

Ligand Substitution Reactions at the Nickel of $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ with Two Water Soluble Phosphines, CO, Br^- , I^- , and NCS^- and the Inertness of the 1,4,7-Triazacyclononane (L) Complex $[\text{Mo}_3(\text{NiL})\text{S}_4(\text{H}_2\text{O})_9]^{4+}$

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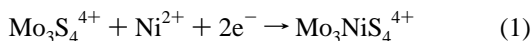
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Comparisons (25 °C) are made of substitution reactions, X replacing H_2O , at the tetrahedral Ni of the heterometallic sulfido cuboidal cluster $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$, $I = 2.00 \text{ M} (\text{LiClO}_4)$. Stopped-flow formation rate constants ($k_f/M^{-1} \text{ s}^{-1}$) for six X reagents, including two water soluble air-stable phosphines, 1,3,5-triaza-7-phosphaadamantane PTA (119) and tris(3-sulfonatophenyl)phosphine TPPTS³⁻ (58), and CO (0.66), Br^- (14.6), I^- (32.3), and NCS^- (44) are reported alongside the previous value for Cl^- (9.4). A dependence on $[\text{H}^+]$ is observed with PTA, which gives an unreactive form confirmed by NMR as N-protonated PTA (acid dissociation constant $K_a = 0.61 \text{ M}$), but in no other cases with $[\text{H}^+]$ in the range 0.30–2.00 M. The narrow spread of rate constants for all but the CO reaction is consistent with an I_d dissociative interchange mechanism. In addition NMR studies with H_2^{17}O enriched solvent are too slow for direct determination of the water-exchange rate constant indicating a value $< 10^3 \text{ s}^{-1}$. Equilibrium constants/ M^{-1} for 1:1 complexing with the different X groups at the Ni are obtained for PTA (2040) and TPPTS³⁻ (8900) by direct spectrophotometry and from kinetic studies (k_f/k_b) for Cl^- (97), Br^- (150), NCS^- (690), and CO (5150). No NCS^- substitution at the Ni is observed in the case of the heterometallic cube $[\text{Mo}_3\text{Ni}(\text{L})\text{S}_4(\text{H}_2\text{O})_9]^{4+}$, with tridentate 1,4,7-triazacyclononane(L) coordinated to the Ni. Substitution of NCS^- for H_2O , at the Mo's of $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ and $[\text{Mo}_3(\text{NiL})\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ are much slower secondary processes, with $k_f = 2.7 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ and $0.94 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ respectively. No substitution of H_2O by TPPTS³⁻ or CO is observed over ~1h at either metal on $[\text{Mo}_3\text{FeS}_4(\text{H}_2\text{O})_{10}]^{4+}$, on $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ or $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$.

Introduction

A property of the trinuclear Mo^{IV}_3 incomplete cuboidal complex $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ which has attracted considerable attention is its tendency to react with metals (and metal ions) to give heterometallic clusters $[\text{Mo}_3\text{MS}_4(\text{H}_2\text{O})_x]^{n+}$ (or related) with $x = 10$ or 12 .^{1–3} The Ni-containing cluster $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ was first prepared using the metal and characterized by X-ray crystallography by Shibahara and colleagues.⁴ However because the reaction with Ni metal is slow (>24 h) an alternative (rapid) reaction involving addition of Ni^{2+} and excess BH_4^- to $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ has also been used, (1).⁵ Only the

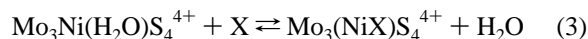


4+ charged product has been identified, and with e.g. $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Co}(\text{dipic})_2]^-$ as oxidants the trinuclear cluster is reformed as indicated in (2).⁶ More recently the carbonyl



complex $[\text{Mo}_3\text{Ni}(\text{CO})\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ has been characterized by X-ray crystallography,⁷ and Hidai and colleagues have prepared

the Pd analogue.⁸ In this work we have studied the kinetics and thermodynamics of substitution reactions, X replacing H_2O coordinated to the Ni in the $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ cube, (3).



Alongside aqueous solution studies with CO as the incoming ligand, two water soluble phosphines have been found to substitute at the Ni and form part of a comparison made with the more conventional aqueous ligands Cl^- , Br^- , I^- , and NCS^- . The studies involving CO and the two phosphines are of wider interest in the context of carrying out industrial catalytic processes in aqueous solution. Thus TPPTS³⁻ has already been used in several important commercial reactions.^{9–11} While the charge on different Mo_3MS_4 clusters is obtained in the course of characterization, the oxidation states applying separately to the Mo_3 unit and the heterometallic atom remain uncertain, as indeed does the whole question of extent of electron delocalization and whether integral oxidation states apply. Although initially a Ni^{II} assignment was assumed for Ni in $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$, more recent studies^{7,8} have raised the question as to whether Ni^0 might be implicated, thereby introducing somewhat different substitution properties.¹² At the same time we have sought confirmation that the substitution is at the Ni

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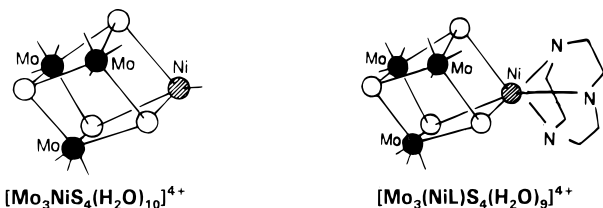
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by synthesizing $[\text{Mo}_3(\text{NiL})\text{S}_4(\text{H}_2\text{O})_9]^{4+}$, where L is the tridentate macrocyclic ligand 1,4,7-triazacyclononane, and demonstrating the substitution inertness of the Ni under these circumstances.

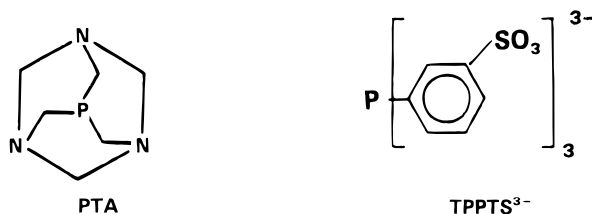
Experimental Section

Preparation of Clusters. Solutions of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$, UV-vis peak at 603 nm ($\epsilon = 362 \text{ M}^{-1} \text{ cm}^{-1}$ per Mo_3), and $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$, peak at 677 nm ($\epsilon = 610 \text{ M}^{-1} \text{ cm}^{-1}$), were prepared and purified by Dowex ion-exchange chromatography as described previously.^{5,13} Stock solutions of $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ were of concentration $\sim 1.5 \text{ mM}$ in 2.0 M perchloric acid. Solutions are air sensitive over times $> 1 \text{ h}$ and were therefore stored under N_2 . The preparation of the $[\text{Mo}_3(\text{NiL})\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ cluster with the 1,4,7-triazacyclononane ligand (L) attached



to the Ni was as follows. A sample of violet colored $\text{NiCl}_2 \cdot 2.5\text{H}_2\text{O}$ was first prepared as described.¹⁴ A solution of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$, pH adjusted to 1.0 by addition of NaHCO_3 (50 mL; $1.7 \times 10^{-3} \text{ M}$), was syphoned onto a mixture of $\text{NiCl}_2 \cdot 2.5\text{H}_2\text{O}$ (0.25 g; 10-fold excess) and $\text{Na}[\text{BH}_4]$ (0.31 g; 100-fold excess) under air-free conditions. The green color of $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ turned to a dark brown. The mixture was stirred for 30 min, diluted four times with 10^{-2} M acid, and loaded onto a carboxymethyl (CM) Sephadex C-25 cation-exchange column (Sigma). This was then washed with 0.5 M Napts (100 mL) followed by 1.0 M Napts (100 mL). These and other Napts solutions used were at pH 2 (Hpts). Unreacted NiL^{2+} and aqua Ni^{2+} were eluted by the 0.5 M Napts. Green $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ was eluted with 1.0 M Napts, and the brownish-green $[\text{Mo}_3\text{NiLS}_4(\text{H}_2\text{O})_9]^{4+}$ was then eluted with 2.0 M Napts. The UV-vis spectrum of the latter gave the following peaks/nm ($\epsilon/\text{M}^{-1} \text{ cm}^{-1}$ per cube) 498 (795), 641 (494). Elemental analysis by inductively coupled plasma (ICP) atomic emission spectroscopy on an AT1 Unicam Model 701 instrument gave a ratio Mo:Ni:S of 3.0:0.89:3.81. The yield was $\sim 10\%$. In air the complex decays only $\sim 5\%$ in 2 days, and there are $< 5\%$ absorbance changes in 0.4 M Hpts over 24 h. The cluster is less stable at higher $[\text{H}^+]$ values, and in 1.0 M HCl the spectrum obtained corresponded to $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ formation with an isosbestic point at 720 nm ($t_{1/2} \sim 30 \text{ min}$ at 25°C). Solutions of $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{3+}$ and $[\text{Mo}_3\text{FeS}_4(\text{H}_2\text{O})_{10}]^{4+}$ were prepared as described in earlier work.^{15,16}

Other Reagents. The air-stable (and water soluble) phosphine 1,3,5-triaza-7-phosphaadamantane (PTA),¹⁷ was prepared as described.¹⁸ We



are most grateful to Professor D. J. Darensbourg at Texas A&M for very generously providing a sample of this phosphine. Cylinder carbon monoxide (BOC technical grade) was very kindly made available to

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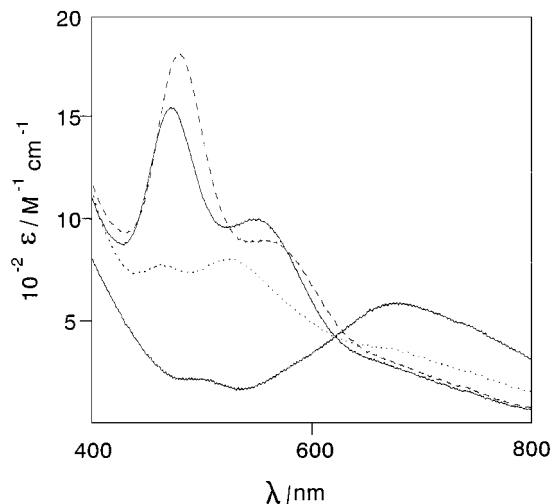


Figure 1. UV-vis absorbance spectra for $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ (—), $[\text{Mo}_3\text{Ni}(\text{CO})\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ (⋯), and the two phosphine complexes $[\text{Mo}_3\text{Ni}(\text{PTA})\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ (—) and $[\text{Mo}_3\text{Ni}(\text{TPPTS})\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ (—) (which are similar) in 2.0 M HClO_4 , in ascending order of intensity at $\sim 500 \text{ nm}$.

us by Dr. N. C. Norman. The water soluble tris(3-sulfonatophenyl)phosphine tetrahydrate, $\text{Na}_3(3\text{-SO}_3\text{C}_6\text{H}_4)_3\text{P} \cdot 4\text{H}_2\text{O}$ (Strem), the anion of which is referred to here as TPPTS^{3-} , was also used.^{9,10} Samples of the latter were shown to contain 10.3% phosphine oxide using ³¹P NMR. This was confirmed as a nonreactive component by adding less than stoichiometric amounts to $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ and quantifying the uniphase absorbance changes. The solubility of CO is 3.5 mL in 100 mL of water at room temperature.¹⁹ Saturated solutions (1.43 mM) were prepared by bubbling CO through water or dilute acidic solutions for 20 min and then leaving to stand overnight in a CO atmosphere. Absorbance changes resulting from the 1:1 complexation of $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ with PTA, TPPTS^{3-} , and CO are shown in Figure 1. The solubility of CO in 2.0 M HClO_4 was checked by adding 0.5 mL of CO saturated solution to 2.5 mL of $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ (1.62 mM), both in 2.0 M HClO_4 , and relating the absorbance changes at 525 nm to the absorbance of $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ ($\epsilon = 194 \text{ M}^{-1} \text{ cm}^{-1}$) and $[\text{Mo}_3\text{Ni}(\text{CO})\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ ($\epsilon = 820 \text{ M}^{-1} \text{ cm}^{-1}$). Assuming complete complexation, CO solubilities of 1.49 and 1.35 mM were obtained in satisfactory agreement with the literature value.¹⁹

Complexing of X with $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$. Equilibrium constants K/M^{-1} (25°C) for 1:1 complexing (eq 3) were determined in three cases with $\text{X} = \text{Br}^-$, PTA, and TPPTS^{3-} , $I = 2.00 \text{ M}$ (HClO_4). Expression 4 can be derived, where A_{aq} , A_{x} and A_{eq} are the initial, 1:1

$$\frac{(A_{\text{eq}} - A_{\text{aq}})}{(A_{\text{x}} - A_{\text{eq}})} = K[\text{X}] \quad (4)$$

product, and equilibrated absorbance readings respectively. For Br^- with the concentration of $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+} \sim 0.50 \times 10^{-4} \text{ M}$, and $[\text{Br}^-]$ in the range 0–0.3 M, a plot to the left-hand side of (4) against $[\text{Br}^-]$ is linear and passes through the origin. From a least-squares treatment $K = 139 \pm 1 \text{ M}^{-1}$. Similarly, in the case of PTA, concentrations in the range 0.070–0.70 mM, a value $K = 2040 \pm 50 \text{ M}^{-1}$ was obtained, and for TPPTS^{3-} , concentration range 0.025–0.100 mM, $K = 8900 \pm 800 \text{ M}^{-1}$. In the case of NCS^- absorbance changes for the second stage of substitution interfere with the determination of K.

Kinetic Studies. These were carried out at $25.0 \pm 0.1^\circ \text{C}$ with ionic strength adjusted to $I = 2.00 \pm 0.01 \text{ M}$ (LiClO_4). Reactions were monitored with the reactant X in large > 10 -fold excess using a Dionex D-110 stopped-flow spectrophotometer, and in one case (CO) by conventional spectrophotometry on a Phillips Unicam PU8700 instrument. From absorbance (A) changes at a fixed wavelength the slopes of $\ln(A_\infty - A_t)$ against time graphs gave first-order rate constants k_{obs} .

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The data conform to the rate-law dependence in (5), defining forward

$$k_{\text{obs}} = k_f[\text{X}] + k_b \quad (5)$$

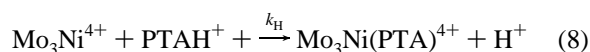
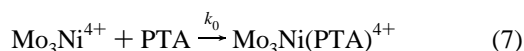
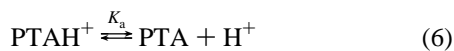
(k_f) and back (k_b) rate constants, although in some cases (PTA and TPPTS³⁻) the latter were small and difficult to detect.

Exchange of $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ with H_2^{17}O . A solution of $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ in 2.0 M HCl was evaporated to dryness using a vacuum line to obtain a sample of the chloride salt. The sample was then taken up in a 4:1 mole ratio of HClO_4 to cube and again evaporated to dryness to remove the remaining chloride as HCl. A solution of 25 mM $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ in 1.50 M HClO_4 with H_2^{17}O (10% ^{17}O enriched sample from Enritech Ltd) at a 5.4% level was prepared, $I = 2.00$ M (LiClO_4). To relax out the free H_2O resonances $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ as the perchlorate salt was added to give a concentration of 0.08 M. Procedures were similar to those used to explore the exchange on $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ using H_2^{17}O -enriched water.²⁰

Treatment of Data. Standard deviations for the various constants were obtained using an unweighted least-squares treatment of data.

Results

Reaction of PTA with $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$. Rate constants k_{obs} with [PTA] in large (>10 -fold) excess are listed in Table 1. Graphs of k_{obs} against total [PTA] indicate an $[\text{H}^+]$ dependence, Figure 2. At each $[\text{H}^+]$ the slope of k_{obs} against [PTA] defines the formation rate constant k_f . No measurable intercepts corresponding to the back-reaction k_b were obtained. Using a smaller range of [PTA] concentrations, K was determined from absorbance changes as 2040 M^{-1} , eq 4. Hence k_b ($=k_f/K$) could be calculated as a small intercept $\sim 0.15 \text{ s}^{-1}$. The nature of the $[\text{H}^+]$ dependence of k_f was explored. The reaction mechanism in (6)–(8) yields the expression in (9). From



$$k_f = \frac{k_0 K_a + k_H [\text{H}^+]}{K_a + [\text{H}^+]} \quad (9)$$

various graphical treatments it can be concluded that k_H makes little or no contribution, and from the linear plot of $1/k_f$ against $[\text{H}^+]$, Figure 3, $k_0 = 119 \pm 8.5 \text{ M}^{-1} \text{ s}^{-1}$ and $K_a = 0.67 \pm 0.08 \text{ M}$. No difference in the ^{31}P NMR was observed for a 10 mM solution of PTA in 2.0 M HClO_4 (-89.7 ppm) and in 0.15 M HClO_4 (-90.1 ppm). It is concluded that N-atom protonation is occurring.

Reaction of CO with $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$. Rate constants k_{obs} are listed in Table 2. From the variations in $[\text{H}^+]$ in the range 0.30–2.00 M, the reaction is independent of $[\text{H}^+]$. From the linear dependence of k_{obs} on [CO], Figure 4, an equilibration process defining k_f (slope) and k_b (intercept) is indicated. The data give $k_f = 0.66 \pm 0.02 \text{ M}^{-1} \text{ s}^{-1}$ and $k_b = (1.28 \pm 0.14) \times 10^{-4} \text{ s}^{-1}$, which are independent of $[\text{H}^+]$. There is therefore no evidence for participation of the protonated form HCO^+ , (10).



Table 1. Variation of Rate Constants k_{obs} (25 °C) for the Reaction of $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ ($1.0 \times 10^{-4} \text{ M}$ except as stated) with 1,3,5-Triaza-7-phosphaadamantane Ligand (PTA), with $I = 2.00 \text{ M}$ (LiClO_4)

$[\text{H}^+]$ (M)	[PTA] (mM)	$10^2 k_{\text{obs}}$ (s^{-1})
2.00	0.25	0.92 ^a
	0.50	1.52 ^a
	1.00	2.93
	1.50	4.5
	2.50	8.1
	3.00	9.2
	4.00	12.1
1.00	1.00	5.2
	2.00	10.3
	3.0	15.2
	4.0	19.2
0.75	0.94	5.5
	1.88	10.6
	2.80	16.1
0.50	1.00	7.2
	2.00	13.8
	3.00	21.1
0.40	1.00	7.4
	2.00	14.4
	3.00	22.2
	3.80	29.0
0.30	1.00	8.0
	1.50	11.0
	3.00	23.5
	3.80	30.0

^a $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}^{4+}] = 0.025 \text{ mM}$.

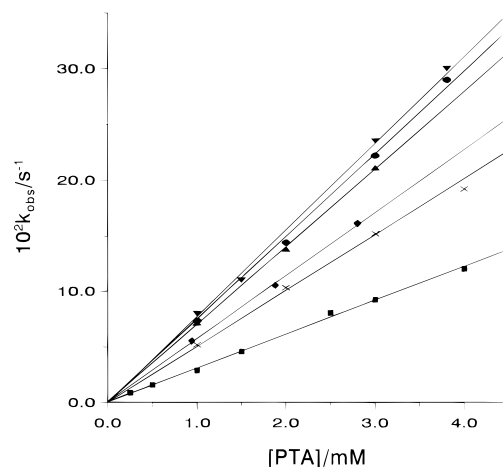


Figure 2. Variation of rate constants k_{obs} (25 °C) for the reaction of $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ with 1,3,5-triaza-7-phosphaadamantane (PTA) at varying $[\text{H}^+] = 2.00$ (■), 1.00 (×), 0.75 (◆), 0.50 (▲), 0.40 (●), and 0.30 M (▼), $I = 2.00 \text{ M}$ (LiClO_4).

Reaction of TPPTS³⁻ with $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$. Rate constants k_{obs} are listed in Table 3. A graph of k_{obs} against [TPPTS³⁻] is linear and gives $k_f = 58 \pm 3 \text{ M}^{-1} \text{ s}^{-1}$. No measurable intercept corresponding to the back reaction k_b is obtained. A small k_b contribution is confirmed by the equilibrium constant K (8900 M^{-1}) determined using eq 4. No dependence on $[\text{H}^+]$ in the range 0.50–2.00 M was observed.

Reactions of Halide Ions with $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$. Rate constants k_{obs} for the reactions with Br^- and I^- are listed in Table 3. No dependencies on $[\text{H}^+]$ are observed. With $[\text{Br}^-]$ up to 0.10 M k_{obs} gives a linear dependence on $[\text{Br}^-]$, Figure 5, where $k_f = 14.6 \pm 0.3 \text{ M}^{-1} \text{ s}^{-1}$ and $k_b = 0.097 \pm 0.035 \text{ s}^{-1}$. The intercept k_b is small and carries a large error. These values give $K = 150 \pm 57 \text{ M}^{-1}$, in satisfactory agreement with the spectrophotometric determination $K = 139 \text{ M}^{-1}$ (experimental section). At higher $[\text{Br}^-]$ to 1.0 M a linear fit gives $k_f = 134 \pm 0.2 \text{ M}^{-1} \text{ s}^{-1}$ and $k_b = 0.23 \pm 0.1 \text{ s}^{-1}$, but $K = 58 \pm 25 \text{ M}^{-1}$

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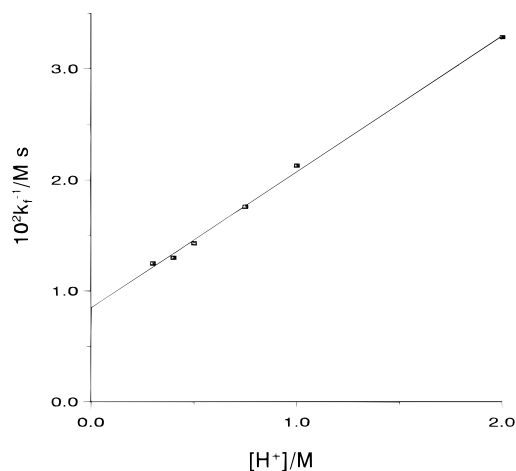


Figure 3. Linear dependence of $(k_t)^{-1}$ on $[H^+]$ for the reaction of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ with 1,3,5-triaza-7-phosphaadamantane (PTA) at 25 °C, $I = 2.00$ M (LiClO₄).

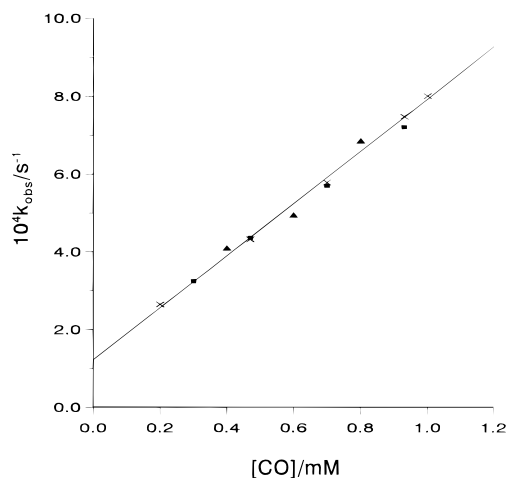
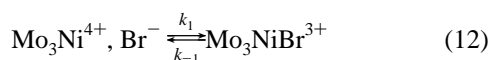


Figure 4. The variation of rate constants k_{obs} (25 °C) for the reaction of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ with [CO] at varying $[H^+] = 2.00$ (x), 1.00 (▲) and 0.30 M (■), $I = 2.00$ M (LiClO₄).

Table 2. Variation of Equilibration Rate Constants k_{obs} (25 °C) for the Reaction of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ (0.030–0.060 mM) with [CO], and Independence of $[H^+]$, with $I = 2.00$ M (LiClO₄)

	At $[H^+] = 2.00$ M				
[CO] (mM)	1.00	0.93	0.70	0.47	0.20
$10^4 k_{obs}$ (s ⁻¹)	8.0	7.5	5.8	4.3	2.65
	At $[H^+] = 1.00$ M				
[CO] (mM)	0.80	0.60	0.40		
$10^4 k_{obs}$ (s ⁻¹)	6.9	5.0	4.1		
	At $[H^+] = 0.30$ M				
[CO] (mM)	0.93	0.70	0.47	0.30	
$10^4 k_{obs}$ (s ⁻¹)	7.2	5.7	4.4	3.3	

is in less good agreement with the independently determined value of 139 M⁻¹. Some curvature is possible, Figure 5, consistent with saturation kinetic behavior as in (11) and (12).



Hence the expression 13 can be obtained. Since k_{-1} is equal

$$k_{obs} - k_{-1} = \frac{K_{os} k_1 [Br^-]}{1 + K_{os} [Br^-]} \quad (13)$$

Table 3. Equilibration Rate Constants k_{obs} (s⁻¹) for the Substitution of Different Reagents (for H₂O) on $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ (1–3 mM) in 2.00 M HClO₄ Except as Stated, with $I = 2.00$ M (H/LiClO₄)

(i) Reaction with TPPTS ³⁻							
$10^3 [TPPTS^{3-}]$ (M) ^a	0.72	1.35	.80	2.60	3.05	4.49	
$10^2 k_{obs}$ (s ⁻¹)	6.0	7.1 ^b	9.8	15.1	17.9	26.7	
(ii) Reaction with Br ⁻							
$10^2 [Br^-]$ (M)	1.0	2.5	2.5	3.0	5.0	7.5	10
k_{obs} (s ⁻¹)	0.21	0.46	0.41 ^c	0.54	0.85	0.79 ^d	1.27
$10^2 [Br^-]$ (M)	30	45	60	65	75	85	90
k_{obs} (s ⁻¹)	4.5	6.7	8.1	8.7	10.1	11.1	12.5
(iii) Reaction with I ⁻							
$10^2 [I^-]$ (M)	1.0	3.0	5.0	5.0	7.5	10.0	
k_{obs} (s ⁻¹)	0.32	1.09	1.53	1.54 ^e	2.39	3.3	
(iv) Reaction with NCS ⁻ ; for Second Stage, see Table 4							
$10^3 [NCS^-]$ (M)	0.5	0.75	1.00	1.50	2.00	2.50	0.50
$10^2 k_{obs}$ (s ⁻¹)	8.1 ^f	9.8 ^f	11.0 ^f	12.9 ^f	14.9 ^f	17.5 ^f	8.3 ^g
$10^3 [NCS^-]$ (M)	1.00	1.50	0.50	1.00	1.50	2.00	
$10^2 k_{obs}$ (s ⁻¹)	11.7 ^g	13.6 ^g	8.6 ^h	10.6 ^h	13.2 ^h	15.2 ^h	

^a [TPPTS³⁻] corrected for unreactive phosphine oxide component. ^b $[H^+] = 0.50$ M. ^c $[H^+] = 0.50$ M. ^d $[H^+] = 1.00$ M. ^e $[H^+] = 0.50$ M. ^f $[H^+] = 2.00$ M (see ref 5). ^g $[H^+] = 1.25$ M. ^h $[H^+] = 0.50$ M.

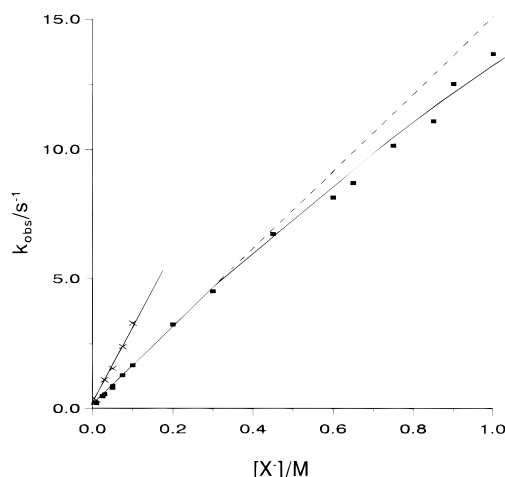


Figure 5. Variation of rate constants k_{obs} (25 °C) for the reaction of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ with X = Br⁻ (■) and I⁻ (x). $I = 2.00$ M (LiClO₄). The broken line indicates the extent of curvature due to ion-pair formation.

to k_b (determined above) a graph of $[Br^-]/(k_{obs} - k_{-1})$ against $[Br^-]$ can be plotted (as in ref 5), and from the intercept ($1/k_1 K_{os}$) and slope ($1/k_1$), $k_1 = 93.5 \pm 110$ s⁻¹ and $K_{os} = 0.16 \pm 0.16$ M⁻¹. The product $k_1 K_{os} = 15.0$ M⁻¹ s⁻¹ is in good agreement with k_f (14.6 M⁻¹ s⁻¹) from the initial slope in Figure 5. The magnitude of K_{os} is similar to that observed in the case of Cl⁻, 0.37 M⁻¹.⁵ However, the errors for k_1 and K_{os} draw attention to the marginal nature of the effect observed.

The reaction with I⁻ was studied under air-free conditions. Rate constants are listed in Table 3. At higher $[I^-]$ we encountered difficulties due to the greater tendency of I₂ to form due to I⁻ oxidation by traces of O₂. Rate constants k_{obs} give a linear dependence on $[I^-]$, Figure 5, from which $k_f = 32.3 \pm 1.3$ M⁻¹ s⁻¹ and $k_b \sim 0.02$ s⁻¹.

Reaction of NCS⁻ with $[Mo_3NiS_4(H_2O)_{10}]^{4+}$. The absorbance changes are large as compared to studies with the halide ions, and for the smaller $[NCS^-]$ values no behavior attributable to saturation kinetics is observed. Results reported in ref 5 indicate a linear dependence of k_{obs} on $[NCS^-]$, consistent with (14). These studies have been extended to include variations of

$$k_{obs} = k_f [NCS^-] + k_b \quad (14)$$

Table 4. Equilibration Rate Constants $k_{2\text{obs}}$ (25 °C) for the Second Phase of the Substitution of NCS^- (for H_2O) on $[\text{MoNiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ (~ 0.1 mM), with $I = 2.00$ M (HClO_4)

$10^3[\text{NCS}^-]$ (M)	1.0	2.0	3.0	5.0	7.0	10.0
$10^3k_{2\text{obs}}$ (s^{-1})	0.33	0.39	0.47	0.57	0.68	0.84

Table 5. Equilibration Rate Constants k_{obs} (25 °C) for the NCS^- Substitution on $[\text{Mo}_3\text{Ni}(\text{L})\text{S}_4(\text{H}_2\text{O})_9]^{4+}$ (0.10 mM) at $[\text{H}^+] = 0.010$ M, with $I = 2.00$ M (Napts), Assigned as Substitution at the Mo

$[\text{NCS}^-]/(\text{mM})$	10^4k_{obs} (s^{-1})	$[\text{NCS}^-]$ (mM)	10^4k_{obs} (s^{-1})
1.16	3.7	4.63	4.1
2.32	3.8	5.05	4.0
2.53	3.8	5.79	4.2
3.47	3.9		

$[\text{H}^+]$ in the range 0.40–2.00 M, Table 3. No dependence on $[\text{H}^+]$ is observed, and the combined data give $k_f = 44 \pm 2 \text{ M}^{-1} \text{ s}^{-1}$ and $k_b = 0.064 \pm 0.002 \text{ s}^{-1}$. A second phase of reaction was monitored at 465 nm, gave rate constants $k_{2\text{obs}}$ as listed in Table 4, and was assigned to NCS^- substitution at Mo. From the equilibration behavior observed, a least-squares treatment gives $k_{2f} = 0.056 \pm 0.002 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{2b} = (2.8 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$ at $I = 2.00$ M (HClO_4). The rate constant k_{2f} is 750 times smaller than k_{1f} . Both Mo and Ni exhibit known thermodynamic preferences for N-bonded NCS^- complexes,^{21,22} and no isomerisation step was observed.

Other Reactions of CO and TPPTS³⁻. No changes in UV–vis spectra were observed on passing CO gas (1 bubble/s) through 2.0 M HClO_4 solutions of (a) $[\text{Mo}_3\text{FeS}_4(\text{H}_2\text{O})_{10}]^{4+}$, (b) $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$, and (c) $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ (all ~ 1.0 mM) in a 1 cm optical cell (volume 2.5 mL) at 25 °C for 20 min. Solutions were left to stand for a further ~ 60 min without any absorbance changes occurring. No reaction with TPPTS³⁻ (10 mM) was observed under similar conditions.

Substitution of NCS^- on $[\text{Mo}_3\text{Ni}(\text{L})\text{S}_4(\text{H}_2\text{O})_9]^{4+}$. For these studies NCS^- (generally a good nucleophile) was chosen. The cluster was ~ 0.10 mM, and $[\text{NCS}^-]$, the reactant in large excess was varied 5-fold, Table 5. No rapid reaction was obtained similar to that for $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$. However small absorbance decreases were observed at 500 nm over reaction times comparable to the second stage of the reaction of NCS^- with $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$. For these studies it was necessary to keep the $[\text{H}^+]$ at a low level (pH 2), so that the cluster retains the ligand L. Rate constants k_{obs} , Table 5, give $k_{2f} = (9.4 \pm 1.5) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ and $k_{2b} = (3.61 \pm 0.02) \times 10^{-4} \text{ s}^{-1}$, eq 14. It is concluded that the 1,4,7-triazacyclononane ligand L blocks reaction at the Ni, and the slow reaction observed corresponds to substitution at Mo. Differences in $K_2 (=k_{2f}/k_{2b})$ for $[\text{Mo}_3(\text{NiL})\text{S}_4(\text{H}_2\text{O})_8]^{4+}$ (26 M^{-1}) as compared to $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ (200 M^{-1}) may originate in part from the different coordination geometries at the Ni.

Discussion

The many studies on substitution reactions X for H_2O on octahedral $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ favor an I_d dissociative interchange mechanism involving the outer-sphere adduct $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}\cdot\text{X}$.^{23–25} The water-exchange rate constant for $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ of $3.2 \times 10^4 \text{ s}^{-1}$ (25 °C) determined by NMR supports this interpretation.^{26,27} Tetrahedral Ni^{II} complexes have been little studied,

Table 6. Summary of Rate Constants (25 °C) for 1:1 Complexing of Different X Reagents with $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$, with $I = 2.00$ M (HClO_4) and Errors Indicated in Parenthesis

X	k_f ($\text{M}^{-1} \text{ s}^{-1}$)	k_b (s^{-1})	K^a (M^{-1})
PTA ^b	119(9)	small ^c	2040(50) ^d
TPPTS ³⁻	58(2)	small ^c	8900(800) ^d
CO ^e	0.66(2)	$1.28(14) \times 10^{-4}$	5150(720)
Cl ⁻	9.4(1)	0.097(7)	97(8) ^e
Br ⁻	14.6(3)	0.097(35)	150(57) ^f
I ⁻	32.3(13)	~ 0.02	
NCS^-	44(2)	0.064(2)	690(50)

^a K is given by ratio k_f/k_b except as stated. ^b Protonated form ($K_a = 0.67$ M) unreactive. ^c Kinetics give no measurable contribution from back-reaction. ^d Spectrophotometrically determined K . ^e Reference 5. $K = 106(2) \text{ M}^{-1}$ by spectrophotometry. ^f This work. $K = 139(1) \text{ M}^{-1}$ by spectrophotometry.

but would be expected to be more labile than $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$. As far as Ni^{II} substitution is concerned, (which we consider below), rate constants for ligand exchange on tetrahedral $[\text{Ni}(\text{CO})_4]$ ($2.0 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ in toluene) are much smaller, and an I_d mechanism has been assigned in keeping with the mutual repulsion of the entering nucleophile and the filled d-orbitals of the d^{10} system.²⁸

In the present studies the assignment of the first stage of reaction as substitution at the Ni requires careful consideration. Substitution of NCS^- for H_2O at the Mo centers on the Mo^{III}_4 cube $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{4+}$ (12-electrons), and on $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$ (11-electrons) are slow, with formation rate constants (k_f) of $1.95 \text{ M}^{-1} \text{ s}^{-1}$ and $0.116 \text{ M}^{-1} \text{ s}^{-1}$ (first stage), respectively.²¹ In contrast with $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$ (10-electrons), k_f is in the stopped-flow range ($13.3 \text{ M}^{-1} \text{ s}^{-1}$).²⁹ The latter reaction is unusually fast, which is believed to relate to the lower electron count. The presence of the Ni will give the cube a higher overall electron count. In the case of the trinuclear Mo^{IV}_3 cluster $[\text{Mo}_3\text{S}_4(\text{H}_2\text{O})_9]^{4+}$, the H_2O 's trans to the μ_2 -S core ligands are labilized and reactions are more rapid than for the H_2O 's trans to μ_3 -S which are inert.¹³ Since all the sulfides are μ_3 -S, the Mo centers in $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ are likely to be inert. With $\text{X} = \text{NCS}^-$ the rate constant for the first stage of substitution on $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ is substantially (750 \times) faster than the second stage. Confirmation of the latter as substitution at the Mo comes from the studies on $[\text{Mo}_3(\text{NiL})\text{S}_4(\text{H}_2\text{O})_9]^{4+}$, where the Ni is coordinated by the tridentate ligand L and the faster of the two substitution reactions is blocked. Therefore, we assign the first stage of substitution to reaction at the Ni and the second to reaction at the Mo centers. The slowness of the second stage is in keeping with slow substitution on $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{4+}$ and $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$.²¹

Substitution of X for H_2O at the Ni on $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ gives formation rate constants k_f for $\text{X} = \text{Cl}^-$, Br^- , I^- , and NCS^- in the narrow range 9.4–44 $\text{M}^{-1} \text{ s}^{-1}$, Table 6. Such behavior is normally interpreted in terms of an I_d mechanism.²⁵ NMR studies with H_2^{17}O enriched solvent gave no ^{17}O line-broadening, and water-exchange processes are therefore too slow to determine by this method. It is concluded that rate constants for the water-exchange are $< 10^3 \text{ s}^{-1}$, which in the Ni case is consistent with the range of values for the different X groups.

Unexpectedly the rate constants obtained for the substitution reactions with $\text{X} = \text{Cl}^-$, Br^- , I^- , and NCS^- substitution at the

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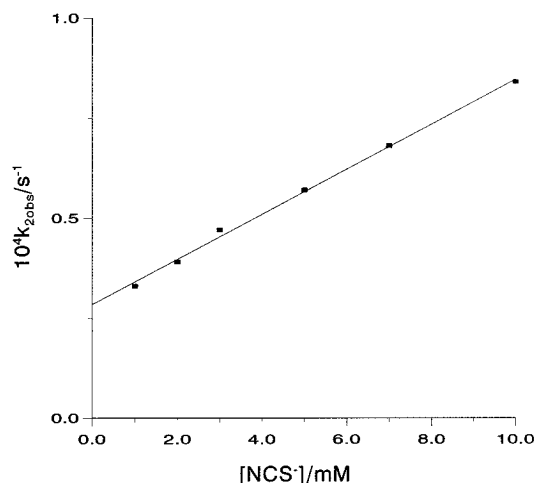


Figure 6. Dependence of $k_{2,obs}$ (25 °C) against $[NCS^-]$ for the second stage of reaction of NCS^- with $[Mo_3NiS_4(H_2O)_{10}]^{4+}$, here assigned to substitution at Mo. $I = 2.00$ M ($HClO_4$).

Ni are $\sim 10^3$ times smaller than for substitution on $[Ni(H_2O)_6]^{2+}$, with every likelihood that an even bigger difference will hold for tetrahedral Ni^{II} . However the Ni in $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ can only be regarded as tetrahedral by neglecting Ni–Mo metal–metal bonds. The two water soluble phosphines PTA and TPPTS³⁻ give k_f values which require a 3-fold extension of the 9–45 $M^{-1} s^{-1}$ range. In contrast CO gives a value of k_f which is $10\times$ smaller, Table 6. It is possible to explain these results while still retaining the essential features of an I_d mechanism. This can be done by considering the interchange process when X is in competition with nearby (outer-sphere) H_2O 's. The bulkiness of both phosphines is such as to impede competition from nearby solvent H_2O 's, thus enhancing rate constants for phosphine substitution. In the case of CO its poor nucleophilic properties (less competitive with H_2O) give rise to a slower reaction. Values of k_b and K for Cl^- , Br^- , and NCS^- , Table 6, are not sufficiently accurate (for reasons given) to give a linear plot of $\ln K$ of slope 1.0 as required for an I_d process.²⁵

It has been found that in the case of $X = TPPTS^{3-}$, Cl^- , Br^- , I^- , and NCS^- there is no $[H^+]$ dependence in the range 0.50–2.00 M. These results can be understood in terms of there being only a single H_2O attached to the Ni, which as leaving group does not have the means to provide a conjugate-base mechanism. In contrast $[Mo_3CrS_4(H_2O)_{12}]^{4+}$ ³⁰ has three H_2O 's coordinated to the Cr and benefits from a conjugate-base (H_2O to OH^-) labilizing effect. The nonlinear dependence of k_{obs} on $[Br^-]$ (and $[Cl^-]$) as the latter approach 1.0 M, Figure 6, provides evidence for K_{os} outer-sphere association with Br^- ($0.16 M^{-1}$) and Cl^- ($0.37 M^{-1}$) prior to inner-sphere complexing, but these values carry large errors and should be viewed as tentative. The K_{os} values obtained are small compared with those calculated for a $4+/1-$ interaction using the Fuoss equation,³¹ suggesting that the local charge on a single metal is more influential with contributions/ shielding provided by S^{2-} core ligands (three for each metal). It was not possible to work at higher concentrations of $TPPTS^{3-}$.

With $X = PTA$, $[H^+]$ was found to inhibit reaction by giving an unreactive protonated form. The acid dissociation constant

for the protonated form is $K_a = 0.67$ M. From NMR measurements protonation is at a N atom of the PTA. Coordination is via the P atom in the case of a Ru complex,¹¹ and if the same applies here also, it would appear that the inhibition is electrostatic in origin. There have been few if any kinetic studies with CO in aqueous solution. In the present case no evidence for the formyl HCO^+ or isoformyl COH^+ cations was obtained.^{32,33} Both processes are believed to be exothermic with the formyl cation calculated to be more stable by $38 kcal mol^{-1}$.³⁴ Thus protonation, as in (15), appears to be confined to the much



more acidic conditions as encountered in superacid solutions e.g. in the SbF_5-HSO_3F system.³³

Finally the question of oxidation states applying to the metal atoms in $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ should be considered and whether a Ni^0 assignment might apply in view of the reactivities observed with the two phosphines and CO. The infrared stretching frequency $\nu(CO)$ reported for $[Mo_3Ni(CO)S_4(H_2O)_9]^{4+}$ ($2060 cm^{-1}$),⁷ is less than for CO itself ($2143 cm^{-1}$), but not sufficiently so to favor a Ni^0 assignment ($\sim 1950 cm^{-1}$). Infrared spectra of a carbon monoxide bound form of the EPR silent Ni^{II} species of hydrogenase isolated from *Chromatium vinosum* also show a band at $2060 cm^{-1}$ which is assigned as a $Ni^{II}-CO$ species.³⁵ The same observations apply in the case of $[Mo_3Pd(CO)S_4(L)_3]^{4+}$ ($2085, 2087 cm^{-1}$) where $L = 1,4,7$ -triazacyclononane.⁸ At the extremes of the transition series, most recently with Ag^+ , the case for nonclassical σ -only CO bonding with little or no π -back-bonding has been made in considering the metal carbonyls $Ag(CO)^+$ and $Ag(CO)_2^+$.³⁶ In such instances there is an increase in $\nu(CO)$ values which range from 2189 to $2220 cm^{-1}$. We note that if C–O bond lengths slightly shorter than 1.128 \AA are indeed indicative of nonclassical metal carbonyl bonding,³⁶ the Ni (1.095 \AA) and Pd (1.10 \AA) clusters might be classified in this way. In kinetic terms, what really emerges from this study is that Ni in the Mo_3NiS_4 cube has distinctive properties of its own, and that substitution constants k_f although supporting an I_d mechanism, do not fall in any of the previously defined ranges for Ni. The μ_3 -S coordination ($\times 3$) of the Ni is unusual and results in a rather special situation. The Ni behaves somewhere in the Ni^0 to Ni^{II} range and on present evidence probably appreciably closer to Ni^{II} .

The observation that $TPPTS^{3-}$ and CO do not react with $[Mo_4S_4(H_2O)_{12}]^{5+}$ and $[Mo_3S_4(H_2O)_9]^{4+}$, or either metal of $[Mo_3FeS_4(H_2O)_{10}]^{4+}$, is also of interest in considering the chemistry of these Mo–S based cuboidal clusters.

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