Kinetics of Substitution of H_2O by NCS^- on μ-Selenido Incomplete Cuboidal $M^{IV}{}_3$ Clusters $[Mo_3O_xSe_{4-x}(H_2O)_9]^{4+}$ and on $[Mo_4Se_4(H_2O)_{12}]^{5+}$ †

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Rate constants ($k_f/M^{-1}\ s^{-1}$) have been determined at 25 °C, $I = 2.00$ M ($LiClO_4$ and in one case Lipts; pts^- = toluene-*p*-sulfonate) for the 1:1 substitution of H_2O by NCS^- at Mo on the trinuclear $Mo^{IV}{}_3$ cluster complexes $[Mo_3O_xSe_{4-x}(H_2O)_9]^{4+}$, $x = 0$–4. The dominant process is substitution of H_2O at the *trans* μ-Se positions with rate constants for $[Mo_3(\mu_3\text{-Se})(\mu\text{-Se})_3(H_2O)_9]^{4+}$ (480) > $[Mo_3(\mu_3\text{-Se})(\mu\text{-O})(\mu\text{-Se})_2(H_2O)_9]^{4+}$ (131 and 52) > $[Mo_3(\mu_3\text{-Se})(\mu\text{-O})_2(\mu\text{-Se})(H_2O)_9]^{4+}$ (13.5 and 2.8) > $[Mo_3(\mu_3\text{-Se})(\mu\text{-O})_3(H_2O)_9]^{4+}$ (0.19), alongside the previously studied $[Mo_3(\mu_3\text{-O})(\mu\text{-O})_3(H_2O)_9]^{4+}$ (2.13) giving a 2530-fold spread of values at $[H^+] = I = 2.00$M. The complexes with $x = 1$ and 2 have non-identical molybdenum centres according to the number of core Se^{2-} and O^{2-} ligands attached, and give biphasic kinetics. Statistical factors of 1, 2 and 3 corresponding to the number of identical centres are defined for the different reactions. The slowness of substitution at positions *trans* to the μ_3-Se ligands is confirmed by studies on cuboidal $[Mo_4Se_4(H_2O)_{12}]^{5+}$, which has all μ_3-Se core ligands. Comparisons are made with results obtained for the $[Mo_3O_xS_{4-x}(H_2O)_9]^{4+}$ series. Labilising effects of electron-rich $\mu\text{-Se}^{2-} > \mu\text{-S}^{2-} > \mu\text{-O}^{2-}$ at the *trans* H_2O ligand are noted. In contrast replacement of the μ_3-O of $[Mo_3O_4(H_2O)_9]^{4+}$ by μ_3-Se and μ_3-S in turn produces 14- and 6-fold retardation effects. Substitution at the H_2O ligands *trans* to μ-Se ligands is increased on decreasing $[H^+]$ consistent with the involvement of conjugate-base forms $Mo_3(OH)^{3+}$ (k_2) alongside $Mo_3{}^{4+}$ (k_1). The kinetics give H_2O ligand acid dissociation constants K_{aM} of 0.32 and 0.44 M for $[Mo_3Se_4(H_2O)_9]^{4+}$ and $[Mo_3O_3Se(H_2O)_9]^{4+}$ respectively. Similar patterns are observed for the aquation rate constants k_{aq}.

In recent work the preparation of the dinuclear di-μ-selenido-dimolybdenum(V) complex $[Mo_2O_2(\mu\text{-Se})_2(cys)_2]^{2-}$ (cys = cysteinate)‡ has enabled the trinuclear $Mo^{IV}{}_3$ incomplete cuboidal (metal-depleted) aqua ions $[Mo_3(\mu_3\text{-Se})(\mu\text{-Se})_3(H_2O)_9]^{4+}$, $[Mo_3(\mu_3\text{-Se})(\mu\text{-O})(\mu\text{-Se})_2(H_2O)_9]^{4+}$, $[Mo_3(\mu_3\text{-Se})(\mu\text{-O})_2(\mu\text{-Se})(H_2O)_9]^{4+}$ as well as the mixed-valence $Mo^{III}{}_3Mo^{IV}$ cuboidal ion $[Mo_4(\mu_3\text{-Se})_4(H_2O)_{12}]^{5+}$ to be isolated.[1,2] By an independent route $[Mo_3(\mu_3\text{-Se})(\mu\text{-O})_3(H_2O)_9]^{4+}$ has also been prepared.[2] Crystal structures have been reported for $[NMe_4]_5[Mo_3(\mu_3\text{-Se})(\mu\text{-Se})_3(NCS)_9]$, $[NMe_4]_5[Mo_3(\mu_3\text{-Se})(\mu\text{-O})_2(\mu\text{-Se})(NCS)_9]$ and $[Mo_4(\mu_3\text{-Se})_4(H_2O)_{12}][pts]_5\cdot 14H_2O$ (pts = toluene-*p*-sulfonate). Formulae for the trinuclear series can be written $[Mo_3O_xSe_{4-x}(H_2O)_9]^{4+}$, $x = 0$–4. As compared to the analogous Mo–S cores, those with Mo–Se have longer bond lengths consistent with known radii for Se^{2-} (1.98), S^{2-} (1.84) and O^{2-} (1.40 Å).[3] Bands in the UV/VIS absorption spectra are red shifted, and in the case of the cube less-positive reduction potentials are observed for the $[Mo_4Se_4(H_2O)_{12}]^{5+/4+}$ and $[Mo_4Se_4(H_2O)_{12}]^{6+/5+}$ couples.[2]

In recent studies Holm and co-workers[4] have reported comprehensive studies on the synthesis and characterisation of binuclear Fe_2Se_2 and cuboidal Fe_4Se_4 clusters with thiolate terminal ligands, and Se^{2-} has been incorporated into heterometal Fe/Mo clusters.[5] Ferredoxins have also been reconstituted with Fe^{II}/Fe^{III} and a selenide source to yield holoproteins containing Fe_2Se_2 and Fe_4Se_4 clusters, a subject which has recently been reviewed.[6] Comparisons of molybdenum and iron clusters are of interest because of the contrasting octahedral (Mo) and tetrahedral (Fe) co-ordination geometries.[7] Stability problems associated with the Fe–S analogues in aqueous solution have restricted the study of solution properties including ligand substitution processes.[8] In contrast the more stable Mo–S counterparts provide a rich and varied aqueous solution chemistry. Also whereas trinuclear Fe_3S_4 incomplete cuboidal clusters have been identified in proteins, Fe_3S_4 complexes which have so far been prepared have a linear FeS_2FeS_2Fe structure. The existence of incomplete cuboidal $Mo^{IV}{}_3$ clusters and the variation of composition of core ligands which can be achieved in aqueous solution are of added interest therefore. The trinuclear molybdenum (and iron) clusters have higher (average) oxidation states than related cuboidal complexes.

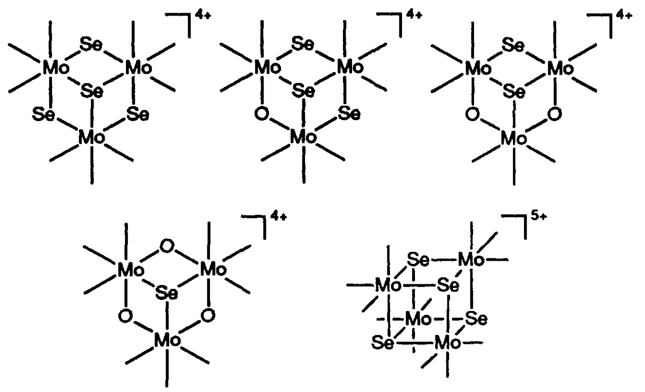

Fig. 1 Structures of trinuclear $[Mo_3O_xSe_{4-x}(H_2O)_9]^{4+}$, $x = 0$–3, and cuboidal $[Mo_4Se_4(H_2O)_{12}]^{5+}$ cluster complexes

A communication has appeared on substitution reactions (NCS^- for H_2O) of the $[Mo_3O_xS_{4-x}(H_2O)_9]^{4+}$ cluster,[9] and more detailed studies[10–12] on $[Mo_3O_4(H_2O)_9]^{4+}$ and

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

‡ Cysteinate here refers to the doubly deprotonated form of cysteine (Cys).

$[Mo_3S_4(H_2O)_9]^{4+}$ as well as on the cuboidal $[Mo_4S_4(H_2O)_{12}]^{4+/5+}$ ions[13] have been carried out. Attention is now focused on the effect of incorporation of Se^{2-} in the molybdenum(IV) core. The clusters studied are indicated in Fig. 1. The preference of sulfide for occupancy of the μ_3 position in *e.g.* the singly substituted trinuclear complexes has been noted,[9] and the same appears to be true also for selenide.[2] Results for the $[W_3O_xS_{4-x}(H_2O)_9]^{4+}$ series[14–16] are also considered for comparison purposes. In a wider context an understanding of the substitution properties of trinuclear and cuboidal complexes is relevant to the behaviour of metal clusters in biological systems.[7]

Experimental

Preparation of $[Mo_3O_xSe_{4-x}(H_2O)_9]^{4+}$ *and* $[Mo_4Se_4(H_2O)_{12}]^{5+}$.—Solutions of the incomplete cuboidal $[Mo_3O_xSe_{4-x}(H_2O)_9]^{4+}$ ions, x = 0–3, and cuboidal $[Mo_4Se_4(H_2O)_{12}]^{5+}$ were prepared by the procedures described.[1,2] Thus $[Mo_3Se_4(H_2O)_9]^{4+}$, $[Mo_3OSe_3(H_2O)_9]^{4+}$, $[Mo_3O_2Se_2(H_2O)_9]^{4+}$ and $[Mo_4Se_4(H_2O)_{12}]^{5+}$ were obtained by $NaBH_4$ reduction of the di-μ-selenido-bis[L-cysteinatooxomolybdate(V)] complex, $Cs_2[Mo_2O_2Se_2(cys)_2]\cdot 4H_2O$. Separation and purification of the products was carried out using Dowex 50W-X2 cation-exchange chromatography. Most of the $[Mo_3O_2Se_2(H_2O)_9]^{4+}$ was prepared by an alternative procedure involving reduction of the molybdenum(V) dinuclear ion $[Mo_2O_2Se_2(cys)_2]^{2-}$ with potassium hexachloromolybdate(III), $K_3[MoCl_6]$ (generously provided by Climax Molybdenum), which gives better yields. Solutions of the trinuclear ion $[Mo_3O_3Se(H_2O)_9]^{4+}$ were prepared by electrochemical reduction of the di-μ-oxo-bis[L-cysteinato-oxomolybdate(V)] complex in the presence of grey selenium powder. The final solution was diluted to ≈0.3 M HCl and loaded onto a Dowex 50W-X2 cation-exchange column. After washing with 0.5 and then 1.0 M Hpts elution was with 2.0 M Hpts. The aqua ions were characterised from the UV/VIS spectra previously reported.[2] All stock solutions in 2.0 M Hpts were stored under N_2 at 4 °C. Immediately prior to use solutions in perchloric acid were obtained by reloading onto a short (3 cm) column; after washing with 0.5 and 1.0 M $HClO_4$ elution was again with 2.0 M acid. Concentrations were determined spectrophotometrically at peak positions λ/nm ($\varepsilon/M^{-1}\ cm^{-1}$ per Mo_3) 648 (263) for $[Mo_3Se_4(H_2O)_9]^{4+}$, 658 (347) for $[Mo_3OSe_3(H_2O)_9]^{4+}$, 634 (398) for $[Mo_3O_2Se_2(H_2O)_9]^{4+}$, and 525 (184) for $[Mo_3O_3Se(H_2O)_9]^{4+}$. The cube (ε per Mo_4) has peaks at 662 (407) and 1188 (117). The $[H^+]$ of stock solutions of all four clusters were determined by passing aliquots down columns (25 × 1.5 cm diameter) of Amberlite IR-120(H) cation-exchange resin, washing off all the acid, and titrating against standard 0.10 M sodium hydroxide.

Other Reagents.—Lithium perchlorate (Aldrich) was recrystallised twice from water, and concentrations of stock solutions were determined using an Amberlite IR-120(H) cation-exchange column (15 × 1.2 cm). Perchloric acid (70%, BDH, AnalaR) determined as 11.8 M was diluted as required. Determination of diluted stock solutions was carried out by direct titration *versus* 0.10 M sodium hydroxide (BDH, Convol) using phenolphthalein as indicator. Solutions of toluene-*p*-sulfonic acid (Hpts, Aldrich) were made up as required. Care was taken in storing the solid out of light, and that samples used were white and not pink. To prepare Lipts the acid was neutralised with Li_2CO_3 and the product recrystallised twice. Sodium thiocyanate (BDH, AnalaR) was used as supplied. Concentrations of ≈0.20 M stock solutions was determined by direct titration against 0.10 M silver nitrate with Fe^{III} as indicator.

Kinetic Studies.—These were carried out at 25.0 ± 0.1 °C, with I adjusted to 2.00 M ($LiClO_4$). Equation (1) defines the

$$[Mo_3O_xSe_{4-x}(H_2O)_9]^{4+} + NCS^- \underset{k_{eq}}{\overset{k_f}{\rightleftharpoons}} [Mo_3O_xSe_{4-x}(H_2O)_8(NCS)]^{3+} + H_2O \quad (1)$$

type of reaction under investigation. Reactions of $[Mo_3Se_4(H_2O)_9]^{4+}$, $[Mo_3OSe_3(H_2O)_9]^{4+}$ and $[Mo_3O_2Se_2(H_2O)_9]^{4+}$ with NCS^- were fast and were monitored on a Dionex D-110 stopped-flow spectrophotometer. Some studies on the second stage of the reaction of $[Mo_3O_2Se_2(H_2O)_9]^{4+}$ were carried out by conventional spectrophotometry on a Perkin Elmer Lambda 9 instrument. Conventional spectrophotometry was also used to study the $[Mo_3O_3Se(H_2O)_9]^{4+}$ and $[Mo_4Se_4(H_2O)_{12}]^{5+}$ reactions. Different wavelengths were used to monitor the reactions: $[Mo_3Se_4(H_2O)_9]^{4+}$ (320 nm with NCS^- in excess and 375 nm with Mo_3 in excess), $[Mo_3OSe_3(H_2O)_9]^{4+}$ (370 nm with NCS^- in excess and 420 nm with Mo_4 in excess), $[Mo_3O_2Se_2(H_2O)_9]^{4+}$ (380 nm in both cases), $[Mo_3O_3Se(H_2O)_9]^{4+}$ (350 nm), and $[Mo_4Se_4(H_2O)_{12}]^{5+}$ (450 nm with NCS^- in excess and 350 nm with Mo_4 in excess). Whereas the $[Mo_3O_3S(H_2O)_9]^{4+}$ complex is noted for its high stability and solutions can be stored over periods of months without any apparent decomposition, the $[Mo_3O_3Se(H_2O)_9]^{4+}$ counterpart is less stable and solutions showed signs of decomposition and had to be recolumned after 24 h. Because ClO_4^- is a possible oxidant, solutions were eluted and stored in Hpts rather than $HClO_4$, and runs were carried out in 2.00 M pts^- instead of ClO_4^-. The kinetic runs are slow however and in spite of these precautions decomposition was observed in the latter stages, and the Guggenheim method was required to evaluate rate constants.

The $[H^+]$ dependence of the reaction of $[Mo_3Se_4(H_2O)_9]^{4+}$ was explored in some detail in order to make comparisons with the previously studied reactions of $[Mo_3S_4(H_2O)_9]^{4+}$ (ref. 12) and $[Mo_3O_4(H_2O)_9]^{4+}$.[10,11] Likewise some $[H^+]$ variations in the range 0.30–2.00 M were carried out in other cases. Studies on $[Mo_3O_2Se_2(H_2O)_9]^{4+}$ were however at $[H^+] = I$ = 2.00 M ($HClO_4$) only. Concentrations of NCS^- were in a range appropriate for 1 : 1 complex formation at any one Mo^{IV}.

Kinetic plots of absorbance changes against time for studies on $[Mo_3O_2Se_2(H_2O)_9]^{4+}$ and $[Mo_3OSe_3(H_2O)_9]^{4+}$ with NCS^- in excess were biphasic, and a concurrent reaction treatment (program by OLIS) was used. With the complex in excess all reactions behaved as uniphasic processes, and a standard reaction treatment was applied. In the cases of $[Mo_3Se_4(H_2O)_9]^{4+}$ and $[Mo_3O_3Se(H_2O)_9]^{4+}$ the traces were uniphasic. A complicating feature with $[Mo_4Se_4(H_2O)_{12}]^{5+}$ was the decay of the cube and release of red Se. This prevented the determination of accurate absorbance A_∞ values, and rate constants are estimates only therefore. The decay is not avoided by working air-free and may be initiated by the presence of perchlorate ions.

Results

Different molybdenum identities e–h are defined in Fig. 2 according to the Se and O attachments. No evidence has been obtained in these studies for isomerisation steps[13,16] resulting from the ambidentate nature of NCS^-

Reaction of $[Mo_3Se_4(H_2O)_9]^{4+}$.—The $[Mo_3Se_4(H_2O)_9]^{4+}$ cluster has three identical Mo^{IV} here designated as h type, Fig. 2. The reaction is uniphasic. A linear dependence of equilibration rate constants k_{eq}, Table 1, on NCS^- (reactant in 10-fold excess) is observed. A statistical factor of three is required to obtain correspondence between rate constants with NCS^- and then $Mo^{IV}{}_3$ in excess, equations (2) and (3) respectively. The effect is illustrated in Fig. 3.

Table 1 First-order equilibration rate constants, k_{eq} (25 °C), for the uniphasic reaction of $[Mo_3Se_4(H_2O)_9]^{4+}$ with NCS^-, I = 2.00 M ($LiClO_4$)

$[H^+]$	$10^3[Mo^{IV}_3]$	$10^3[NCS^-]$	
	M		$10k_{eq}/s^{-1}$
2.00	0.040	0.50	2.81
	0.040	1.00	3.6
	0.040	1.25	4.1
	0.040	1.50	4.4
	0.040	1.83	4.9
	0.040	2.00	5.2
	0.150	0.040	2.67
	0.160	0.040	2.75
	0.35	0.040	3.7
1.70	0.020	0.50	3.00
	0.030	1.00	3.8
	0.040	1.50	4.7
	0.040	2.00	5.50
1.20	0.040	0.40	3.50
	0.030	0.50	3.7
	0.040	0.80	4.4
	0.040	1.20	5.2
	0.040	1.50	5.8
1.00	0.040	0.40	3.8
	0.040	0.80	4.9
	0.040	1.20	5.5
	0.040	1.50	6.4
0.8	0.040	0.40	4.0
	0.020	0.75	5.0
	0.040	0.80	5.2
	0.040	1.20	6.2
	0.040	1.35	6.5
	0.040	1.50	7.0
0.40	0.020	0.40	4.6
	0.040	0.75	5.7
	0.040	1.00	6.6
	0.040	1.35	7.8
	0.170	0.04	5.0
0.30	0.040	0.50	5.7
	0.040	0.75	6.9
	0.040	1.00	7.9
	0.040	1.30	8.8

Table 2 Formation (k_f) and aquation (k_{aq}) rate constants (25 °C) for the equilibration of $[Mo_3Se_4(H_2O)_9]^{4+}$ with NCS^- corresponding to the slope and intercept respectively in Fig. 3, I = 2.00 M ($LiClO_4$)

$[H^+]$/M	$k_f/M^{-1}\,s^{-1}$	$10k_{aq}/s^{-1}$
2.00	480 ± 11	2.00 ± 0.05
1.70	510 ± 17	2.14 ± 0.08
1.20	630 ± 6	2.67 ± 0.02
1.00	680 ± 40	2.90 ± 0.12
0.80	780 ± 50	3.02 ± 0.18
0.40	1010 ± 15	3.20 ± 0.04
0.30	1140 ± 70	3.90 ± 0.21

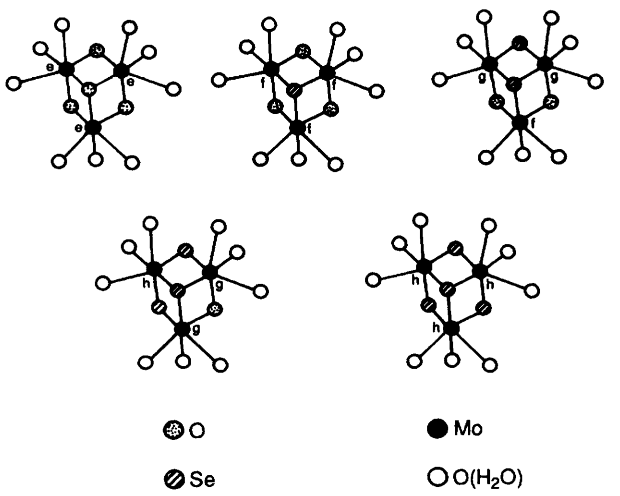


Fig. 2 Different molybdenum identities e–h in cluster complexes $[Mo_3O_xSe_{4-x}(H_2O)_9]^{4+}$, x = 0–4, defined by the number of core oxo and selenido groups attached, *e.g.* the Mo atoms in $Mo_3Se_4^{4+}$ are all of the h type

$$k_{eq} = (k_f[NCS^-]/3) + k_{aq} \tag{2}$$

$$k_{eq} = k_f[Mo^{IV}_3] + k_{aq} \tag{3}$$

The dependence of rate constants k_{eq} upon $[H^+]$ in the range 0.30–2.00 M was investigated with NCS^- in excess. Values of k_f and k_{aq} for the formation and aquation steps as defined in equation (1) are listed in Table 2. A graph of k_f *versus* $[H^+]^{-1}$ is curved with intercept > 0 indicating the existence of an $[H^+]$-independent step in addition to the conjugate-base pathway.

The reaction scheme proposed, with $[Mo_3Se_4(H_2O)_9]^{4+}$ written as Mo_3^{4+} and the conjugate-base form as $Mo_3(OH)^{3+}$, is as in equations (4)–(7). From this scheme the expression (8) is

$$Mo_3^{4+} \xrightleftharpoons{K_{aM}} Mo_3(OH)^{3+} + H^+ \tag{4}$$

$$Mo_3^{4+} + NCS^- \xrightleftharpoons[k_{-1}]{k_1} Mo_3(NCS)^{3+} \tag{5}$$

$$Mo_3(OH)^{3+} + NCS^- \xrightleftharpoons[k_{-2}]{k_2} Mo_3(OH)(NCS)^{2+} \tag{6}$$

$$Mo_3(NCS)^{3+} \xrightleftharpoons{K_{aMT}} Mo_3(OH)(NCS)^{2+} + H^+ \tag{7}$$

$$k_f = \frac{k_1[H^+] + k_2K_{aM}}{[H^+] + K_{aM}} \tag{8}$$

obtained. To test for this dependence, $k_f([H^+] + K_{aM})$ *versus* $[H^+]$ was plotted in an iterative manner using K_{aM} values in the range 0.15–0.40 M, Fig. 4. A linear best fit was obtained with K_{aM} = 0.32 ± 0.2 M, which gives k_1 = 237 ± 18 $M^{-1}\,s^{-1}$ and k_2 = 2000 ± 210 $M^{-1}\,s^{-1}$. An equation of the same form can be derived for k_{aq}. Values obtained for k_{aq} do not allow a precise determination of K_{aMT}. However using the same iterative procedure as above suggests that K_{aMT} is small and maybe of magnitude $\approx 10^{-3}$ M.

Reaction of $[Mo_3OSe_3(H_2O)_9]^{4+}$.—The reaction is biphasic consistent with two different molybdenum identities g and h, Fig. 2. Equilibration rate constants k_{1eq} and k_{2eq} at $[H^+]$ = 0.50–2.00 M are listed in Table 3. The treatment for each phase is the same as previously indicated for $[Mo_3Se_4(H_2O)_9]^{4+}$. For k_{1eq} equations (9) and (10) apply (no statistical factor), Fig. 5.

$$k_{1eq} = k_{1f}[Mo_3OSe_3^{4+}] + k_{1aq} \tag{9}$$

$$k_{1eq} = k_{1f}[NCS^-] + k_{1aq} \tag{10}$$

For k_{2eq} equations (11) and (12) hold, and a statistical factor of

$$k_{2eq} = k_{2f}[Mo_3OSe_3^{4+}] + k_{2aq} \tag{11}$$

$$k_{2eq} = (k_{2f}[NCS^-]/2) + k_{2aq} \tag{12}$$

2 is required in (12), Fig. 6. Rate constants k_{1f}, k_{1aq} and k_{2f}, k_{2aq} from the slopes and intercepts are listed in Table 4. Rate

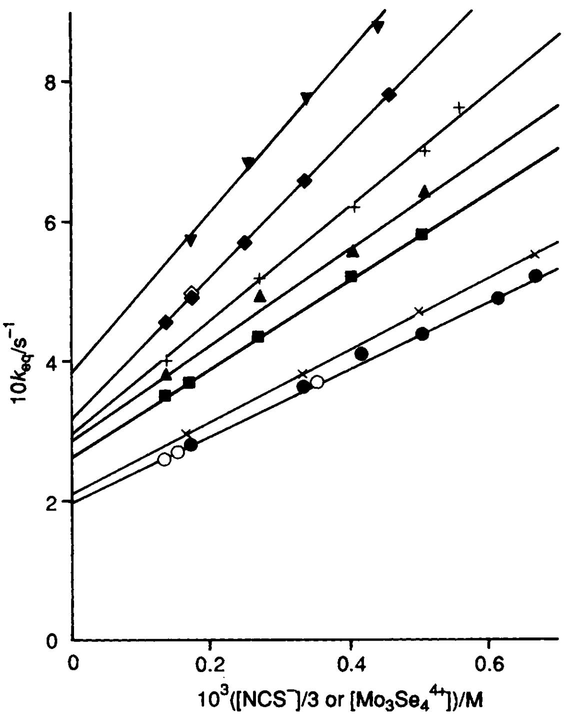


Fig. 3 First-order rate constants, k_{eq} (25 °C), for the equilibration of $[Mo_3Se_4(H_2O)_9]^{4+}$ with NCS^-, the reactant in excess (solid symbols, + and x) and with the $Mo^{IV}{}_3$ reactant in excess (open symbols). A statistical factor of 3 is required: $[H^+]$ = 0.30 (▼), 0.40 (◆), 0.80 (+), 1.00 (▲), 1.20 (■), 1.70 (×), and 2.00 M (●), with I = 2.00 M($LiClO_4$)

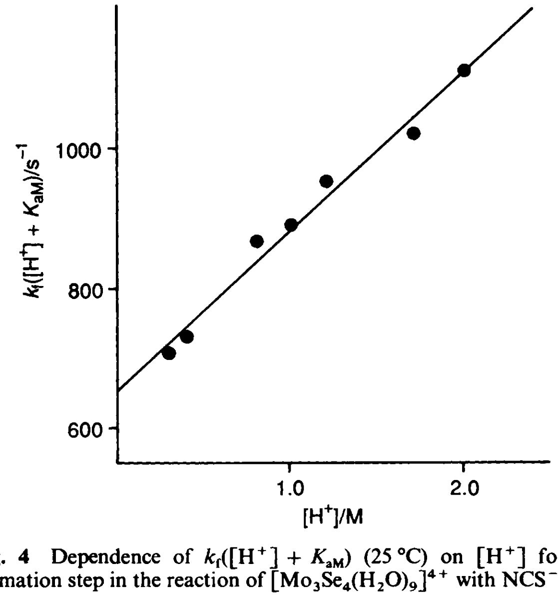


Fig. 4 Dependence of $k_f([H^+] + K_{aM})$ (25 °C) on $[H^+]$ for the formation step in the reaction of $[Mo_3Se_4(H_2O)_9]^{4+}$ with NCS^-, I = 2.00 M ($LiClO_4$)

Table 3 First-order rate constants k_{1eq} and k_{2eq} (25 °C) for the first and second stages of the reaction of $[Mo_3OSe_3(H_2O)_9]^{4+}$ with NCS^-, I = 2.00 M ($LiClO_4$)

$[H^+]$	$10^3[Mo^{IV}{}_3]$	$10^3[NCS^-]$	$10k_{1eq}$	10^2k_{2eq}
	M		s^{-1}	
2.00	0.19	0.03	1.22	—
	0.38	0.03	1.34	—
	0.04	0.50	1.66	4.3
	0.04	1.00	2.18	5.5
	0.04	1.50	2.97	7.1
	0.04	2.00	3.49	8.1
	0.04	2.50	4.3	9.2
	0.04	3.00	4.8	11.0
1.00	0.04	1.00	2.91	7.1
	0.04	2.00	4.5	9.9
	0.04	3.00	6.1	13.0
0.50	0.05	1.00	4.4	10.2
	0.05	2.00	6.8	14.1
	0.05	2.50	8.1	15.8

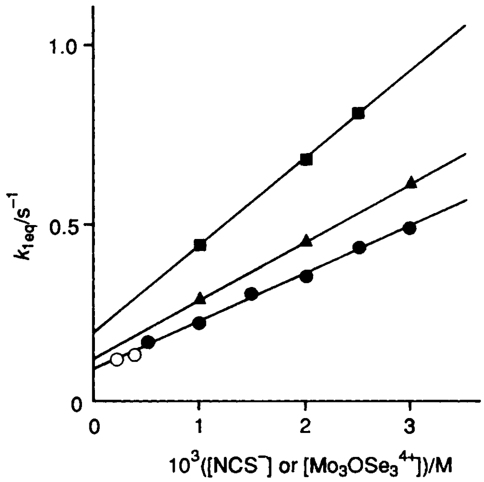


Fig. 5 Dependence of rate constants k_{1eq} (25 °C) for the first stage in the equilibrium of $[Mo_3OSe_3(H_2O)_9]^{4+}$ with NCS^- (reactant in excess) on $[NCS^-]$ at $[H^+]$ = 2.00 (●), 1.00 (▲) and 0.50 M (○), I = 2.00 M ($LiClO_4$). Runs with $[Mo_3OSe_3(H_2O)_9]^{4+}$ in excess are indicated by open symbols

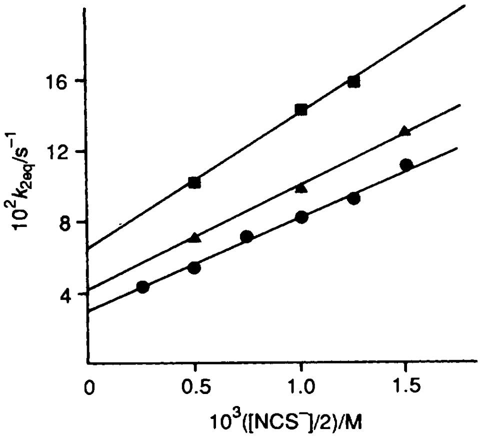


Fig. 6 Dependence of rate constants k_{2eq} (25 °C) for the slower stage of the equilibrium of $[Mo_3OSe_3(H_2O)_9]^{4+}$ with NCS^- (reactant in excess) on $[NCS^-]$ at $[H^+]$ = 2.00 (●), 1.00 (▲) and 0.50 M (■), I = 2.00 M ($LiClO_4$). A statistical factor of 2 is applied

constants k_f and k_{aq}, for both stages, are dependent on $[H^+]^{-1}$. Although studies were less detailed than for $[Mo_3Se_4(H_2O)_9]^{4+}$ the dependences are certainly of the kind $[H^+]^{-1}$, and possibly of the same form as equation (8).

Reaction of $[Mo_3O_2Se_2(H_2O)_9]^{4+}$.—Biphasic kinetics consistent with different Mo atoms, f and g in Fig. 2, was observed with statistical factors of 2 and 1 respectively. Rate constants k_{1eq} and k_{2eq} obtained in 2.00 M $HClO_4$, I = 2.00 M, are listed in Table 5. Their dependences on concentrations are illustrated in Fig. 7. From the slopes and intercepts $k_{1f} = 13.5 \pm 0.4$ M^{-1} s^{-1}, $k_{1aq} = (5.9 \pm 0.3) \times 10^{-3}$ s^{-1}, $k_{2f} = 2.8 \pm 0.1$ M^{-1} s^{-1}, and $k_{2aq} = (6.2 \pm 0.9) \times 10^{-4}$ s^{-1}. Preliminary runs at lower $[H^+]$

Table 4 Summary of rate constants k_{1f}, k_{1aq} and k_{2f}, k_{2aq} (25 °C) for the first and second phases of the reaction of $[Mo_3OSe_3(H_2O)_9]^{4+}$ with NCS^- at different $[H^+]$ values, I = 2.00 M ($LiClO_4$)

$[H^+]$/ M	k_{1f}/ M^{-1} s^{-1}	k_{1aq}/ s^{-1}	k_{2f}/ M^{-1} s^{-1}	k_{2aq}/ s^{-1}
2.00	131 ± 3	0.093 ± 0.005	52 ± 2	0.030 ± 0.002
1.00	161 ± 2	0.131 ± 0.003	59 ± 2	0.041 ± 0.002
0.40	242 ± 6	0.199 ± 0.011	75 ± 3	0.065 ± 0.002

Table 5 Equilibration rate constants, k_{1eq} and k_{2eq} (25 °C), for the first and second stages of the reaction of $[Mo_3O_2Se_2(H_2O)_9]^{4+}$ with NCS^- in 2.00 M $HClO_4$, I = 2.00 M

$10^3[Mo^{IV}_3]$	$10^3[NCS^-]$	10^2k_{1eq}	10^3k_{2eq}
M		s^{-1}	
0.30	0.04	1.00	—
0.50	0.04	1.22	—
0.75	0.04	1.62	—
1.00	0.04	1.94	—
0.03	0.50	0.95	2.1
0.04	0.75	1.12	2.72
0.04	1.00	1.30	3.4
0.04	1.25	1.45	4.0
0.04	1.50	1.55	4.8
0.04	2.00	1.98	6.3

Table 6 First-order equilibration rate constants k_{eq} (25 °C) for the uniphasic reaction of $[Mo_3O_3Se(H_2O)_9]^{4+}$ with NCS^-, I = 2.00 M [Li(pts)]

$[H^+]$/M								
2.00	$10^3[NCS^-]$/M	1.00	0.09[a]	2.00	0.09[b]	3.00	4.00	
	$10^4k_{obs}/s^{-1}$	1.65	2.06	2.49	2.71	2.91	3.7	
1.50	$10^3[NCS^-]$/M	1.00	0.27[c]	2.49	3.00			
	$10^4k_{obs}/s^{-1}$	2.29	3.2	3.4	3.8			
1.25	$10^3[NCS^-]$/M	1.00	2.49	3.00	3.00	4.00		
	$10^4k_{obs}/s^{-1}$	2.8	3.9	4.4	4.5	5.3		
1.00	$10^3[NCS^-]$/M	1.00	1.50	2.55	3.00	3.90		
	$10^4k_{obs}/s^{-1}$	3.3	3.9	4.9	5.4	6.2		
0.80	$10^3[NCS^-]$/M	1.00	1.50	2.00	2.10	2.55	3.00	3.90
	$10^4k_{obs}/s^{-1}$	4.1	4.8	5.4	5.4	6.1	6.4	8.0
0.50	$10^3[NCS^-]$/M	1.00	1.50	2.00	2.55	3.00	3.90	
	$10^4k_{obs}/s^{-1}$	5.2	6.2	6.5	8.1	8.5	9.7	
0.30	$10^3[NCS^-]$/M	1.00	1.50	2.00	2.55	3.00	3.90	
	$10^4k_{obs}/s^{-1}$	6.2	7.9	8.1	9.2	9.8	12.0	

[a] $[Mo^{IV}_3]$ = 4.4 × 10^{-4} M. [b] $[Mo^{IV}_3]$ = 8.8 × 10^{-4} M. [c] $[Mo^{IV}_3]$ = 6.0 × 10^{-4} M.

Table 7 Formation (k_f) and aquation (k_{aq}) rate constants (25 °C) for the reaction of $[Mo_3O_3Se(H_2O)_9]^{4+}$ with NCS^-, I = 2.00 M [Li(pts)]

$[H^+]$/M	$10^2k_f/M^{-1}\ s^{-1}$	$10^4k_{aq}/s^{-1}$
2.00	18.5	1.25
1.50	21.1	1.65
1.25	25.3	1.92
1.00	30.5	2.32
0.80	39	2.79
0.50	47	3.7
0.30	56	4.5

indicated an inverse $[H^+]$ dependence, but this was not studied further.

Table 8 Estimates of approximate equilibration rate constants, k_{1eq} and k_{2eq} (25 °C), for the reaction of NCS^- with $[Mo_4Se_4(H_2O)_{12}]^{5+}$, $I = [H^+]$ = 2.00 M $HClO_4$

$10^3[NCS^-]$	$10^3[Mo_4Se_4(H_2O)_{12}]^{5+}$	10^4k_{1eq}	10^4k_{2eq}
	M	s^{-1}	
0.08	0.35	6.1	1.25
1.30	0.040	8.1	1.78
1.97	0.090	11.6	2.80
2.96	0.090	17.1	4.1
3.94	0.090	20.8	5.1

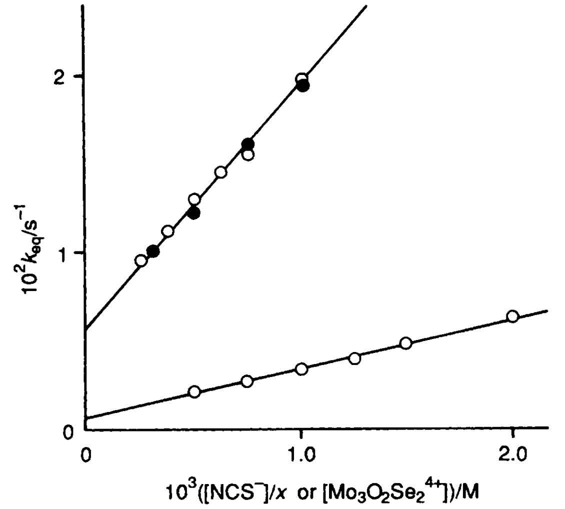


Fig. 7 First-order rate constants, k_{eq} (25 °C), for the two stages k_{1eq} (upper) and k_{2eq} (lower) of the equilibration of $[Mo_3O_2Se_2(H_2O)_9]^{4+}$ with NCS^- (reactant in excess), $[H^+] = I$ = 2.00 M. A statistical factor $x = 2$ is used for k_{1eq} and $x = 1$ for k_{2eq}. Runs with the Mo^{IV}_3 reactant in excess are also indicated (solid symbols)

Reaction of $[Mo_3O_3Se(H_2O)_9]^{4+}$.—Because of some early recognition of instability of this complex and the slowness of kinetic runs it was decided to study the reaction in 2.00 M pts^- instead of ClO_4^-. Uniphasic kinetics and a statistical factor of 3 apply. The $[H^+]$ dependence was investigated in some detail as illustrated in Fig. 8. Equilibration rate constants are listed in Table 6, and k_f and k_{aq} values in Table 7. As in the case of $[Mo_3O_4(H_2O)_9]^{4+}$ the conjugate-base pathway only was detected, k_1 and k_{-1} are zero in equation (5), and a satisfactory fit of k_f is obtained with K_{aM} = 0.44 ± 0.05 M and k_2 = 1.00 ± 0.16 M^{-1} s^{-1}. For the corresponding treatment of k_{aq}, K_{aMT} is 0.19 ± 0.08 M and k_{-2} = (1.38 ± 0.18) × 10^{-3} s^{-1}. Previously the effect of replacing pts^- for ClO_4^- was investigated for the reactions of NCS^- with $[Mo_3O_4(H_2O)_9]^{4+}$,[10] and it was found that k_f is approximately three times larger and k_{aq} 40% larger in ClO_4^- solutions. Similar factors are expected to contribute here also and are to be borne in mind in making comparisons.

Reaction of $[Mo_4Se_4(H_2O)_{12}]^{5+}$.—All the selenide ligands in the cube are of the μ_3 type, and a study of substitution of this mixed-valence $Mo^{III}{}_3Mo^{IV}$ complex is important to define the magnitude of effects stemming from the μ_3 ligands. All runs were carried out under rigorous air-free conditions, and were very slow compared to those of the Mo^{IV}_3 complexes. The data obtained are not as precise as we would have wished because of decomposition of the cube with release of red Se over the long reaction times required. We note however that the initial part of absorbance *vs.* time curves, Fig. 9, is of a similar shape to that observed in studies on $[Mo_4S_4(H_2O)_{12}]^{5+}$.[13] Rate constants were estimated using the Guggenheim method and with a biphasic fit (ignoring decomposition), Table 8. From our treatment the two stages appear to have statistical factors of 3

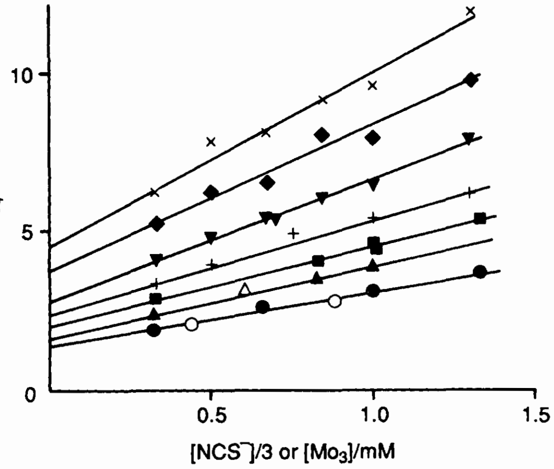


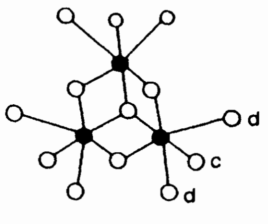
Fig. 8 First-order rate constants, k_{eq} (25 °C), for the equilibration of $[Mo_3O_3Se(H_2O)_9]^{4+}$ with NCS^- the reactant (solid symbols), and with the Mo^{IV}_3 reactant in excess (open symbols), I = 2.00 M [Li(pts)]. $[H^+]$ = 2.00 (●), 1.50 (▲), 1.25 (■), 1.00 (+), 0.80 (▼), 0.50 (◆) and 0.30 M (×). A statistical factor of 3 is required for runs with NCS^- in excess

and 1, and can be assigned as substitution at Mo^{III} and Mo^{IV} respectively as in the case of $[Mo_4S_4(H_2O)_{12}]^{5+}$.[13] For the first stage of substitution at Mo^{III}, $k_{1f} \approx 1.5$ M^{-1} s^{-1} and $k_{1aq} \approx 1.3 \times 10^{-4}$ s^{-1}, and for the second at Mo^{IV}, $k_{2f} \approx 0.11$ M^{-1} s^{-1} and $k_{2aq} \approx 6.3 \times 10^{-5}$ s^{-1}. We have confidence in these numbers to factors of within 2–3 only.

Discussion

Studies on the substitution of H_2O by NCS^- in the case of the all μ_3-Se cube $[Mo_4Se_4(H_2O)_{12}]^{5+}$ confirm in the most emphatic way possible that substitution at H_2O *trans* to μ_3-Se is relatively slow at both the molybdenum-(III) (≈ 1.5 M^{-1} s^{-1}) and -(IV) (≈ 0.11 M^{-1} s^{-1}) centres. The latter is particularly relevant to the Mo^{IV}_3 studies described in this paper, and supports earlier findings from ^{18}O labelling,[17] as well as NMR experiments on $[Mo_3O_4(H_2O)_9]^{4+}$,[18] that positions *trans* to μ_3 core ligands are more inert than those which are *trans* to μ_2 ligands.

The molecular structures of the Mo^{IV}_3 ions $[Mo_3O_2Se_2(NCS)_9]^{5-}$ and $[Mo_3Se_4(NCS)_9]^{5-}$ determined by X-ray diffraction[2] have established that the NCS^- is *N*-bonded to the Mo^{IV}, which is likely therefore to be thermodynamically the most stable form. The corresponding aqua ions have three H_2O molecules bonded to each Mo^{IV}, one *trans* to the μ_3-ligand (designated type c), and two *trans* to μ-ligands (designated type d). The structures are not regular cubic shapes. Thus as in the case of the Mo/S analogues,[19] the trinuclear incomplete cuboidal (metal-depleted) cluster $[Mo_3Se_4(H_2O)_9]^{4+}$ is related to the cuboidal ion $[Mo_4Se_4(H_2O)_{12}]^{5+}$, which can be viewed as made up of two regular interpenetrating Se_4 and Mo_4 tetrahedra which are of different sizes. Additional distortions result on interchanging O for Se in the $[Mo_3O_xSe_{4-x}(H_2O)_9]^{4+}$ series, which is the main focus of the present paper.



Different molybdenum(IV) identities result from the bonding of core oxo and selenido ligands, Fig. 2. A single Se^{2-} (or S^{2-}) ligand occupies preferentially the μ_3 position.[20] A Mo^{IV} bound to three oxo ligands, as in $[Mo_3O_4(H_2O)_9]^{4+}$, is designated e, one to μ_3-Se and two μ-O is designated f, one to μ_3-Se, μ-Se and μ-O as g, and one to three selenido core ligands as in $[Mo_3Se_4(H_2O)_9]^{4+}$ as h. For all runs with Mo^{IV}_3 in excess only one stage was observed. This is because the absorbance changes are relatively small and solutions become depleted in NCS^- before the second stage is incident.

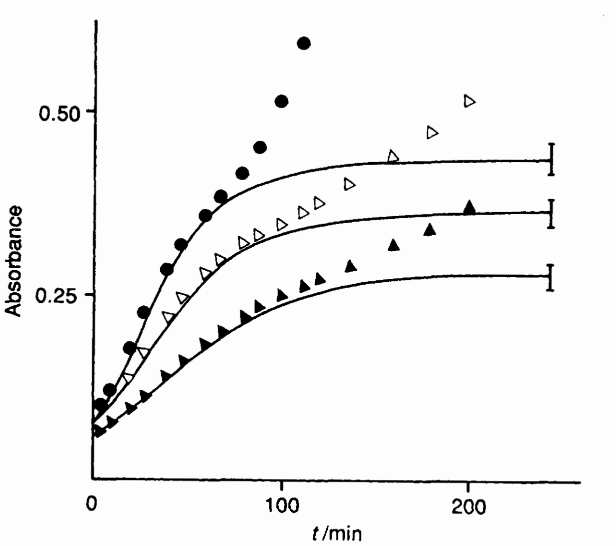


Fig. 9 The change in absorbance with time (λ = 450 nm) for the reaction (25 °C) of $[Mo_4Se_4(H_2O)_{12}]^{5+}$ (0.09 mM) with NCS^-, $I = [H^+]$ = 2.00 M ($HClO_4$), $[NCS^-]$ = 3.94 (●), 2.96 (▽), and 1.97 mM (▼)

Studies of the NCS^- substitution on $[Mo_3Se_4(H_2O)_9]^{4+}$, which has three h-type Mo^{IV}, have led to the identification of a statistical factor of three. This allows for the fact that with NCS^- in excess 1 : 1 substitution occurs simultaneously at all three Mo. The behaviour observed is similar to that of the $[Mo_3S_4(H_2O)_9]^{4+}$ (refs. 10 and 11) and $[W_3S_4(H_2O)_9]^{4+}$ analogues.[15] Formation rate constants k_f for the $[NCS^-]$-dependent substitution on $[Mo_3Se_4(H_2O)_9]^{4+}$ likewise exhibit an $[H^+]$ dependence which implicates both the aqua and conjugate-base forms written as Mo_3 and $Mo_3(OH)$ in equations (5) and (6). The reverse steps together constitute the aquation process. All these reactions are believed to occur at the d-H_2O, and are the result of the *trans*-labilisation effect of relatively electron-rich μ-Se ligands. The behaviour is similar to that observed for $[Mo_3S_4(H_2O)_9]^{4+}$ and with $[Mo_3O_4(H_2O)_9]^{4+}$, except that in the latter contributions from the conjugate-base pathway only are detected.[10–12] This suggests a greater relative importance of the μ-Se (and μ-S) *trans*-labilising effect, which enhances substitution on the aqua ion to a rate comparable to that observed for the conjugate-base pathway. The present studies gave a kinetic value of the acid dissociation constant, K_{aM} = 0.32 M for $[Mo_3Se_4(H_2O)_9]^{4+}$, comparable to the previously determined values of 0.22,[17] 0.42[11] and 0.34 M[17] for $[Mo_3S_4(H_2O)_9]^{4+}$, $[Mo_3O_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$ respectively. A value of similar magnitude (0.44 M) is indicated for $[Mo_3O_3Se(H_2O)_9]^{4+}$. The NMR studies of Merbach and co-workers[18] on $[Mo_3O_4(H_2O)_9]^{4+}$ have demonstrated that acid dissociation occurs at the d-H_2O, and the conjugate-base pathway results from the effect of acid dissocation at one d-H_2O on substitution at the other d-H_2O of any one Mo^{IV}. While $[H^+]$ was not varied for studies on $[Mo_4Se_4(H_2O)_{12}]^{5+}$, for the same range of $[H^+]$ the ions $[Mo_4S_4(H_2O)_{12}]^{4+/5+}$ exhibit no $[H^+]$ dependence,[13] and this and other evidence[19] indicates that acid dissociation of c-type H_2O *trans* to μ_3 core ligands is much less extensive.

The X-ray crystal structure of $[Mo_3O_2Se_2(NCS)_9]^{5-}$ clearly demonstrates[2] the presence of a μ_3-selenido ligand with two g- and one f-type Mo^{IV}. Since the molybdenum(IV) centres differ

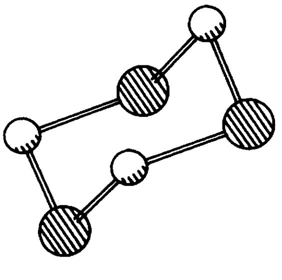
Table 9 Summary of rate constants (25 °C) for the equilibration of $[Mo_3O_xSe_{4-x}(H_2O)_9]^{4+}$ and $[Mo_3O_xS_{4-x}(H_2O)_9]^{4+}$ (ref. 9) and $[W_3O_xS_{4-x}(H_2O)_9]^{4+}$ (refs. 14–16) (x = 0–4) trinuclear cluster complexes with NCS^- in 2.00 M $HClO_4$, I = 2.00 M, and in one case with $[Mo_3O_3Se(H_2O)_9]^{4+}$ in 2.00 M Hpts

		Mo–Se			Mo–S			W–S		
x	M^{IV} Type	k_f/M^{-1} s^{-1}	k_{aq}/s^{-1}	K/M^{-1}	k_f/M^{-1} s^{-1}	k_{aq}/s^{-1}	K/M^{-1}	k_f/M^{-1} s^{-1}	k_{aq}/s^{-1}	K/M^{-1}
4	e	2.13	2.20×10^{-3}	970	2.13	2.20×10^{-3}	970	0.110	0.35×10^{-4}	3140
3	f	0.19	1.25×10^{-4}	1520	0.37	1.6×10^{-4}	2310	0.008	5.4×10^{-6}	1480
2	f	2.8	6.2×10^{-4}	4520		Not determined		0.045	6.0×10^{-5}	750
	g	13.5	5.9×10^{-3}	2290	7.7	2.7×10^{-3}	2850	0.50	1.3×10^{-4}	3850
1	g	52	3.0×10^{-2}	1730	23	1.4×10^{-2}	1640	0.212	4.1×10^{-4}	540
	h	131	9.3×10^{-2}	1410	82	2.4×10^{-2}	3420	1.24	2.3×10^{-3}	520
0	h	480	2.0×10^{-1}	2400	212	9.2×10^{-2}	2300	38.4	2.5×10^{-2}	1520

it is not surprising that the equilibration of NCS^- with $[Mo_3O_2Se_2(H_2O)_9]^{4+}$ is biphasic. A statistical factor of two is required to obtain coincidence of rate constants calculated for the first stage (13.5 M^{-1} s^{-1}) with first $[Mo_3O_2Se_2(H_2O)_9]^{4+}$ and then NCS^- in excess, demonstrating that this process is substitution at the more labile g-type Mo^{IV} co-ordinated to one μ-Se and one μ-O. The second slower stage (2.80 M^{-1} s^{-1}) is assigned as substitution at the single f-type molybdenum centre with a statistical factor of one. Substitution on $[Mo_3OSe_3(H_2O)_9]^{4+}$ is also biphasic, and statistical factors of one and two respectively can likewise be assigned. In the case of $[Mo_3O_3Se(H_2O)_9]^{4+}$ substitution is substantially slower than is observed for $[Mo_3O_4(H_2O)_9]^{4+}$. Uniphasic kinetics is observed, and the statistical factor of three is consistent with a μ_3-Se structure and three identical Mo^{IV}.

Rate constants k_f and k_{aq} (and related K values) at $[H^+]$ = I = 2.00 M are summarised in Table 9, alongside corresponding values for $[Mo_3O_xS_{4-x}(H_2O)_9]^{4+}$ (ref. 9) and $[W_3O_xS_{4-x}(H_2O)_9]^{4+}$.[14–16] While this is a relatively easy comparison to make at $[H^+]$ = 2.00 M there is a distortion, because the $[Mo_3O_xSe_{4-x}(H_2O)_9]^{4+}$ (x = 0–3) complexes have k_1 and k_2 contributions to k_f at $[H^+]$ = 2.0 M, whereas only the k_2 component is detected for $[Mo_3O_4(H_2O)_9]^{4+}$. The same is true in the case of k_{aq} values. However a comparison of known k_2/M^{-1} s^{-1} values for $[Mo_3Se_4(H_2O)_9]^{4+}$ (2000), $[Mo_3O_3Se(H_2O)_9]^{4+}$ (1.05) and $[Mo_3O_4(H_2O)_9]^{4+}$ (4.8)[11] indicates a comparable span of rate constants of 2240 to that of 2530 from k_f values in Table 9.

A particularly important observation is the increase in k_f values as the number of μ-Se (and μ-S) core atoms increase. It is evident that the replacement of μ-O with μ-Se enhances the labilisation of d-H_2O molecules. Replacement of the μ_3-O of $[Mo_3O_4(H_2O)_9]^{4+}$ by μ_3-Se to give $[Mo_3O_3Se(H_2O)_9]^{4+}$ is however accompanied by a decrease in k_f by a factor of 14, Table 9. Since substitution at the d-H_2O positions is clearly less, it can be concluded that there is a *cis* retardation effect. A similar effect is observed for the μ_3-S of $[Mo_3O_3S(H_2O)_9]^{4+}$ in the sulfido series. On the other hand replacement of μ-O by μ-Se gives quite the opposite trend in rate constants with $Se^{2-} > S^{2-} > O^{2-}$, demonstrating a substantial *trans*-labilising effect. A 2530-fold increase in k_f values is observed from the most inert $[Mo_3O_3Se(H_2O)_9]^{4+}$ to the most labile $[Mo_3Se_4(H_2O)_9]^{4+}$. A smaller 570-fold spread of k_f is observed for the $[Mo_3O_xS_{4-x}(H_2O)_9]^{4+}$ series. While Se^{2-} is seen to be more influential than S^{2-} at 25 °C the differences are not sufficiently marked to ensure that they will be retained as the temperature is varied, since different $\Delta H^\ddagger$ values are likely to apply. Similar opposing effects are observed on replacing O^{2-} by S^{2-} in the case of $[W_3O_xS_{4-x}(H_2O)_9]^{4+}$ (4800-fold effect).[14–16] The effects observed draw attention to the different bonding of μ-O as compared to μ-Se and μ-S for which d-orbital participation is possible. Distortions from regular geometric shapes resulting from different effective ionic radii for O^{2-} (1.40), S^{2-} (1.84), and Se^{2-} (1.98 Å)[3] may also contribute. Average bond lengths of 2.03 Å for Mo–μ_3-O, 2.35 Å for Mo–μ_3-S, and 2.45 Å for Mo–μ_3-Se are noted.[19]



From an inspection of Table 9 it is clear that the rate constants for substitution at metal atoms designated f, g or h in any one series are not identical. The introduction of μ-Se or μ-S core ligands at a remote core position appears to have beneficial effects on substitution at a particular metal site. One way of rationalising such effects is in terms of the quasi-aromaticity approach of Lu[21] in which bonding in the Mo_3S_3 ring of $Mo_3S_4{}^{4+}$ is compared to that of C_6 aromatic rings. In this approach the ability of μ core ligands to form multiple bonds to Mo^{IV} is taken into account. The μ_3-S core ligand is assumed to have little or no influence and is excluded. Bond lengths in the puckered Mo_3S_3 ring (≈2.28 Å) are identical and intermediate between those of single (2.44 Å) and double Mo–S bonds (2.02 Å). They are also less than the Mo–μ_3-S bond lengths of 2.36 Å.[19] Similar discussion is expected to hold for Mo_3Se_3 and Mo/Se/O six-membered rings with different bond lengths applying in the latter case because of ring delocalisation effects. It seems reasonable that rate constants at *e.g.* the h metal atoms of $[Mo_3Se_4(H_2O)_9]^{4+}$ and $[Mo_3OSe_3(H_2O)_9]^{4+}$ are not identical. Ring delocalisation in non-planar Mo_3Se_3 is possible due to metal d orbital participation, whereas with C_6 planar rings are required.

When a comparison of rate constants for molybdenum-chalcogenide and W–S trinuclear clusters is made a significant difference (≈10-fold) is clearly evident. This pattern has been observed for the substitution reactions of metal(V) $[M_2O_4(H_2O)_6]^{2+}$ (refs. 23 and 24) and metal(IV) ions $[M_3O_4(H_2O)_9]^{4+}$ (M = Mo or W),[10–12,14] and is attributed to the relativistic effect of 5d as compared with 4d orbitals.[24]

No evidence was obtained in the present studies for substitution of a second NCS^- at a single Mo. This would be evident in the case of *e.g.* $[Mo_3Se_4(H_2O)_9]^{4+}$ and $[Mo_3O_3Se(H_2O)_9]^{4+}$ as a second stage of reaction.

A comparison of aquation rate constants in Table 9 indicates similar trends to k_f, with a decrease in k_{aq} as μ_3-O is replaced by μ_3-S or μ_3-Se and overall increases as the number of μ-chalcogenide ligands increases. There is a strong correspondence of k_f and k_{aq} in all three cluster series. In particular, plots of rate constants against the number of core-S or -Se ligands for the molybdenum sulfido and molybdenum selenido series show a marked similarity in appearance.

Equilibrium constants have been calculated for the NCS^- substitution on each cluster, Table 9. No clearly discernible trends are observed, the spread of values in the two molybdenum series being very similar, and that of the tungsten series approximately twice as big. Overall the scatter in equilibrium constants almost certainly reflects the greater uncertainty in determining k_{aq} (intercept) as opposed to k_f (slope) values.

Acknowledgements

We are most grateful to Professors G. Henkel and B. Krebs for samples of the $Mo^V{}_2$ complex, the SERC and Laporte Industries for a CASE post-graduate studentship (to C. A. R), the British Council for financial support and the University of Barcelona for leave of absence (to M. M.), the University of the Orange Free State in South Africa (G. J. L.) and the University of Kuwait (N.A.-S.) also for leave of absence. We also thank Mari-Angel Pitarque of the University of Barcelona for carrying out some check kinetic runs.

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Received 28*th July* 1992; *Paper* 2/04052B