at the second d-H_2O should also be occurring, this has not so far been detected in spectrophotometric investigations.

We now consider the stopped-flow results obtained in this study. A comparison of rate constants for $[Mo_2WS_4(H_2O)_9]^{4+}$ and $[MoW_2S_4(H_2O)_9]^{4+}$ alongside those for $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$, all in 2.00 M $HClO_4$, is made in Table 5. This approach using a single (high) $[H^+]$ has been used previously (since it avoids carrying out a very large number of runs), and is justified as long as the pK_a values are about the same for the molybdenum and tungsten centres, which appears to be the case.[1,2] In total, four formation steps might be anticipated, involving events occurring at the d-H_2O sites of the Mo and W. Much slower substitution at the c-H_2O sites would be expected to contribute two more steps. In Table 5 we compare the first stages for $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$ with the two stopped-flow stages studied for each of the Mo/W hetero complexes. The assignments are reasonably straightforward with the first substitution occurring at Mo for both the Mo/W clusters, which is confirmed by the statistical factors of 2 for Mo_2W and 1 for MoW_2. The pattern of behaviour with the substitution at Mo about an order of magnitude faster than at W is retained, and there appears to be little or no influence of W on Mo (and *vice versa*) when the two occur in the same trinuclear unit.

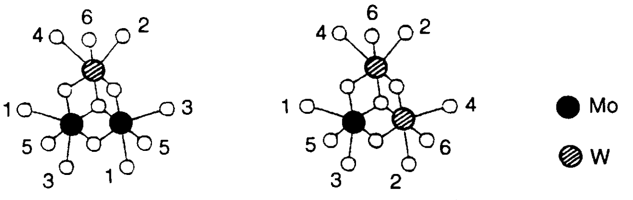


Fig. 8 Summary of the order of substitution of H_2O ligands at Mo and W on $[Mo_2WS_4(H_2O)_9]^{4+}$ and $[MoW_2S_4(H_2O)_9]^{4+}$. In the former, the positions 1 and 3, and 2 and 4 respectively are equivalent at the outset. The first stage 1 has a conjugate-base contribution from position 3 (and 2 from 4), but 3 shows no $[H^+]$ dependence. Processes 5 and 6 are slow and at present less well defined. Similar observations hold for the MoW_2 complex, in which case there may in addition be a thiocyanate isomerisation process at W

A much fuller study was carried out on the Mo_2W than on the MoW_2 complex, including an investigation of the effect of $[H^+]$ on k_{1eq} and k_{2eq}. Conjugate-base pathways involving Mo–OH and W–OH respectively contribute to both stages. The acid dissociation constant K_{1a} of 0.27 M from studies on the first stage (Mo) of the Mo_2W reaction is in very good agreement with the corresponding value for the Mo_3 ion of 0.22 M.[1,14] Likewise $K_{2a} = 0.45$ M for the second stage (W) compares with 0.35 M from studies on the W_3 ion.[2] The values obtained for W are greater than those for Mo, see also ref. 6. From the treatment given, K'_{1a} and K'_{2a} are much smaller and $\leqslant 10^{-2}$ M, a trend which can be explained by the presence of NCS^- in the same co-ordination sphere.

With the information available from these and other studies the order of six substitution processes can be defined for each of the Mo_2W and MoW_2 ions. Fig. 8 summarises the reaction sequences involved. While it is possible to study the kinetics of at least the third and fourth stages of the Mo_2W reaction by conventional spectrophotometry, we did not see the need further to establish these processes at this time.

Recent results for the substitution by NCS^- on the μ-oxo trinuclear analogue $[Mo_2WO_4(H_2O)_9]^{4+}$ are also of interest.[15] Unfortunately only one stage was detected, where it is noted that the rate constant obtained is in this case more like that for substitution on $[W_3O_4(H_2O)_9]^{4+}$ than on $[Mo_3O_4(H_2O)_9]^{4+}$.[4,16]

Whereas substitution on $[Mo_3O_xS_{4-x}(H_2O)_9]^{4+}$ and $[W_3O_xS_{4-x}(H_2O)_9]^{4+}$ mixed oxo–sulfido bridged trinuclear complexes indicates an influence of oxo and sulfido ligands on substitution at a remote metal centre to which they are not attached,[6] the metals Mo and W in the heterometal Mo_2W and MoW_2 clusters do not produce similar effects. From Table 5 it would appear that substitution rates at Mo and W remain essentially unchanged. Thus rate constants for the substitution at Mo in Mo_3, Mo_2W and MoW_2 complexes are in the range 171–300 M^{-1} s^{-1}, and those for W in W_3, Mo_2W and MoW_2 complexes are in the range 23.7–39.0 M^{-1} s^{-1}. Also of interest are the consistently smaller formation constants K for complexing of NCS^- at W as compared to Mo, Table 5.

Finally Mo^{IV} and W^{IV} have identical radii and there are no structural changes on replacing one metal by another. Thus from X-ray crystallography the dimensions of $[Mo_3S_4(H_2O)_9][pts]_4 \cdot 9H_2O$ (Mo–Mo 2.73, Mo–μ_3-S 2.33, Mo–μ-S 2.29 Å)[17] and $[W_3S_4(H_2O)_9][pts]_4 \cdot 7H_2O$ (W–W 2.72, W–μ_3-S 2.35, W–μ-S 2.28 Å),[18] as well as of the Mo_2W and MoW_2 complexes (see Introduction) are identical. The differences in substitution rate constants for Mo and W of about an order of magnitude originate in large part from the different sizes of 4d and 5d orbitals respectively.[19] The influence of heterometal atoms from different groups in the Periodic Table remains to be fully appraised for incomplete and cuboidal clusters.[20,21]

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