

(except for the oxygen atom) and the anion have been omitted from the bottom portion of 4. Room-temperature magnetic moments for these complexes are near those for magnetically dilute copper(II) ions, $\sim 1.9 \mu_B$ (see ref 33 and references therein). A recent report¹⁹ has described a Cu_4O_4 complex, $[\text{Cu}_4(\text{OH})_4(\text{SO}_3\text{CF}_3)_2(\text{py})_3\text{N}]_4(\text{SO}_3\text{CF}_3)_2$, which contains tris(2-pyridyl)amine instead of a (dialkylamino)ethanol derivative; the $(\text{py})_3\text{N}$ coordinates as a bidentate ligand bound via the pyridyl groups, and the OH^- ions provide the oxygen bridging atoms.

The $(\text{py})_2\text{PhCOH}$ ligand can provide both the pyridyl groups for coordination to the copper(II) as in the complex above and the bridging oxygen atom to obtain a cubane-like structure. The data for this complex are consistent with such a Cu_4O_4 unit as (1) the stoichiometry suggests there must be some sharing of the donor atoms between copper(II) ions, (2) limited solubility in both nitromethane and acetonitrile suggests some association of copper(II)-(py)₂PhCO⁻ units, (3) the room-temperature magnetic moment (Table II) is consistent with the magnetic moments of other Cu_4O_4 clusters, (4) infrared bands in the 1600–1400-cm⁻¹, 1000–980-cm⁻¹, and 800–700-cm⁻¹ regions suggest coordinated and nearly equivalent pyridyl rings while there are no bands above 3200 cm⁻¹ assignable to the carbinol group, and (5) perchlorate bands are broad but do not show any pronounced splitting, in-

dicating only slight distortion from T_d symmetry. Molecular models show that steric considerations do not preclude such a structure. We are currently trying to obtain suitable crystals for an X-ray structure analysis to provide an unambiguous assignment to this complex.

Conclusions

This investigation has shown that the ligand bis(2-pyridyl)phenylcarbinol can function as a tridentate ligand (N,N,O) regardless of whether the carbinol group remains protonated. Complexes of varying stoichiometry are easily obtained depending upon the metal ion and/or the reaction conditions employed. Finally, a cluster complex $[\text{M}((\text{py})_2\text{PhCO}^-)]_4^{4+}$ unique for copper(II) with this particular ligand has been prepared.

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Registry No. Ni((py)₂PhCOH)₂(ClO₄)₂, 97633-54-0; Co((py)₂PhCOH)((py)₂PhCO⁻)(ClO₄), 97644-25-2; Ni((py)₂PhCOH)((py)₂PhCO⁻)(ClO₄), 97644-27-4; Zn((py)₂PhCOH)((py)₂PhCO⁻)(ClO₄), 97644-29-6.

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Effect of Equivalent and Nonequivalent Sites on the Kinetics of Equilibration of Thiocyanate with $[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$

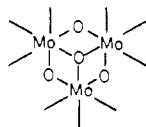
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Unique kinetic situations arise in considering substitution reactions of the triangular Mo(IV) ion $[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$. For the condition in which $[\text{NCS}^-]$ is in large (≥ 10 -fold) excess a statistically corrected rate constant is used, assuming three equivalent sites on the $\text{Mo}_3\text{O}_4^{4+}$ ion, and equilibration rate constants k_{eq} can be expressed as $k_{\text{eq}} = (k_1/3)[\text{NCS}^-] + k_{-1}$. With $[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$ in excess the reaction is constrained by the low $[\text{NCS}^-]$ to form only $\text{Mo}_3\text{O}_4(\text{NCS})^{3+}$, and $k_{\text{eq}} = k_1[\text{Mo}_3\text{O}_4^{4+}] + k_{-1}$. A comparison is made by using different anions, *p*-toluenesulfonate; trifluoromethanesulfonate, and perchlorate, $I = 2.0 \text{ M}$ (Li⁺ salt). At 25 °C forward and backward rate constants at $[\text{H}^+] = 2.0 \text{ M}$ are $k_1 = 0.78, 1.02, 2.13 \text{ M}^{-1} \text{ s}^{-1}$ and $10^3 k_{-1} = 1.57, 1.94, 2.18 \text{ s}^{-1}$ for the three anions, respectively. Rate constants k_1 and k_{-1} (and the aquation step k_{-2}) have $[\text{H}^+]$ dependences of the kind $a + b[\text{H}^+]^{-1}$, with b dominant for $[\text{H}^+] = 0.8\text{--}2.0 \text{ M}$. Solutions containing higher complexes obtained by equilibrating $\text{Mo}_3\text{O}_4^{4+}$ ($1.3 \times 10^{-3} \text{ M}$) with NCS^- ($5 \times 10^{-3} \text{ M}$) give, on ion exchange, bands that in order of elution (Mo and NCS^-) analyze for $\text{Mo}_3\text{O}_4(\text{NCS})_2^{2+}$, $\text{Mo}_3\text{O}_4(\text{NCS})^{3+}$, and $\text{Mo}_3\text{O}_4^{4+}$. A fraction not held on the column at $[\text{H}^+] = 0.3 \text{ M}$ is believed to contain $\text{Mo}_3\text{O}_4(\text{NCS})_3^+$ as well as free NCS^- . Two kinetic stages are observed for aquation of $\text{Mo}_3\text{O}_4(\text{NCS})_2^{2+}$, which are assigned (for 2 M HPTS) to k_{-1} (here $1.7 \times 10^{-3} \text{ s}^{-1}$) and $k_{-2} = 0.24 \times 10^{-3} \text{ s}^{-1}$. Consistent with these assignments, the faster and not the slower rate constant is observed in the aquation of $\text{Mo}_3\text{O}_4(\text{NCS})_2^{2+}$. Implications regarding different isomeric forms of $\text{Mo}_3\text{O}_4(\text{NCS})^{3+}$ and $\text{Mo}_3\text{O}_4(\text{NCS})_2^{2+}$ are considered.

Introduction

The trimeric Mo_3O_4 core in Mo(IV) is now well characterized, a notable feature being the apical μ_3 -oxo ligand.¹⁻³ The aqua



ion $[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$ is unusual in that four different types of O atoms are attached to each Mo. Murmann and colleagues,^{4,5}

using ¹⁸O-labeling techniques, have obtained information regarding exchange rates. At 25 °C and in 1 M methanesulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$) the half-time for exchange of the μ_3 -oxo is 5 days, for the three μ_2 -oxo's >3 years, for the three H_2O 's trans to the μ_3 -oxo 1.1 h, and for the six H_2O 's trans to the μ_2 -oxo's ~ 20 min (at 0 °C). We now extend these studies to include NCS^- anation of $[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$ and related aquation reactions. For the duration of the experiments considered the four core O atoms of $\text{Mo}_3\text{O}_4^{4+}$ can be assumed to be inert. Previous studies from this laboratory on $\text{Mo}_3\text{O}_4^{4+}$ have been reported.⁶⁻⁹ The instability

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(to oxidation) of $\text{Mo}_3\text{O}_4^{4+}$ in perchlorate over long periods,⁷ and our intention to ion exchange the products obtained on equilibration of $\text{Mo}_3\text{O}_4^{4+}$ with NCS^- , led to studies with alternative anions having poor donor properties, namely *p*-toluenesulfonate (PTS^-), used in most studies, and trifluoromethanesulfonate (TFMS^-).

Experimental Section

Materials. Sodium molybdate $\text{Na}_2[\text{MoO}_4] \cdot 2\text{H}_2\text{O}$ (Analar, BDH), potassium hexachloromolybdate(III), $\text{K}_3[\text{MoCl}_6]$ (a gift from Climax Molybdenum Co.), sodium thiocyanate (Technical, BDH) recrystallized once from ethanol, *p*-toluenesulfonic acid (Sigma Chemicals), and trifluoromethanesulfonic acid (Aldrich and 3M) were used. The lithium salt of HPTS was prepared by addition of Li_2CO_3 (Reagent Grade) and recrystallizing 2–3 times. All other chemicals were of Analar grade purity.

Preparation of Mo^{IV} . A solution of $\text{Na}_2[\text{MoO}_4] \cdot 2\text{H}_2\text{O}$ in 2 M HCl (25 mL, 0.3 M) was added to $\text{K}_3[\text{MoCl}_6]$ in 2 M HCl (50 mL, 0.3 M). Both solutions were deoxygenated prior to mixing. The reaction mixture was kept at 90 °C for ~1 h,¹⁰ and the resultant red solution of $\text{Mo}(\text{IV})$ trimer was stored under N_2 . Portions of this stock solution (5–10 mL) were diluted 50 times with 0.5 M HPTS and left to stand at room temperature for at least 1 day to allow aquation of coordinated chloride. To separate the aqua ion the solution was transferred to a Dowex 50W-X2 cation-exchange column (12 cm \times 1.2-cm diameter). A red band was held on the column, and a diffuse yellow-brown band of $\text{Mo}(\text{V})_2$ dimer formed below this. Elution of the Mo^{V}_2 was achieved with 0.5 M HPTS. The red band moved slowly under these conditions and split into two bands, the first of which was eluted with 1.0 M HPTS. This was shown to contain Cl^- . The second band, containing the $[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$ ion, was eluted with 2.0 M HPTS. To obtain $\text{Mo}_3\text{O}_4^{4+}$ in HClO_4 and HTFMS , the HPTS solution was again ion exchanged onto a Dowex 50W-X2 resin, this time by using a very short column (2 cm long) and eluting with 2.0 M HClO_4 (or HTFMS) after first washing off the HPTS and then moving the band to the bottom of the column with 1.0 M HClO_4 (or HTFMS). The $\text{Mo}_3\text{O}_4^{4+}$ has a peak at 505 nm ($\epsilon = 63 \text{ M}^{-1} \text{ cm}^{-1} / \text{Mo}$).

Kinetic Studies. Formation of the 1:1 complex was monitored at $\lambda = 370 \text{ nm}$ in acidic HPTS reactant solution, $I = 2.00\text{--}2.02 \text{ M}$ (LiPTS). Runs were carried out with first $\text{Mo}_3\text{O}_4^{4+}$ and then NCS^- in excess. The concentration of $[\text{NCS}^-]$ was restricted to $\leq 4 \times 10^{-3} \text{ M}$ to avoid extensive formation of the higher thiocyanato complexes. Final absorbances (A_∞) were measured for each run, and the slopes of plots of $\ln(A_\infty - A_t)$ against time (linearity >85% completion) gave equilibration rate constants k_{eq} . The Guggenheim method was also used.^{11a} With increasing $[\text{NCS}^-]$ ($\geq 5 \times 10^{-3} \text{ M}$) the linearity decreased to <75%. Aquation studies at 340 nm (sometimes 380 nm) were carried out on $\text{Mo}_3\text{O}_4(\text{NCS})^{3+}$ and $\text{Mo}_3\text{O}_4(\text{NCS})_2^{2+}$ obtained by the ion-exchange procedures described below. At the dilutions used these reactions were assumed to yield the fully aquated product. Runs in which NCS^- was at a higher concentration (0.005–0.050 M) with $\text{Mo}_3\text{O}_4^{4+}$ at $1.0 \times 10^{-4} \text{ M}$ gave biphasic kinetics consistent with more extensive coordination of the NCS^- . Because of the complexity of a rigorous treatment for consecutive equilibria these conditions were not explored further.

Ion-Exchange Separation of Products. Reactant solutions (50 mL) with $[\text{NCS}^-] = 5 \times 10^{-3} \text{ M}$, $[\text{Mo}_3\text{O}_4^{4+}] = 1.3 \times 10^{-3} \text{ M}$, and $[\text{HPTS}] = 0.3 \text{ M}$ (ionic strength not adjusted) were thermostated at 25 °C for 1 h. Ion-exchange separation of the products was carried out on an air-free, ice-cooled Dowex 50W-X2 column (16 cm \times 1.2-cm diameter). The reaction mixture was loaded onto the column, and elution was commenced with 0.5 M HPTS. All eluant solutions were collected and analyzed. The first fraction collected was not held by the column. Other bands that separated on the column were a diffuse brown band, which was eluted with 0.5 M HPTS, a dark brown band (eluted with 1.0 M HPTS), and a red band (2.0 M HPTS). The same procedure was carried out by using HClO_4 instead of HPTS when an identical number of bands was observed. Analyses obtained by the procedures described below are given in Table I.

Analysis of Products. The center of each band was collected separately and made up to a known volume with water and HPTS so that the final $[\text{H}^+]$ was approximately 0.50 M. The $\text{Mo}(\text{IV})$ was analyzed by titrating an aliquot against cerium(IV) with ferroin as the indicator.

Table I. Analyses of Different Fractions Obtained following Ion-Exchange Separation (0 °C) of a Solution of $\text{Mo}_3\text{O}_4^{4+}$ ($1.3 \times 10^{-3} \text{ M}$) and NCS^- ($5 \times 10^{-3} \text{ M}$) Equilibrated at Room Temperature ($\sim 20 \text{ }^\circ\text{C}$)^e

band	Mo:NCS ⁻	% total Mo	dominant form
low-charged product ^a	<i>b</i>	15	
diffuse brown band	1.65:1 ^c	31	$\text{Mo}_3\text{O}_4(\text{NCS})_2^{2+}$
dark brown band	3.7:1 ^d	30	$\text{Mo}_3\text{O}_4(\text{NCS})^{3+}$
red band	no NCS^-	19	$\text{Mo}_3\text{O}_4^{4+}$

^aNot held by column. ^bContains free NCS^- . ^c1.64:1 for solution equilibrated in 0.30 M HClO_4 . ^d3.5:1 for solution equilibrated in 0.30 M HClO_4 . ^e $[\text{H}^+] = 0.30 \text{ M}$.

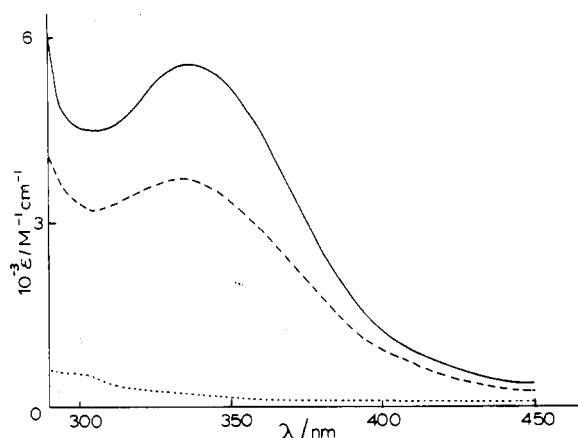


Figure 1. Electronic spectra of $\text{Mo}_3\text{O}_4(\text{NCS})_2^{2+}$ (—), $\text{Mo}_3\text{O}_4(\text{NCS})^{3+}$ (---), and $\text{Mo}_3\text{O}_4^{4+}$ (···) in 2 M HPTS.

Thiocyanate was determined spectrophotometrically at 470 nm as $\text{Fe}(\text{NCS})^{2+}$ by the following procedure. A calibration line (25 °C) of absorbance against $[\text{NCS}^-]$ (range up to $2.5 \times 10^{-4} \text{ M}$) was determined by adding 2 mL of NCS^- stock solutions to 5 mL of iron(III) sulfate (0.20 M) in 2.0 M H_2SO_4 , and made up to 10 mL with H_2O . The $[\text{NCS}^-]$ could then be read off the line when 2 mL of an unknown solution was treated in the same way. A large excess of $\text{Fe}(\text{III})$ (as prescribed) is essential. Variations in $[\text{H}^+]$ (0.2–0.7 M) for the NCS^- solutions had negligible effect on the absorbance. Spectra of thiocyanato products are shown in Figure 1. Peak positions at 335 nm give ϵ ($\text{M}^{-1} \text{ cm}^{-1} / \text{Mo}$) for $\text{Mo}_3\text{O}_4(\text{NCS})_2^{2+}$ (5650; average of two determinations within 2% of each other) and $\text{Mo}_3\text{O}_4(\text{NCS})^{3+}$ (3830; average of two values within 8% of each other), which can be compared with ϵ for $\text{Mo}_3\text{O}_4^{4+}$ (520 at 300 nm). Solutions were 2.0 M in HPTS, which absorbs strongly below 300 nm.

Results

1:1 Anation of $\text{Mo}_3\text{O}_4^{4+}$. Earlier data⁷ for the equilibration of $\text{Mo}_3\text{O}_4^{4+}$ with NCS^- to give $\text{Mo}_3\text{O}_4(\text{NCS})^{3+}$ (in perchlorate solutions), which were obtained prior to establishing the trimer structure, have been modified to include the statistical factor.¹² Equilibration rate constants, k_{eq} , at 25 °C with (a) NCS^- (≥ 10 -fold excess) and (b) Mo^{IV} (≥ 10 -fold excess expressed as monomer) in PTS^- and TFMS^- are listed in Table II. Rate constants k_1 and k_{-1} are defined by the rate law

$$-\frac{d[\text{Mo}_3\text{O}_4^{4+}]}{dt} = k_1[\text{Mo}_3\text{O}_4^{4+}][\text{NCS}^-] - k_{-1}[\text{Mo}_3\text{O}_4(\text{NCS})^{3+}] \quad (1)$$

With NCS^- in ≥ 10 -fold excess a study of the approach of equilibrium is described by (2), assuming three equivalent sites

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

that are accessible to NCS^- on $\text{Mo}_3\text{O}_4^{4+}$. In the presence of excess $\text{Mo}_3\text{O}_4^{4+}$ the reaction is constrained (by the lower $[\text{NCS}^-]$) to form only $\text{Mo}_3\text{O}_4(\text{NCS})^{3+}$, and the rate constant for approach to equilibrium is governed by (3). Rate constants k_1 and k_{-1} from

$$k_{\text{eq}} = k_1[\text{Mo}_3\text{O}_4^{4+}] + k_{-1} \quad (3)$$

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Table II. Equilibrated Rate Constants, k_{eq} (25 °C), for the Reaction of NCS^- with $[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$ ^c

$10^3[\text{Mo}^{\text{IV}}_3]$, M	$10^3[\text{NCS}^-]$, M	10^3k_{eq} , s ⁻¹
Reaction in 2 M HPTS (Except as Indicated)		
0.033	1.05	1.91
0.033	1.60	1.92
0.033	2.00	2.08
0.033	2.96	2.20
0.033	3.8	2.62
0.41	0.10	1.84
0.41	0.10	3.3 ^a
0.41	0.10	4.5 ^b
0.42	0.10	1.85
0.71	0.10	2.06
0.73	0.10	2.20
0.73	0.10	2.21
0.99	0.10	2.29
0.99	0.10	4.3 ^a
0.99	0.10	5.7 ^b
1.00	0.10	2.35
1.33	0.10	4.7 ^a
1.33	0.10	2.55
1.67	0.10	5.5 ^a
1.79	0.10	2.86
Reaction in 2 M HTFMS		
0.033	2.8	3.00
0.033	3.4	3.10
0.033	4.0	3.30
0.36	0.10	2.25

^a[HPTS] = 1.5 M. ^b[HPTS] = 1.0 M. ^c $I = 2.0$ M.

Table III. Summary of Rate Constants k_1 and k_{-1} (25 °C) for the Reaction of NCS^- with $\text{Mo}_3\text{O}_4^{4+}$ in 2 M Aqueous Acid Solutions

acid	k_1 , M ⁻¹ s ⁻¹	10^3k_{-1} , s ⁻¹	K_1 , ^a M ⁻¹
HPTS	0.78 ± 0.12	1.57 ± 0.14	498
HTFMS	1.02 ± 0.15	1.94 ± 0.21	546
HClO ₄	2.13 ± 0.15	2.18 ± 0.18	987

^aFrom the ratio $k_1:k_{-1}$

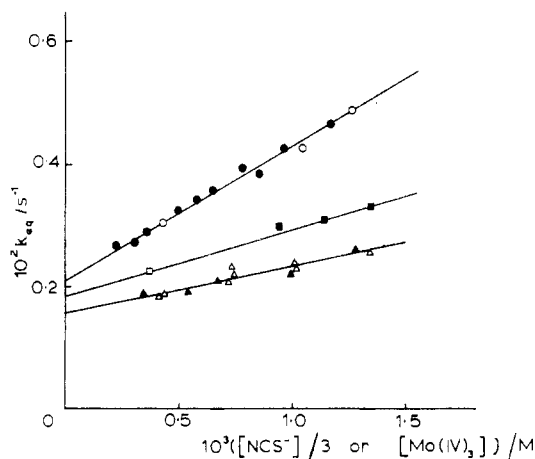


Figure 2. Equilibration rate constants, k_{eq} (25 °C), for the 1:1 reaction of NCS^- with $\text{Mo}_3\text{O}_4^{4+}$. $I = 2.0$ M. Points are shown for NCS^- corrected for the statistical factor (solid) or $\text{Mo}_3\text{O}_4^{4+}$ (open) in large excess and are for runs in 2 M HPTS (Δ and \blacktriangle), 2 M HTFMS (\square and \blacksquare), or 2 M HClO_4 (\circ and \bullet).

(2) and (3) (for any one anion of PTS^- , TFMS^- , or ClO_4^-) are in agreement. Table III is a listing of such values. Rate constants k_{eq} (in PTS^-) increase on decreasing $[\text{H}^+]$ from 2.0 to 1.0 M, consistent with a dependence $k_1 = a + b[\text{H}^+]^{-1}$ as previously reported for perchlorate.⁷ The term in b is also dominant for PTS^- solutions and, from the less extensive data, is close to 1.8 s^{-1} (cf. 3.63 s^{-1} for perchlorate). With $[\text{NCS}^-] \leq 4 \times 10^{-3} \text{ M}$ (reactant in excess), the linearity of plots was $\geq 80\%$ completion. Formation of the 2+ ion is not excluded since statistical relationships for the different Mo's can apply.¹³

Table IV. Summary of Rate Constants (25 °C) for the NCS^- Anation of $\text{Mo}_3\text{O}_4^{4+}$ (k_1) and Aqueation Studies (k_{-1} and k_{-2}) in HPTS Solutions (Source of $[\text{H}^+]$), except Where Anion Has Been Changed (As Indicated)^a

$[\text{H}^+]$, M	k_1 , M ⁻¹ s ⁻¹	10^3k_{-1} , s ⁻¹	10^3k_{-2} , s ⁻¹
Equilibration Kinetics ^b			
1.0	2.07	3.7	
1.5	1.56	2.7	
2.0	0.78	1.6	
2.0 (TFMS ⁻)	1.02	1.9	
2.0 (ClO_4^-)	2.13	2.2	
Aqueation of $\text{Mo}_3\text{O}_4(\text{NCS})^{3+}$			
0.8		3.8	
1.0		3.5	
1.25		2.8	
1.5		2.1	
2.0		1.7 (2)	
2.0 (ClO_4^-)		2.5	
Aqueation of $\text{Mo}_3\text{O}_4(\text{NCS})_2^{2+}$			
0.8		4.0	0.49
1.0		3.1	0.40
1.5		2.3	0.30
2.0		1.6	0.24
2.0 (ClO_4^-)		2.5 (2)	0.34

^aNumber of runs averaged indicated in parentheses. $I = 2.0$ M (LiPTS). ^bAs illustrated in Figure 2.

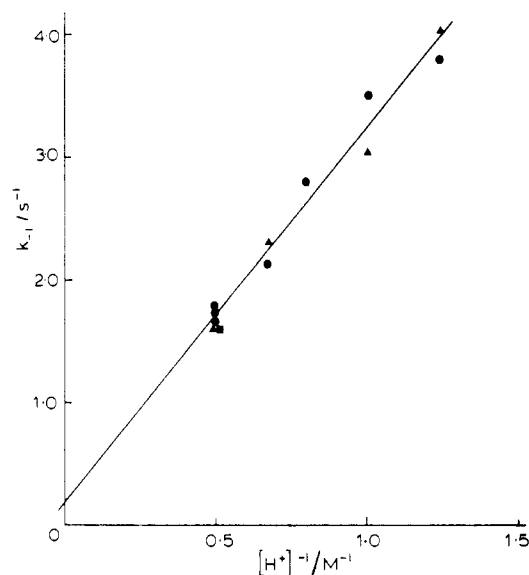


Figure 3. $[\text{H}^+]$ dependence of rate constants k_{-1} (25 °C) from equilibration studies (Figure 2) (\blacksquare), from the aqueation of $\text{Mo}_3\text{O}_4(\text{NCS})_2^{2+}$ (\blacktriangle), and from the aqueation of $\text{Mo}_3\text{O}_4(\text{NCS})^{3+}$ (\bullet). $I = 2.0$ M (LiPTS).

Aqueation of $\text{Mo}_3\text{O}_4(\text{NCS})^{3+}$. For the concentration range adopted, $(1.0\text{--}1.3) \times 10^{-4}$ M trimer, $\text{Mo}_3\text{O}_4^{4+}$ was the sole product, and aqueation was complete. Kinetic plots were linear to $>87\%$ completion, consistent with a single dominant aqueation process identified as k_{-1} in (1). Rate constants in PTS^- (Table IV) are dependent on $[\text{H}^+]^{-1}$, which can be expressed as in (4). Figure

$$k_{-1} = c + d[\text{H}^+]^{-1} \quad (4)$$

3 includes k_{-1} values obtained from k_{eq} and from the aqueation of $\text{Mo}_3\text{O}_4(\text{NCS})_2^{2+}$ (see below). From an unweighted least-squares fit $c = (0.26 \pm 0.3) \times 10^{-3} \text{ s}^{-1}$ and $d = (2.97 \pm 0.32) \times$

(13) Instances in which a sequence of two (pseudo-) first-order reactions conform to a monophasic rather than a biphasic equation and the conditions that need to be satisfied have been considered previously: (a) Buckingham, D. A.; Frances, D. J.; Sargeson, A. M. *Inorg. Chem.* **1974**, *13*, 2630. (b) Pohl, M. C.; Espenson, J. H. *Inorg. Chem.* **1980**, *19*, 235. (c) Armstrong, F. A.; Henderson, R. A.; Sykes, A. G. *J. Am. Chem. Soc.* **1980**, *102*, 6545. (d) Marty, W.; Espenson, J. H. *Inorg. Chem.* **1979**, *18*, 1246.

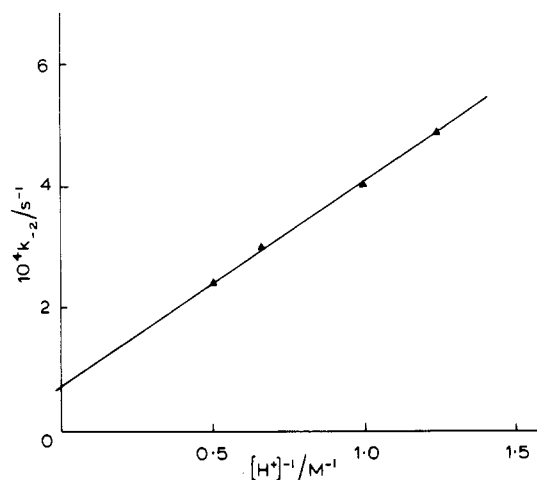
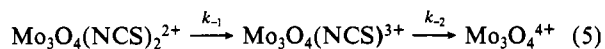


Figure 4. $[\text{H}^+]$ dependence of rate constants k_{-2} (25 °C), for the slower stage in the aquation of $\text{Mo}_3\text{O}_4(\text{NCS})_2^{2+}$. $I = 2.0 \text{ M}$ (LiPTS).

10^{-3} M s^{-1} . Rate constants obtained for solutions 2.0 M in HClO_4 are also included in Table IV.

Aquation of $\text{Mo}_3\text{O}_4(\text{NCS})_2^{2+}$. For the range of concentrations $(1.0\text{--}1.3) \times 10^{-4} \text{ M}$ the final product was identified as $>90\%$ $\text{Mo}_3\text{O}_4^{4+}$. Two kinetic stages were observed, which were fitted to a consecutive treatment (5).^{11b} The first of the two constants



corresponds to k_{-1} for the aquation of $\text{Mo}_3\text{O}_4(\text{NCS})^{3+}$, and the second (slower) process is designated as k_{-2} .¹⁴ This suggests that $\text{Mo}_3\text{O}_4(\text{NCS})^{3+}$ in (5) is not identical with $\text{Mo}_3\text{O}_4(\text{NCS})^{3+}$ as obtained by ion-exchange chromatography. By analyzing absorbances a spectrum of the intermediate $\text{Mo}_3\text{O}_4(\text{NCS})^{3+}$ can be generated with a shape similar to that of $\text{Mo}_3\text{O}_4(\text{NCS})^{3+}$ but with ϵ values about two-thirds less. The $[\text{H}^+]^{-1}$ dependence of k_{-2} , (6)

$$k_{-2} = e + f[\text{H}^+]^{-1} \quad (6)$$

illustrated in Figure 4, gives $e = (0.08 \pm 0.03) \times 10^{-3} \text{ s}^{-1}$ and $f = (0.33 \pm 0.03) \times 10^{-3} \text{ M s}^{-1}$.

Discussion

X-ray crystallographic studies,^{1,2} solution studies using ^{18}O labeling,^{4,5} the characterization of a mixed-valence $\text{Mo}(\text{III},\text{III},\text{IV})$ form,⁹ and EXAFS measurements,¹⁵ have established unequivocally that the aquated $\text{Mo}(\text{IV})$ ion is trimeric with three equivalent Mo's. Consistent with these experiments we have also demonstrated that a 0.1 M solution of $[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$ in 4 M HPTS at 25 °C is diamagnetic.¹⁶ Earlier, the correspondence of data in (2) and (3) was used as an argument for monomeric $\text{Mo}(\text{IV})$.⁶ There is no evidence in our studies or those of Murmann and colleagues^{4,5} for other than the trimer, and the existence of monomeric and dimeric forms can now be firmly excluded.

The interpretation requires that there are three equivalent sites on the trimer which NCS^- has access to. A possible interpretation is that NCS^- substitutes only the three H_2O 's that are trans to the μ_3 -oxo ligand. A different situation applies if the six equivalent sites trans to the μ_2 -oxo ligands are involved. If, however, reaction proceeds by NCS^- ion pairing to the single octahedral face incorporating the three H_2O ligands on each Mo, regardless of which type of H_2O is to be replaced, then the three-equivalent-site interpretation is valid. The rate constant k_1 corresponds to reaction at any one such site on the trimer. Rate constants from ref 7 in perchlorate are included in Figure 2 with an adjustment for the statistical factor. The three anions, selected because of their poor donor properties, give different values for k_1 and k_{-1} (Table III).

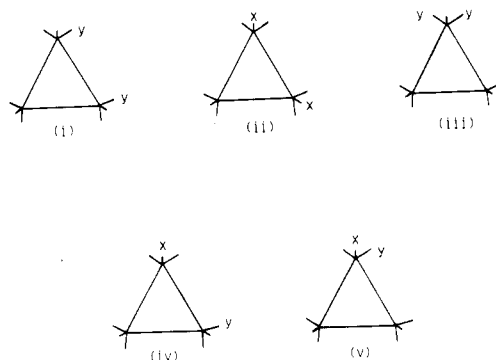


Figure 5. Different isomers for $\text{Mo}_3\text{O}_4(\text{NCS})_2^{2+}$, where x and y are positions trans to μ_3 - and μ_2 -oxo ligands, respectively.

Both k_1 and k_{-1} have dominant $[\text{H}^+]^{-1}$ terms, as previously established for ClO_4^- , consistent with conjugate-base pathways. These are presumed to be operative from the cis position, and the effect must therefore originate from the cis position, a fact that is often far from clear in considering substitution reactions of mononuclear hexaqua or acido pentaammine complexes. Of the three H_2O ligands attached to each Mo, that trans to the μ_3 -oxo has a shorter Mo–O bond⁵ and would be expected to be more acidic than the other two. Anation processes in which the other two H_2O 's are (preferentially) substituted are envisaged therefore. Whether isomerisation can take place once substitution has occurred is a possibility we consider further below. Conjugate-base pathways are generally believed to be dissociative in character,^{17,18} an observation that is supported by recent volumes of activation.¹⁹ The large contributions from conjugate-base pathways in the present studies suggest that associative processes are unfavorable, which is of considerable interest in view of the low d-electron population of each $\text{Mo}(\text{IV})$ (d^2). However $\text{Mo}_3\text{O}_4^{4+}$ is diamagnetic, and this and crystallographic information¹ are consistent with metal–metal bonding, which in effect increases the coordination number around each Mo to eight. Under these circumstances an associative process would be expected to be much less favorable. For the anation process k_1 , the acid-independent contribution a is small and no reliable activation parameters are available; for the $[\text{H}^+]^{-1}$ -dependent term b , which is composite, parameters $\Delta H^\ddagger = 14.9 \text{ kcal mol}^{-1}$ and $\Delta S^\ddagger = -6.1 \text{ cal K}^{-1} \text{ mol}^{-1}$ have been obtained in perchlorate, $I = 2.0 \text{ M}$.⁷

X-ray crystallographic studies on $[\text{Mo}_3\text{O}_4(\text{NCS})_8(\text{H}_2\text{O})]^{4-2}$ as well as the $\text{Mo}(\text{V})$ dimer $[\text{Mo}_2\text{O}_4(\text{NCS})_6]^{4-20}$ and $[\text{Mo}(\text{NCS})_6]^{3-}$, indicate N-bonded thiocyanate. No evidence has been obtained for any involvement of S-bonded isomers. It is also apparent that the charge density on $\text{Mo}_3\text{O}_4^{4+}$ does not give sufficiently extensive 1:1 ion pair formation with NCS^- for this to be influential in the kinetics ($K_{\text{IP}} < 30 \text{ M}^{-1}$). It is not certain whether different values of rate constants for studies in PTS^- , TFMS^- , and ClO_4^- are due to inner- or outer-sphere complexing of these anions to $[\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9]^{4+}$. A size effect $\text{ClO}_4^- < \text{TFMS}^- < \text{PTS}^-$ is noted.

A particularly interesting aspect of this work concerns the assignment of rate constants for the aquation of $\text{Mo}_3\text{O}_4(\text{NCS})_2^{2+}$, since the faster and not the slower process is observed in separate studies on $\text{Mo}_3\text{O}_4(\text{NCS})^{3+}$. Possible isomers for $\text{Mo}_3\text{O}_4(\text{NCS})_2^{2+}$ are indicated in Figure 5, where x denotes positions trans to the μ_3 -oxo and y denotes positions trans to the μ_2 -oxo ligands. Rapid

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interconversion is not suggested by the results of Murmann and colleagues.⁵ For aquation studies, providing the Mo's behave independently, isomers i and ii would be expected to give uniphase (statistical) kinetics²³⁻²⁵ and not the behavior observed. Isomer iii is likewise unable to explain the rate constant pattern for $\text{Mo}_3\text{O}_4(\text{NCS})_2^{2+}$ and $\text{Mo}_3\text{O}_4(\text{NCS})_3^+$. The remaining formulations, iv (for which there are two isomers) and v, provide reasonable explanations, although it is not clear how occupancy of the x position comes about. If isomerization is the result of the second substitution occurring at the same Mo, which would favor isomer v, then microscopic reversibility requires that the reverse events must occur in the aquation process. However it is less likely that a second substitution occurs at the same Mo since that Mo will already have four negatively charged ligands coordinated to it. Single y and x occupancy might be favored because separation of the two negatively charged NCS^- ligands will be maximized. However, this then raises the question as to whether the Mo sites are behaving as three equivalent independent sites. A mixture of isomers including isomers i-iii may of course be present and may contribute to the effects observed. We were unable to separate into different forms the $\text{Mo}_3\text{O}_4(\text{NCS})_3^+$ and $\text{Mo}_3\text{O}_4(\text{NCS})_2^{2+}$ bands in further ion-exchange experiments. The amplitude of absorbance changes for the first and second aquation steps of $\text{Mo}_3\text{O}_4(\text{NCS})_2^{2+}$ are about equal in magnitude. The possibility of using NMR to comment further on these effects is currently being explored.

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Equilibrium constants for (1:1) complexing from k_1 and k_{-1} values in Table III are 498 (2 M HPTS), 546 (2 M HTFMS), and 987 M^{-1} (2 M HClO_4) at 25 °C. The equilibration experiment referred to in Table I can be used to calculate K_1 , K_2 , and K_3 , assuming that the low-charged species (15%) is $\text{Mo}_3\text{O}_4(\text{NCS})_3^+$. The calculated molarity of free NCS^- is $3.2 \times 10^{-3} \text{ M}$, so that $K_1 = 490 \text{ M}^{-1}$ in agreement with the kinetic value of 498 M^{-1} in Table III. From product analyses indicated in Table III, relative values of the equilibrium constants $K_1:K_2:K_3$ are 1.5:1:0.47 whereas for a statistical relationship ratios 3:1:0.33 would be expected to apply. Also $(\epsilon_1 - \epsilon_0)$ should be equal to $1/2(\epsilon_2 - \epsilon_0)$ (the subscripts refer to the number of thiocyanates bound), and this does not seem to be the case from the information obtained. This draws attention to the involvement of x and y positions and again raises the question as to whether the x substituent is generated directly or by isomerization. For the highest NCS^- concentration ($4 \times 10^{-3} \text{ M}$), the equilibrium constant K_1 indicates ~67% 1:1 complexation to $\text{Mo}_3\text{O}_4^{4+}$. Some further anation to give the 2:1 thiocyanato product would be expected to contribute at this stage, which is not apparent in kinetic plots consistent with a statistical situation applying. At $[\text{NCS}^-] = 5 \times 10^{-3} \text{ M}$ reduced linearity (to 75%) in kinetic plots is observed, from which point runs become increasingly biphasic with increasing $[\text{NCS}^-]$.

Acknowledgment. We are particularly indebted to Professor E. L. King for his most helpful comments and correspondence, to Professor R. K. Murmann for information prior to publication,⁵ and to Professors J. H. Espenson and R. G. Pearson for comments. SERC postgraduate (A.B.S) and postdoctoral (D.T.R.) support is gratefully acknowledged.

Registry No. $\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_9^{4+}$, 74353-85-8; $\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_7(\text{NCS})_2^{2+}$, 97059-48-8; $\text{Mo}_3\text{O}_4(\text{H}_2\text{O})_8(\text{NCS})_3^+$, 97042-91-6; NCS , 302-04-5.

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Kinetics and Equilibria for Reactions of the Hexachloroiridate Redox Couple in Nitrous Acid

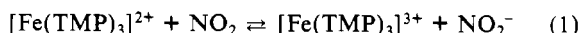
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The equilibria, kinetics, and mechanisms of the reactions of the $\text{IrCl}_6^{2-/3-}$ redox couple in nitrous acid have been investigated in aqueous solution at 25.0 °C in nitric and perchloric acid media by conventional and stopped-flow spectrophotometry. In 1 M HClO_4 , when IrCl_6^{3-} and HNO_2 are mixed, the equilibrium $\text{HNO}_2 + \text{H}^+ + \text{IrCl}_6^{3-} \rightleftharpoons \text{NO} + \text{H}_2\text{O} + \text{IrCl}_6^{2-}$ is established in a few milliseconds, with $d[\text{IrCl}_6^{2-}]/dt = k_f[\text{H}^+][\text{HNO}_2][\text{IrCl}_6^{3-}] - k_r[\text{NO}][\text{IrCl}_6^{2-}]$, where $k_f = 1.8 \times 10^4 \text{ M}^{-2} \text{ s}^{-1}$ and $k_r = 1.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$. At high $[\text{HNO}_2]$, this reaction precedes a slow loss of IrCl_6^{2-} that is due to formation of NO_3^- . In 1 M NO_3^- with $[\text{HNO}_2] > [\text{IrCl}_6^{3-}]$ the rapid equilibrium is followed by zero-order formation of IrCl_6^{2-} , and with $[\text{IrCl}_6^{3-}] > [\text{HNO}_2]$ the process is autocatalytic. When IrCl_6^{2-} is mixed with N(III) at pH ≥ 2 , IrCl_6^{2-} is consumed with rates that increase with acidity; at pH < 2 the rates become less, the kinetics become non first order, and IrCl_6^{2-} is only partially consumed. All of these phenomena have been accurately simulated by numerical integration of the set of differential equations that arise from k_f and k_r as defined above and several previously established processes intrinsic to nitrous acid/nitric acid mixtures. The k_f step is interpreted as rate-limiting diffusion-controlled electron transfer from IrCl_6^{3-} to NO^+ . The reaction of NO_2 with $[\text{Fe}(\text{TMP})_3]^{2+}$ (TMP = 3,4,7,8-tetramethylphenanthroline), observed directly by pulse radiolysis, has a rate constant of $1.0 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$; this rate constant, in conjunction with the results of a prior study of the reaction of NO_2^- with $[\text{Fe}(\text{TMP})_3]^{3+}$, has confirmed the choice of thermodynamic data used to analyze the $\text{IrCl}_6^{2-/3-}$ reactions.

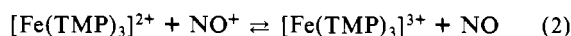
Introduction

This is the second of our reports on the behavior of substitution-inert one-electron redox couples in aqueous nitrous acid. The first report, which described the reactions of $[\text{Fe}(\text{TMP})_3]^{2+/3+}$ (TMP = 3,4,7,8-tetramethylphenanthroline), showed that reaction 1 was central in the mechanism.¹ No evidence could be found



for a significant role being played by the nitrosonium ion as in

eq 2. Reaction 2 was eagerly sought, because of the expectation



that nuclear tunneling would have a major influence on its rate constant.

In continuation of the search for a reaction proceeding through a NO^+/NO pathway, as in eq 2, the $\text{IrCl}_6^{2-/3-}$ system was selected because it is anionic, it has a higher reduction potential, and it has a lower self-exchange rate than the $[\text{Fe}(\text{TMP})_3]^{2+/3+}$ system. This system has proven to be remarkably complex, with analytical solutions to the kinetics only under quite limited conditions. However, by means of numerical integration the entire gamut of

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