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Nature of the Interaction and Photophysical Properties of $[Mo_6Cl^i_8(SO_3CF_3)^a_6]^{2-}$ and $[Mo_6Cl^i_8Cl^a_6]^{2-}$ on Silica Gel

L. M. Robinson, H. Lu, J. T. Hupp, and D. F. Shriver*

Department of Chemistry and Materials Research Center, Northwestern University, Evanston, Illinois 60208

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The nature of the interaction between silica gel and $[Mo_6Cl^i_8(SO_3CF_3)^a_6]^{2-}$ (**1**) and $[Mo_6Cl^i_8Cl^a_6]^{2-}$ (**2**) in organic media is described. Silica gel, which contains a high density of Si–OH groups, strongly adsorbs clusters **1** and **2**. Although **1** is adsorbed from CH_2Cl_2 and solvents of high dielectric constant, such as CH_3OH, **2** is adsorbed only from CH_2Cl_2 solution. In CH_2Cl_2, basic silica gel, containing a small percentage of anionic Si–O⁻ sites, coordinates with Mo atoms of **1** by replacement of labile triflate groups. In more polar solvents, such as CH_3OH and CH_3CN, the triflate ligands of **1** are replaced by solvent molecules to produce $[Mo_6Cl^i_8(\text{solvent})^a_6]^{4+}$, which can then covalently attach to the silica gel surface. Presumably, Si–OH ionization is promoted in these polar media to yield SiO⁻ surface sites. Under the same conditions, the less substitutionally labile cluster, $[Mo_6Cl^i_8Cl^a_6]^{2-}$, is not covalently attached to silica gel. The supported systems are stable to atmospheric moisture and O_2 but undergo decomposition in the presence of liquid water. Clusters bound by either electrostatic or covalent interaction display absorption and emission profiles virtually identical to those of solution species, indicating that the clusters are intact. Transient emission measurements reveal that supported **1** retains the characteristic long-lived excited state in **1** in solution: $\tau_{gel} = 100\ \mu s$ and $\tau_{soln} = 110\ \mu s$. The photochemical properties of the silica gel bound molybdenum cluster are retained, as indicated by luminescence quenching by O_2 and phenothiazine.

Introduction

The present work was designed to explore the interaction of silica gel with the hexanuclear molybdenum clusters $(Bu_4N)_2[Mo_6Cl^i_8L^a_6]$ (i and a refer to face-bridging and axial ligands, respectively, and L = $SO_3CF_3^-$, Cl^-; Figure 1) to yield porous solids that might exhibit useful redox and photophysical properties. The molybdenum halide clusters are particularly interesting because of their unusually long exicted-state lifetimes ($\tau = 180\ \mu s$ for $[Mo_6Cl^i_8Cl^a_6]^{2-}$),[1a] which are among the longest known for any transition-metal complex. Upon absorption of visible or near-UV light, the electronically excited cluster can undergo electron transfer with electron acceptors or donors to generate $[Mo_6Cl^i_8Cl^a_6]^-$, a powerful oxidant, or $[Mo_6Cl^i_8Cl^a_6]^{3-}$ a powerful reductant (Figure 2).[1] The clusters have been examined as possible candidates for use in catalytic and photocatalytic redox cycles.[1] Although the behavior of the octahedral molybdenum halide clusters in solution has been studied extensively,[1] we are aware of only two attempts to support these systems. Newsham et al. reported that Mo_6Cl_{12} encapsulated in a sol–gel matrix or incorporated into poly(vinylpyridine) polymers retains a long emissive lifetime.[2a,b] Recently, Golden et al. copolymerized *n*-vinylimidazole (NVI) with $[Mo_6Cl^i_8(NVI)^a_6]^{4+}$ to form a cross-linked polymer matrix.[2c]

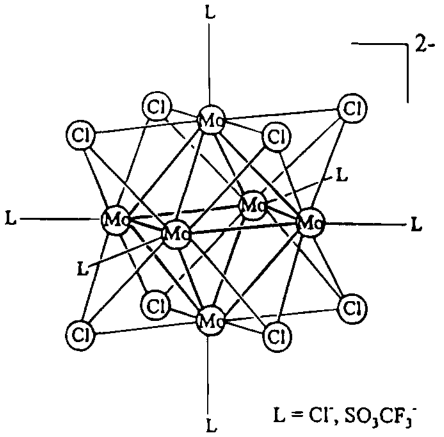

Figure 1. Representation of the $[Mo_6Cl^i_8L^a_6]^{2-}$ clusters. Six molybdenum clusters form an octahedral metal core. Eight face-bridging chlorides, designated by the i superscript, cap the faces of the metal octahedron. Six additional ligands occupy the axial positions, which are designated by superscript a.

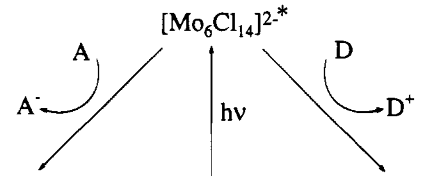

Figure 2. Redox and photochemistry of the $[Mo_6Cl^i_8Cl^a_6]^{2-}$ clusters. Reduction potentials are reported vs SCE in dichloromethane. Data from ref 1e.

Silica gel, a microporous solid, readily adsorbs a variety of organic and inorganic compounds from the

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gas phase or solution.[3-6] Nonspecific dispersion forces as well as weak electrostatic interactions[3] promote adsorption of molecules.[6] Additionally, chemical interaction resulting in formation of covalent bonds may occur between the adsorbate and Si−OH groups on the silica gel.[3]

The silanol groups of silica gel are weakly acidic ($pK_a = 7.1 \pm 0.5$)[7] and readily undergo exchange with simple cations (i.e., Na^+, Ca^{2+}, etc.) in basic aqueous solution. Burwell et al. extended this chemistry to the ion-exchange of transition-metal coordination complexes on "basic" silica gel containing a small percentage of anionic $Si-O^-$ sites.[8] Cations such as $[Cr(NH_3)_6]^{3+}$, $[Co(en)_2Cl_2]^+$, and $[Co(en)_2Cl(H_2O)]^{2+}$ are readily ion-exchanged onto base-treated silica gel in aqueous media.[8] Similarly, silica gel adsorbs $[Ru(bpy)_3]^{2+}$ from basic aqueous solution.[9] Examples of chemical reaction between adsorbate and silanol groups include the adsorption of FeTPPCl, MnTPPCl, and CoTPPCl (TPP = tetraphenylporphyrin) with subsequent formation of HCl.[10] Similarly, complexes such as $Rh(allyl)_3$[11] and $MoCl_5$[12] react with silanol groups, forming Si−O−M bonds with loss of C_3H_6 and HCl, respectively.

Silanol groups also serve as strong hydrogen bond donors, rendering silica gel a polar, microporous medium. Chronister et al. determined, with use of Reichardt's dye,[13] that silica gel is more polar than methanol and slightly less polar than 2,2,2-trifluoroethanol or water.[14] Accordingly, many polar organic molecules, such as 1,5-dinitronaphthalene and 1-acetonaphthalene, are strongly adsorbed.[15] The adsorption of organometallic species, such as $Os_3(CO)_{12}$ and $Fe_3(CO)_{12}$, on silica gel is also well documented.[3-5,16,17]

The affinity of a molecule or ion pair for silica gel may be described by a partition coefficient (K'), which is the ratio (moles of solute per gram of adsorbent)/(moles of solute per milliliter of solvent phase).[18] Adsorption of a solute is strongly influenced by the number, identity and arrangement of substituents, as well as the eluting strength of the solvent.[18,19]

In the present study, $[Mo_6Cl^i_8(SO_3CF_3)^a_6]^{2-}$ (**1**)[20] was employed as the solute because the $SO_3CF_3^-$ ligands are readily displaced. This presents the opportunity to coordinate the cluster to $Si-O^-$ groups of basic silica gel or adsorb the solvated $[Mo_6Cl^i_8(solvent)^a_6]^{4+}$ cluster cation by ion exchange. Simple adsorption of the clusters without covalent bond formation to silica gel was also explored with the much less substitutionally labile cluster $[Mo_6Cl^i_8Cl^a_6]^{2-}$ (**2**).

Experimental Section

General Experimental. The tetrabutylammonium salts of $[Mo_6Cl^i_8(SO_3CF_3)^a_6]^{2-}$ (**1**) and $[Mo_6Cl^i_8Cl^a_6]^{2-}$ (**2**) were synthesized by methods described in the literature.[20,21] Silica gel (Davisil, 100−200 mesh, 150 Å pore size, 300 m^2/g) was supplied by Aldrich and pretreated before use as detailed below. Sodium hydroxide, tetrabutylammonium hydroxide, and phenothiazine were used as received from Aldrich. Tetrabutylammonium chloride hydrate (Aldrich) was heated under vacuum to remove associated water. Except for the pretreatment of the silica gel supports, all reactions were conducted under prepurified dinitrogen. The solvents (1,2-dichloroethane, acetonitrile, methanol, methylene chloride, tetrahydrofuran) were dried and freshly distilled. Moisture sensitive reactants were stored in a drybox.

Preparation of Supports. To prepare the *acidic gel*, approximately 10 g of silica gel was washed repeatedly with a 0.1 M solution of $HOSO_2CF_3$, triflic acid, in order to remove basic impurities. This gel suspension was washed to neutrality with deionized water to remove excess triflic acid. The acidic gel was dried at 150 °C in an oven for at least 5 h, followed by an additional drying step at 175 °C, under vacuum, for at least 12 h. The dehydrated acidic gel was stored in a drybox until further use.

In the preparation of the *basic gel*, adapted from the procedure of Burwell et al.,[8b] approximately 10 g of silica gel was washed several times with a 0.1 M HNO_3 or $HOSO_2CF_3$ solution and then washed with deionized water to neutrality. The gel was then washed repeatedly with a pH 10 solution of NaOH or Bu_4NOH (more basic solutions dissolve the silica gel) until the washings tested basic. This basic gel was again washed with deionized water to remove excess base. This procedure converts a small percentage of surface silanol groups to basic $Si-O^-\ C^+$ ($C^+ = Na^+, Bu_4N^+$) siloxide sites.[8b] The concentration of basic sites on the gel (approximately 4.4×10^{-5} mol/g of SiO_2) was determined by stirring a 1.0 g sample of the gel with 0.010 M HCl and back-titrating the supernatant solution with 0.010 M NaOH, by the method of Burwell et al.[8b] The basic gel was then dried as described in the preparation of the acidic gel.

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(3) In this paper, we employ the term *electrostatic interactions* to denote polar interactions between $[Bu_4N]_2[Mo_6Cl^i_8Cl^a_6]$ or $[Bu_4N]_2[Mo_6Cl^i_8(SO_3CF_3)^a_6]$ and the silica gel surface by charge−dipole, dipole−dipole, or hydrogen-bonding interactions. As used here, the term *covalent interaction* denotes the coordination of the molybdenum cluster to the silica gel surface by one or more Si−O−Mo bonds.

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Table 1. Adsorption of $(Bu_4N)_2[Mo_6Cl^i_8(SO_3CF_3)^a_6]$ and $(Bu_4N)_2[Mo_6Cl^i_8Cl^a_6]$ to Silica Gel

			$(Bu_4N)_2[Mo_6Cl^i_8(SO_3CF_3)^a_6]$		$(Bu_4N)_2[Mo_6Cl^i_8Cl^a_6]$	
solvent	donor no.	ϵ	mol of cluster × 10^5/g of basic SiO_2	mol of cluster × 10^5/g of acidic SiO_2	mol of cluster × 10^5/g of basic SiO_2	mol of cluster × 10^5/g of acidic SiO_2
CH_2Cl_2			4.3	4.5	3.3	3.4
CH_3CN	14.1	36	2.4	2.6	0.0	0.0
CH_3OH	20.0	32.6	4.0	4.2	0.0	0.0

Synthesis of Supported Cluster Systems. A 0.050 g (2.3×10^{-5} mol) sample of **1** or 0.025 g (2.3×10^{-5} mol) sample of **2** and 0.50 g of SiO_2 were suspended in 15 mL of solvent (CH_2Cl_2, CH_3CN, or CH_3OH) and stirred for approximately 30 min. The supernatant was removed, an additional 10 mL of the appropriate solvent was added to the gel, and the suspension was stirred for at least 10 min to wash the gel free of any unsupported cluster. This process was repeated and the combined supernatants were filtered through a glass frit covered with a layer of Celite to remove any SiO_2. Solvent was removed under vacuum, and the residue redissolved in 5.0 mL CH_2Cl_2 for subsequent UV−vis analysis.

Competitive Adsorption Studies with Bu_4NCl and $Bu_4NSO_3CF_3$. The supported cluster systems, obtained as described above, were washed with 4 × 10 mL portions of a 0.02 M Bu_4NCl solution in CH_2Cl_2. For each addition of Bu_4NCl, the suspension was stirred for approximately 20 min, and the supernatant removed. All supernatant fractions were combined and filtered through a sintered glass frit covered with a layer of Celite to remove fine SiO_2 particles. All solvent was removed, and the residue redissolved in 10.0 mL of CH_2Cl_2. The concentration of the cluster in the combined fractions was determined by UV−vis spectroscopy. A similar experiment was performed with $Bu_4NSO_3CF_3$ as the eluent. The amount of cluster eluted was comparable to that obtained with Bu_4NCl, indicating that the chloride ion does not promote Mo−O−Si bond cleavage.

Adsorption Studies with $Bu_4NSO_3CF_3$. A 0.010 g sample of $Bu_4NSO_3CF_3$ (2.6×10^{-5} mol) was stirred with a suspension of 0.50 g SiO_2. The supernatant solution was removed and the gel washed with 3 × 10 mL portions CH_2Cl_2. All supernatants were combined and filtered as described above. After removal of solvent under vacuum, the residue was redissolved in CD_2Cl_2 and ^{19}F NMR was used to determine the amount of $Bu_4NSO_3CF_3$ present, with $(Bu_4N)_2[Mo_6Cl^i_8(SO_3CF_3)^a_6]$ as an internal standard. Approximately 0.1×10^{-5} mol uncoordinated $SO_3CF_3^-$ was found in the supernatant, with 2.5×10^{-5} mol remaining adsorbed to the silica gel ($K' = 900$ mL/g).

pH Determination of Cluster/Gel Supernatant Solutions. A 0.020 g sample of $(Bu_4N)_2[Mo_6Cl^i_8(SO_3CF_3)^a_6]$ (9.0×10^{-6} mol) was stirred with 0.50 g of SiO_2 in 10.0 mL CH_2Cl_2, CH_3CN, or CH_3OH for approximately 30 min. For CH_3CN and CH_3OH suspensions, 1.0 mL of the supernatant was removed and added to 25.0 mL of deionized H_2O, and the pH of the mixture was determined. As CH_2Cl_2 is immiscible with H_2O, all of the CH_2Cl_2 supernatant was added to 10.0 mL of CH_3OH and stirred to extract any acid present. A 1.0 mL aliquot of the mixture was then added to 25.0 mL of deionized H_2O. The CH_2Cl_2 was allowed to settle out of the aqueous layer before the pH was measured.

Luminescence Quenching Studies with O_2 and Phenothiazine. A sample of silica gel supported cluster was suspended in O_2 saturated 1,2-dichloroethane, loaded into a 1.0 cm path-length quartz cuvette, and analyzed by fluorescence spectroscopy. For the phenothiazine quencher study, a sample of silica gel supported cluster and approximately 1.0×10^{-3} mol of phenothiazine were placed in a 1.0 cm path-length quartz cuvette, suspended in rigorously degassed 1,2-dichloroethane and analyzed by fluorescence spectroscopy.

Electronic Spectra. UV−vis spectra were acquired on a Varian Cary 1E spectrophotometer. Solution spectra were measured in CH_2Cl_2, using matched cells of 1.0 cm path length. The cells were capped with rubber septa and purged with nitrogen prior to use. Spectra of the SiO_2 supported clusters were obtained on a suspension of the gel in CH_2Cl_2 in a sample cell of 0.1 cm path length. A short path length was necessary to avoid excessive scattering by the suspended gel, which does not exactly match the index of refraction of CH_2Cl_2. A suspension of untreated SiO_2 in CH_2Cl_2 was used as the reference.

Table 2. $(Bu_4N)_2[Mo_6Cl^i_8(SO_3CF_3)^a_6]$ Covalently Bound to Silica Gel[a]

solvent	mol of cluster × 10^5/g of basic SiO_2	mol of cluster × 10^5/g of acidic SiO_2
CH_2Cl_2	1.1	0.0
CH_3CN	2.0	2.1
CH_3OH	3.4	3.6

[a] As determined by competitive adsorption studies with Bu_4NCl.

Fluorescence measurements were performed on a SPEX Fluoromax fluorimeter equipped with a 150 W Xe lamp, and a Czerny-Turner spectrometer was employed to provide monochromatic excitation ($\lambda_{exc} = 420$ nm). SiO_2-supported clusters were suspended in 1,2-dichloroethane or CH_2Cl_2 in 1.0 cm quartz cells, yielding fairly transparent samples. Solution spectra of **1** and **2** were determined in CH_2Cl_2. Features described as "fluorescence tails" did not move when the excitation wavelength was varied, indicating that they do not originate from light scattering (scattering varies as ν^4). ^{19}F NMR experiments were conducted on a Varian Gemini 300 MHz instrument with a $CFCl_3$ reference. Emissive lifetimes were determined by transient emission spectroscopy with pulsed N_2 laser excitation ($\lambda_{exc} = 337$ nm). Luminescence was monitored at 670 nm. Lifetimes were derived by using standard least-squares linear regression statistics. Pure cluster and cluster/gel samples were loaded, in a drybox, into 5 mm quartz tubes equipped with Teflon glass valves. Rigorously degassed 1,2-dichloroethane (at least five freeze−pump−thaw cycles) was then vacuum transferred into the tubes, which were flame sealed under vacuum.

Results

Supported $(Bu_4N)_2[Mo_6Cl^i_8(SO_3CF_3)^a_6]$ (1). The compound $(Bu_4N)_2[Mo_6Cl^i_8(SO_3CF_3)^a_6]$ (**1**) was adsorbed by stirring the dissolved cluster with a suspension of silica gel. The adsorption data are summarized in Table 1. Uptake of the cluster was rapid; the color of the initially bright yellow solution decreased significantly while the gel became intensely colored.

For a given solvent system, the uptake of **1** by the gel does not vary with the pretreatment of the silica gel, within experimental error (Table 1). Changes in the nature of the solvent employed as the suspending medium do influence the degree of initial cluster uptake, but the effect is not large under the conditions reported here. Acetonitrile disfavors adsorption by silica gel as compared with CH_2Cl_2 and CH_3OH.

Supported **1** is not removed by repeated washings with solvent; however, introduction of excess Bu_4NCl to the suspension results in significant desorption of the cluster, as reported in Table 2. In the CH_2Cl_2 suspensions, only 1.2×10^{-5} mol of cluster/g of silica gel (approximately 2 molecules/100 nm^2) is retained by the basic gel after repeated washings with Bu_4NCl solution, while none of the cluster is retained by the acidic gel. Interestingly, in the more polar solvents (CH_3CN and

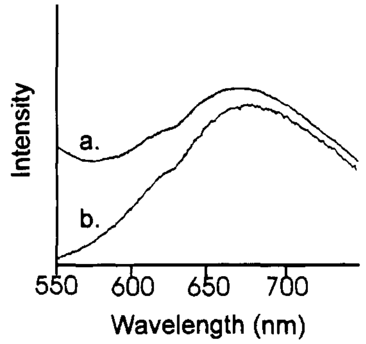

Figure 3. Comparison of fluorescence spectra of $(Bu_4N)_2[Mo_6Cl^{i}_8(SO_3CF_3)^{a}_6]$ supported on silica gel (a) and in solution (b). The fluorescence tail above 500 nm is due to fluorescence of surface hydroxyl groups or impurities on the silica gel.[24,25] Samples were run in 1,2-dichloroethane (λ_{exc} = 420 nm).

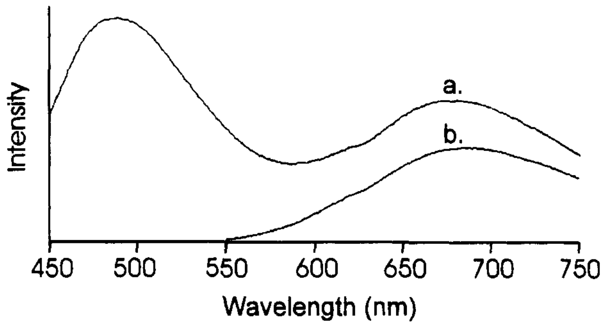

Figure 4. Comparison of fluorescence spectra of $(Bu_4N)_2[Mo_6Cl^{i}_8Cl^{a}_6]$ supported on silica gel (a) and in solution (b). The fluorescence tail at 480 nm is due to fluorescence of surface hydroxyl groups or impurities on the silica gel.[24,25] Samples were suspended or dissolved in 1,2-dichloroethane (λ_{exc} = 420 nm).

CH_3OH), less desorption of cluster is observed upon introduction of excess Bu_4NCl. With CH_3CN as solvent, approximately 2.1×10^{-5} mol of cluster/g of silica gel (approximately 4 molecules/100 nm^2) is retained on both acidic and basic gels. With CH_3OH as solvent, approximately 3.6×10^{-5} mol of cluster/g of silica gel (approximately 7 molecules/100 nm^2) is retained on both acidic and basic gels.

Supported $(Bu_4N)_2[Mo_6Cl^{i}_8Cl^{a}_6]$ (2). The compound $(Bu_4N)_2[Mo_6Cl^{i}_8Cl^{a}_6]$ (**2**) can be supported on basic or acidic silica gel, when CH_2Cl_2 is the suspending solvent (Table 2). No uptake of **2** by the gel is observed in more polar solvents such as CH_3CN or CH_3OH. The uptake of **2** from CH_2Cl_2 into silica gel is less than that of **1**; the partitioning coefficients are approximately 100 and 800 mL/g, respectively. Adsorbed **2** was completely removed from both acidic and basic silica gel by addition of excess Bu_4NCl.

Stability of the Supported Cluster Systems. The UV–vis absorption spectra of the silica gel/cluster systems are very similar to those of the clusters in homogeneous solution, differing only in the increased breadth of the absorption peaks. UV–vis spectra also indicate that supported **1** and **2** are stable for several months when suspended in organic solvents or subjected to atmospheric moisture and oxygen. In CH_2Cl_2 solution, the onset of absorption occurs at approximately 450 nm with λ_{max} at 297 and 313 nm for **1** and **2**, respectively. These absorption bands are broad and rather featureless at room temperature. The main absorption peak for the SiO_2/cluster suspensions in CH_2Cl_2 is very broad; however, the onset of absorption is also observed at 450 nm for both cluster systems. The range of λ_{max} is 290–300 nm for supported **1** and 310–315 nm for supported **2**. Diffuse reflectance measurements of the supported cluster systems also reveal broad, featureless absorption peaks. Similarly, fluorescence experiments conducted on suspensions of the silica gel supported clusters in CH_2Cl_2 reveal spectra virtually identical to the fluorescence spectra of **1** and **2** in solution. Very broad emission lines, with maxima at approximately 675 (**1**) and 685 nm (**2**) are observed for both supported and unsupported clusters as shown in Figures 3 and 4. The solution resulting from multiple washings of $[Mo_6Cl^{i}_8Cl^{a}_6]^{2-}$ or $[Mo_6Cl^{i}_8(SO_3CF_3)^{a}_6]^{2-}$/silica gel with Bu_4NCl has a UV–vis spectrum identical to that of $(Bu_4N)_2[Mo_6Cl^{i}_8Cl^{a}_6]$. These observations provide strong evidence of the integrity of the supported cluster.

Upon immersion in water while exposed to air, both supported **1** and **2** show signs of degradation. The color of the gel gradually changes from bright yellow to orange and finally brown over a period of several weeks. UV–vis spectra of the brown materials reveal completely featureless absorption profiles with an onset near 450 nm and lack of a distinct absorption maximum in the 300 nm region. This degradation is likely caused by hydrolysis leading to destruction of the hexanuclear cluster core. Similar behavior has been observed for **1** dissolved in organic solvents upon introduction of H_2O; however, degradation of the solution species occurs almost immediately.

Discussion

A major issue in this research was to distinguish cluster species that are retained on silica gel by electrostatic interactions from clusters that are covalently bound to silica gel. IR and Raman spectra are of limited utility in making this distinction. High background signals from SiO_2 and the breadth of the UV–vis and fluorescence spectra render these techniques insensitive to the nature of the cluster–SiO_2 interaction. Moreover, solvent effect on the uptake of **1** and **2** by silica gel offered no clear evidence of covalent as opposed to electrostatic interaction. The eluting strengths (expressed as relative adsorption energy of solvent per unit area silica gel, with *n*-pentane as the 0.0 reference point) of CH_2Cl_2, CH_3CN and CH_3OH on silica gel are 0.42, 0.65, and 0.95, respectively.[18] The uptake of cluster **2** was found to be substantial in the least eluting solvent, CH_2Cl_2. By contrast, the uptake of the cluster **1**, varies only slightly with the dielectric and eluting strength of the solvent.

Cluster Interaction with Acidic Silica Gel. The literature on the uptake of simple metal complexes by silica gel indicates that the interaction between acidic silica gel and the molybdenum clusters may arise from (1) replacement of axial triflate or chloride ions by silanol groups, (2) deprotonation of silanol groups with displacement of $SO_3CF_3^-$ or Cl^- ligands and the formation of Si–O–Mo bonds, or (3) partitioning of the clusters between the support and solvent. Each of these possibilities were examined.

Interaction of $(Bu_4N)_2[Mo_6Cl^{i}_8Cl^{a}_6]$ with Acidic Silica Gel. In CH_2Cl_2, the interaction of **2** with acidic silica gel is due to electrostatic interactions and can be expressed in terms of the partition coefficient, K' (K' = moles of solute per gram of adsorbent/moles solute per milliliter of solvent phase). The observed value is large (100 mL/g), indicating that association of the cluster with the polar silica gel medium is favored over interaction with the solvent phase. In more polar media, such as CH_3CN and CH_3OH, the affinity of the support for solvent molecules is greater than its affinity for the cluster, and **2** is not adsorbed by the silica gel ($K' \approx 0$ mL/g). Compound **2** is quantitatively eluted from the acidic gel upon addition of a solution of Bu_4NCl or $Bu_4NSO_3CF_3$ in CH_2Cl_2, indicating that **2** is not covalently bound to silica gel. Given that the chloride ligands of $[Mo_6Cl^i{}_8Cl^a{}_6]^{2-}$ are relatively strongly bound to the molybdenum,[1] it is logical that axial chloride ligands are not replaced by the acidic silanol groups and do not undergo reaction to form HCl and Si−O−Mo bonds. We conclude that the equilibrium for reaction of acidic silica gel (A) silanol protons with $[Mo_6Cl_{14}]^{2-}$ lies far to the left (eq 1). The present results are consistent with

$$A{-}(SiOH)_n + [Mo_6Cl^i{}_8Cl^a{}_6]^{2-} \overset{CH_2Cl_2}{\rightleftharpoons} [A{-}(SiO)_n{}^a\, Mo_6Cl^i{}_8Cl^a{}_{6-n}]^{2-} + nHCl \quad (1)$$

numerous examples of adsorption of ions, polar organics and transition-metal complexes on silica gel.[3-8]

Interaction of $(Bu_4N)_2[Mo_6Cl^i{}_8(SO_3CF_3)^a{}_6]$ with Acidic Silica Gel. In noncoordinating solvents such as CH_2Cl_2, the axial triflate ligands of $[Mo_6Cl^i{}_8(SO_3CF_3)^a{}_6]^{2-}$ remain bound to the cluster core.[20] In solvents of moderate to high Lewis basicity ("donor number") such as CH_3OH, the triflate ligands are displaced by solvent molecules to form the solvated cluster cation $[Mo_6Cl^i{}_8(solvent)^a{}_6]^{4+}$.[20] In CH_3CN, the cluster species exists between these two extremes, retaining approximately half the triflate ligands as $[Mo_6Cl^i{}_8(SO_3CF_3)^a{}_x(CH_3CN)^a{}_{6-x}]^{(4-x)+}$.[20] The partitioning of **1** between the silica gel and solvent phases may, therefore, be influenced by both the relative polarity of the silica gel and solvent phase and by the nature of the solvated cluster. The CH_2Cl_2 solvent system and the more basic, polar media (CH_3CN, CH_3OH) will be discussed separately.

In CH_2Cl_2, **2** is strongly adsorbed by acidic silica gel (K' = 100 mL/g), and the acidic silica gel has an even higher affinity for the triflate cluster, with K' = 800 mL/g. The unusually high partition coefficient of the triflate cluster appears to arise from the affinity of silica gel for salts having large cations and anions, and triflate salts in particular. As determined by ^{19}F NMR experiments described in the Experimental Section, tetrabutylammonium triflate, $Bu_4NSO_3CF_3$, has approximately the same partition coefficient (K' = 900 mL/g) as $(Bu_4N)_2[Mo_6Cl^i{}_8(SO_3CF_3)^a{}_6]$ in the silica gel phase suspended in CH_2Cl_2.

Several lines of evidence indicate that in CH_2Cl_2 the large partition coefficient of **1** on acidic silica gel is not due to coordinative attachment through Si−O−Mo bonds. First, complete elution of the cluster from the support can be achieved with solutions of excess Bu_4NCl or $Bu_4NSO_3CF_3$ (Table 2). Second, for a suspension of silica gel in a CH_2Cl_2 solution of **1**, ^{19}F NMR experiments reveal only traces of free triflate ligand in the supernatant CH_2Cl_2. The UV−vis spectrum of this supernatant shows the presence of a small amount of molyb-denum cluster with a main absorption peak approximately 30 nm above that of **1**. This indicates that **1** has been attacked by some impurity "ligand" (L) present on the gel (perhaps trace H_2O or silicate fragments) and that the trace of triflate ligand observed in the NMR experiments serves as a counterion for a $[Mo_6Cl^i{}_8(L)^a{}_6]^{n+}$ species. Thus, the axial triflate ligands are not displaced by the acidic silanol groups. Finally, the remote possibility of reaction between silanol groups and triflate ligands to form triflic acid ($HOSO_2CF_3$) was investigated and discounted. No change in the pH of the supernatant of a CH_2Cl_2 suspension of supported **1** was observed. Negligible formation of $HOSO_2CF_3$ is reasonable, given that $HOSO_2CF_3$ is a much stronger acid than the silanol groups on silica gel. We conclude that for acidic silica gel, in low polarity solvents such as CH_2Cl_2, the triflate cluster is adsorbed by electrostatic interactions, rather than coordination of the cluster to the silica gel.

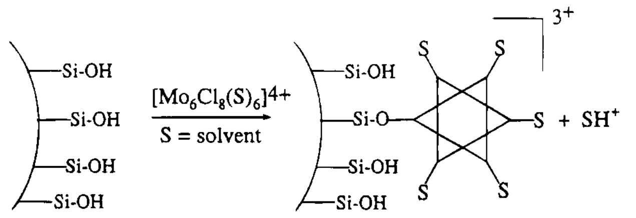

Figure 5. Proposed covalent bond formation between the solvated triflate cluster cation $[Mo_6Cl^i{}_8S^a{}_6]^{4+}$ and silica gel at deprotonated silanol sites (S = solvent molecule).

In more polar, basic solvents such as CH_3CN and CH_3OH, the interaction between acidic silica gel and $[Mo_6Cl^i{}_8(SO_3CF_3)^a{}_6]^{2-}$ is due to a combination of Si−O−Mo coordination and electrostatic interactions. As shown in Table 2, washing the silica gel supported cluster with excess Bu_4NCl solution removes only a fraction of **1** initially adsorbed from CH_3CN and CH_3OH solutions. These results suggest that a portion of **1** is not coordinated to the gel and is eluted with Bu_4NCl, while the cluster that remains on the silica gel is covalently bound to the support.

The chemisorption of **1** on acidic silica gel (A) likely arises from deprotonation of silanol groups in solvents such as CH_3OH and CH_3CN (eqs 2 and 3). This limited

$$A{-}(SiOH)_n \xrightarrow[CH_3OH]{CH_3CN} A{-}(SiO^-)_n + nH^+ \quad (2)$$

$$A{-}(SiO^-)_n + [Mo_6Cl^i{}_8(SO_3CF_3)^a{}_x(S)^a{}_{6-x}]^{(4-x)+} \xrightarrow[CH_3OH]{CH_3CN} [A{-}(SiO)_n{}^aMo_6Cl^i{}_8(SO_3CF_3)^a{}_x(S)^a{}_{6-x-n}]^{(4-x-n)+} + n(S) + xSO_3CF_3{}^- \quad (3)$$

dissociation of the weakly acidic silanol groups is followed by exchange of the solvated cluster cation $[Mo_6Cl^i{}_8(SO_3CF_3)^a{}_x\,(solvent)^a{}_{6-x}]^{(4-x)+}$ onto the deprotonated sites. Covalent attachment of the cluster to the deprotonated, anionic site on the silica gel then occurs by replacement of a solvent molecule or triflate group (Figure 5). Deprotonation of the silanol groups was monitored by pH measurements, as described in the Experimental Section. A decrease in pH corresponding to approximately 1.6 mol of H^+ released/mol of cluster adsorbed on the gel is observed for the CH_3OH suspension, after 30 min of stirring. For the CH_3CN system, only 0.5 mol of H^+/mol of cluster adsorbed is observed. After 24 h, the ratio increases slightly to 1.8 mol of H^+/mol of cluster adsorbed for the CH_3OH system. The $[H^+]$/[cluster] ratio is unchanged for the CH_3CN system.

These results are consistent with the idea that the CH_3OH solvated cluster cation $[Mo_6Cl^i_8(CH_3OH)^a_6]^{4+}$ possesses a higher charge than that of the CH_3CN solvated cluster cation $[Mo_6Cl^i_8(SO_3CF_3)^a_x(CH_3CN)^a_{6-x}]^{(4-x)+}$. Ion exchange of $[Mo_6Cl^i_8(CH_3OH)^a_6]^{4+}$ with silica gel would release up to four protons from surface silanol groups, in order to maintain charge neutrality. However, studies involving exchange of multipositive ($n+$) cations onto silica gel reveal that $n - 1$ or fewer protons are released per cation.[22] The $[H^+]$/[cluster] ratio for the CH_3OH system is consistent with this trend. Because the average charge on the CH_3CN solvated cluster is only 1+ (corresponding to replacement of one-half the triflate groups), exchange of only one proton per cluster ion is expected. The observed ratio, $[H^+]$/[cluster] = 0.5, indicates incomplete ion-exchange with surface Si–OH groups.

Cluster Interaction with Basic Silica Gel. The presence of anionic siloxide sites on the basic silica gel (approximately 4.4×10^{-5} mol/g of silica gel) presents the possibility of replacing axial chloride or triflate ligands of the clusters with siloxide groups, forming covalently bound clusters. This mode of interaction was also investigated.

Interaction of $(Bu_4N)_2[Mo_6Cl^i_8Cl^a_6]$ with Basic Silica Gel. Although potentially coordinating basic sites are available on the basic silica gel, **2** is not expected to be substitutionally labile under these reaction conditions. Complete substitution of axial Cl^- ligands by methoxide ligands, which are much more basic than the siloxide sites present on silica gel, requires reflux in methanol with excess sodium methoxide.[23] The main evidence against covalent attachment of **2** to the silica gel is the fact that no cluster is adsorbed on the gel from CH_3CN or CH_3OH solutions. The cluster is adsorbed on basic silica gel in CH_2Cl_2, but introduction of Bu_4NCl completely removes **2** from the gel. These results indicate that **2** is not coordinatively bound to the basic gel.

Interaction of $(Bu_4N)_2[Mo_6Cl^i_8(SO_3CF_3)^a_6]$ with Basic Silica Gel. As detailed below, a portion of the triflate cluster, **1**, in CH_2Cl_2 is weakly retained in the silica gel by nonspecific electrostatic forces, and another portion is bound by specific coordination of molybdenum atoms to surface siloxide donor sites. Unlike **2**, **1** has a high affinity for oxygen donor ligands, and alkoxides in particular.[20] Chemisorption occurs when one or more axial triflate ligands are replaced by basic siloxide sites on the silica gel (Figure 6). Competitive adsorption studies with Bu_4NCl (Table 2) reveal that the basic gel/cluster system synthesized in CH_2Cl_2 retains approximately 1.1×10^{-5} mol of **1**/g SiO_2. Given that the acidic gel, containing no basic siloxide sites, retains none of the cluster adsorbed from CH_2Cl_2 when treated with Bu_4NCl, we infer that **1** remaining on the basic gel (B) is coordinatively linked to the support through the replacement of weak $Mo-OSO_2CF_3$ bonds with stronger Si–O–Mo bonds (eq 4). The cluster eluted from the gel is merely adsorbed to the support by electrostatic interactions, as in the acidic silica gel system.

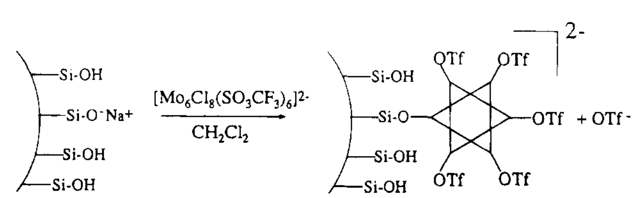

Figure 6. Proposed covalent bond formation between $(Bu_4N)_2[Mo_6Cl^i_8(SO_3CF_3)^a_6]$ and basic silica gel by replacement of axial triflate ligands.

$$B-(SiO^-)_n + [Mo_6Cl^i_8(SO_3CF_3)^a_6]^{2-} \rightarrow [B-(SiO)^a_nMo_6Cl^i_8(SO_3CF_3)^a_{(6-n)}]^{2-} + n(SO_3CF_3)^- \quad (4)$$

Additional evidence that triflate ligands are displaced by basic sites on the silica gel is provided by ^{19}F NMR experiments. The supernatant solution from the adsorption of $[Mo_6Cl^i_8(SO_3CF_3)^a_6]^{2-}$ on basic silica gel contains uncoordinated triflate ligand (on the order of 2×10^{-6} mol). This amount of free triflate is less than would be expected if one or more triflate ligands per cluster were replaced by silica gel siloxide sites to form 1.1×10^{-5} mol of covalently anchored triflate cluster (on the order of 1.1×10^{-5} mol of triflate ligand expected). Presumably, the "missing" triflate salt is adsorbed by polar interaction with the gel and is not readily removed by washing with solvent.

In CH_3CN and CH_3OH solvents, the interaction between the basic silica gel and **1** is also due to a combination of Mo–O–Si coordination and electrostatic interactions. As summarized in Table 2, a much larger percentage of **1** is coordinated to the basic silica gel in the CH_3CN and CH_3OH media than in CH_2Cl_2. In fact, the basic gels retain the same amount of **1** as the acidic gels after introduction of Bu_4NCl (approximately 2.1×10^{-5} mol of cluster/g of basic SiO_2 for the CH_3CN system and 3.6×10^{-5} mol of cluster/g of basic SiO_2 for the CH_3OH system). Covalent attachment of the cluster may occur by two related reactions. Replacement of axial triflate ligands (or solvent molecules) by siloxide sites on the basic gel is possible, as discussed for the CH_2Cl_2 solvent system (eq 4). The basic gel also contains a large percentage of silanol groups (only a small fraction are converted to basic sites upon treatment with base),[8] and coordination of the cluster to silica gel may also occur by dissociation of silanol groups, with subsequent covalent attachment of the solvated cluster cation (eqs 2 and 3). This second process is promoted only in polar, basic media and increases the chemisorption of **1**.

Photophysical Properties of Supported $(Bu_4N)_2[Mo_6Cl^i_8(SO_3CF_3)^a_6]$ (1). Transient emission spectroscopy reveals that supported **1** displays a long-lived excited state. In 1,2-dichloroethane solution, it has an excited-state lifetime (τ) of 110 μs. The triflate cluster coordinated to acidic or basic silica gel (σ) that was washed with Bu_4NCl solution to form $[\sigma\text{-}(SiO)^a_nMo_6Cl^i_8Cl^a_{6-n}]^{2-}$ has $\tau = 100$ μs. Upon heating the supported cluster for approximately 12 h at 150 °C under vacuum, the lifetime decreases to 24 μs. This attenuation of τ indicates that either the cluster has begun to degrade,

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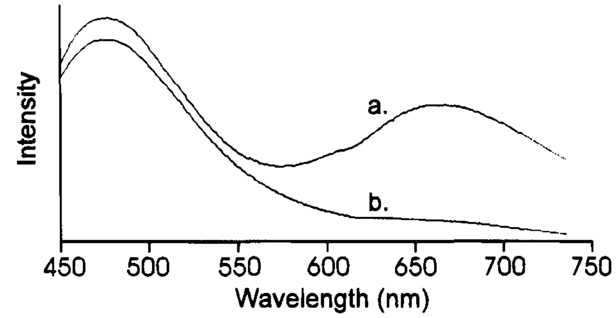

Figure 7. Comparison of fluorescence spectra (λ_{exc} = 420 nm) of $(Bu_4N)_2[Mo_6Cl^i_8(SO_3CF_3)^a_6]$ chemisorbed on silica gel and then reacted with excess Bu_4NCl, forming $[\sigma-(SiO)^a{}_nMo_6Cl^i_8Cl^a_{6-n}]^{2-}$, under (a) N_2 atmosphere and (b) O_2 atmosphere. The peak at 480 nm is due to fluorescence of surface hydroxyl groups or impurities on silica gel and is not quenched by O_2.[24,25]

or additional linkages between the silica gel and the cluster form at elevated temperatures.

Experiments were conducted to determine if the excited-state luminescence of the supported clusters could be quenched by either energy or electron transfer to other species in solution. Jackson et al. report that the luminescence of $[Mo_6Cl^i_8Cl^a_6]^{2-}$ in solution is efficiently quenched by energy transfer to oxygen.[1f] As illustrated in Figure 7, steady-state fluorescence experiments reveal the luminescence of the supported cluster is also quenched by oxygen. Similarly, phenothiazine, which has been shown to reductively quench the excited state of $[Mo_6Cl^i_8Cl^a_6]^{2-}$ in solution,[1e] quenches the luminescence of the supported cluster, as shown in Figure 8. Transient emission spectroscopy reveals that the excited-state lifetime of the supported cluster decreases with increasing concentration of quencher, providing further evidence that the excited state can participate in electron- and energy-transfer reactions while covalently bound to silica gel. These studies indicate that silica gel supported clusters are a potentially useful medium for photochemical transformations.

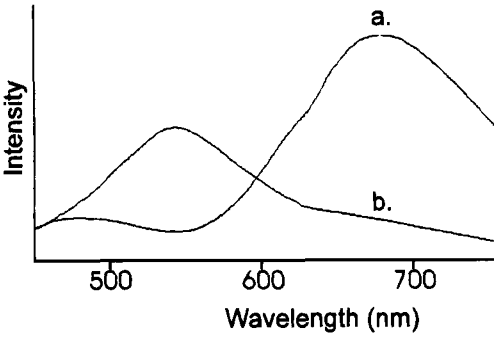

Figure 8. Comparison of fluorescence spectra (λ_{exc} = 420 nm) of $(Bu_4N)_2[Mo_6Cl^i_8(SO_3CF_3)^a_6]$ chemisorbed on silica gel and then reacted with excess Bu_4NCl, forming $[\sigma-(SiO)_nMo_6Cl^i_8Cl^a_{6-n}]^{2-}$, in the absence (a) and presence (b) of phenothiazine (3×10^{-3} M). The peak at 545 nm is due to phenothiazine fluorescence.

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