Mechanism of Substitution on Trinuclear Incomplete Cuboidal $[M_3X_4(OH_2)_9]^{4+}$ Ions: Kinetic Studies of Water Exchange and Substitution by Cl^- on $[Mo_3S_4(OH_2)_9]^{4+}$†

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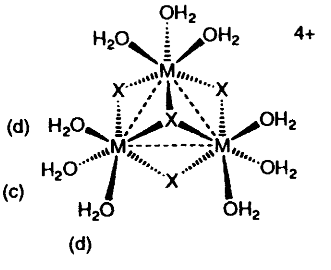
The complex $[Mo_3S_4(OH_2)_9]^{4+}$ possesses non-equivalent H_2O ligands with those (d, two per Mo) which are *trans* to μ-S undergoing water exchange 10^5 faster than those (c, one per Mo) which are *trans* to μ_3-S. The former arises from a labilising pathway involving the monohydroxo conjugate base $[Mo_3S_4(OH_2)_8(OH)]^{3+}$ ($K_{aM} \approx 0.2$ mol dm^{-3}). The chloride anation reaction has also been studied and comparisons are made with data previously reported for the thiocyanate anation. Together the results suggest an I_d mechanism for substitution at the d sites on $[Mo_3S_4(OH_2)_8(OH)]^{3+}$. For water exchange on $[Mo_3S_4(OH_2)_9]^{4+}$ at both the d and c sites, an I_a mechanism is tentatively suggested from comparisons with complex-formation data.

It is now well established that molybdenum and tungsten in oxidation state IV form trinuclear incomplete cuboidal aqua ions $[M_3X_4(OH_2)_9]^{4+}$ **I** (X = O or S) in non-complexing acidic aqueous solution.[1-5] Crystal structure determinations on the $Mo_3O_4{}^{4+}$,[6] $Mo_3S_4{}^{4+}$ (ref. 7) and $W_3S_4{}^{4+}$ (ref. 8) aqua ions and related complexes, in conjunction with ^{17}O NMR studies[6,9] and ^{18}O isotopic labelling,[10] have shown that the basic trinuclear unit **I** is retained in solution.



I

Subsequently a number of kinetic studies have sought to investigate the mechanism of substitution of the co-ordinated terminal water ligands.[6,11-14] Complex **I** has non-identical H_2O groups designated c and d which occupy positions approximately *trans* to the μ_3-capping and μ-bridging X ligands respectively. It has been demonstrated that electron-rich μ-S ligands bring about a more significant labilising effect than does μ-O.[11] Cuboidal $[Mo_4S_4(OH_2)_{12}]^{5+/4+}$ complexes on the other hand have only μ_3-S ligands and the H_2O groups are relatively inert.[15]

Previous water-exchange studies have been carried out on $[Mo_3O_4(OH_2)_9]^{4+}$ in toluene-*p*-sulfonate (pts$^-$) solutions using ^{17}O NMR spectroscopy. It has been demonstrated that rate constants are a factor of 2 smaller in 2.0 mol dm^{-3} pts$^-$ than in 2.0 mol dm^{-3} $ClO_4{}^-$ in studies on the complexing of $[Mo_3O_4(OH_2)_9]^{4+}$ by NCS^-.[16] This may be associated with the outer-sphere association of pts$^-$ with $Mo_3O_4{}^{4+}$. A feature of the crystal structures of $[Mo_3O_4(OH_2)_9][pts]_4{\cdot}13H_2O$[6] and $[Mo_3S_4(OH_2)_9][pts]_4{\cdot}9H_2O$[7] is the extensive network of hydrogen bonds of the water molecules to pts$^-$. Studies in the presence of the more weakly complexing $ClO_4{}^-$ are thus to be preferred. Moreover the lower viscosity of $ClO_4{}^-$ solutions is desirable for NMR linewidth measurements employing quadrupolar nuclei like ^{17}O. Unfortunately the longer-duration studies on $[Mo_3O_4(OH_2)_9]^{4+}$ in $ClO_4{}^-$ are hindered by oxidation to Mo^V. On the other hand $[Mo_3S_4(OH_2)_9]^{4+}$ is quite stable under similar conditions to $ClO_4{}^-$.[11] Moreover we find it is possible to monitor spectrophotometrically the replacement of H_2O by Cl^- in the case of $[Mo_3S_4(OH_2)_9]^{4+}$. With the development of improved techniques for obtaining more concentrated solutions of $[Mo_3S_4(OH_2)_9]^{4+}$ in $ClO_4{}^-$ we have been able to study water exchange of both c and d H_2O groups of $[Mo_3S_4(OH_2)_9]^{4+}$ using ^{17}O NMR spectroscopy. The results obtained, together with those from the chloride anation study, are presented in this paper. From a comparison of rate constants for water exchange and anation by Cl^- and NCS^- it is possible to discuss the mechanism of substitution.[17,18]

Experimental

Preparation of Perchlorate Solutions of $[Mo_3S_4(OH_2)_9]^{4+}$.—Stock solutions of $[Mo_3S_4(OH_2)_9]^{4+}$ were obtained by air oxidation of $[Mo_4S_4(OH_2)_{12}]^{5+}$ (2 h at ≈90 °C) as previously described.[19] Solutions were purified by Dowex 50W-X2 cation-exchange chromatography. The complex was eluted first in 2.0 mol dm^{-3} HCl, and then after recolumning and washing with 0.5 and 1.0 mol dm^{-3} $HClO_4$, eluted in 2.0 mol dm^{-3} $HClO_4$. Reproducible kinetics was obtained only with very pure complex. The peak ratio $A_{366}:A_{603} = 15.3:1$ in 2.0 mol dm^{-3} $HClO_4$ was used as a guide to purity. Concentrations were determined from the absorbance at the 603 nm peak, $\varepsilon = 362$ dm^3 mol^{-1} cm^{-1} per trimer at 25 °C.[11] Stock solutions used for

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† *Supplementary data available* (No. SUP 56954, 3 pp.): relaxation times. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

the complex-formation study with Cl^- were $\approx 1 \times 10^{-3}$ mol dm^{-3} in $[Mo_3S_4(OH_2)_9]^{4+}$.

For the water-exchange study, solutions 50 times more concentrated in $[Mo_3S_4(OH_2)_9]^{4+}$ were required. Such concentrations are not normally attainable by elution from Dowex cation-exchange columns using $HClO_4$, and so an alternative method was devised. This involved preparing pure solutions of $[Mo_3S_4(OH_2)_9]^{4+}$ in 2.0 mol dm^{-3} $HClO_4$, recolumning and eluting with 2.0 mol dm^{-3} HCl. Solutions were then evaporated to dryness on a vacuum line (10^{-3} Torr, *ca.* 0.133 Pa) to leave a green residue of $[Mo_3S_4Cl_x(OH_2)_{9-x}]$ ($x \approx 4$). The solid was dissolved in 3.0 mol dm^{-3} $HClO_4$ and left to equilibrate for 1 d to give $[Mo_3S_4(OH_2)_9]^{4+}$ at the higher concentrations desired. The $[H^+]$ of solutions so prepared was adjusted to be in at least a 50-fold excess over $Mo_3S_4^{4+}$ in order to safeguard against any hydrolysis products. Typical stock solutions so prepared contained ≈ 0.05 mol dm^{-3} $[Mo_3S_4(OH_2)_9]^{4+}$ in ≈ 2.5 mol dm^{-3} $HClO_4$. Concentrations of $[Mo_3S_4(OH_2)_9]^{4+}$ were determined as before by standardisation at 603 nm following a 10-fold dilution into 2.0 mol dm^{-3} $HClO_4$.

Other Reagents.—The salt $LiClO_4 \cdot 3H_2O$ (Aldrich) was recrystallised twice from water; $Mn(ClO_4)_2 \cdot 6H_2O$, 70% $HClO_4$, LiCl and HCl (all AnalaR grade) were used as supplied by Aldrich. The degree of hydration in the perchlorate salts, together with the background $[H^+]$ of $[Mo_3S_4(OH_2)_9]^{4+}$ stock solutions, was determined by cation exchange with $[H^+]$ and titration of the liberated acid with standard NaOH. All solutions for kinetics were adjusted to ionic strength 2.0 mol dm^{-3} using $LiClO_4$.

Kinetics of Complex Formation with Cl^-.—All runs were conducted with Cl^- in large excess (0.2–1.0 mol dm^{-3}) over $[Mo_3S_4(OH_2)_9]^{4+}$ ($\approx 1 \times 10^{-4}$ mol dm^{-3}). Absorbance changes were monitored at 603 and 460 nm at 25.0 ± 0.1 °C using stopped-flow techniques as described previously.[11] Preliminary runs monitored at 603 nm with $[Cl^-] = 1.0$ mol dm^{-3} indicated a biphasic process, both phases giving a decrease in absorbance. At 460 nm an initial increase was observed followed by a decrease. Typical stopped-flow reaction times with 1.0 mol dm^{-3} Cl^- were 0.1 s and 45 s respectively. For the second phase, isosbestic points were observed at 522 and 638 nm. Equilibrium constants for chloride complexing (and absorbance changes) are much smaller than with NCS^- and preclude studies with $[Mo_3S_4(OH_2)_9]^{4+}$ in excess. Equilibration rate constants k_{1eq} and k_{2eq} were determined at 460 nm. A plot of absorbance changes $\ln(A_\infty - A_t)$ *vs.* t gave k_{2eq} from the linear portion. The intercept of the latter on the $\ln(A_\infty - A_t)$ axis gave x and from a plot of $\ln(A_\infty - A_t - xe^{-kt})$ *vs.* t the rate constant k_{1eq} was obtained. The treatment used[20] applies to consecutive or concurrent reactions (see below). With the inclusion of a statistical factor of 3,[16] rate constants k_{1eq} are dependent on $[Cl^-]$, equation (1), where k_{1f} and k_{1aq} define the formation

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

and aquation processes at each Mo. For the second phase the corresponding relationship is (2), where the statistical factor remains to be confirmed and $n = 1$ has been used for the present.

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

*Dynamic Oxygen-*17 *NMR Measurements.*—The transverse relaxation rates, $1/T_{2b}$, for both the c- and d-H_2O ligands were evaluated by measurement of the linewidths of their corresponding ^{17}O NMR resonances, Fig. 1, from 2.0 cm^3 samples in 10 mm o.d. tubes using a Bruker AM-300 instrument operating at 40.69 MHz. A non-linear least-squares fit of two Lorentzian lines was used to simulate the overlapping resonances of the two H_2O ligands for the purpose of linewidth evaluation as a function of temperature and $[H^+]$. Thermostatting was achieved by blowing a stream of air or N_2 through the probe. The temperature (± 0.5 °C) was measured by calibration using the ^1H NMR chemical shifts of an ethylene glycol standard. The concentration of $[Mo_3S_4(OH_2)_9]^{4+}$ varied between 1.1×10^{-2} and 2.9×10^{-2} mol dm^{-3} with the $[H^+]$ varying between 0.545 and 1.56 mol dm^{-3}, $I = 2.0$ mol dm^{-3} ($LiClO_4$). The ^{17}O enrichment varied between 3.8 {highest $[Mo_3S_4(OH_2)_9]^{4+}$ concentration} to 8.6 atom% (lowest). Amounts of Mn^{2+} (0.05–0.1 mol dm^{-3}) were added to each solution in order to relax out the intense resonance line of free H_2O.[21] The temperature was varied between 5 and 50 °C. The upper limit of 50 °C (highest acidity) was set by the difficulty of measuring the linewidth of the d-H_2O resonance at higher temperatures (too broad) as well as the increased risk of generating unwanted products. The lower limit of 5 °C was used to avoid the increasing viscosity of the solutions. The use of $[H^+] < 0.5$ mol dm^{-3} was also avoided in order to decrease the risk of generating hydrolysis products at the high $[Mo_3S_4(OH_2)_9]^{4+}$ concentrations employed. Typically, between 1×10^5 and 2×10^5 transients were added using 2000 data points, pulse width 27 μs, in order to get an acceptable signal-to-noise ratio for the lineshape simulations. Spectral widths were typically 62.5 kHz.

The slower chemical exchange of the c-H_2O ligands was studied at 25 °C using an isotope-labelling technique[22] with the help of a fast-injection apparatus[23] mounted within the probe of a wide-bore Bruker AM-400 instrument operating at 54.24 MHz. Two solutions of roughly equal volumes, consisting of acidified natural-abundance solutions of $[Mo_3S_4(OH_2)_9]^{4+}$ and $\approx$ 10–12 atom% $H_2{}^{17}O$ containing $LiClO_4 + Mn(ClO_4)_2$, both at 25 °C, were rapidly mixed to a final volume of 2.0 cm^3, $I = 2.0$ mol dm^{-3}, in a static 10 mm o.d. tube. The temperature of the probe was monitored by a substitution technique.[24] The concentration ranges of $[Mo_3S_4(OH_2)_9]^{4+}$, Mn^{2+} and H^+ and the level of ^{17}O enrichment were as for the study of the d-H_2O exchange. Up to 30 spectra (width 62.5 kHz) were taken (1000 transients added, pulse width 25 μs) each accumulated over a 9.7 s time interval using 256 data points in order to monitor the increase with time of the ^{17}O NMR resonance line of the c-H_2O ligands.

Results

Complexation by Cl^-.—Equilibration rate constants for the first (k_{1eq}) and second (k_{2eq}) phases at varying $[H^+]$ and $[Cl^-]$ are listed in Tables 1 and 2 respectively. From plots of k_{1eq} against $[Cl^-]$, k_{1f} and k_{1aq} at different $[H^+]$ values have been obtained, Table 3. The reaction scheme (3)–(6) is the same as

$$[Mo_3S_4(OH_2)_9]^{4+} \xrightleftharpoons{K_{aM}} [Mo_3S_4(OH_2)_8(OH)]^{3+} + H^+ \qquad (3)$$

$$[Mo_3S_4(OH_2)_9]^{4+} + Cl^- \xrightleftharpoons[k_{-1}]{k_1} [Mo_3S_4(OH_2)_8Cl]^{3+} + H_2O \qquad (4)$$

$$[Mo_3S_4(OH_2)_8(OH)]^{3+} + Cl^- \xrightleftharpoons[k_{-OH}]{k_{OH}} [Mo_3S_4(OH_2)_7(OH)Cl]^{2+} + H_2O \qquad (5)$$

$$[Mo_3S_4(OH_2)_8Cl]^{3+} \xrightleftharpoons{K_{aMC}} [Mo_3S_4(OH_2)_7(OH)Cl]^{2+} + H^+ \qquad (6)$$

that found for complexation of NCS^-. The variation of k_{1f} with $[H^+]^{-1}$ is shown in Fig. 2. From the sequence (3)–(6) k_{1f} can be expressed as in equation (7). A good fit is obtained with

$$k_{1f} = \frac{k_1[H^+] + k_{OH}K_{aM}}{[H^+] + K_{aM}} \qquad (7)$$

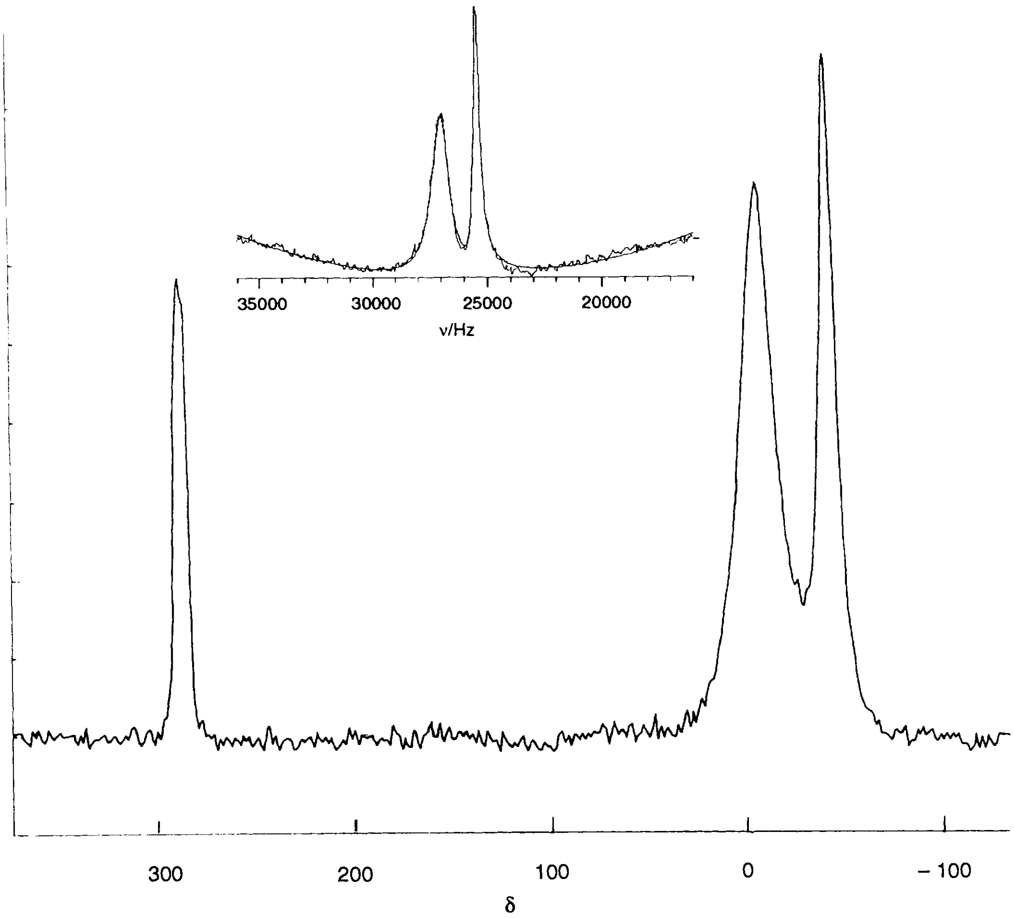

Fig. 1 The 40.56 MHz ^{17}O NMR spectrum for a solution (5 atom% enriched) of $[Mo_3S_4(OH_2)_9]^{4+}$ (0.02 mol dm^{-3}) at $[H^+] = 1.56$ mol dm^{-3}, $I = 2.00$ mol dm^{-3} ($LiClO_4$) at 25 °C; ^{17}O chemical shifts referenced to ClO_4^- (δ 288) are δ −7.4 ± 0.1 (d-H_2O) and −43.4 ± 0.1 (c-H_2O). Inset: fit of the two overlapping resonances of bound H_2O by two Lorentzian lines

Table 1 Equilibration rate constants, k_{1eq}/s^{-1} (25 °C), for the first phase of chloride substitution on $[Mo_3S_4(OH_2)_9]^{4+}$, $I = 2.00$ mol dm^{-3} ($LiClO_4$)

	$[H^+]$/mol dm^{-3}					
$[Cl^-]$/mol dm^{-3}	2.00	1.50	1.00	0.75	0.625	0.5
0.20	61	71	90	101	114	134
0.30	67					
0.40	68	82			133	
0.50	77	90	110	127	142	165
0.60	83					
0.70	87	100				
0.80	94	107	135	153	170	196
0.90	97					
1.00	104	122	147	170	188	216

Table 2 Equilibration rate constants, $10^2k_{2eq}/s^{-1}$ (25 °C), for the second phase of chloride substitution on $[Mo_3S_4(OH_2)_9]^{4+}$, $I = 2.00$ mol dm^{-3} ($LiClO_4$)

	$[H^+]$/mol dm^{-3}		
$[Cl^-]$/mol dm^{-3}	2.00	1.00	0.50
0.20	4.5	5.0	5.0
0.50	6.8	6.3	6.4
0.70	8.2		
0.80	8.6	8.2	8.9
0.90	9.4		
1.00	10.0	9.6	9.4

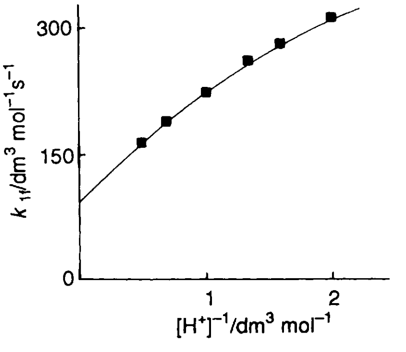

Fig. 2 Variation of k_{1f} (25 °C) with $[H^+]^{-1}$ for the first phase of reaction of Cl^- with $[Mo_3S_4(OH_2)_9]^{4+}$, $I = 2.00$ mol dm^{-3} ($LiClO_4$)

Table 3 Variation of the formation (k_{1f}) and aquation (k_{1aq}) rate constants (25 °C) for the first phase of the reaction of Cl^- with $[Mo_3S_4(OH_2)_9]^{4+}$ with $[H^+]$, $I = 2.00$ mol dm^{-3} ($LiClO_4$)

$[H^+]$/mol dm^{-3}	k_{1f}/dm^3 mol^{-1} s^{-1}	k_{1aq}/s^{-1}
2.00	162	50
1.50	189	58
1.00	222	74
0.75	258	84
0.625	276	96
0.50	309	113

$k_1 = 91 \pm 1$ dm^3 mol^{-1} s^{-1}, $k_{OH} = 790 \pm 10$ dm^3 mol^{-1} s^{-1} and $K_{aM} = 0.23$ mol dm^{-3} (as in the NCS$^-$ study[11]). Data for the aquation step k_{1aq} have also been evaluated. From an expression for k_{1aq} as in equation (7), $k_{-1} = 30.1 \pm 2.5$ s^{-1}, $k_{-OH}K_{aMC} = 41 \pm 1$ dm^3 mol^{-1} s^{-1} and K_{aMC} is $< 10^{-2}$ mol dm^{-3}. For the [H$^+$] range explored, 0.5–2.00 mol dm^{-3}, k_{2eq} was independent of [H$^+$], Fig. 3, with k_{2f} (25 °C) = (6.3 ± 0.5) × 10^{-2} dm^3 mol^{-1} s^{-1} and k_{2aq} = (3.4 ± 0.4) × 10^{-2} s^{-1}.

Water Exchange at the d-H_2O *Ligands of* $[Mo_3S_4(OH_2)_9]^{4+}$.—The temperature and [H$^+$] dependences of the ^{17}O transverse relaxation rate, $1/T_{2b}$, for both the slow-exchanging c-H_2O ligands and fast-exchanging d-H_2O ligands are shown in Fig. 4. For the c-H_2O ligands, $1/T_{2b}(c)$ is dominated by quadrupolar relaxation, $1/T_{2b}(c) = 1/T_{2Q}(c)$. For the d-$H_2O$ ligands $1/T_{2b}(d)$ is made up of contributions from both quadrupolar relaxation, $1/T_{2Q}(d)$, and chemical exchange, k_{ex}, according to equation (8), the exact extent of each contribution being

$$1/T_{2b}(d) = 1/T_{2Q}(d) + k_{ex} \qquad (8)$$

dependent upon both the temperature and the [H$^+$]. Below 17 °C, $1/T_{2b}(d)$ is dominated by quadrupolar relaxation. Above 17 °C line broadening occurs due to chemical exchange. Values for $1/T_{2Q}$(c or d) were found to be independent of [H$^+$] and were fitted by an Arrhenius temperature dependence [equation (9)][6] where $1/T_{2Q}{}^{298}$ is the contribution at 25 °C (298.15 K)

$$1/T_{2Q} = 1/T_{2Q}{}^{298}\exp\{E_Q/R[(1/T) - 1/298.15]\} \qquad (9)$$

and E_Q is the corresponding activation energy. The difference in the observed quadrupolar relaxation rate for each arises from the different quadrupolar coupling constants for the two sites.[25]

For $k_{ex}(d)$ however a significant dependence on [H$^+$] is seen, Fig. 4, consistent with the reaction scheme (10)–(12) and same general rate expression (13) as found for complexation of Cl$^-$

$$[Mo_3S_4(OH_2)_9]^{4+} \xrightleftharpoons{K_{aM}} [Mo_3S_4(OH_2)_8(OH)]^{3+} + H^+ \qquad (10)$$

$$[Mo_3S_4(OH_2)_9]^{4+} + H_2O^{17} \xrightleftharpoons{k_1} [Mo_3S_4(OH_2)_8(d\text{-}O^{17}H_2)]^{4+} + H_2O \qquad (11)$$

$$[Mo_3S_4(OH_2)_8(OH)]^{3+} + H_2O^{17} \xrightleftharpoons{k_{OH}} [Mo_3S_4(OH_2)_7(OH)(d\text{-}O^{17}H_2)]^{3+} + H_2O \qquad (12)$$

$$k_{ex}(d) = \frac{k_1[H^+] + k_{OH}K_{aM}}{[H^+] + K_{aM}} \qquad (13)$$

and NCS$^-$, implying significant involvement of the monohydroxo species $Mo_3(OH)^{3+}$. The temperature dependence of rate constants k_1 and k_{OH} in equation (13) was fitted by the Eyring equation. Analysis of $\ln(1/T_{2b})$ values for both the c- and d-H_2O ligands using equations (8), (9) and (13) yielded constant values (25 °C) for E_Q, $1/T_{2Q}(c)$ and $1/T_{2Q}(d)$ whatever the values of k_1, k_{OH} and K_{aM}. The value of $1/T_{2Q}(d)$ was thus calculated from the known values of E_Q and $1/T_{2Q}(d)$ (25 °C) and subtracted from $1/T_{2b}(d)$ to obtain values of k_{ex}. Only k_{ex} values representing a contribution of more than 20% to $1/T_{2b}(d)$ were considered as reliable in the fit of the temperature and [H$^+$] dependences. For each temperature a fit by equation (13) indicated that k_1 was not significantly contributing to k_{ex} [k_1 (25 °C) < 10 s^{-1}] such that a value of $k_1 = 0$ could be set. Thus the contribution from the term $k_{OH}K_{aM}$ is found to be dominant. For the iterative fit of the data by equations (8), (9) and (13) it was not possible to allow both the value of K_{aM} and its temperature coefficient, the enthalpy of hydrolysis ΔH°_{aM}, to 'float'. The value of ΔH°_{aM} was thus fixed at +3.9 kJ mol^{-1}.* It was subsequently found that the value assumed for ΔH°_{aM} had little effect on the value of K_{aM} (25 °C) obtained from the fit.

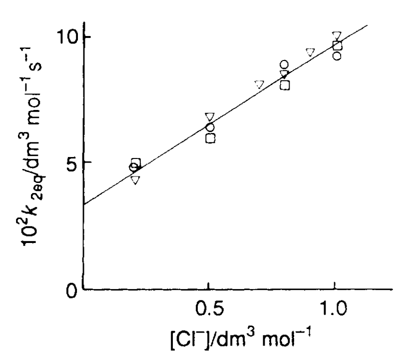

Fig. 3 Variation of k_{2eq} (25 °C) with Cl$^-$ for the second phase of the reaction of Cl$^-$ with $[Mo_3S_4(OH_2)_9]^{4+}$ at different [H$^+$], I = 2.00 mol dm^{-3} ($LiClO_4$): (▽) 2.00, (□) 1.00 and (○) 0.50 mol dm^{-3}

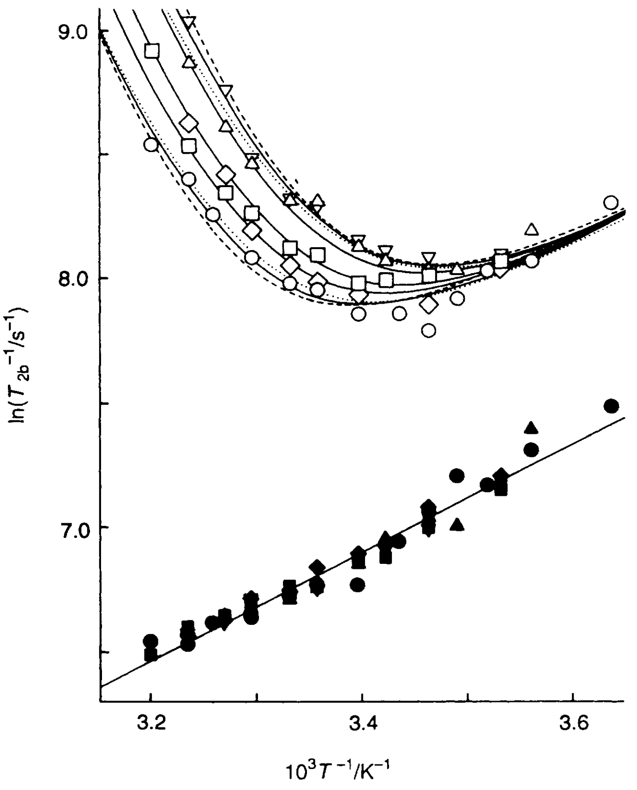

Fig. 4 Temperature and [H$^+$] dependences of the transverse relaxation rate [$\ln(1/T_{2b})$] for the ^{17}O resonances of the d-H_2O ligands of $[Mo_3S_4(OH_2)_9]^{4+}$ (0.011–0.029 mol dm^{-3}) *trans* to the μ-sulfido groups (open symbols) and the c-H_2O ligands *trans* to the μ$_3$-sulfido groups (filled symbols). The [H$^+$] values are 1.56 (○), 1.18 (□), 0.945 (◇), 0.664 (△) and 0.545 mol dm^{-3} (▽); the solutions were enriched in $^{17}OH_2$ (3.8–8.6 atom% ^{17}O) and contained $Mn(ClO_4)_2$ (0.1 mol dm^{-3}) at I = 2.00 mol dm^{-3} ($LiClO_4$). The curves result from simultaneous non-linear least-squares fits; the full lines were obtained from a fit with K_{aM} as an adjustable parameter; the other lines were obtained from fits with fixed values of K_{aM} (– – –, 1.0 × 10^{-3}; · · ·, 0.4 mol dm^{-3}) and are represented only for the two extreme [H$^+$] values, 1.56 and 0.545 mol dm^{-3}

Three analyses of the data were performed and the parameters obtained are listed in Table 4. In Fig. 4 a comparison of the

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* A recent reinvestigation[26] of the acid dissociation process on $[Mo_3O_4(OH_2)_9]^{4+}$, carried out using UV/VIS spectrophotometry at 505 nm in I = 2.0 mol dm^{-3} pts$^-$ media (adjustment of [H$^+$] carried out by dilution at 273 K), gave rise to the following parameters: $K_{aM}{}^{298}$ = (0.43 ± 0.04) mol dm^{-3}, ΔH°_{aM} = +3.9 kJ mol^{-1}, ε^{505}-($Mo_3O_4{}^{4+}$) = 217 ± 3.6 dm^3 mol^{-1} cm^{-1}, $\varepsilon^{505}[Mo_3O_4(OH)^{3+}]$ = 106 ± 1.1 dm^3 mol^{-1} cm^{-1}.

Table 4 Water-exchange parameters (25 °C) obtained for $[Mo_3S_4(OH_2)_9]^{4+}$ in the $[H^+]$ range 0.545–1.56 mol dm^{-3}, $I = 2.00$ mol dm^{-3} ($LiClO_4$). The parameters listed in the second and third columns were obtained by using fixed values for both K_{aM} and $\Delta H^{\ominus}_{aM}$

k_{OH}/s^{-1}	$(7.5 \pm 2.1) \times 10^3$	$(4.4 \pm 0.2) \times 10^3$	$(1.01 \pm 0.06) \times 10^6$
K_{aM}/mol dm^{-3}	0.18 ± 0.07	0.40^a	$1.00 \times 10^{-3\,a}$
k_2/s^{-1}	$1.36 \times 10^{3\,b}$	$1.76 \times 10^{3\,b}$	$1.00 \times 10^{3\,b}$
$\Delta H^{\ominus}_{aM}$/kJ mol^{-1}	$+3.9^a$	$+3.9^a$	$+3.9^a$
$\Delta H^{\ddagger}_{OH}$/kJ mol^{-1}	83.0 ± 4.0	78.4 ± 3.6	89.3 ± 3.8
$\Delta S^{\ddagger}_{OH}$/J K^{-1} mol^{-1}	107.6 ± 15	87.6 ± 12	170 ± 13
$1/T_{2Q}{}^b$ (d)/s^{-1}	2017 ± 53	1957 ± 51	2097 ± 47
$1/T_{2Q}{}^b$ (c)/s^{-1}	900 ± 7	899 ± 7	901 ± 7
E_Q/kJ mol^{-1}	18.2 ± 0.06	18.5 ± 0.6	17.7 ± 0.6
Residual R	0.70×10^{-2}	0.73×10^{-2}	0.74×10^{-2}

Values were computed from a non-linear least-squares fit using the Gauss–Newton algorithm. The residual R is the χ^2 of Pearson.
^{a} Fixed. ^{b} Calculated according to $k_{OH}K_{aM}$.

three treatments is only illustrated for the data representing the two extreme $[H^+]$ values 1.56 and 0.545 mol dm^{-3}. In the first treatment (solid line), shown over all the data, $\Delta H^{\ominus}_{aM}$ was fixed at +3.9 kJ mol^{-1} with all other parameters allowed to float. In the second treatment (dotted line), K_{aM} was additionally fixed at 0.40 mol dm^{-3} and for the third treatment (dashed line), K_{aM} was fixed at 0.001 mol dm^{-3} (smaller values of K_{aM} produce the same $k_{OH}K_{aM}$ product). The results in Table 4 show that a shallow minimum in the fit (lowest residual $R = 0.7 \times 10^{-2}$) is obtained for the first treatment with $k_{OH} = (7.5 \pm 2.1) \times 10^3$ s^{-1} and $K_{aM} = 0.18 \pm 0.07$ mol dm^{-3} (25 °C). However, as Fig. 4 illustrates, the nature of the shallow minimum appears to allow a reasonable fit of the data to any value for K_{aM} up to 0.4 mol dm^{-3} and a corresponding k_{OH} larger than 4.4×10^3 s^{-1}. Their product $k_{OH}K_{aM}$ is however well defined: $1.00 < 10^{-3}k_2 < 1.76$.

Water Exchange at the c-H_2O *Ligands of* $[Mo_3S_4(OH_2)_9]^{4+}$.—The rate constant for exchange at the c-H_2O ligands was obtained by fitting the increase in intensity of their ^{17}O NMR resonance line by a standard exponential function. As reference the resonance line of the d-H_2O ligands was used which was already at isotopic equilibrium due to its much faster exchange rate (factor of 10^5). Rate constants for the c-H_2O exchange (25 °C) evaluated for three acidities in the range 0.57–1.56 mol dm^{-3} showed no discernible dependence on $[H^+]$ within the limit of measurement. Unfortunately rate constants of the magnitude obtained ($\approx 10^{-2}$ s^{-1}) are right on the limit of detection by fast-injection ^{17}O NMR spectroscopy at these levels of signal intensity and as a result the quality of data did not permit a more detailed investigation of any slight $[H^+]$ dependence. From the data obtained the c-H_2O exchange rate constant (25 °C) in 2.0 mol dm^{-3} ClO_4^- solution is estimated to have a value $(1.8 \pm 0.4) \times 10^{-2}$ s^{-1} (independent of $[H^+]$).

Discussion

The reaction of $[Mo_3S_4(OH_2)_9]^{4+}$ with Cl^- is much less favourable thermodynamically than that with NCS^-. The ratio of rate constants for the two stages of chloride complexation, $[H^+] = 2.0$ mol dm^{-3}, give formation constants $K = 3.24$ (first) and 1.85 dm^3 mol^{-1} (second). With NCS^- the corresponding values are 2300 (first) and 2150 dm^3 mol^{-1} (second). Therefore in this study larger chloride concentrations have to be used. In addition absorbance changes are smaller.

A useful diagnostic approach in assigning the mechanism of substitution at a mononuclear hexaaqua metal ion, and whether this has dissociative or associative features, has been to determine the ratio of rate constants k_{NCS}/k_{Cl}. For an associative interchange (I_a) process the ratio is generally substantially > 10:1, but for a dissociative interchange (I_d) process it is close to unity. In the case of the low d-electron population d^3 ion $[Mo(OH_2)_6]^{3+}$ the ratio is 59:1.[17,27] Evidence has been obtained for other low d-electron population ions $[Ti(OH_2)_6]^{3+}$ (d^1) and $[V(OH_2)_6]^{3+}$ (d^2) reacting by an I_a process.[28] It is assumed that the same arguments apply for reactions on the trinuclear aqua ion $[Mo_3S_4(OH_2)_9]^{4+}$. For complexation of Cl^- and NCS^- on $[Mo_3S_4(OH_2)_9]^{4+}$ the corresponding ratios for the first stage of reaction are 1.2 (k_1 path) and 1.4:1 (k_{OH} path). For the conjugate-base path k_{OH} a ratio of 1.4:1 and an I_d assignment causes no surprise. However an interesting outcome is that for the k_1 path (aqua ion) a ratio close to unity is also observed which is diagnostic of an I_d process. For the purpose of further verifying these assignments one can attempt to compare the rate parameters for complex formation on $[Mo_3S_4(OH_2)_9]^{4+}$ with those for water exchange.

As found in the previous water-exchange study on $[Mo_3O_4(OH_2)_9]^{4+}$ the d-H_2O ligands are much more labile (factor of 10^5 at 25 °C) than the c-H_2O ligands. As a result a d-H_2O is implied as the site for the first phase of substitution by NCS^- and Cl^-. However an interesting feature of the present results is the markedly differing $[H^+]$ dependences for water exchange at the two types of H_2O ligand. Whereas exchange at the more inert c-H_2O ligands occurs solely through the aqua ion {k_{ex} (25 °C) $= 1.8 \times 10^{-2}$ s^{-1}, independent of $[H^+]$}, exchange at the d-H_2O ligands is strongly promoted through the monohydroxo species, $Mo_3S_4(OH)^{3+}$ ($k_{OH} = 7.5 \times 10^3$ s^{-1}, $K_{aM} = 0.18$ mol dm^{-3}).

For the purpose of comparing rate constants for complex formation with that for d-H_2O exchange one can attempt to apply the Eigen–Wilkins model (14).[29] It is necessary to consider k_I, the rate constant for interchange, with $k_{ex}(H_2O)$ in order to comment further on the mechanism.

$$k_1 \text{ (or } k_{OH}) = k_I K_{os} \qquad (14)$$

Unfortunately estimates of K_{os}, the ion-pair association constant, *e.g.* from electrostatic theory,[30] are not straightforward for such a large non-spherical metal cluster ion. There is also an uncertainty as the exact magnitude of the local positive charge relevant on any interacting molybdenum centre which could range from +0.33 [single deprotonated centre on $Mo_3S_4(OH)^{3+}$] to +4.0. An even lower limiting value may be relevant if some of the positive charge is delocalised onto the capping μ_3-S atom.[31,32] From complex-formation runs on $[Mo_3S_4(OH_2)_9]^{4+}$ with up to 1.0 mol dm^{-3} Cl^- no curvature is detected in plots of k_f *vs.* $[Cl^-]$. It can thus be assumed that values of K_{os} are likely to be quite small and probably < 0.5 dm^3 mol^{-1}. A value of 0.2 dm^3 mol^{-1} has been assumed for the purpose of comparing the data in Table 5 (25 °C). Values of k_I so estimated are of comparable magnitude to, and certainly no greater than, k_{OH} for substitution at a d-H_2O on $Mo_3S_4(OH)^{3+}$ in keeping with the I_d mechanism. Likewise an I_d process would be consistent with the values for $\Delta H^{\ddagger}_{OH}$ (83 kJ mol^{-1}) and $\Delta S^{\ddagger}_{OH}$ (+108 J K^{-1} mol^{-1}) (Table 4). On the other hand, the k_1 values (25 °C) for the first stage of substitution by NCS^- and Cl^- on $[Mo_3S_4(OH_2)_9]^{4+}$ are, despite a k_{NCS}/k_{Cl} ratio close to unity, seemingly several orders of magnitude larger than the estimated rate constant for d-H_2O exchange (< 10 s^{-1}) suggesting an I_a process. In this regard such a changeover in mechanism between aqua ion and conjugate base is well established in the substitution behaviour of $[Fe(OH_2)_6]^{3+}$ (I_a) and $[Fe(OH_2)_5(OH)]^{2+}$ (I_d).[28]

The second phase of reaction observed with Cl^- and NCS^- is ambiguous in that from the evidence obtained we do not know whether this stage corresponds to substitution at a second d-H_2O or at a c-H_2O. The extent of involvement of $Mo_3S_4(OH)Y^{2+}$ ($Y = NCS^-$ or Cl^-) towards a second incoming Y ligand at a d site is not known and so a clear-cut distinction between the two is not easy. The ratio ≈ 20:1 (Table 5) suggests an I_a process.

The agreement in the kinetic values for K_{aM} (0.18 mol dm^{-3}, d-H_2O exchange; 0.23 mol dm^{-3}, complex formation) is

Table 5 Comparison of water-exchange and complex-formation data for $[Mo_3S_4(OH_2)_9]^{4+}$ in 2.0 mol dm^{-3} ClO_4^- at 25 °C

Rate constant	NCS^-	Cl^-	k_{NCS}/k_{Cl}	d-H_2O	c-H_2O
k_1/dm^3 mol^{-1} s^{-1}	108[a]	91	1.2	< 10[f]	2×10^{-2}[b,c]
k_{OH}/dm^3 mol^{-1} s^{-1}	1120[a]	790	1.4		
k_I/s^{-1}	≈5600[d]	≈3975[d]		7500 (k_{OH})[e]	
K_{aM}/mol dm^{-3}	0.23[a]	0.23		0.18[e]	
k_{2f}/dm^3 mol^{-1} s^{-1}	1.24[b,f,g]	6.3×10^{-2}[g]	19.7		

[a] Ref. 11. [b] No $[H^+]$ dependence detected. [c] Units of s^{-1}. [d] Value of K_{os} in equation (14) assumed to be ≈0.2 dm^3 mol^{-1}. [e] k_{OH} $> 4.4 \times 10^3$ dm^3 mol^{-1} s^{-1}, K_{aM} < 0.4 mol dm^{-3}, $1.00 < 10^{-3}k_{OH}K_{aM} < 1.76$, see text. [f] Ref. 12. [g] No statistical factor applied.

gratifying and gives weight to the significance of the former value estimated in the present study despite the poorly defined minimum residual. Unfortunately it has not proved possible to obtain an independent thermodynamic value of K_{aM} for verification, for example, by monitoring changes to the UV/VIS spectrum. The UV/VIS chromophore of $[Mo_3S_4(OH_2)_9]^{4+}$ is found to be insensitive to changes in $[H^+]$ in the range 0.02–1.995 mol dm^{-3}, I = 2.00 mol dm^{-3} ClO_4^-. Perhaps more surprisingly the ^{17}O NMR chemical shifts of the c- and d-H_2O ligands are also found to be unaffected by changes to $[H^+]$ in the range 0.29–1.56 mol dm^{-3}. This is in contrast to the behaviour found previously in the case of $[Mo_3O_4(OH_2)_9]^{4+}$ wherein clear evidence was obtained for deprotonation at a d-H_2O.[6] It would seem not unreasonable to assume that a similar deprotonation at a d-H_2O is relevant to the formation of $Mo_3S_4(OH)^{3+}$ in the present case despite the lack of direct evidence. If this is so then the apparent labilisation at the d site (but not the c site) in these $Mo_3X_4^{4+}$ species by the presence of an OH^- group at the adjacent d site could conceivably be occurring *via* charge transfer through a molecular orbital common to only the d sites.[31–33]

The insensitivity of the $Mo_3S_4^{4+}$ UV/VIS chromophore in distinguishing terminal OH^- from H_2O contrasts with quite distinct changes observed in the case of the μ-oxo analogue, $[Mo_3O_4(OH_2)_9]^{4+}$. A possible explanation is that the core molecular orbitals (MOs) for $Mo_3X_4^{4+}$ are dominated by contributions from Mo–X–Mo interactions.[31,32] Thus when X = S (not O) these MOs will be of significantly different energy from those involved with bonding to the terminal H_2O ligands and so the interaction and hence sensitivity towards the presence of terminal OH^- *versus* H_2O will be less. Significantly different band maxima energies occurring for $[Mo_3S_4(OH_2)_9]^{4+}$ (366 and 603 nm) and $[Mo_3O_4(OH_2)_9]^{4+}$ (290 and 505 nm) have been noted.

The use of perchlorate media has been highly desirable in the present study. Considerable medium effects have been detected on going from ClO_4^- to pts^- in complex-forming reactions, the differences being attributable to strong ion-pair association of $[Mo_3X_4(OH_2)_9]^{4+}$ with the counter anion in the case of pts^-. Significantly smaller rates of water exchange have been detected in parallel studies in 2.0 mol dm^{-3} pts^- media *versus* the present study.* Further evidence of stronger ion-pair association of $Mo_3X_4^{4+}$ ions with pts^- can also be seen in the attainment of significantly more concentrated solutions of $Mo_3X_4^{4+}$ ions (factor of 10) *via* elution from Dowex 50W X2 cation-exchange columns using a given concentration of Hpts as opposed to the same concentration of $HClO_4$.

The crystal structures of pts^- salts of the three aqua ions $[Mo_3O_4(OH_2)_9]^{4+}$, $[Mo_3S_4(OH_2)_9]^{4+}$ and $[W_3S_4(OH_2)_9]^{4+}$ are all consistent with no detectable difference in Mo–OH_2 bond length occurring between the c and d sites.[6–8] As a result the factor 10^5 in the water-exchange rate constants at the two sites has been difficult to rationalise. It is clear now from the present results that the much faster exchange occurring at the d-H_2O ligands is due to the activation *via* the monohydroxo form, $Mo_3S_4(OH)^{3+}$. Moreover the crystallographic Mo–OH_2 bond lengths should only relate to properties of the aqua ion $Mo_3S_4^{4+}$ itself and in this regard the present results are not inconsistent with a water-exchange rate constant of a comparable magnitude at either site. Indeed fixing a value for k_1 (d-H_2O) = 2×10^{-2} s^{-1} in equation (13) has *no effect* on the d-H_2O exchange parameters listed in Table 4.

Conclusion

The present study has shown that the complex $[Mo_3S_4(OH_2)_9]^{4+}$ possesses non-equivalent H_2O ligands with those labelled d (two per Mo), *trans* to μ-S, undergoing H_2O exchange much faster (factor of 10^5) when compared with those labelled c (one per Mo), *trans* to μ_3-S. The faster reaction is directly attributable to the presence of the monohydroxo conjugate base $Mo_3S_4(OH)^{3+}$. Comparisons made with data for the NCS^- and Cl^- anation reactions suggest an I_d mechanism for substitution at the d sites on $Mo_3S_4(OH)^{3+}$. Rate constants for H_2O exchange at both d and c sites on the parent $Mo_3S_4^{4+}$ aqua ion are of similar magnitude (≈10^{-2} s^{-1}) in agreement with the identical crystallographically determined Mo–OH_2 bond lengths. Here an I_a mechanism is tentatively suggested from comparisons with complex-formation data. The H_2O ligands of $[Mo_3S_4(OH_2)_9]^{4+}$ are more labile than those of the μ-oxo analogue probably due to effective σ-electron donation from the electron-rich μ-S ligands.

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* Rate constants for water exchange on $[Mo_3S_4(OH_2)_9]^{4+}$ in 2.0 mol dm^{-3} pts^- media are significantly slower, factor of 6 (k_{OH}, d-H_2O), factor of 14 (k_1, c-H_2O), than those obtained in the present study in 2.0 mol dm^{-3} ClO_4^-.[34]

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