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Aqueous Solution Chemistry of the Mo_3PdS_4 Cube: Substitution Reactions and the Double to Single Cube Interconversion Induced by CO, Two Phosphines, Cl^-, Br^-, and NCS^-

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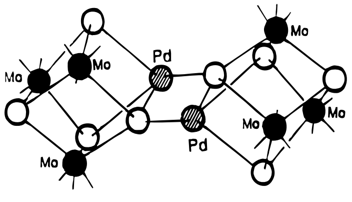
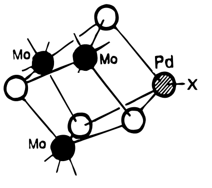
The kinetics of conversion of an edge-linked double cube, in this case $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$, to the corresponding single cube $[Mo_3(PdX)S_4(H_2O)_9]^{4+}$, has been studied for the first time. Reaction is induced by six reagents X = CO, two water-soluble phosphines, Cl^-, Br^-, and NCS^-, which complex at the tetrahedral Pd. The first stage of reaction is fast and is accompanied by color changes, e.g. purple to dark blue in the case of Cl^-, assigned as double to single cube conversion. With X = CO and the two phosphines, when absorbance changes are intense enough for stopped-flow monitoring with reactants at ≤1 mM, rate constants $10^{-5}\ k/M^{-1}\ s^{-1}$ at 25 °C are as follows: CO, 1.11; PTA, 27.8; $P(C_6H_4SO_3)_3{}^{3-}$, 9.6; at $I = 2.00$ (Li(pts)). The reactions are independent of $[H^+]$ in the range 0.30−2.00 M, and no substitution at the Mo's is observed. The first stages with X = Cl^-, Br^-, and NCS^- were too fast to monitor, but equilibrium constants K_1/M^{-1} were determined, Cl^- (490), Br^- (8040), and NCS^- (630), by UV−vis spectrophotometry. Two subsequent kinetic stages are assigned to substitution at the Mo's. Similar behavior is observed for $[Mo_3FeS_4(H_2O)_{10}]^{4+}$, which was selected because substitution at the Fe is also fast and there is no known double-cube formation. For both Mo_3Pd and Mo_3Fe the latter two stages can be explained by substitution at nonidentical (two α and one β) H_2O's on each Mo or by the presence of mixed-valent $Mo^{III}{}_2Mo^{IV}$ forms which are sufficiently long-lived to give a kinetic discrimination. In the case of NCS^- an additional step, $0.015\ s^{-1}$, independent of $[NCS^-]$ is assigned to the isomerization Pd−NCS → Pd−SCN. On removal of e.g. Cl^- by chromatography or addition of Ag^+, the double cube re-forms.

Introduction

Incorporation of palladium as freshly prepared palladium black into the well-characterized[1] incomplete cuboidal $Mo^{IV}{}_3$ cluster $[Mo_3S_4(H_2O)_9]^{4+}$ results, in HCl solution, in the formation of the heterometallic cuboidal cluster $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$.[2] Changing the acid to the less complexing *p*-toluenesulfonic acid (Hpts) gives the related edge-linked double cube $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$. Hidai and colleagues[2] have characterized both forms by X-ray crystallography on $[Mo_3(PdCl)S_4L_3]Cl_3{\cdot}4H_2O$ (where L is tridentate 1,4,7-triazacyclononane) and $[\{Mo_3PdS_4(H_2O)_9\}_2](pts)_8{\cdot}24H_2O$, and the two structures relevant to the present study are as illustrated.



$[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$



$[Mo_3(PdX)S_4(H_2O)_9]^{4+}$

Distinctive colors, purple and blue (X = Cl^-), respectively, are observed for the double- and single-cube aqua ions. The X-ray crystal structure of the carbonyl complex $[Mo_3(PdCO)S_4(H_2O)_9]^{4+}$ has also been determined.[2] The heterometal oxidation state has been assigned as Pd^{II} largely on the basis of infrared ν(C═O) properties.[2] Although two other double cubes $[\{Mo_3MS_4(H_2O)_9\}_2]^{8+}$, M = Co, Cu, have been characterized by crystallography,[3,4] no information concerning quantitative aspects of double/single cube interconversions have so far been determined.[5] The greater stability in air makes the interconversion of Pd single and double clusters ideal for study. Other heterometallic Mo_3MS_4 clusters appear to exist exclusively as the single cube, e.g. M = Fe, Ni with the heterometal atom tetrahedral,[6,7] or in one case M = Cr (alongside M = Mo) octahedral.[8] With M = Hg, Sn, Sb, an alternative double-cube structure $[(H_2O)_9Mo_3S_3MS_4Mo_3(H_2O)_9]^{8+}$, which has the heterometallic atom in a central corner-shared (or sandwich) position, is obtained.[3,9,10] Conversion of the corner-shared double cube, M = Sn, to give the single-cube $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ and $[Mo_3S_4(H_2O)_9]^{4+}$ and the reverse have been shown to be redox controlled.[11,12]

In the present paper the reactions of six reagents X = CO, two water-soluble phosphines, Cl^-, Br^-, and NCS^- with $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ are explored, all of which induce reaction to form 2 mol of the single-cube $[Mo_3(PdX)S_4(H_2O)_9]^{4+}$. The two phosphines are 1,3,5-triaza-7-phosphaadamantane (PTA) and

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tris(3-sulfonatophenyl)phosphine (previously abbreviated to $TPPTS^{3-}$). Kinetic and thermodynamics studies on heterometallic single cubes, M = Cr,[13] Fe,[14] Ni,[15] Cu,[5] Co,[16] have been carried out,[12] and review papers have appeared.[16,17] Some comparisons with $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ are included in this study to help with the assignment of substitution processes at the Mo_3 component of $[Mo_3(PdX)S_4(H_2O)_9]^{4+}$ clusters.

Experimental Section

Preparation of $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$. Solutions of green $[Mo_3S_4(H_2O)_9]^{4+}$, typically 10mM in 2M HCl, were prepared as described previously.[18] Stock solutions in 2 M *p*-toluenesulfonic acid (Hpts) gave UV−vis absorbance peaks λ/nm (ϵ/M^{-1} cm^{-1} per Mo_3) at 366 (5550) and 603 (362). Palladium black was freshly prepared by reduction of a solution of $PdCl_2$ (0.15 M; Johnson Matthey) in water, with hydrazine hydrochloride. Conversion of $[Mo_3S_4(H_2O)_9]^{4+}$ (0.01 M) in 2 M HCl was accomplished by adding a large excess of Pd black and leaving the mixture under N_2 with stirring for 3−4 days. Excess Pd black was filtered off, and the blue/green filtrate was purified by Dowex 50W-X2 cation-exchange chromatography. The solution was first diluted to 0.5 M HCl for satisfactory loading. The column was then washed with 100mL amounts of first 0.50 M followed by 1.0 M HCl, when the blue $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ separated from unreacted $[Mo_3S_4(H_2O)_9]^{4+}$. Elution of the 3+ product was carried out with 2.0 M HCl. Typical yields were 70−80% based on the conversion of $[Mo_3S_4(H_2O)_9]^{4+}$, with concentrations of $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ stock solutions in the range 5−8 mM in 2.0M HCl.

Conversion to $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$. The single cube with an Mo_3PdS_4 core (as above) was loaded onto a Dowex column and washed with 100 mL each of 0.5, 1.0, and 2.0 M Hpts, before elution with 4.0 M Hpts. Concentrations obtained were in the range 0.7−1.2 mM. Solutions were stored under N_2 at ~4 °C.

UV−Vis Spectra. Peak positions λ/nm (ϵ/M^{-1} cm^{-1}) for the blue (3+) chloro-complexed single cube (ϵ's per Mo_3) are 450 (1013) and 580 (1382) and for the purple double cube (ϵ's per Mo_6) are 456 (2310) and 572 (2786), Figure 1. The peak positions for the single cube are the same as those reported previously.[2] In the case of the double cube however the present ϵ's are ~30% larger. No absorbance bands were observed in the near-IR up to 1200 nm. Due to interference from Hpts, spectra were not recorded below 300 nm. The Mo:Pd:S ratio for the single cube was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) as 3.04:1:4.11. To determine ϵ values, solutions of the single and double cubes were oxidized by $[Co(dipic)_2]^-$ to give $[Mo_3S_4(H_2O)_9]^{4+}$, (1), the UV−vis spectrum of which is well-known.[1]

$$\mathrm{Mo_3PdS_4}^{4+} + 2\mathrm{Co^{III}} \rightarrow \mathrm{Mo_3S_4}^{4+} + \mathrm{Pd^{II}} + 2\mathrm{Co^{II}} \qquad (1)$$

Other Reactants. Cylinder carbon monoxide (BOC technical grade) was made available to us by Dr. N. C. Norman. 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 acid for 20 min and then leaving the mixtures to stand overnight. The air-stable (and water-soluble) phosphine 1,3,5-triaza-7-phosphaadamantane (PTA) was prepared as described.[20,21] We are grateful to Prof. D. J. Darensbourg (Texas A&M) for generously providing a sample of this phosphine. Tris(3-sulfonatophenyl)phosphine tetrahydrate, $Na_3(3\text{-}SO_3C_6H_4)_3P{\cdot}4H_2O$ (Strem), referred to here as $TPPTS^{3-}$, was also used.[22,23] Samples of the latter have been shown to contain 10.5% of phosphine oxide.[15] Solutions of HCl, HBr and NaNCS, all of AnalaR grade purity, were used to prepare solutions of anions. Lithium *p*-toluenesulfonate was prepared by neutralization of 4M Hpts (Aldrich) with Li_2CO_3 (BDH). The product was recrystallized twice from water.

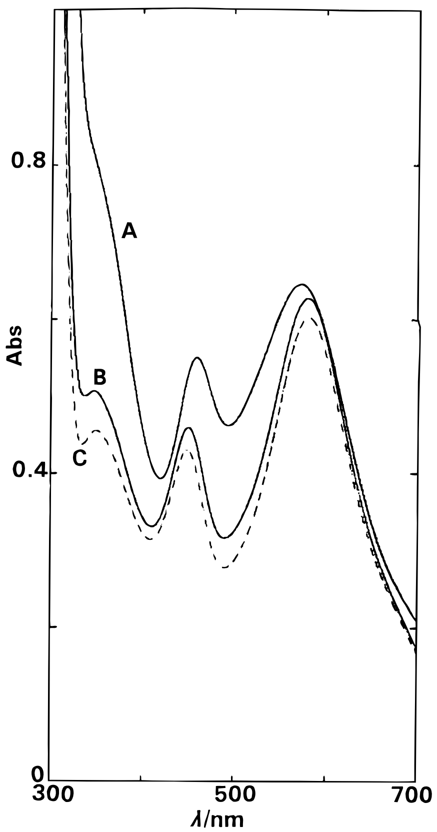

Figure 1. Absorbance spectrum (1 cm path pength) of the purple double cube $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ (~0.23 mM) (A) and changes observed on addition of a 10-fold excess of Cl^- to give the single cube $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ (B), followed by a large excess (1.0 M) giving Cl^- complexing at the Mo's (C). Both solutions (B) and (C) are dark blue; ϵ's are as in text.

Preparation of $[Mo_3FeS_4(H_2O)_{10}]^{4+}$. Iron wire (1 g; Johnson Matthey Specpure) was added to $[Mo_3S_4(H_2O)_9]^{4+}$ (50 mL of 1 mM) in 2.0M $HClO_4$, and the mixture was allowed to react for ~1 h under N_2 gas.[14] Purification was by loading a solution diluted to <0.5M $HClO_4$ onto an O_2-free Dowex 50W-X2 cation-exchange column (1 cm × 20 cm). The column was washed with 0.5 M (100 mL) followed by 1.0 M $HClO_4$ (100 mL) and then eluted with 2.0 M $HClO_4$. The gray/purple $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ product was eluted prior to green $[Mo_3S_4(H_2O)_9]^{4+}$. Storage was done at 4 °C under N_2. UV−vis spectrum, λ/nm (ϵ/M^{-1} cm^{-1} per cube): 503 (730), 603 (448), 970 (122). Solutions were generally used within 24 h of preparation.

Electrochemistry. Electrodes used were a Metrohm glassy-carbon working electrode, Pt secondary electrode, and standard calomel reference electrode. No meaningful redox properties were observed using cyclic voltammetry. The chloride-based reference electrode initiates conversion of the double to single cube, and the single cube starts to decompose at E_{pa} = 0.714 V.

Stability. Both the single and double Mo_3PdS_4 cubes are air stable over long periods. The single cube $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ in 2.0 M HCl takes 3−4 weeks to decompose completely to $[Mo_3S_4(H_2O)_9]^{4+}$, (2). The double cube requires several months for a similar conversion to occur.

Kinetic Studies. Reactions were carried out at 25.0 ± 0.1 °C and ionic strength I = 2.00 ± 0.010 M adjusted with Li(pts). Reactions of

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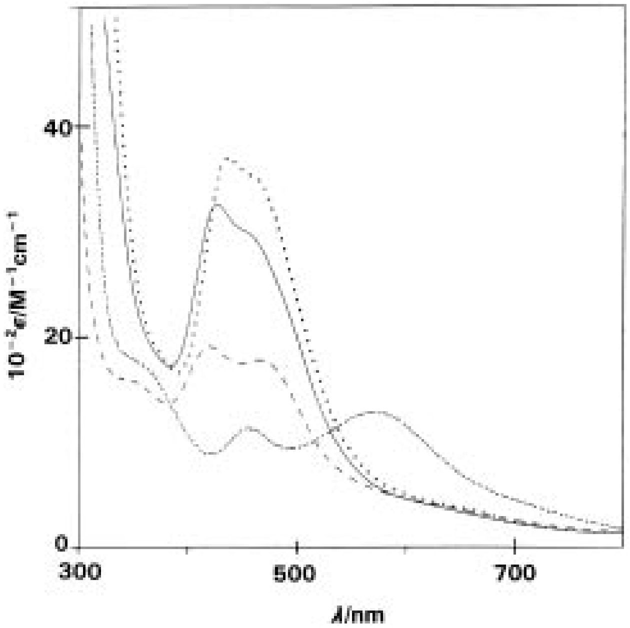

Figure 2. UV−vis absorbance spectra in 2.0M Hpts of the double cube $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ (− • −) and the products of the reactions with CO, PTA, and $TPPTS^{3-}$, assigned the formulas $[Mo_3(PdCO)S_4(H_2O)_9]^{4+}$ (---), $[Mo_3(PdPTA)S_4(H_2O)_9]^{4+}$ (—), and $[Mo_3(PdTPPTS)S_4(H_2O)_9]^{+}$ (···), respectively.

$$2Mo_3PdS_4^{\ 4+} + O_2 + 4H^+ \rightarrow 2Mo_3S_4^{\ 4+} + Pd^{2+} + 2H_2O \quad (2)$$

the double cube with CO (420 nm) and with the two phosphines (440 nm), all of which give purple to orange color changes, were monitored using Dionex D-110 and Applied Photophysics stopped-flow spectrophotometers. Absorbance changes for complete reactions are as indicated in Figure 2. First-order rate constants obtained for the first stage are defined as k_{1obs}. The phosphine reactions are at the limit of the stopped-flow range and require an instrument with dead-time/mixing ~1 ms.

In the case of the anionic reactants Cl^-, Br^-, and NCS^-, absorbance changes were not sufficiently large, and the rates were too fast for the double to single cube conversion to be monitored. With Cl^- and Br^-, secondary changes at the lower limit of the stopped-flow range gave biphasic equilibration kinetic behavior (~66% and ~33% absorbance changes respectively). The spectrophotometer was interfaced to an IBM PC/AT-X computer for data acquisition using software from On-Line Instrument Systems (OLIS, Bogart, GA). For the NCS^- reaction, two stages (both ~30% absorbance contributions), one of them corresponding an isomerization step (k_{isom}), were determined by the stopped-flow method, and a further rate constant (~40% change) was obtained by conventional spectrophotometry. From the dependencies of measured rate constants on [X], forward and back rate constants were evaluated. Those for the forward reactions k_{2f}, k_{3f} are considered relevant in the context of this paper.

Stability Constants for the Complexing of X with $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$. These were determined from spectrophotometric changes observed on addition of Cl^-, Br^-, and NCS^- to the double cube. For anion concentrations up to ~10-fold those of the double cube, complexing occurs at the Pd. Complexing brings about the dimer to monomer change. The equilibration processes can be expressed as in (3), which defines the constant K_1. Values of K_1 (25 °C) were determined at $I = 2.00 \pm 0.010$ M (Li(pts)).

$$[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+} + 2X \rightleftarrows [Mo_3(PdX)S_4(H_2O)_9]^{4+} \quad (3)$$

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

Results

Reaction of $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ with CO. Upon bubbling of CO through solutions of the double cube $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$, a yellow-orange product is obtained. The same product is observed for the reaction of the single cube $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$, which has been characterized by X-ray crystallography with 1,4,7-triazacyclononane (abbreviated to tacn or 9-aneN_3) coordinated to give $[Mo_3(PdCO)S_4(tacn)_3]^{4+}$.[2] The overall reaction is as in (4). For stopped-flow kinetic

$$[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+} + 2CO \rightarrow 2[Mo_3(PdCO)S_4(H_2O)_9]^{4+} \quad (4)$$

studies aliquots of a saturated aqueous stock solution of CO (1.43 mM) were used with no apparent losses over >1 h. From absorbance changes at 420 nm (increase) and 570 nm (decrease), satisfactory uniphasic first-order fits were obtained, giving rate constants k_{obs} with CO in >20-fold excess of the double cube. The extent of reaction was >94% in all cases. The reaction is first-order in [CO], Figure 3, and no dependence on $[H^+]$ in the range $[H^+] = 0.30-2.00$ M was observed. The second-order rate constant (25 °C) for the reaction of CO with the double cube is $(1.11 \pm 0.02) \times 10^5$ M^{-1} s^{-1}. No intercept corresponding to the back-reaction was detected, and it is concluded that the carbonyl product $[Mo_3(PdCO)S_4(H_2O)_9]^{4+}$ is very stable ($K_1 > 5 \times 10^4$ M^{-1}) with no tendency to aquate under the conditions studied.

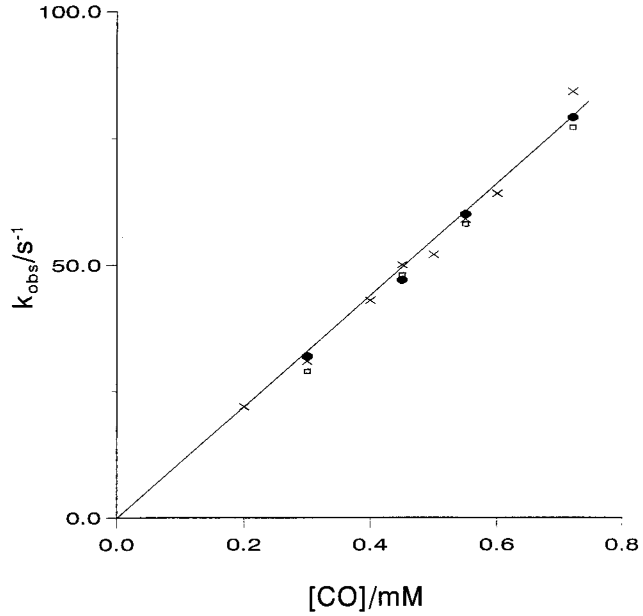

Figure 3. Dependence of first-order rate constants k_{obs} (25 °C) on [CO] for the reaction of the double cube $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ (0.02 mM) with CO, at $[H^+]$/M = 2.00 (×), 1.00 (●), 0.50 (□), and 0.30 (▲), I = 2.00 M (Li(pts)).

Reaction of $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ with the Two Phosphines. Both reactions are uniphasic and close to the upper limit of the stopped-flow range. Using a single-exponential fitting procedure, second-order rate constants were obtained (Table 1). No phosphine-independent contributions were observed, and second-order rate constants are assigned to the forward reaction (k_f). These are (average values) 2.78×10^6 M^{-1} s^{-1} (for PTA) and 9.6×10^5 M^{-1} s^{-1} (for $TPPTS^{3-}$).

Reaction of $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ with Cl^-. The two stages of reaction are as indicated in Figure 1. In this experiment the Cl^- was in sufficient excess (~10-fold) to complete stage 1 and then in large 1 M excess for complexing at the Mo, stage 2. The latter, a biphasic equilibration process, is considered later. The first stage of reaction at the Pd (purple to blue color change) is too fast for rate constants to be

Table 1. First-Order Rate Constants k_{obs} (25 °C) for the Complexing of Two Water-Soluble Phosphines with $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ in 2.00 M Hpts, I = 2000 M

reaction of 1,3,5-triaza-7-phosphaadamantane (PTA)			reaction of tris(3-sulfonatophenyl)phosphine ($TPPTS^{3-}$)		
[PTA]/mM	$[\{Mo_3PdS_4\}_2]$/mM	$10^{-6}k_f/M^{-1}\ s^{-1}$	$[TPPTS^{3-}]$/mM	$[\{Mo_3PdS_4\}_2]$/mM	$10^{-5}k_f/M^{-1}\ s^{-1}$
0.40	0.020	2.75	0.80	0.040	9.6
0.20	0.020	2.80	0.75	0.040	9.7
			0.40	0.040	9.5

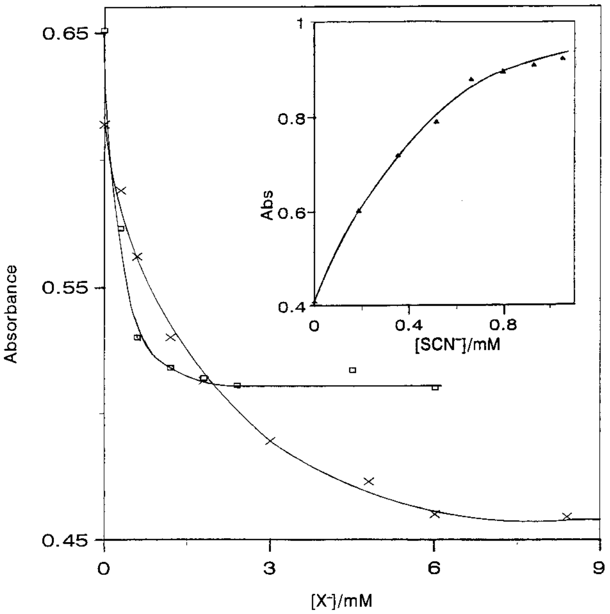

Figure 4. Absorbance changes (0.5 cm path length) at 500 nm indicating the extent of conversion of the double cube $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ (~0.70 mM) to the single cube as $[Mo_3(PdX)S_4(H_2O)_9]^{4+}$ with increasing amounts of X = Cl^- (×) and Br^- (□). Inset: absorbance changes at 425 nm for NCS^- (▲).

determined ($k > 10^5\ M^{-1}\ s^{-1}$). Small concentrations of Cl^- are able to induce the conversion of double to single cube, Figure 4. From these effects K as defined in (5), can be evaluated as 490 ± 90 M^{-1}.

$$[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+} + 2Cl^- \overset{K_1}{\rightleftharpoons} 2[Mo_3(PdCl)S_4(H_2O)_9]^{3+} \quad (5)$$

Reaction of $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ with Br^- and NCS^-. Similar features are observed with Br^-, which is more effective than Cl^- in inducing the double to single cube conversion, Figure 4. The color change is purple to green. From the data given, K_1 was determined as (8.04 ± 2.00) × $10^3\ M^{-1}$. For the reaction with NCS^- an identical treatment was used yielding K_1 = 630 ± 100 M^{-1}.

Further Complexing of Cl^-, Br^-, and NCS^- with $[Mo_3(PdX)S_4(H_2O)_9]^{4+}$. Smaller absorbance changes are observed after formation of the single-cube products $[Mo_3(PdX)S_4(H_2O)_9]^{4+}$ with X = Cl^-, Br^-, and NCS^-, e.g. Figure 1. Two further Mo substitution equilibria are observed. The latter are thermodynamically ~10^2 times less favorable than the first stages. From the linear dependences on [X], formation rate constants defined as $k_{2f}/M^{-1}\ s^{-1}$, $k_{3f}/M^{-1}\ s^{-1}$ are 2.8(1), ~0.2 for $[Cl^-]$ in the range 0.06–0.50 M; 8.6(3), ~1.0 for $[Br^-]$ in the range 0.01–0.12 M; and 17(1), ~0.2 for $[NCS^-]$ in the range 0.5–3.0 mM. Rate constants for the reverse aquation steps from the intercepts are less precise; see ref 24. With NCS^- an additional step independent of NCS^- is observed. This is assigned to isomerization, $k_{isom} = 0.015\ s^{-1}$, most likely a sequel to the first stage (k_{1f}) and a reaction corresponding to linkage isomerization PdNCS → PdSCN. The latter S-bonded form is thermodynamically more stable in terms of hard–soft acid–base theory, using a soft metal such as Pd in a lower oxidation state.[25]

Reformation of $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ from $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$. A solution of the chloro complex of the single cube $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ in 2.00 M Hpts was prepared by addition of Cl^- (10 mM) to $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ (1 mM). The Cl^- was removed by loading onto a Dowex cation-exchange column and eluting with 4 M Hpts or by adding an excess of $AgClO_4$ solution and filtering off the AgCl precipitate. In both cases, the resultant solution gave the color (purple) and spectrum of the double cube $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$.

Complexing of NCS^- with $[Mo_3FeS_4(H_2O)_{10}]^{4+}$. This reaction was studied to provide a comparison with the reactions in the previous section and help make assignments. Complexing of Cl^- at the Fe of $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ has previously been shown to be rapid with rate constants >2 × $10^4\ M^{-1}\ s^{-1}$.[14] Here we chose to study the complexing of $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ (0.25 mM) with NCS^- in the range 4.0–10.0 mM at 25 °C, I = 2.00 M ($HClO_4$). Following the rapid complexing of NCS^- at the Fe, it was of interest to explore other subsequent substitution processes. Biphasic kinetics were observed, and equilibria monitored at 435 nm were assigned to complexing at Mo. From the linear dependencies on $[NCS^-]$ formation rate constants are k_{2f} = 0.38(3) $M^{-1}\ s^{-1}$ and k_{3f} ~0.06 $M^{-1}\ s^{-1}$.

Discussion

The edge-linked double cube $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ (purple), which exists in the weakly coordinating acids $HClO_4$ and Hpts, is converted into single-cube forms by six reagents X. Products obtained with for example Cl^- and CO are $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ (blue) and $[Mo_3(PdCO)S_4H_2O)_9]^{4+}$ (yellow-brown), respectively. With CO and the two water-soluble phosphines, 1,3,5-triaza-7-phosphaadamantane (PTA) and tris(3-sulfonatophenyl)phosphine ($TPPTS^{3-}$), complexing is at the Pd only. It has been noted previously that CO and $TPPTS^{3-}$ do not react with the all-Mo clusters $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_4S_4(H_2O)_{12}]^{5+}$.[15]

The products of the reactions with CO and the two phosphines have sufficiently intense absorbance bands, Figure 2, for the fast first stage of reaction to be monitored. The rate laws are first-order in double cube and reagent X and support a mechanism in which X induces formation of the single cube. No back-reaction (i.e. intercept in Figure 3) is observed, and it can be concluded that in the case of CO the formation constant K_1 defined by (3) is >5 × $10^4\ M^{-1}$. Stepwise cleavage of the intercube links (broken lines) can be written as in (6) and (7). If (7) proceeds with involvement of H_2O rather than a second X, then a subsequent (rapid) step involving substitution of X for H_2O is required. An alternative mechanism in which the double cube is involved in a dissociation equilibrium process

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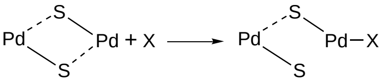
[24] Saysell, D. M. Ph.D. Thesis, University of Newcastle, Newcastle upon Tyne, U.K., 1996.

[25] E.g.: Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry*, 4th ed.; Harper and Collins College Publishers: New York, 1993; pp 350–355.

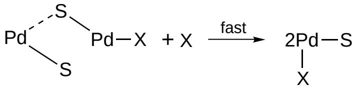
Table 2. Comparisons of Kinetic and Thermodynamic Data (25 °C) for X-Induced Conversions of $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ to the Related Single-Cube Forms $[Mo_3(PdX)S_4(H_2O)_9]^{4+}$, $I = 2.00$ M (Li(pts))[a]

reactant X	k_{1f}/ $M^{-1}\,s^{-1}$	K/ M^{-1}	reactant X	k_{1f}/ $M^{-1}\,s^{-1}$	K/ M^{-1}
CO	1.11×10^5	$>5 \times 10^4$	Cl^-	$>10^{5}$[c]	490
PTA	27.8×10^5	*b*	Br^-	fast[c]	8040
$P(C_6H_4SO_3)_3^{3-}$	9.6×10^5	*b*	NCS^-	fast[c]	630

[a] No dependences on $[H^+] = 1.0{-}2.0$ M are observed. [b] Also very favorable. [c] Absorbance changes smaller; too fast to follow.



(6)



(7)

(8) followed by reaction with X, (9), can be ruled out, since it would give a half-order dependence on $[\{Mo_3PdS_4(H_2O)_9\}_2{}^{8+}]$.

$$[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+} + 2H_2O \rightleftarrows 2[Mo_3PdS_4(H_2O)_{10}]^{4+} \tag{8}$$

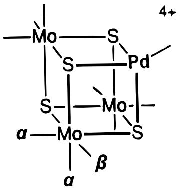
$$[Mo_3PdS_4(H_2O)_{10}]^{4+} + X \rightarrow [Mo_3(PdX)S_4(H_2O)_9]^{4+} \tag{9}$$

The first stage of reaction of Cl^-, Br^-, and NCS^- with the double cube is too fast to monitor by the stopped-flow method. A high affinity of X for Pd is indicated by the following K_1/M^{-1} values: Cl^-, 490; Br^-, 8040; NCS^- (630). These parallel but are $\sim 10^2$ times greater than corresponding K/M^{-1} values (25 °C) obtained for the 1:1 complexing of Cl^- (2.98) and Br^- (14.7) to square-planar $[Pd(H_2O)_4]^{2+}$, (10); $I = 1.00$ M

$$[Pd(H_2O)_4]^{2+} + X \rightleftarrows [Pd(H_2O)_3X]^{2+} + H_2O \tag{10}$$

($HClO_4$).[26] The rate constants k_f for the forward reactions with $[Pd(H_2O)_4]^{2+}$ are 1.83×10^4 $M^{-1}\,s^{-1}$ (Cl^-) and 9.2×10^4 $M^{-1}\,s^{-1}$ (Br^-), the ratio indicating a controlling influence of k_f on the magnitude of K.[27] The rate constants $k_1/M^{-1}\,s^{-1}$ for CO (1.1×10^5), PTA (27.8×10^5), and $TPPTS^{3-}$ (9.6×10^5) and the lower limit for Cl^- ($>10^5$ $M^{-1}\,s^{-1}$) indicate a facile double-cube-cleavage process. With Ni as the heterometal in $[Mo_3NiS_4(H_2O)_9]^{4+}$, there is no edge-linked double cube, and substitution of H_2O at the Ni is appreciably slower than the k_1 step in the present studies, with the following rate constants/ $M^{-1}\,s^{-1}$: CO, 0.66; PTA, 119; $TPPTS^{3-}$, 58; Cl^-, 9.4; Br^-, 14.6; NCS, 44.[15]

With X = Cl^-, Br^-, NCS^- at levels greater than those required to give $[Mo_3(PdX)S_4(H_2O)_9]^{4+}$, further absorbance changes are observed. This is illustrated for Cl^- in Figure 1. The occurrence of biphasic kinetics for the subsequent step was confirmed by prior addition of a sufficent excess of X (Cl^- or Br^-) to give $[Mo_3(PdX)S_4(H_2O)_9]^{4+}$, followed by stopped-flow mixing with a second amount of X. The reaction steps observed are assigned to substitution at Mo. Initial complexing of NCS^- at the Fe on $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ is also fast, and slower biphasic kinetics were again observed in a second stage. The biphasic steps are due either to nonidentical (α and *β*) H_2O's on each Mo as illustrated



or to nonidentical Mo's. If Fe, like Pd, is in oxidation state II,[28] then the Mo_3 component can be written as $Mo^{III}{}_2Mo^{IV}$ and the possibility of nonidentical Mo's arises. This has been observed previously in the case of $[Mo_4S_4(H_2O)_{12}]^{5+}$ giving rise to two different kinetic (substitution) processes.[29,30] At present, although inclined to favor the latter, we are not able to distinguish between the two possibilities. The rate constants $k_{2f}/M^{-1}\,s^{-1}$ for Cl^- (2.8), Br^- (8.6), and NCS^- (17), and similarly for k_{3f}, are within a factor of 6 of each other and indicate a dissociative I_d mechanism.[31]

To summarize conversion of the edge-linked double cube $[\{Mo_3PdS_4(H_2O)_9\}_2]^{8+}$ to the single cube $[Mo_3(PdX)S_4(H_2O)_9]^{4+}$, induced by X = CO, PTA, $TPPTS^{3-}$, Cl^-, Br^-, and NCS^-, is rapid and is at the limit of the stopped-flow range. Removal of X leads to re-formation of the double cube. Formation constants K_1 are high and indicate a preference for complexing of X over H_2O, which is not able to retain the single-cube structure. With Cl^-, Br^-, and NCS^- a slower biphasic stage corresponding to Mo substitution is observed. Similar behavior is noted also for NCS^- with $[Mo_3FeS_4(H_2O)_{10}]^{4+}$. Interconversions of other edge-linked double cubes $[\{Mo_3MS_4(H_2O)_9\}_2]^{8+}$ with M = $Co^{3,4}$ and $Cu^{5,32}$ are more difficult to study because of air sensitivity. Other recent examples of edge-linked structures have been noted in studies on Fe_3Mo and Re_6 chalcogenide/halide clusters.[33,34]

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Supporting Information Available: Listings of kinetic data and a figure showing plots of k_{2eq} and k_{3eq} vs $[Cl^-]$ (7 pages). Ordering information is given on any current masthead page.

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