# Preparation and Properties of the Tungsten(V) Aqua Dimer $[W_2O_4(H_2O)_6]^{2+}$: Kinetic Studies on the 1 : 1 Reaction with $NCS^-$ †

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A procedure is described for the preparation of chromatographically pure tungsten(V) aqua dimer, absorption maxima, $\lambda$/nm ($\varepsilon$/M$^{-1}$ cm$^{-1}$ per dimer), at 430 (193) and 340 (278), in 2 M *p*-toluenesulphonic acid (Hpts). The aqua ion is readily converted to the $[W_2O_4(edta)]^{2-}$ (edta = ethylenediamine-*NNN'N'*-tetra-acetate) complex, the crystal structure of which has been determined previously, and this and other evidence suggests an aqua–oxo structure, $[W_2O_4(H_2O)_6]^{2+}$, analogous to $[Mo_2O_4(H_2O)_6]^{2+}$. Reactions with $O_2$ and $ClO_4^-$ give precipitates of blue mixed-valence $W^V/W^{VI}$ complexes. A stopped-flow kinetic study of the 1 : 1 equilibration of $W_2O_4^{2+}$ with $NCS^-$ has been carried out. Conditions with first $W_2O_4^{2+}$ (> 5-fold) and then $NCS^-$ (> 10-fold) in excess have been investigated, and a statistical factor (× 2) identified in this and the corresponding $Mo_2O_4^{2+}$ reaction. Rate constants are independent of $[H^+]$ in the range investigated (1.0—2.0 M), and at 25 °C are, for formation, $k_1$ = 2 520 M$^{-1}$ s$^{-1}$ ($\Delta H_1^\ddagger$ = 13.3 kcal mol$^{-1}$, $\Delta S_1^\ddagger$ = 1.4 cal K$^{-1}$ mol$^{-1}$), and aquation, $k_{-1}$ = 3.8 s$^{-1}$ ($\Delta H_{-1}^\ddagger$ = 7.1 kcal mol$^{-1}$, $\Delta S_{-1}^\ddagger$ = −32.1 cal K$^{-1}$ mol$^{-1}$), $I$ = 2.0 M [Li(pts)], with $k_1$ some 10 times smaller than for the corresponding reaction of $Mo_2O_4^{2+}$. A mechanism of rapid equilibration in the axial position followed by rate-determining axial to equatorial isomerisation is believed to apply. Comparisons are also made with kinetic data for 1 : 1 substitution reactions of $NCS^-$ with other oxo cations.

The aqua (or aqua–oxo) ions of different oxidation states of tungsten are more difficult to prepare than those of molybdenum.[1] Difficulties are highlighted by attempts (reported herein) to obtain the $W^V$ aqua ion *via* oxalato, cysteinato, and ethylenediamine-*NNN'N'*-tetra-acetate (edta) complexes, in which removal of the organic ligands is clearly not straightforward. In earlier studies with $Mo^V$ difficulties of this kind were not encountered.[2]

We report in this paper a procedure for the preparation of the $W^V$ aqua ion from $[WOCl_5]^{2-}$. Earlier studies on the structure[3] and solution chemistry[4] of $[W_2O_4(edta)]^{2-}$ have been reported. The method recently described for the preparation of the $W^{IV}$ aqua ion of $[W_3O_4(H_2O)_9]^{4+}$ also involves a chloro precursor complex, $[WCl_6]^{4-}$,[5] and is different to the procedure used for the $[Mo_3O_4(H_2O)_9]^{4+}$ analogue.[1] No tungsten(III) aqua ions have yet been reported.

The substitution properties of the $[W_2O_4(H_2O)_6]^{2+}$ ion (hereafter $W_2O_4^{2+}$)‡ are of interest alongside similar studies for other oxo-metal ions, which have been recently reviewed.[6]

## Experimental

Air-free conditions were employed extensively for the preparation of $W^V$ products, using $N_2$ gas, rubber septa, and Teflon needles, as well as glove-bag techniques.

*Reagents*.—Ammonium tungstate, $[NH_4]_{10}[W_{12}O_{41}]\cdot 5H_2O$ (BDH, GPR), oxalic acid (BDH, AnalaR), ammonium oxalate (May and Baker), tin powder (BDH, Reagent Grade), ammonium chloride (BDH, AnalaR), and *p*-toluenesulphonic acid (Hpts; Sigma Chemicals) were used. Lithium *p*-toluenesulphonate was prepared by neutralising the acid with $Li_2CO_3$(Koch-Light) followed by recrystallisation three times. Sodium thiocyanate (BDH, Reagent Grade), was recrystallised from ethanol. Solutions of the aqua ion of $Mo_2O_4^{2+}$ (in $HClO_4$), and $LiClO_4$ were prepared as previously described.[7] The aqua ion of $Mo_2O_4^{2+}$ has absorption maxima, $\lambda$/nm($\varepsilon$/M$^{-1}$ cm$^{-1}$ per dimer), at 295 (3 546) and 384 (103).

*Preparation of Tungsten*(V) *Oxalato Complex*.—A procedure similar to that described by Collenberg[8] was used. Oxalic acid (10 g) and ammonium oxalate (5 g) were dissolved in $H_2O$ (100 cm$^3$). Ammonium tungstate (6.2 g) was added and the solution brought to the boil. Powdered tin (8 g) was slowly added with stirring. Air-free conditions were maintained throughout. The solution was heated on a steam bath for 3 h, during which time the colour changed from blue to red, and the volume reduced to 50—70 cm$^3$. Free oxalic acid and ammonium oxalate crystallised out on cooling to 0 °C and were filtered off. Tin(II) sulphide was precipitated by passing $H_2S$ through the solution for 3—5 min at 0 °C, and air-free methanol (20 cm$^3$) added to precipitate any remaining oxalate. The filtrate was then shaken with the same volume of 95% ethanol, which precipitated a red oil. The solution and the oil were left at room temperature for 12 h after which 95% ethanol (100 cm$^3$) was added. A deep orange coloured powder was filtered off, and washed with ethanol and diethyl ether.

*Preparation of* $[NH_4]_2[WOCl_5]$.—Ammonium chloride (1 g) was dissolved in concentrated HCl (11.2 M, 30 cm$^3$) and heated to 55—60 °C. The tungsten(V) oxalato complex (5 g) was added (slowly), and dissolved to give a deep blue coloured solution. This was kept at 60 °C until green crystals began to form on the surface. After cooling to room temperature, and then to 0 °C in ice, solutions were saturated with gaseous HCl (30 min). Green crystals obtained after 12 h at 0 °C were filtered off (under $N_2$), washed with ice-cold, $O_2$-free concentrated HCl (30 cm$^3$), and dried in a desiccator over concentrated $H_2SO_4$;

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† *Non-S.I. units employed:* M = mol dm$^{-3}$, cal = 4.184 J.

‡ Throughout this paper, the formulae of aqua–oxo ions of tungsten (and other transition metals) do not always include water molecules; other ligands are specified, however.

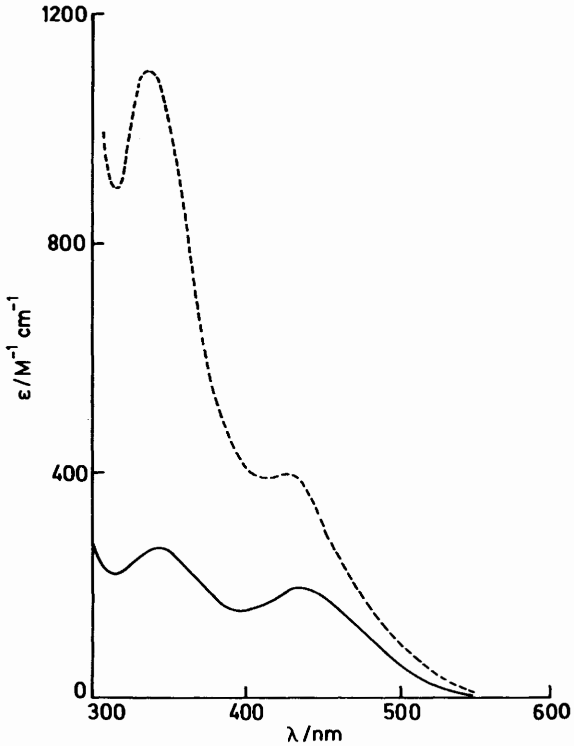


**Figure 1.** Comparison of u.v.–visible spectra of the $W_2O_4^{2+}$ aqua ion in 2 M Hpts (——) and $[W_2O_4(edta)]^{2-}$ in $H_2O$ (– – –) (ε values per dimer)

HCl was later removed by purging with dry $N_2$ and the bright green powder was stored under $N_2$.

*Preparation of the Tungsten*(V) *Aqua Ion.*—This was obtained by dissolving $[NH_4]_2[WOCl_5]$ (0.2 g) in $O_2$-free Hpts (100 cm$^3$), working in a glove-bag. After millipore filtration (pore size 8 μm) to remove a blue precipitate, the yellow-green solution was transferred (by syphoning) and loaded onto an $O_2$-free, ice-cooled Dowex 50W-X2 cation-exchange column (10 × 1.5 cm), outside the glove-bag. The $W^V$ binds as a compact yellow band with a blue impurity above it. The column was washed with $O_2$-free 0.5 M Hpts (50 cm$^3$) to remove chloro complexes, and the $W^V$ eluted as a yellow band with $O_2$-free 2 M Hpts. Solutions used for kinetic studies were recolumned immediately before use. Stock solutions of $W^V$ (1.0 × 10$^{-2}$ M) in 2 M Hpts (*ca.* 20 cm$^3$) were obtained, and were stored at *ca.* 4 °C under rigorous air-free conditions. The solution could be stored for several hours in this form. More concentrated solutions gave blue precipitates.

*Properties of the Tungsten*(V) *Aqua Ion.*—The yellow solution has absorption maxima, λ/nm (ε/M$^{-1}$ cm$^{-1}$ per dimer), at 430 (193) and 340 (278) and a spectrum similar in appearance to that of $[W_2O_4(edta)]^{2-}$, 423 (401) and 340 (1 115), Figure 1. Absorption coefficients for the aqua ion were determined by a procedure involving oxidation with excess $Ce^{IV}$ and back-titrating with $Fe^{II}$ assuming the oxidation state to be $W^V$. Ion-exchange elution characteristics are similar to those observed for the aqua ion of $Mo_2O_4^{2+}$, suggesting a 2+ ion $[W_2O_4(H_2O)_6]^{2+}$. Addition of a five-fold excess of edta to a 6.45 mM solution of aqua ion, and adjustment of $[H^+]$ to 0.1 M with 1 M NaOH, gave quantitative formation of $[W_2O_4(edta)]^{2-}$ in <3 min.

*Stability.* Even on storing under $N_2$ at 4 °C solutions of aqua $W^V$ showed signs of deterioration, with formation of a blue colour, probably due to ingress of traces of $O_2$. On leaving a 2 × 10$^{-3}$ M solution in 2 M Hpts in a 1-cm optical cell under air at 25 °C, a 50% increase in absorbance at 430 nm was observed after 1 h, and after several hours a blue precipitate was obtained. This behaviour is not consistent with a simple $W^V$ (yellow) $\longrightarrow$ $W^{VI}$ (colourless) conversion, and suggests that mixed-valence $W^V/W^{VI}$ ('tungsten blues') are formed.[9] Absorbance increases were also noted on addition of $ClO_4^-$ (final concentration 1.0 M) to a solution of $W_2O_4^{2+}$ (2 × 10$^{-3}$ M) at $[H^+]$ = 1.0 M, and after 30 min a blue precipitate was obtained. Also of interest are experiments in which concentrated HCl is added to $Mo_2O_4^{2+}$ and $W_2O_4^{2+}$ respectively. Whereas 10$^{-3}$ M $Mo_2O_4^{2+}$ (yellow) reacted instantly in 10 M HCl to give green $[MoOCl_5]^{2-}$,[10] $W_2O_4^{2+}$ under identical conditions required at least 10 s to give a visible blue colouration, confirmed as $[WOCl_5]^{2-}$ by u.v.–visible spectroscopy.

*Other Attempts to prepare the Tungsten*(V) *Aqua Ion.*—In an earlier study[4] it was noted that addition of HCl (2 M or 3 M) to $[W_2O_4(edta)]^{2-}$ gave a product with absorption maxima, λ/nm (ε/M$^{-1}$ cm$^{-1}$ per dimer), at 439 (*ca.* 200) and 347 (*ca.* 300). There are close similarities between this spectrum and that of the $W_2O_4^{2+}$ aqua ion reported herein. However it was found that the product obtained could not be separated from the edta by loading onto a cation-exchange column, because on decreasing $[H^+]$ for loading, the edta rapidly re-co-ordinated. Before commencing the present study we tried unsuccessfully to remove the edta by Sephadex G-10 gel filtration of a solution at $[H^+]$ = 2.0 M.

We also attempted to remove oxalate from a solution of the oxalato $W^V$ complex (as described in the Experimental section) by addition of 2 M HCl followed by gel filtration using a Sephadex G-10 column. In this instance the product had only one absorption maximum (at 430 nm) and clearly was not the required aqua ion. Moreover the product was not held by a Dowex cation-exchange column indicating that oxalate was still present. This was confirmed by titration with $Ce^{IV}$, to oxidise both $W^V$ and oxalate, and $[IrCl_6]^{2-}$, to oxidise the $W^V$ only, which indicated a $W^V$ to oxalate ratio of 2:1.

Also prior to the present study Drs. Kathirgamanathan and Ramam in this laboratory attempted to prepare the $W^V$ aqua ion by the electrochemical reduction of tungstate(VI), in the presence of cysteine as a 'protective' ligand to stabilise the $W^V$ state. In a typical procedure sodium tungstate(VI), $Na_2[WO_4]\cdot 2H_2O$ (BDH, AnalaR; 5.2 g), and L-cysteine hydrochloride (Sigma; 2.5 g) were dissolved in $H_2O$ (75 cm$^3$), and electrolysed at a potential of −1.1 V [*vs.* saturated calomel electrode (s.c.e.)] at a Hg cathode under $N_2$ for >18 h. The brown-green solution was exposed to air for 15 min, diluted to 300 cm$^3$ with $H_2O$, and loaded onto an air-free Dowex 50W-X2 cation-exchange column. Dark blue products were removed by washing with $H_2O$ and then 0.5 M Hpts. With further 0.5 M Hpts a compact yellow band and an orange band were obtained, believed to be tungsten(V) and tungsten(IV) forms respectively.[5] The yellow band was eluted with 1 M Hpts and the orange band with 2 M Hpts; yields were variable. A more highly charged red-brown product was also noted in some experiments. After recolumning the yellow solution a product with a peak at 436 nm (no peak at *ca.* 340 nm) was obtained. On addition of edta, quantitative conversion to $[W_2O_4(edta)]^{2-}$ was not observed. Moreover spectrophotometric titration with $[IrCl_6]^{2-}$ (peak at 487 nm, ε = 4 075 M$^{-1}$ cm$^{-1}$) gave two distinct stages, one rapid corresponding to the $W^V \longrightarrow W^{VI}$ change, and another, believed to correspond to the oxidation of cysteine. Therefore, again this complex does not give satisfactory purity, and chelating organic ligands are not always readily removed from

**Table 1.** First-order equilibration rate constants ($k_{eq}$) for the reaction of $NCS^-$ with the aqua ion $W_2O_4^{2+}$; $[H^+]$ = 1.0 M (except as indicated), $I$ = 2.0 M [Li(pts)]

| Temp. (°C) | $10^3[NCS^-]$/M | $10^3[W_2O_4^{2+}]$/M | $k_{eq}/s^{-1}$ |
|---|---|---|---|
| 14.0 | 7.5 | 0.25 | 5.7 |
| | 15.0 | 0.25 | 9.6 |
| | 20.0 | 0.25 | 11.9 |
| 17.0 | 7.5 | 0.25 | 7.2 |
| | 10.0 | 0.25 | 9.1 |
| | 20.0 | 0.25 | 14.8 |
| 20.0 | 7.5 | 0.25 | 9.1 |
| | 10.0 | 0.25 | 11.3 |
| | 20.0 | 0.25 | 19.6 |
| 25.0 | 1.0 | 5.40 | 17.1 |
| | 7.5 | 0.23 | 13.7 |
| | 10.0 | 0.23 | 15.9 |
| | 10.0 | 0.13 | 16.7[a] |
| | 10.0 | 0.13 | 16.7[b] |
| | 15.0 | 0.23 | 23.1 |
| | 20.0 | 0.23 | 28.9 |
| | 25.0 | 0.23 | 35.3 |
| 30.8 | 7.5 | 0.25 | 19.5 |
| | 10.0 | 0.25 | 24.0 |
| | 15.0 | 0.25 | 34.0 |

[a] $[H^+]$ = 1.5 M. [b] $[H^+]$ = 2.0 M.

**Table 2.** The variation of $k_1$ and $k_{-1}$ with temperature for the equilibration of $NCS^-$ with $W_2O_4^{2+}$; $I$ = 2.0 M [Li(pts)]

| Temp. (°C) | $k_1/M^{-1}\ s^{-1}$ | $k_{-1}/s^{-1}$ |
|---|---|---|
| 14.0 | 995 ± 210 | 2.0 ± 1.5 |
| 17.0 | 1 190 ± 400 | 2.9 ± 2.7 |
| 20.0 | 1 670 ± 60 | 3.0 ± 0.4 |
| 25.0 | 2 520 ± 120 | 3.8 ± 1.2 |
| 30.8 | 3 890 ± 630 | 4.7 ± 3.5 |

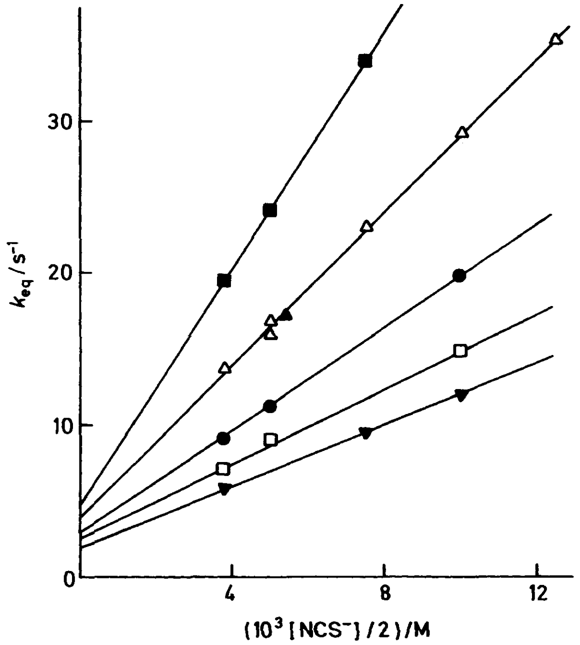


**Figure 2.** The variation of first-order equilibration rate constants, $k_{eq}$ (25 °C), for the reaction of $NCS^-$ with the $W^V$ aqua dimer, $[W_2O_4(H_2O)_6]^{2+}$, $I$ = 2.0 M [Li(pts)]: $T$ = 14.0 (▼), 17.0 (□), 20.0 (●), 25.0 (△), and 30.8 °C (■); (▲) run with $[W_2O_4(H_2O)_6]^{2+}$ in large excess, the ordinate axis (same numerical scale) being $[W_2O_4(H_2O)_6{}^{2+}]$ in this case

$W^V$ by addition of acid. Rate constants for the equilibration of the product with $NCS^-$ were *ca.* twice those reported herein.

*Kinetic Studies.*—Absorbance changes at 430 nm ($NCS^-$ excess) and 455 nm ($W_2O_4^{2+}$ excess) were monitored on a Dionex D-110 stopped-flow spectrophotometer with both reactant solutions air-free. The ionic strength was made up to 2.0 M with Hpts and Li(pts) as required. When adjusting the $[H^+]$ of $W_2O_4^{2+}$ solutions to 2.0 M using 4 M Hpts, small amounts of a blue precipitate appeared, which were removed by millipore (8 μm) filtration. Solutions were standardised spectrophotometrically before use. Further formation of precipitate was avoided by working with $W_2O_4^{2+}$ solutions in 2 M Hpts and diluting only with acid (< 2 M Hpts) as required. Absorbance-time data obtained were treated 'on-line' as previously described in papers from this laboratory. First-order plots of absorbance ($A$) changes for ln ($A_\infty - A_t$) against time were linear to 3—4 half-lives.

Further studies on the $Mo_2O_4^{2+}$ reaction with $NCS^-$, using the stopped-flow rather than the temperature-jump method, required a temperature less than 25 °C (here 7.7 °C). The reaction was monitored at 380 nm in perchlorate solutions, $I$ = 2.0 M ($LiClO_4$).

*Treatment of data.* Unweighted linear least-squares programs were used. Activation parameters were obtained from an Eyring plot of log ($k/t$) *vs.* $1/T$.

## Results

*Kinetics of* $W_2O_4^{2+}$ *with* $NCS^-$.—With $NCS^-$ in a large (> 10-fold) excess of $W_2O_4^{2+}$, first-order equilibration rate constants ($k_{eq}$) at 25 °C are independent of $[H^+]$ in the range 1.0—2.0 M, Table 1. On varying the concentration of $NCS^-$ a linear dependence of $k_{eq}$ on $[NCS^-]$ was observed. One run with $W_2O_4^{2+}$ in large (> 5-fold) excess was carried out, which identified the statistical factor, of 2. Thus rate constants $k_1$ and $k_{-1}$ are defined by the rate law (1).[11] With $NCS^-$ in excess, assuming two equivalent sites, the relationship (2) holds. In the presence of excess of $W_2O_4^{2+}$ the reaction is constrained (by the lower $[NCS^-]$) to form only $W_2O_4(NCS)^+$, and the rate constant for approach to equilibrium is governed by equation (3).

$$-d[W_2O_4{}^{2+}]/dt = k_1[W_2O_4{}^{2+}][NCS^-] - k_{-1}[W_2O_4(NCS)^+] \quad (1)$$

$$k_{eq} = (k_1/2)[NCS^-] + k_{-1} \quad (2)$$

$$k_{eq} = k_1[W_2O_4{}^{2+}] + k_{-1} \quad (3)$$

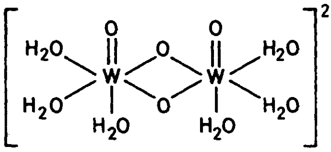
The slope for the data at 25 °C in Figure 2 gives $k_1$ = 2 520 ± 120 $M^{-1}$ $s^{-1}$, and $k_{-1}$ = 3.8 ± 1.2 $s^{-1}$, $I$ = 2.0 M [Li(pts)]. A listing of $k_1$ and $k_{-1}$ values is given in Table 2. From these values activation parameters are: $\Delta H_1^{\ddagger}$ = 13.3 ± 1.2 kcal $mol^{-1}$, $\Delta S_1^{\ddagger}$ = 1.4 ± 3.9 cal $K^{-1}$ $mol^{-1}$, $\Delta H_{-1}^{\ddagger}$ = 7.1 ± 3.2 kcal $mol^{-1}$, and $\Delta S_{-1}^{\ddagger}$ = −32.1 ± 10.9 cal $K^{-1}$ $mol^{-1}$.

*Kinetics of* $Mo_2O_4^{2+}$ *with* $NCS^-$.—Previous studies were made using the temperature-jump technique.[7] Here we use the stopped-flow method, but at 7.7 °C so that the reaction was sufficiently slow to monitor. It was demonstrated that runs at

$[H^+] = 2.0$ M in perchlorate solutions, $I = 2.0$ M ($LiClO_4$), with $[Mo_2O_4{}^{2+}] = 0.50 \times 10^{-3}$ M, $[NCS^-] = 1.0 \times 10^{-2}$ M, and with $[Mo_2O_4{}^{2+}] = 5.0 \times 10^{-3}$ M, $[NCS^-] = 0.50 \times 10^{-3}$ M gave rate constants of 68.4 and 67.1 $s^{-1}$ respectively in good agreement with previous data.[7] These runs were sufficient to establish that the statistical factor of 2 applies also in this study. Runs at $[H^+] = 1.0$ and 0.5 M ($NCS^-$ in excess) gave rate constants of 67.4 $s^{-1}$, confirming that there is no $[H^+]$ dependence over this range.

## Discussion

An aqua ion of $W^V$ has been prepared for the first time in a chromatographically pure form in 2.0 M Hpts. Ion-exchange elution characteristics, spectroscopic properties, and one-stage conversion to the structurally characterised $[W_2O_4(edta)]^{2-}$, all indicate that the aqua ion has a di-μ-oxo structure, $[W_2O_4(H_2O)_6]^{2+}$ (below). From the structure of the edta complex,[3] and by analogy with complexes of $Mo_2O_4{}^{2+}$, elongation of the bond to the axial $H_2O$ is likely. In an *X*-ray crystal structure determination of $[Mo_2O_4(NCS)_6]^{4-}$ it has been demonstrated that the axial Mo–N bonds are 0.15 Å longer than those to the equatorial (*i.e.* basal plane) ligands.[12] It is also well established that there is a similar elongation for mononuclear complexes of $VO^{2+}$ of around 0.18 Å.[13]



At 25 °C the rate constant for the 1:1 reaction of $NCS^-$ with $W_2O_4{}^{2+}$ ($2.52 \times 10^3$ $M^{-1}$ $s^{-1}$) is some 10 times smaller than that for $Mo_2O_4{}^{2+}$ ($2.9 \times 10^4$ $M^{-1}$ $s^{-1}$). Consistent with this it has been demonstrated that the aquation of $[W_2O_4(edta)]^{2-}$ ($1.6 \times 10^{-4}$ $s^{-1}$) is some 60 times slower than that of $[Mo_2O_4(edta)]^{2-}$ ($6.9 \times 10^{-3}$ $s^{-1}$).[2,3] The latter comparison is less precise because different conditions were used in the two cases (2 M HCl for W and 2 M $HClO_4$ in the Mo case). The direction and magnitude of the effect are significant, however. The trend is not readily explained because Mo and W not only have virtually identical atomic radii, but the single $d^1$ electron on each $M^V$ ion is involved in metal–metal bonding in the dimeric structures. Enhanced 5*d* participation due to the previously discussed[14] relativistic expansion effect is expected to strengthen the W–$OH_2$ bonds, making the tungsten more substitution inert. In this context the higher $\Delta H^‡$ value of 13.3 kcal $mol^{-1}$ for $W_2O_4{}^{2+}$, compared to 11.3 ± 0.9 kcal $mol^{-1}$ for $Mo_2O_4{}^{2+}$ is noted. Both reactions relating to the present study are independent of $[H^+]$ over the ranges investigated, for $W_2O_4{}^{2+}$ (1.0—2.0 M) and $Mo_2O_4{}^{2+}$ (0.50—2.0 M). No information has been obtained as to the magnitude of the acid dissociation constant for either 2 + cation, and it is concluded that conjugate-base forms do not contribute under the conditions investigated.

**Table 3.** Comparison of kinetic data for the 1:1 complexation of $NCS^-$ with metal oxo ions

| Reaction | $10^{-3}k_1$/ $M^{-1}$ $s^{-1}$ | $\Delta H^‡$/ kcal $mol^{-1}$ | $\Delta S^‡$/ cal $K^{-1}$ $mol^{-1}$ | Ref. |
|---|---|---|---|---|
| $Mo_2O_4{}^{2+} + NCS^{-\,a}$ | 29 | 11.3 | −0.3 | 7 |
| $W_2O_4{}^{2+} + NCS^{-\,a}$ | 2.52 | 13.3 | 1.4 | This work |
| $VO^{2+} + NCS^{-\,b}$ | 11.5 | 10.8 | −3.7 | 15 |
| $TiO^{2+} + NCS^{-\,c}$ | 2.21 | 11.7 | −4.0 | 16 |

[a] $I = 2.0$ M [Li(pts)]. [b] $I \longrightarrow 0$. [c] $I = 0.50$ M ($LiClO_4$).

Kinetic data for the complexation of $NCS^-$ to $d^0$ or $d^1$ aqua–oxo ions[7,15,16] are summarised in Table 3. While it has been demonstrated that in dilute solutions, pH < 1, aquatitanium(IV) is present as $TiO^{2+}$,[17–19] more recent n.m.r. studies have indicated that for the conditions pertaining to previous kinetic studies $Ti(OH)_2{}^{2+}$ is also present.[20] At higher $Ti^{IV}$ concentrations more complex oligomeric forms are also present. It appears that there is rapid interconversion of $TiO^{2+}$ and $Ti(OH)_2{}^{2+}$ by an internal proton-transfer mechanism resulting in rapid exchange of the oxo group of $TiO^{2+}$, which is *ca.* $10^6$ times faster than that observed for $VO^{2+}$. The Ti–O bond, confirmed in Raman and EXAFS studies,[18,19] is likely to have a labile trans $H_2O$ ligand (as in the case of $VO^{2+}$), and $TiO^{2+}$ rather than $Ti(OH)_2{}^{2+}$ might be expected to remain the dominant component as far as substitution is concerned. The presence of $Ti(OH)_2{}^{2+}$ will decrease the effective concentration of $TiO^{2+}$, but it is possible that there is little or no other effect. This is supported by the comparison of data in Table 3, which are remarkably similar for the four ions listed. In the case of $VO^{2+}$ it has been established that complex formation occurs in two stages. Thus rapid equilibration at the labile axial position ($H_2O$ exchange rate constant $> 10^7$ $s^{-1}$)[21] is followed by axial to equatorial (*i.e.* basal plane) isomerisation. This mechanism has been established by studies on the $[VO(pmida)(H_2O)]$ complex, which has the quadridentate (2-pyridylmethyl)iminodiacetate(2−)[22] ligand co-ordinated in the axial position, leaving only a single $H_2O$ in the equatorial plane. A much smaller exchange rate constant of 0.1 $s^{-1}$ is observed for such a water molecule, excluding in the case of $[VO(H_2O)_5]^{2+}$ the direct route for substitution at an equatorial $H_2O$.

For the two-stage mechanism proposed, the experimental rate constants $k_1$ are the product of the equilibrium constant for (rapid) complex formation at the axial position ($K$), and the rate constant for the axial to equatorial isomerisation ($k_{isom}$). The rate constants $k_1$ and corresponding activation parameters, Table 3, suggest that similar influences are contributing to the reactivity pattern. As compared to $Mo_2O_4{}^{2+}$ the $\Delta H^‡$ value for $W_2O_4{}^{2+}$ gives a rate constant two orders of magnitude smaller with the difference in $\Delta S^‡$ compensating by an order of magnitude. To explain such a narrow range of rate constants (within a factor of 13), for metals from the first, second, and third transition series, a similar mechanism is possible.

The present study has also demonstrated that, as in the complexing of $NCS^-$ to $Mo_3O_4{}^{4+}$,[11] a statistical factor must be taken into account in considering rate constants with first $NCS^-$ and then the metal ion reactant in excess. This factor was not detected in the previous temperature-jump study on the reaction of $Mo_2O_4{}^{2+}$ with $NCS^-$.[7] The results from the latter study given in Table 3 are with $Mo_2O_4{}^{2+}$ in excess and therefore need no correction.

Experiments relating to the stability of the $W^V$ aqua dimer to $O_2$ and $ClO_4{}^-$ have been reported in this paper; redox properties will be considered in a wider context in a subsequent publication.

## Acknowledgements

We thank the S.E.R.C. for a postgraduate studentship (to E. F. H.), and the Climax Molybdenum Co. for a C.A.S.E. studentship (to C. S.).

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*Received* 1st *April* 1986; *Paper* 6/625