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Kinetic Studies on the NCS⁻ Substitution of H₂O on Two Incomplete Cuboidal W^{IV}₃ Complexes: [W₃O₂S₂(H₂O)₉]⁴⁺ and [W₃OS₃(H₂O)₉]⁴⁺

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Three kinetic stages have been detected in studies on the 1:1 NCS⁻ substitution of H₂O (at each W) on [W₃(μ₃-S)(μ-S)(μ-O)₂(H₂O)₉]⁴⁺ (A) and [W₃(μ₃-S)(μ-S)₂(μ-O)(H₂O)₉]⁴⁺ (B). Both A and B have two tungstens of one type and one of another determined by the identity of core oxo/sulfido ligands. From studies with first W^{IV}₃ and then NCS⁻ in large excess, statistical factors of 2 and 1, respectively, are obtained for the first stages. These are assigned to substitution at the tungsten with the most core sulfides attached. Together with the previously detected factor of 3 for the reactions of [W₃(μ₃-O)(μ-O)₃(H₂O)₉]⁴⁺ and [W₃(μ₃-S)(μ-S)₃(H₂O)₉]⁴⁺, three different situations have now been identified. With NCS⁻ in excess, second and third stages are observed for A and B. The second is [NCS⁻]-dependent and corresponds to substitution at the more inert of the tungsten sites. The third is independent of [NCS⁻] and may correspond to isomerization of S- to N-bonded NCS⁻. The kinetics are consistent with concurrent and/or consecutive reactions for the different stages. A comparison of data for substitution (k_f) on five [W₃O_xS_{4-x}(H₂O)₉]⁴⁺ complexes indicates a 350-fold labilization effect on replacing the three μ₂-O ligands by electron-rich μ₂-S. A 14-fold inhibition is observed on replacing μ₃-O by μ₃-S.

Introduction

Rate constants for NCS⁻ substitution on incomplete cuboidal complexes [M₃(μ₃-O)(μ-O)₃(H₂O)₉]⁴⁺,^{1,2} [M₃(μ₃-S)(μ-O)₃(H₂O)₉]⁴⁺,^{3,4} and [M₃(μ₃-S)(μ-S)(H₂O)₉]⁴⁺^{5,6} (M = Mo, W), with first NCS⁻ and then the trinuclear complex in large (>10-fold) excess have been shown to differ by a factor of 3, the statistical factor. Thus, identical k_f and k_b values are obtained only if equilibration rate constants k_{eq} are expressed as in (1) and (2),

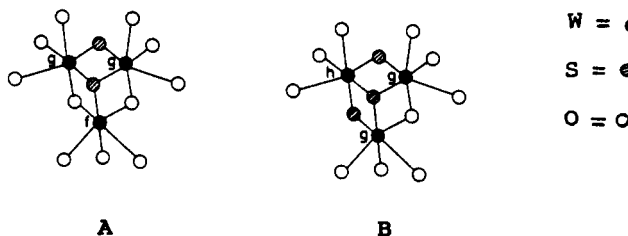
$$k_{eq} = (k_f[\text{NCS}^-]/x) + k_b \quad (1)$$

$$k_{eq} = k_f[M_3] + k_b \quad (2)$$

respectively, with x = 3. Such kinetic behavior is consistent with monomer structures, but in the case of [Mo₃(μ₃-O)(μ-O)₃(H₂O)₉]⁴⁺ extensive studies including X-ray crystallography,⁷ ¹⁸O-labeling,⁸ NMR spectroscopy,⁹ and EXAFS have excluded this possibility.¹⁰ The effect is explained by the existence of identical metal sites (in this case three) on each trinuclear complex, which with NCS⁻ in excess are substituted simultaneously.

Two mixed oxo/sulfido core trinuclear complexes leading to nonidentical W atoms, [W₃(μ₃-S)(μ-S)(μ-O)₂(H₂O)₉]⁴⁺ (A)¹¹ and [W₃(μ₃-S)(μ-S)₂(μ-O)(H₂O)₉]⁴⁺ (B),¹² are the subject of the present study. These have been characterized by X-ray crystallography as Ba[W₃(μ₃-S)(μ-S)(μ-O)₂(Hnta)₃]·9H₂O and K₂[W₃(μ₃-S)(μ-S)₂(μ-O)(Hnta)₃]KCl·7H₂O (Hnta is nitrilotriacetate with one acetate protonated). In each case there are two W's of

one type and one of another determined by the identity of the attached core atoms. Different statistical factors are expected for each W type, and are a prime focus in this paper. Terms used are as in previous studies.³ Thus the trinuclear complexes, e.g. [W₃(μ₃-O)(μ-O)₃(H₂O)₉]⁴⁺ and [Mo₃(μ₃-O)(μ-O)₃(H₂O)₉]⁴⁺, have different core O atoms (a and b) and different H₂O sites (c and d) depending on whether these are trans μ₃-O or trans μ₂-O. Different metal sites e–h are also designated, depending on the identity of core atoms to which they are bound. For complexes A and B the W's are of types f, g and h as illustrated. From



earlier studies³ it appears that a metal center labeled h on [Mo₃(μ₃-S)(μ₂-S)₃(H₂O)₉]⁴⁺ does not give a rate constant identical to that of h on [Mo₃(μ₃-S)(μ₂-S)₂(μ₂-O)(H₂O)₉]⁴⁺. This and related questions, including a comparison of W and Mo, are also addressed in the present study. One interesting outcome is the detection of a [NCS⁻]-independent step for both A and B.

No variations of [H⁺] were carried out in the present work. Inverse dependences on [H⁺] have been reported previously for the trinuclear clusters written henceforth as W₃O₄⁴⁺ and W₃S₄⁴⁺ etc.^{2,4} and presumably apply here also.^{2,4} We do not consider such dependences merit further study at this time.

Experimental Section

Preparation of Trinuclear Complexes. The W(VI) and W(III) complexes (NH₄)₂[WS₄] and K₃[W₂Cl₉] were first prepared using literature methods.^{13,14} To obtain the two W(IV) clusters, a procedure similar to that described in refs 11 and 12 was used. Air-free solutions of (N-H₄)₂[WS₄] (1 g) in H₂O (10 mL) and K₃[W₂Cl₉] (3 g) in 3 M HCl (50 mL) were mixed. The solution obtained was heated at ~90 °C for 2 h, cooled, and filtered. After filtration, the solution was loaded onto a Dowex 50W-X2 cation-exchange column. Extensive washing with 0.5 M HCl (200 mL) and then 1.0 M HCl (100 mL) gave three bands. Elution with 2 M HCl gave first a (red) band, which was identified as [W₃O₂S₂(H₂O)₉]⁴⁺, peak at 506 nm (ε 381 M⁻¹ cm⁻¹ per trimer),¹¹ and then a second (red-purple) band, peak at 540 nm, identified as [W₃OS₃(H₂O)₉]⁴⁺, previously reported peak at 535 nm (ε 408 M⁻¹ cm⁻¹).¹¹ Both were purified on a second Dowex 50W-X2 column (10

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Table I. Equilibration Rate Constants k_1 (25 °C) for the Reaction of $[\text{W}_3\text{O}_2\text{S}_2(\text{H}_2\text{O})_9]^{4+}$ (>10-fold Excess) with NCS^- in Aqueous Solution in 2.00 M HClO_4 , $I = 2.00$ M

$10^4[\text{W}_3\text{O}_2\text{S}_2^{4+}]$, M	$10^4[\text{NCS}^-]$, M	10^4k_1 , s^{-1}
1.99	0.178	2.33
4.00	0.356	3.30
5.23	0.475	3.98
6.13	0.593	4.4
7.30	0.593	4.8
9.66	0.593	6.2

cm), the final elution being with 2 M HCl. Solutions in perchloric acid were obtained from a further column, which was loaded, washed with 0.5 M and then 1.0 M HClO_4 , and eluted with 2.0 M HClO_4 . A third purple band with a peak at 563 nm, identified as $[\text{W}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$, literature peak at 557 nm (ϵ 446 $\text{M}^{-1}\text{cm}^{-1}$ per trimer), was also obtained. Stock solutions in 2.0 M HClO_4 , stored at 4 °C in air, were stable indefinitely.

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. The NCS^- solutions were standardized by titration against Ag(I) (BDH, Convol) with Fe(III) as indicator.

Kinetic Runs. These were followed by conventional UV-vis spectrophotometry. The reaction of $[\text{W}_3\text{O}_2\text{S}_2(\text{H}_2\text{O})_9]^{4+}$ (A) was monitored at 320 nm, and that of $[\text{W}_3\text{OS}_3(\text{H}_2\text{O})_9]^{4+}$ (B) at 280 nm (NCS^- in excess) or 325 nm (W in excess). Concentrations of NCS^- were $<2 \times 10^{-3}$ M to confine reaction to 1:1 substitution at any one W(IV). All runs were at 25.0 ± 0.1 °C, in 2.00 M HClO_4 , $I = 2.00$ M. Kinetic runs were of long duration, taking up to 4 days in the case of $\text{W}_3\text{O}_2\text{S}_2^{4+}$ and 1 day in the case of $\text{W}_3\text{OS}_3^{4+}$, and there was therefore a need to check the stability of NCS^- in acidic solutions. This was done by aging $(0.5\text{--}1.5) \times 10^{-3}$ M solutions in 2.00 M HClO_4 at 25 °C for 1.5 and 4 days, respectively. Check runs carried out using such stock solutions gave the same number of stages and behavior identical to that of existing runs.

For both the $[\text{W}_3\text{O}_2\text{S}_2(\text{H}_2\text{O})_9]^{4+}$ and $[\text{W}_3\text{OS}_3(\text{H}_2\text{O})_9]^{4+}$ runs, triphasic behavior was observed. Rate constants for the third stage (designated k_3) were obtained first from absorbance (A) plots of $\ln(A_\infty - A_t)$ against time. This plot gave an intercept x at $t = \text{zero}$. Considerable care was required to ensure that equilibration was complete and that correct final absorbance A_∞ values were used. Equilibration rate constants for the second stage were obtained from plots of $\ln(A_\infty - A_t - xe^{-k_3t})$ against time, using a standard consecutive reaction treatment.¹⁵ The procedure was repeated to obtain the rate constant for the first stage. A check on the accuracy of rate constants for the first stage, which makes by far the largest contribution to absorbance changes, was possible, since only this stage is observed with W^{IV} present in large excess.¹⁶ With $[\text{W}_3\text{O}_2\text{S}_2(\text{H}_2\text{O})_9]^{4+}$ in excess, an isosbestic point was observed at 365 nm, consistent with a single stage. First-order plots were linear to >3 half-lives. Rate constants for the first and third stages are believed to be the more accurate. Rate constants for the second stage are dependent on those obtained for the third and, because of cumulative errors, may be less reliable than the $\pm 6\%$ range indicated.

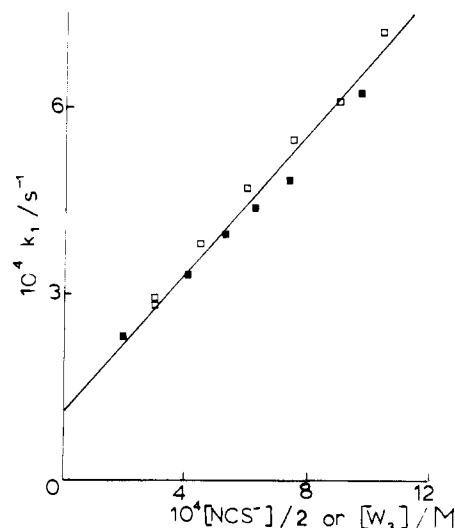
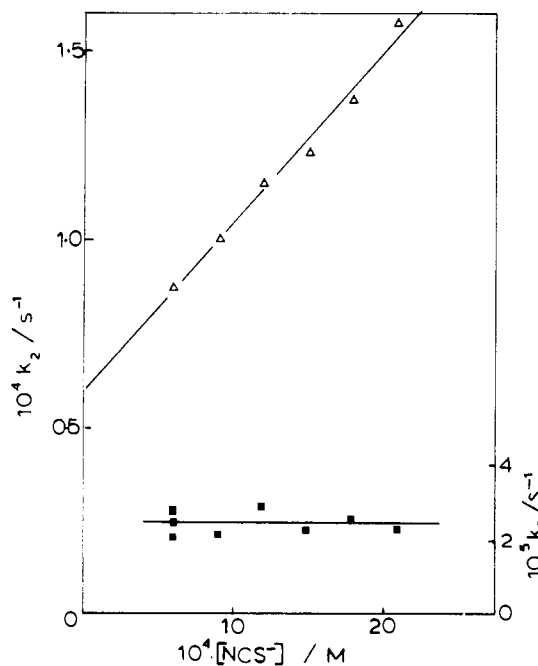
Product Analysis. For the reaction of $[\text{W}_3\text{S}_2\text{O}_2(\text{H}_2\text{O})_9]^{4+}$ (5.9×10^{-5} M) with NCS^- (11.9×10^{-4} M) at 25 °C in 2.0 M HClO_4 , the solution was cooled in ice on completion of the first phase (4 h). The solution was then loaded onto an ice-cooled Dowex 50W-X2 column (1 \times 10 cm). On elution with 0.5 M HClO_4 , three bands were obtained; the first two were purple, and the third was red, corresponding to unreacted 4+ complex. Thiocyanate in the product was determined spectrophotometrically as FeNCS^{2+} within 1–2 min of addition of Fe^{3+} . A calibration curve was obtained using free NCS^- and iron(III) sulfate. W(IV) was analyzed for by titrating an aliquot against Ce(IV) with ferroin as indicator. Products identified were of composition in order of elution $\text{W}_3(\text{NCS})_2^{2+}$ (32%), $\text{W}_3(\text{NCS})_3^{3+}$ (59%) and W_3^{4+} (9%). In less extensive studies on the corresponding $[\text{W}_3\text{OS}_3(\text{H}_2\text{O})_9]^{4+}$ reaction, $\text{W}_3(\text{NCS})_2^{2+}$ and $\text{W}_3(\text{NCS})_3^{3+}$ products were again obtained.

Typically, the third stage corresponds to 8% of the total absorbance change. No other product, e.g. a second $\text{W}_3(\text{NCS})_3^{3+}$ band, was identified which could be assigned to an S-bonded form, thus helping to better characterize this stage.

Table II. Equilibration First-Order Rate Constants (25 °C) for Three Stages of the Reaction of $\text{W}_3\text{O}_2\text{S}_2^{4+}$ (5.9×10^{-5} M) with NCS^- in >10-fold Excess in 2.00 M HClO_4 , $I = 2.00$ M

$10^4[\text{NCS}^-]$, M	10^4k_1 , s^{-1}	10^4k_2 , s^{-1}	10^5k_3 , s^{-1}
5.95	2.67		2.50
5.95 ^a	2.89	0.88	2.04
8.93	3.80	1.00	2.18
11.9	4.69	1.15	2.91
14.9	5.46	1.23	2.27
17.9	6.08	1.37	2.50
20.8	7.21	1.58	2.35

^a $[\text{W}_3\text{O}_2\text{S}_2^{4+}] = 4.0 \times 10^{-5}$ M.

**Figure 1.** First-order rate constants (25 °C) k_1 for the reaction of $\text{W}_3\text{O}_2\text{S}_2^{4+}$ with NCS^- in 2.00 M HClO_4 , $I = 2.00$ M. Runs with $\text{W}_3\text{O}_2\text{S}_2^{4+}$ (●) and NCS^- (□), respectively, in large excess are indicated. A satisfactory correspondence is observed with a statistical factor of 2.**Figure 2.** Dependence of first-order rate constants (25 °C) for the second (▲) and third (■) stages of the NCS^- (reactant in excess) substitution of H_2O of $\text{W}_3\text{O}_2\text{S}_2^{4+}$ on $[\text{NCS}^-]$ in 2.00 M HClO_4 , $I = 2.00$ M.

Treatment of Data. Unweighted linear least-squares fitting procedures were used.

Results

Equilibration rate constants k_1 , k_2 , and k_3 were obtained for three stages of reaction of $[\text{W}_3\text{O}_2\text{S}_2(\text{H}_2\text{O})_9]^{4+}$, and k_1' , k_2' , and

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- (16) In an earlier study on the reaction of $[\text{Mo}_2\text{OS}_3(\text{H}_2\text{O})_9]^{4+}$ with NCS^- with Mo^{IV} in large excess, absorbance changes assigned to the second stage were very small.
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Table III. Equilibration Rate Constants (25 °C) for Three Stages in the Reaction of [W₃(S)OS₂(H₂O)₉]⁴⁺ with NCS⁻ in 2.00 M HClO₄, I = 2.00 M

10 ³ [NCS ⁻], M	10 ³ [W ₃ OS ₃ ⁴⁺], M	10 ³ k ₁ ', s ⁻¹	10 ⁴ k ₂ ', s ⁻¹	10 ⁵ k ₃ ', s ⁻¹
0.040	0.38	2.40		
0.040	0.43	3.00		
0.040	0.54	3.30		
0.040	1.18	3.90		
0.40	0.040	2.65	4.5	6.6
0.60	0.050	3.10	4.8	6.3
0.75	0.050	3.40	4.7	6.5
1.00	0.050	3.60	5.0	6.4
1.25	0.050	3.90	5.5	6.1
1.50	0.050	4.00	5.5	6.1

Table IV. Summary of Rate Constants (25 °C) for Substitution of NCS⁻ at d-H₂O of W(IV) Trimers in 2.00 M HClO₄^a

complex	W type	x ^b	k _f , M ⁻¹ s ⁻¹	k _b , s ⁻¹	K, M
[W ₃ O ₄ (H ₂ O) ₉] ⁴⁺ ^c	e	3	0.110	0.35 × 10 ⁻⁴	3140
[W ₃ O ₃ S(H ₂ O) ₉] ⁴⁺ ^d	f	3	0.0080	5.4 × 10 ⁻⁶	1480
[W ₃ O ₂ S ₂ (H ₂ O) ₉] ⁴⁺ ^e	g	2	0.50	1.3 × 10 ⁻⁴	3820
	f	(1)	0.045	6.0 × 10 ⁻⁵	750
[W ₃ OS ₃ (H ₂ O) ₉] ⁴⁺ ^f	h	1	1.24	2.3 × 10 ⁻³	540
	g	(2)	0.212	4.1 × 10 ⁻⁴	520
[W ₃ S ₄ (H ₂ O) ₉] ⁴⁺ ^g	h	3	38.4	2.5 × 10 ⁻²	1520

^aType of W is defined by the number of core oxo/sulfido ligands attached (see formulas in text). Statistical factor (x) is as defined in eq 1. ^bStatistical factor used. Value confirmed except when parenthesized. ^c(μ₃-O)(μ₂-O)₃. ^d(μ₃-S)(μ₂-O)₃. ^e(μ₃-S)(μ₂-O)₂(μ₂-S). ^f(μ₃-S)(μ₂-O)(μ₂-S)₂. ^g(μ₃-S)(μ₂-S)₃.

k₃' for reaction of [W₃OS₃(H₂O)₉]⁴⁺. Rate constants k₁ (Table I), with [W₃O₂S₂(H₂O)₉]⁴⁺ in large excess, define k_{1f} and k_{1b} (eq 3). With NCS⁻ in excess (Table II), a statistical factor of 2 is

$$k_1 = k_{1f}[\text{W}_3\text{O}_2\text{S}_2^{4+}] + k_{1b} \quad (3)$$

required (eq 4) to define the same k_{1f} and k_{1b} values (Figure 2).

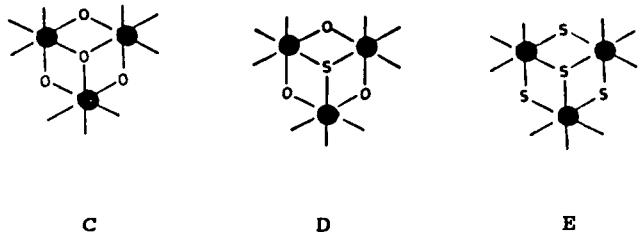
$$k_1 = (k_{1f}[\text{NCS}^-]/2) + k_{1b} \quad (4)$$

From the graph in Figure 1, k_{1f} = 0.50 ± 0.02 M⁻¹ s⁻¹ and k_{1b} = (1.3 ± 0.1) × 10⁻⁴ s⁻¹. For the rate constants k₂ (Table II) obtained with NCS⁻ in excess, we have no measurements indicating the statistical factor. Consistent with the structure, a value of 1 can be assumed (Figure 2), giving k_{2f} = 0.045 ± 0.003 M⁻¹ s⁻¹ and k_{2b} = (6.0 ± 0.4) × 10⁻⁵ s⁻¹. The rate constant k₃ is independent of [NCS⁻] and is assigned to isomerization, k_{isom} = (2.4 ± 0.5) × 10⁻⁵ s⁻¹.

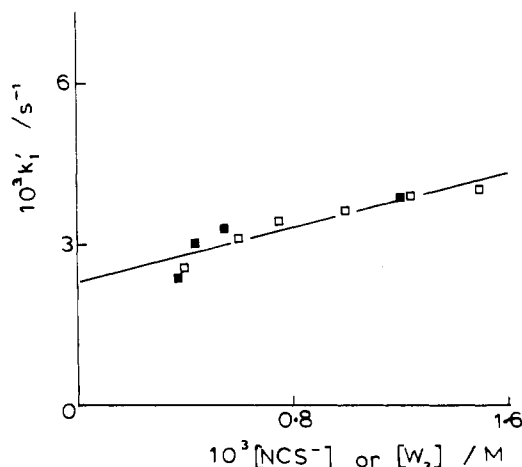
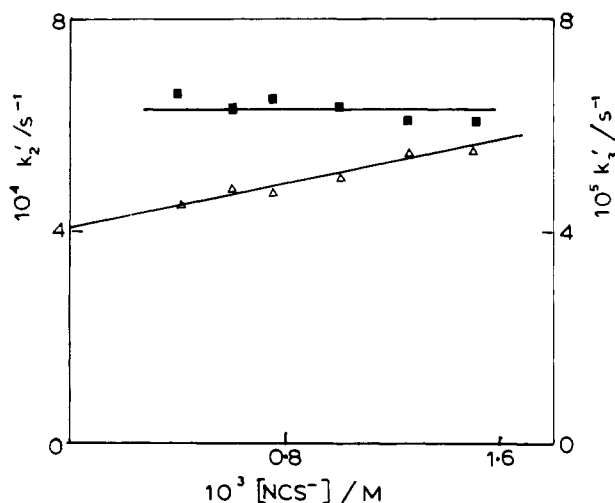
In the case of [W₃OS₃(H₂O)₉]⁴⁺ a statistical factor of 1 is required on comparing rate constants k₁' (Table III) with first W₃OS₃⁴⁺ and then NCS⁻ in large excess (Figure 3): k_{1f}' = 1.24 ± 0.19 M⁻¹ s⁻¹ and k_{1b}' = (2.30 ± 0.17) × 10⁻³ s⁻¹. Here, in view of the factor required for the first stage, a value of 2 is assumed for the second, giving k_{2f}' = 0.212 ± 0.015 M⁻¹ s⁻¹ and k_{2b}' = (4.1 ± 0.1) × 10⁻⁴ s⁻¹ (Figure 4). The third-stage k₃' is independent of [NCS⁻] and again is assigned to isomerization, k_{isom}' = (6.4 ± 0.3) × 10⁻⁵ s⁻¹.

Discussion

Results obtained for [W₃O₂S₂(H₂O)₉]⁴⁺ and [W₃OS₃(H₂O)₉]⁴⁺ are summarized in Table IV alongside those for [W₃O₃S(H₂O)₉]⁴⁺ (D) and the more symmetrical [W₃O₄(H₂O)₉]⁴⁺ (C) and



[W₃S₄(H₂O)₉]⁴⁺ (E) clusters.⁴ Different W(IV)'s e, f, and h can

**Figure 3.** First-order rate constants k₁ (25 °C) for the reaction of W₃OS₃⁴⁺ with NCS⁻ in 2.00 M HClO₄, I = 2.00 M. Runs with W₃OS₃⁴⁺ (■) and NCS⁻ (□), respectively, in large excess are indicated. A satisfactory correspondence is observed with a statistical factor of 1.**Figure 4.** Dependence of first-order rate constants (25 °C) for the second (Δ) and third (■) stages of the NCS⁻ (reactant in excess) substitution of H₂O of W₃OS₃⁴⁺ on [NCS⁻] in 2.00 M HClO₄, I = 2.00 M.

be defined alongside f, g, and h for A and B.

Statistical factors of 1, 2, and 3 have now been identified in studies on A–E. In the case of A and B, such information is only forthcoming for the first stage, when it is possible to explore the effect of having first W^{IV}₃ and then NCS⁻ in large excess. Studies with W^{IV}₃ in large excess give relatively small absorbance changes and yield rate constants for the first stage only, after which [NCS⁻] is small and subsequent changes are not readily detected.

The first stage of the [W₃O₂S₂(H₂O)₉]⁴⁺ reaction with a statistical factor of 2 (Figure 1) is assigned as substitution at the two equivalent g W's which have the greater number of μ₂-S ligands attached. The observation (Figure 2) that no statistical factor is required in the first stage of the [W₃OS₃(H₂O)₉]⁴⁺ reaction clearly differentiates the more labile h center from the (two) less labile g centers.

The third stage of reaction requires up to 4 days for completion, and considerable care is required in obtaining data. In the treatment used, rate constants for stage 3 are the first to be evaluated, and those for stage 1 the last. For the latter, the fact that there is a good correspondence of data with first W^{IV}₃ and then NCS⁻ in excess is an important check on the procedures used. Second-stage k_f and k_b terms corresponding to the [W₃O₂S₂(H₂O)₉]⁴⁺ site f and the [W₃OS₃(H₂O)₉]⁴⁺ site g are included in the summary (Table IV). There are significant differences in k_f and k_b values for the different g and h sites. The accuracy with which the three rate constants can be evaluated is of crucial importance. We note that discrepancies of similar magnitude are

observed in studies on $[\text{Mo}_3\text{O}_x\text{S}_{4-x}(\text{H}_2\text{O})_9]^{4+}$,³ when there are no complications from a third stage involving isomerization. This suggests that the effects are real and there are interactions between individual metal centers as the number of core sulfido ligand varies and/or structure deformations determined by the different number (and size) of oxo/sulfido core atoms prevent a better agreement.

There are clearly discernible trends to higher k_f rate constants as the number of μ_2 -S core atoms increases. As in the case of the $[\text{Mo}_3\text{O}_x\text{S}_{4-x}(\text{H}_2\text{O})_9]^{4+}$ clusters,³ replacement of μ_3 -O by μ_3 -S in $[\text{W}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$ has an inhibitory effect. The total spread of rate constants for W is 4800, with $[\text{W}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ reacting 350 times faster than $[\text{W}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$. For Mo, the spread of 570 is significantly less, with $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ reacting $\sim 10^2$ times faster than $[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$.³ Overall, the trends observed are in excellent agreement and are consistent with a strong transbilabilization by the electron-rich μ_2 -S ligands.

The third stages in the reactions of $[\text{W}_3\text{O}_2\text{S}_2(\text{H}_2\text{O})_9]^{4+}$ and $[\text{W}_3\text{OS}_3(\text{H}_2\text{O})_9]^{4+}$ are independent of $[\text{NCS}^-]$. The trinuclear complexes are themselves extremely stable, showing no signs of decomposition over the duration of experiments here described. Indeed, the complexes can be stored indefinitely, which is an indication of the stabilizing influence of core S atoms on W(IV). The most likely process would therefore seem to be isomerization although this is a surprisingly slow process. There are two possible mechanisms. The first is that S- and/or N-bonded thiocyanato products are obtained in the first stage, and isomerization then occurs. Crystal structures of thiocyanato complexes of W (and Mo) are all N-bonded, and it is reasonable therefore to assume that the N-bonded isomer is the more stable. A second explanation would involve a positional change of N-bonded NCS^- from a

d- H_2O to the much less labile trans c- H_2O position. At present, we are unable to distinguish between these possibilities. Under similar conditions, only a single stage has been identified in the substitution of the $[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$ and $[\text{W}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$ clusters.¹⁸ Isomerization has recently been detected in the case of $[\text{W}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ ($k_{\text{isom}} = 10.2 \times 10^{-5} \text{ s}^{-1}$), but not the Mo analogue,¹⁹ and appears to be effective for μ_2 -S-containing W but not Mo trimers. Since W is expected to be softer than Mo, linkage isomerization can be explained in terms of hard-soft (or class a and b) acid-base theory.^{20,21} There are more core S atoms attached to the W's implicated in the first stage, and it is these W's which are likely to generate more of the S-bonded isomer and contribute most significantly to isomerization. Isomerization involving S- to N-bonded thiocyanate has been studied previously for Co(III) complexes.^{22,23}

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- (18) In a recent check on the reaction of NCS^- ($< 3.5 \times 10^{-3} \text{ M}$) with $\text{Mo}_3\text{O}_4^{4+}$ ($4 \times 10^{-5} \text{ M}$), we find plots linear to $> 90\%$ with no evidence for a second stage.
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Notes

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$\eta^1(\text{S})$ - and η^6 -Coordination of Dibenzothiophene (DBT) in $\text{Cp}^*\text{MCl}_2[\eta^1(\text{S})\text{-DBT}]$ and $\text{Cp}^*\text{M}(\eta^6\text{-DBT})^{2+}$ ($\text{M} = \text{Ir}, \text{Rh}$)

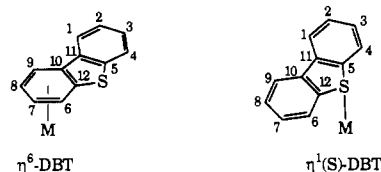
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As part of our studies of the mechanism of thiophene hydrodesulfurization (HDS) on heterogeneous transition-metal catalysts, we have recently explored² the coordination and reactivity of η^6 -coordinated (Chart I) dibenzothiophene (DBT) in $[\text{CpRu}(\eta^6\text{-DBT})\text{PF}_6]$ and $[(\text{CpRu})_2(\mu\text{-}\eta^6, \eta^6\text{-DBT})](\text{PF}_6)_2$. While other η^6 -DBT complexes are known, e.g., $\text{Cr}(\text{CO})_3(\eta^6\text{-DBT})$,³ $\text{CpFe}(\eta^6\text{-DBT})^+$,⁴ and $[(\text{CpFe})_2(\mu\text{-}\eta^6, \eta^6\text{-DBT})]^{2+}$,⁴ there are no reactions of these η^6 -derivatives that suggest² η^6 -coordination activates DBT to desulfurization on HDS catalysts.

A recent report⁵ describes a $\text{Cp}^*\text{Rh}(\text{PMe}_3)$ -promoted DBT C-S cleavage which is proposed to occur through an $\eta^1(\text{S})$ -coordinated (Chart I) DBT intermediate. Only three isolated complexes containing $\eta^1(\text{S})$ -DBT have been reported: $\text{Cp}(\text{CO})_2\text{Re}(\eta^1(\text{S})\text{-DBT})$,⁶ $\text{Cl}_2\text{Ru}[4\text{-R}_2\text{P}(\text{DBT})]_2$,⁷ in which the DBT is part of a

Chart I



phosphine chelating ligand, and $\text{Cp}(\text{CO})_2\text{Fe}(\eta^1(\text{S})\text{-DBT})^+$.⁸ The last two complexes have been characterized by crystallography and show pyramidal sulfur coordination such that the metal does not lie in the plane of the DBT.

In a recent kinetic study^{9a} of the rate of dissociation of $\eta^1(\text{S})$ -thiophenes (Th) from $\text{Cp}(\text{CO})_2\text{Re}(\eta^1(\text{S})\text{-Th})$, it was observed that DBT dissociates more slowly than benzo[*b*]thiophene (BT) or thiophene; this result suggested that DBT coordinates through the sulfur more strongly than the other thiophenes to transition metals. In the present note, we describe further evidence for the stronger coordinating ability of DBT and report the synthesis of $\eta^1(\text{S})$ -DBT complexes of Ir and Rh and their interconversion to η^6 -DBT derivatives.

Experimental Section

The ¹H and ¹³C NMR and mass spectra were recorded on Varian VXR-300 and Kratos MS-50 spectrometers, respectively. The ¹H and ¹³C chemical shifts are given in δ units relative to the internal standard

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