Thiocyanate Substitution on the Incomplete Cuboidal Clusters $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$†

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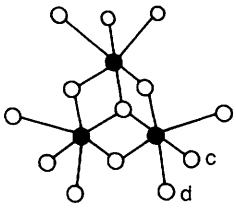
Absorbance changes at ~300 nm corresponding to the second stage in the reaction of excess of thiocyanate (millimolar amounts) with $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$ have been studied for the first time. The Mo^{IV}_3 reaction, which is $[NCS^-]$ dependent and independent of $[H^+] = 0.70–2.00$ M, corresponds to substitution of a second H_2O at Mo. In the W^{IV}_3 case no $[NCS^-]$ dependence is observed, and the dominant process is assigned as isomerisation of S- to N-bonded thiocyanate or a positional change. The kinetics exhibit an $[H^+]^{-1}$ dependence from which it can be concluded that an acid dissociation process with $K_a < 0.008$ M applies. The latter is assumed to be at an H_2O on the same W to which thiocyanate is attached. Spectrophotometric measurements on the unsubstituted reactants give acid dissociation constants of 0.18 and 0.26 M for $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$ respectively. The kinetic results obtained illustrate differences in the behaviour of Mo and W, and are rationalised in terms of hard–soft acid–base theory.

Thiocyanate has been used extensively to define substitution properties of the aqua ions $[Mo^{II}_2(H_2O)_8]^{4+}$,[1] $[Mo^{III}(H_2O)_6]^{3+}$,[2] $[Mo^{IV}_3O_4(H_2O)_9]^{4+}$,[3] and $[Mo^{V}_2O_4(H_2O)_6]^{2+}$,[4] respectively. It has also been used in similar studies on the tungsten analogues $[W_3O_4(H_2O)_9]^{4+}$ (ref. 5) and $[W_2O_4(H_2O)_6]^{2+}$,[6] and for oxo/sulfido analogues of the IV state trimers, including $[Mo_3S_4(H_2O)_9]^{4+}$ (ref. 7) and $[W_3S_4(H_2O)_9]^{4+}$ (ref. 8) which are the subject of this report. Advantages in using NCS^- are the thermodynamically favourable nature of reactions, and the relatively large absorbance changes making reactions easier to monitor. Surprisingly, for the trimers with sulfur-rich cores at least, there is no structural evidence for S-bonded thiocyanato products. Thus all the X-ray crystallographic studies on NCS^--containing molybdenum complexes, including those of oxidation states III–V, $K_3[Mo(NCS)_6]\cdot MeCO_2H\cdot H_2O$,[9] $[NMe_4]_4[Mo_3O_4(NCS)_8(H_2O)]\cdot 3H_2O$,[10] $[Hpy]_5[Mo_3O_2S_2(NCS)_9]\cdot 2H_2O$ (py = pyridine),[11] $[NH_4]_6[Mo_4S_4(NCS)_{12}]\cdot 10H_2O$,[12] $[Hpy]_4[Mo_2O_4(NCS)_6]$[13] and $[Hpy]_3[Mo_2O_4(HCO_2)(NCS)_4]\cdot 2H_2O$,[14] indicate N-bonded thiocyanate. Similarly in the case of W^{IV}_3, crystal structures of $[NH_4]_2[NEt_4]_3[W_3O_4(NCS)_9]\cdot H_2O$,[15] $[W_3O_3S(NCS)_9]^{5-}$,[16] and $[Hbipy]_5[W_3S_4(NCS)_9]\cdot 3H_2O$ (bipy = 2,2′-bipyridyl)[17] have been reported, which all have N-bonded thiocyanate. Significantly, on eluting $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$ with 1 M NCS^- from ice-cooled Dowex 50W-X2 cation-exchange columns, a condition which is expected to give complete NCS^- replacement of H_2O ligands, green and red fractions have been observed. It has been suggested that these contain N- and S-bonded forms respectively.[7] Initial quite rapid absorbance changes of the red product are followed by slower changes, giving after several days the spectrum of the green band. So far this is the only evidence consistent with the existence of S-bonded thiocyanato complexes. There are two different types of co-ordinated H_2O on $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$ which are *trans* to the core μ_3-S and μ-S as illustrated. These are designated as c and d respectively.[18] In the case of the H_2O exchange on $[Mo_3O_4(H_2O)_9]^{4+}$ it has been demonstrated that the d position is ~10^4 times more labile than c.[19] From previous studies on 1:1 NCS^- substitution at Mo and W the rate constants k_f give $[H^+]^{-1}$ dependences of the type $k_f = a + b[H^+]^{-1}$. At 25 °C and in 2.00 M $HClO_4$ (I = 2.00 M), k_f values (assigned as substitution at d)[20] are 212 and 38.4 $M^{-1}\,s^{-1}$ for $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$ respectively.[5,7] It is now appropriate to consider absorbance changes corresponding to the second stage of reaction.



From X-ray crystal structures of $Mo_3S_4^{4+}$ and $W_3S_4^{4+}$ trimers, it has been demonstrated that the cores have very similar dimensions. Thus the metal–metal distances in the case of $Mo_3S_4^{4+}$ (31 structures) average 2.76 Å and for $W_3S_4^{4+}$ (three structures) the corresponding distance is 2.75 Å.[21]

Experimental

Preparation of $[Mo_3S_4(H_2O)_9]^{4+}$.—The procedure for the preparation and purification was as described previously.[7] The $[H^+]$ was determined by exchanging an aliquot of $[Mo_3S_4(H_2O)_9]^{4+}$ onto an Amberlite 1R(H)120 cation-exchange column, and titrating the total H^+ collected against NaOH (BDH, Convol). Stock solutions having a peak at 603 nm (ε 362 $M^{-1}\,cm^{-1}$), typically 3 mM $[Mo_3S_4(H_2O)_9]^{4+}$ in ~2 M $HClO_4$, were stable in air and stored without any special precautions.

Preparation of $[W_3S_4(H_2O)_9]^{4+}$.—Using the earlier procedure,[8] the first trimer to be eluted with 2 M $HClO_4$ is red-purple $[W_3OS_3(H_2O)_9]^{4+}$, having a peak at 540 nm (ε 407 $M^{-1}\,cm^{-1}$), followed by purple $[W_3S_4(H_2O)_9]^{4+}$, having a peak at 563 nm (ε 446 $M^{-1}\,cm^{-1}$). The absorption coefficients are as in ref. 22. Stock solutions were typically 2–3 mM $[W_3S_4(H_2O)_9]^{4+}$ in ~2 M $HClO_4$ (the latter determined as for the molybdenum analogue). The aqua ion was stable in air and stored over long periods without any special precautions.

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

Table 1 The variation with $[NCS^-]$ of equilibration rate constants k_{Mo} (25 °C) for the second stage of the reaction of NCS^- with $[Mo_3S_4(H_2O)_9]^{4+}$ ($\sim 4.0 \times 10^{-5}$ M), in 2.00 M $HClO_4$, $I = 2.00$ M

$[H^+]$/M	$10^3[NCS^-]$/M	$10^3k_{Mo}/s^{-1}$
2.0	0.4	0.96*
		1.02
		1.08
	0.6	1.30
	0.7	1.40
		1.45
	0.8	1.57
	1.0	1.75
		1.88
	1.2	1.98
	1.3	2.05
1.4	0.4	1.20*
	0.8	1.65
	1.2	2.15
1.0	0.7	1.40
	1.1	2.00
0.7	0.4	2.00
	0.8	1.70
	1.2	2.10

* $[Mo_3S_4^{4+}] = 2 \times 10^{-5}$ M.

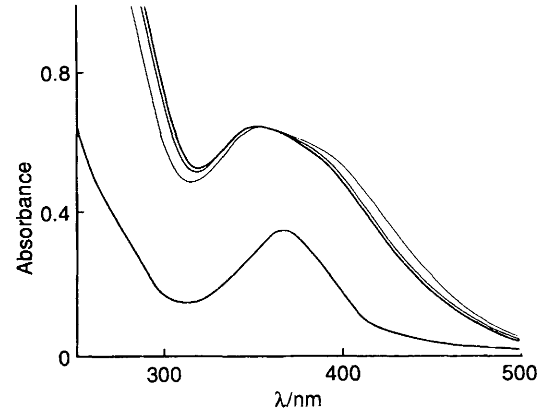


Fig. 1 UV/VIS scan spectra for the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ (1×10^{-4} M) with NCS^- (3×10^{-3} M) in 2.0 M $HClO_4$. There is a rapid initial increase in absorbance from the lower spectrum in a split cell, second scan taken 14 s after mixing. Further scans were recorded at 5 min intervals (increase in absorbance at 300 nm, decrease at 400 nm); 25 °C, $I = 2.00$ M

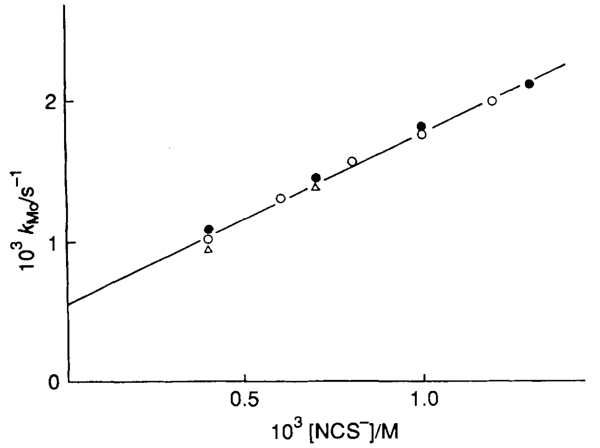


Fig. 2 Plot of rate constants k_{Mo} against $[NCS^-]$ for the second phase of the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with NCS^- (reactant in excess) at 25 °C in 2.0 M $HClO_4$, $I = 2.00$ M. Rate constants were determined from absorbance data at 260 (●), 300 (○) and 430 nm (△)

Titration of Trimer Solutions.—To decrease the $[H^+]$ of stock solutions, saturated (7 g per 100 cm^3) $NaHCO_3$ (BDH, Analar) was slowly added with mechanical stirring until the required pH (~1.3) was reached. This neutralisation procedure has the advantage that the $NaHCO_3$ solution added is acidic. For some measurements sub-stock solutions were first prepared; in others the ionic strength of the $NaHCO_3$ was adjusted to 2.00 M with $LiClO_4$ prior to mixing. A typical procedure was as follows. Trimer stock solutions were first diluted ×4 to decrease $[H^+]$ from 2.0 to 0.5 M, and I adjusted to 2.00 M ($LiClO_4$). The calculated amount (1.64 cm^3) of 0.83 M $NaHCO_3$ at $I = 2.00$ M ($LiClO_4$) was then added slowly to 3.36 cm^3 of trimer with stirring over ~40 min. For the actual titration, amounts of 3.77 M $HClO_4$ were added using a Hamilton microsyringe, total volume added ~0.5 cm^3. After each addition 20 min were allowed for equilibration. The spectrum was recorded, and the absorbance at fixed wavelengths noted, see Figs. 6 and 7. Allowances were made for dilution of the stock solution. The spectrum generated after titration indicated a reversible change. In an alternative procedure the $[H^+]$ (3.5 M) of trimer stock (5 mM) solutions was slowly decreased by dilution with an appropriate solution of ~1.8 M $LiClO_4$, to give a final $I = 2.00$ M ($LiClO_4$). The solution was stirred throughout.

Other Reagents.—Sodium thiocyanate (BDH, Analar), tungstic acid (Aldrich, Reagent Grade), hydrochloric acid (BDH, Analar), and 70% perchloric acid (BDH, Analar) were used as supplied. Lithium perchlorate (Aldrich, Reagent Grade) was recrystallised twice from water.

Kinetic Studies.—Previous studies have been concerned with the first phase of the reactions of $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$ as monitored by stopped-flow spectrophotometry.[7,8] The focus now is on the smaller absorbance changes corresponding to the second phase. Studies at 25.0 ± 0.1 °C were by conventional time-range spectrophotometry. Perchlorate solutions, generally 2.0 M $HClO_4$ with ionic strength $I = 2.00$ M, were used. For those runs in which $[H^+]$ was varied the ionic strength was adjusted with $LiClO_4$.

Results

Reactivity of $[Mo_3S_4(H_2O)_9]^{4+}$.—Scan spectra, as in Fig. 1, indicate the completion of the first phase, and incidence of the second with an isosbestic at 363 nm. Absorbance changes for the second phase were much smaller. The latter was monitored at 300 nm with checks at 260 and 430 nm. Plots of absorbance (A) changes $\ln(A_\infty - A_t)$ against time gave slopes corresponding to equilibration rate constants k_{Mo}, Table 1. Fig. 2 indicates the $[NCS^-]$ dependence, equation (1). From a non-weighted least-squares fit $k_f = 1.24 \pm 0.06$ M^{-1} s^{-1} and $k_{aq} = (5.8 \pm 0.5) \times 10^{-4}$ s^{-1}. Hence the equilibrium constant is 2.14×10^3 M^{-1}. The $[H^+]$ was varied in the range 0.7–2.0 M with little or no variation in k_{Mo} (Table 1).

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

Reactivity of $[W_3S_4(H_2O)_9]^{4+}$.—Scan spectra are shown in Fig. 3. Rate constants k_w (25 °C) for the second phase obtained as above are listed in Table 2. Here there is no dependence on $[NCS^-]$, Fig. 4, and k_w is assigned as an isomerisation process, $k_w = (1.02 \pm 0.11) \times 10^{-4}$ s^{-1}. On varying $[H^+]$, Table 2, the dependence (2) is observed, Fig. 5. This gives $a = (0.92 \pm 0.03) \times 10^{-4}$ s^{-1} and $b = (1.00 \pm 0.05) \times 10^{-6}$ M^{-1} s^{-1}. Since Fig. 5 gives no curvature it can be concluded that the acid dissociation constant for

$$k_w = a + b[H^+]^{-1} \qquad (2)$$

Table 2 The variation with $[NCS^-]$ of rate constants k_w (25 °C) for the second stage of the reaction of NCS^- with $[W_3S_4(H_2O)_9]^{4+}$ (4×10^{-5} M) in 2.00 M $HClO_4$, I = 2.00 M ($LiClO_4$)

$10^3[NCS^-]$/M	10^4k_w/s^{-1}
0.40	1.06
0.60	0.94
0.80	1.00
1.00	1.14
1.20	1.03

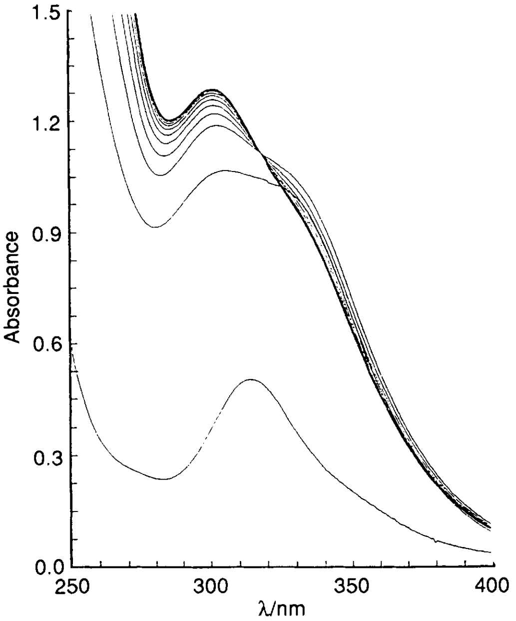


Fig. 3 UV/VIS scan spectra for the reaction of $[W_3S_4(H_2O)_9]^{4+}$ (1×10^{-4} M) with NCS^- (3×10^{-3} M) in 2.0 M $HClO_4$. There is a rapid initial increase in absorbance from the lower spectrum, with the second scan recorded 20 s after mixing. Further scans were recorded at 20 min intervals (increase in absorbance at 300 nm, decrease at 350 nm); 25 °C, I = 2.00 M

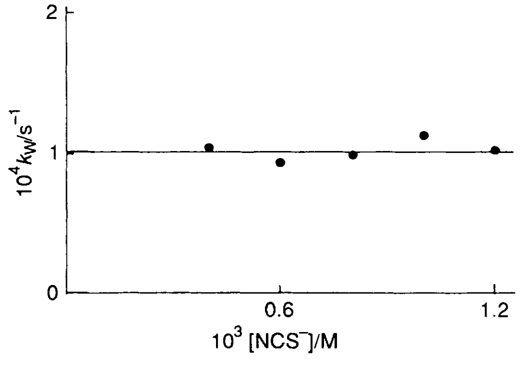


Fig. 4 Plot of rate constants k_w against $[NCS^-]$ for the second phase of the reaction of $[W_3S_4(H_2O)_9]^{4+}$ with NCS^- (reactant in excess) at 25 °C in 2.0 M $HClO_4$, I = 2.00 M

$[W_3S_4(H_2O)_8(SCN)]^{3+}$ is <0.008 M. Absorbance changes for the second stage were all ~15% of the total.

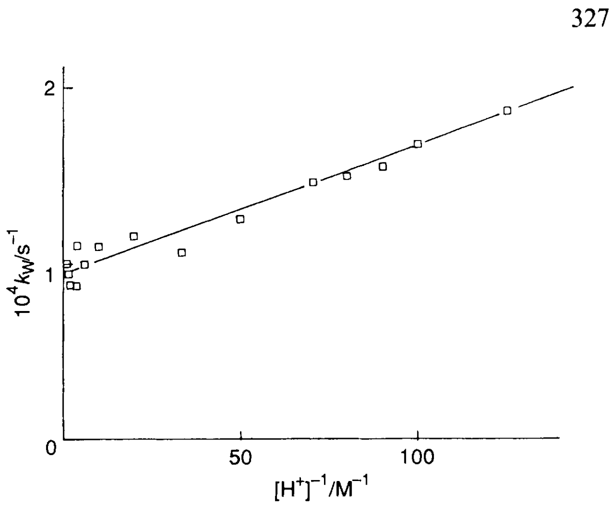


Fig. 5 Dependence of the rate constant k_w for the second phase of the reaction of $[W_3S_4(H_2O)_9]^{4+}$ (4×10^{-4} M) with NCS^- (8×10^{-4} M) on $[H^+]^{-1}$ at 25 °C, I = 2.00 M ($LiClO_4$)

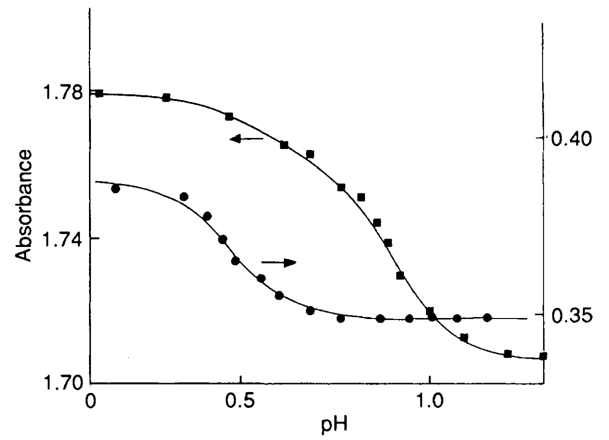


Fig. 6 Determination of the pK_a of $[Mo_3S_4(H_2O)_9]^{4+}$ by titration of a solution at pH ~1.3 with H^+ and monitoring spectrophotometrically at 400 nm (right-hand scale, ●), and a similar experiment for $[W_3S_4(H_2O)_9]^{4+}$ monitored at 280 nm (left-hand scale, ■)

Determination of pK_a *Values.*—In a separate series of experiments solutions of $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$ at pH ~1.3 were titrated against $[H^+]$ and absorbance changes monitored at 400 and 280 nm respectively, Fig. 6. The changes observed define a single deprotonation step, *e.g.* (3).

$$Mo_3S_4^{4+} \overset{K_a}{\rightleftharpoons} Mo_3S_4(OH)^{3+} + H^+ \qquad (3)$$

Values of K_a from determinations on $[Mo_3S_4(H_2O)_9]^{4+}$ were 0.13 and 0.14 M using the first procedure for adjusting the $[H^+]$, and for the second (which yields more dilute solutions) 0.21 and 0.23 M. The average is 0.18 ± 0.08 M. Two determinations on $[W_3S_4(H_2O)_9]^{4+}$ gave 0.25 and 0.28, average 0.26 ± 0.1 M. At lower H^+ values dimerisation and/or oligomerisation is observed, and at $[H^+]$ <0.008 M precipitation occurs.

Discussion

Scan spectra, Figs. 1 and 3, record spectrophotometric absorbance changes for the reactions of NCS^- (3×10^{-3} M) with $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$ (both 1×10^{-4} M). At, *e.g.*, 300 nm, the initial rapid absorbance increases due to the first phase of reaction are followed by slower (and smaller) conventional time-range changes which are the subject of the present studies. Although the absorbance changes observed for the second phase are similar, those for $[W_3S_4(H_2O)_9]^{4+}$ are somewhat greater.

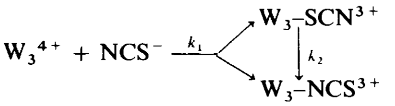
In the case of the $[Mo_3S_4(H_2O)_9]^{4+}$ reaction there is a dependence on $[NCS^-]$ for the second (as well as first) stage, and equilibration kinetics apply. There is however no dependence on $[H^+]^{-1}$ over the range 0.70–2.00 M, which range gives a clear-cut dependence for the first stage. The kinetic analysis indicates no $[NCS^-]$ dependence for the second stage

Table 3 Variation of rate constants (25 °C) with $[H^+]$ for the second stage (k_w) of the reaction of $[W_3S_4(H_2O)_9]^{4+}$ (4.0×10^{-5} M) with NCS^- (8×10^{-4} M), here assigned as k_{isom}, $I = 2.00$ M ($LiClO_4$)

$[H^+]$/M	$10^4k_{isom}/s^{-1}$	$10^2[H^+]$/M	$10^4k_{isom}/s^{-1}$
2.00	1.00	3.0	1.06
1.00	0.95	2.0	1.25
0.40	0.88	1.40	1.46
0.30	0.88	1.25	1.50
0.25	1.10	1.11	1.55
0.20	1.00	1.00	1.67
0.10	1.10	0.80	1.86
0.050	1.16		

of the $[W_3S_4(H_2O)_9]^{4+}$ reaction. In neither case did we detect any evidence for further stages. There are two possible sites for the second NCS^- substitution on $[Mo_3S_4(H_2O)_9]^{4+}$. These are the second of the d-H_2O ligands, with the first position already occupied by NCS^-, or the c-H_2O position. Substitution at the d-H_2O is expected to be slower because of the electrostatic influence of the existing NCS^-. Also acid dissociation will be less,[19] and whichever of the H_2O ligands is replaced a conjugate-base pathway is unlikely to be as pronounced as for the first stage. On present information we have no means of choosing between these two possibilities.

For the $[NCS^-]$-independent second stage of the $[W_3S_4(H_2O)_9]^{4+}$ reaction there are again two possible explanations. The first involves isomerisation of S-bonded W–SCN, formed in the first stage alongside W–NCS, to the more stable we assume N-bonded form W–NCS. Thus the mechanism can be written as in (4), where k_2 is for equilibration isomerisation, which may or may not have a significant component from the reverse process. The second explanation involves positional isomerisation, with NCS^- re-equilibrating to give occupancy of both the d and c positions.



$$W_3^{4+} + NCS^- \xrightarrow{k_1} \begin{cases} W_3\text{–}SCN^{3+} \\ \downarrow k_2 \\ W_3\text{–}NCS^{3+} \end{cases} \qquad (4)$$

Linkage isomerisation has been proposed in recent studies on the NCS^- substitution of the molybdenum(III) cuboidal ion $[Mo_4S_4(H_2O)_{12}]^{4+}$,[23] in which all the H_2O ligands are *trans* to μ_3(S) core ligands and identical. The second stage cannot therefore be assigned as d- to c-isomerisation, and S- to N-bonded isomerisation provides an acceptable explanation. In the present study we believe isomerisation to be the more likely.

There have been a number of previous reports on NCS^- isomerisation notably by Sargeson, Jackson and co-workers.[24,25] These studies on cobalt(III) complexes have indicated an $[H^+]^{-1}$ dependence for the isomerisation step. Since substitution on $[W_3S_4(H_2O)_9]^{4+}$ is known to exhibit conjugate-base effects,[8] it was no surprise that an $[H^+]^{-1}$ dependence was detected. However it was necessary to work over a wider than usual range of $[H^+]$ down to 0.008 M. The linearity in Fig. 5 implies that $K_a < 0.008$ M, which is not unreasonable since (as already discussed) both the remaining H_2O ligands on the W to which NCS^- is already attached are expected to be less acidic.

Because of the magnitude of the above we have checked by spectrophotometry the acid dissociation constants of $[Mo_3S_4(H_2O)_9]^{4+}$ (0.23 M) and $[W_3S_4(H_2O)_9]^{4+}$ (0.35 M), previously obtained from kinetic studies.[7,8] The procedure used involved the adjustment of pH to ~1.3 and then titration with H^+. Values of 0.18 and 0.26 M respectively were obtained. Bearing in mind the difficulties in adjusting the pH of such solutions and resultant dilution effects the agreement is regarded as satisfactory, and adequate confirmation that the same acid dissociation process is occurring. From NMR studies on $[Mo_3O_4(H_2O)_9]^{4+}$ it has been concluded that the d-H_2O are more acidic than the c-H_2O ligands, and we have no reason to suppose a different interpretation for $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$. To summarise, the pK_a values observed for $[Mo_3S_4(H_2O)_9]^{4+}$ and $[W_3S_4(H_2O)_9]^{4+}$ are attributed to acid dissociation of the first d-H_2O, K_a in the range 0.18–0.35 M. After complexation with NCS^- a second pK_a is <0.008 M. In all these studies HNCS behaves as a strong acid,[26,27] with no evidence for substantial protonation of NCS^-.[28]

Equilibration constants for the first thiocyanate complexing with oxo/sulfido W^{IV}_3 and Mo^{IV}_3 trimers are favourable and in the range 500–4000 M^{-1}.[29] In the case of $[Mo_3S_4(H_2O)_9]^{4+}$ the equilibrium constant of 2300 M^{-1} reported for substitution of the first NCS^- compares with 1370 M^{-1} obtained in this work for the second substitution process at the same Mo^{IV}.[7]

Finally we need to comment on why there should be a measurable isomerisation process for $[W_3S_4(H_2O)_9]^{4+}$ but not $[Mo_3S_4(H_2O)_9]^{4+}$. Soft–hard acid–base (or class a/b) considerations[30,31] would predict that W is softer than Mo, resulting in the formation of larger amounts of S-bonded thiocyanate, and a more readily observable isomerisation process. The fact that in other work isomerisation is observed for NCS^- substitution on cuboidal $[Mo_4S_4(H_2O)_{12}]^{4+}$ suggests that the behaviour for Mo/S clusters is very borderline. Because of the higher electron density and polarisability of Mo^{III} in $[Mo_4S_4(H_2O)_{12}]^{4+}$ it is possible to rationalise the behaviour observed.

Acknowledgements

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