Design and Synthesis of Selective Mesoporous Anion Traps

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Arsenic contamination of groundwater has recently commanded widespread public attention. Under many conditions, arsenic, and certain other environmentally relevant toxic metals such as chromium, exist in nature as oxyanions. Selective binding of anions is one of the most challenging problems in chemistry, biology, and materials and environmental science. In this paper we report the synthesis and use of metal-chelated ligands immobilized on mesoporous silica as novel anion binding materials. Nearly complete removal of arsenate and chromate has been achieved in the presence of competing anions for solutions containing more than 100 mg/L (ppm) toxic metal anions under a variety of conditions. Anion loading of more than 120 mg (anion)/g of adsorption materials is observed. A binding mechanism is also proposed on the basis of computer modeling. First, Cu(II) ions are bonded to ethylenediamine (EDA) ligands to form octahedral complexes on the surface of the mesoporous silica. This gives rise to positively charged hosts with 3-fold symmetry that match the geometry of tetrahedral anions. The anion binding involves initial electrosteric coordination, followed by displacement of one ligand and direct binding with the Cu(II) center.

Introduction

Recent reports of the crisis caused by arsenic contamination of drinking water in Bangladesh, India, and other parts of the world have attracted wide public attention.[1,2] In Bangladesh alone, health officials estimated that 50−70 million people could be affected by drinking water contaminated by natural arsenic sources.

Arsenic, along with other toxic metals such as chromium and selenium, are included in the U.S. Environmental Protection Agency's list of priority pollutants. These contaminating species, unlike many heavy metals and transition metals, can exist in nature as tetrahedral oxyanions (arsenate ions $HAsO_4^{2-}$, $H_2AsO_4^{-}$, and chromate ions $HCrO_4^{-}$, CrO_4^{2-}).[3,4] In many cases, trace amounts of arsenate and chromate need to be removed from waste solutions containing high concentrations of competing anions, sulfate and chloride in particular.

Currently, the development of effective anion-binding materials is an important subject in chemistry, biochemistry, and materials and environmental science.[5,6] So far, a wide range of ion-exchange resins (based on ammonium ion exchange sites) and inorganic adsorbing materials (alumina, phosphate, and zeolytic materials) have been used,[7] but their selectivity and capacity is usually far behind the performance of typical cation-adsorbing materials. For example, Sessler et al.[5] reviewed various adsorbing materials (activated carbon, alumina, and ion exchangers) for arsenate and chromate and concluded that they were not effective. Recently Ramana et al. reported the copper-chelated pyridyl and tertiary ammonium polymers as anion exchangers for arsenate and selenite and demonstrated high affinity toward these anions over sulfate and chloride.[8] In addition to traditional ion-exchange materials, families of synthetic cyclic compounds have shown promise as anion traps.[5,9]

In the past few years, a new class of ordered mesoporous materials have attracted wide attention for many industrial and environmental applications. The ordered mesoporous materials were synthesized using surfactant micellar structures as templates.[10] Ordered mesoporous silica can be prepared under a range of experi-

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mental conditions, and many excellent papers have been published.[11,12] More recently, the templates were extended to include block copolymers.[13] In order for the mesoporous silica to have specific surface chemistry for catalytic activities and binding, the silica surface must be modified. The surface modification can be achieved either by cocondensation or by direct silanation. Except for some latest publications,[14] many of these efforts have recently been summarized in an excellent review by Moller and Bein[15] and will not be discussed in this paper. There have been several studies on the cation-binding properties of modified mesoporous silica. For example, we[16] and others[17] reported the synthesis of alkanethiol-functionalized mesoporous silica, which showed high-binding efficiency for mercury and other "soft" heavy metals. One big advantage of mesoporous materials over traditional sol–gel materials is that all the pore surfaces are accessible.[17] Fully dense monolayer coverage loading capacities of 700 mg of Hg/g (adsorbing materials) and distribution coefficients as high as 10^8 [defined as the amount of metal adsorbed (in micrograms) on 1 g of adsorbing materials divided by the metal concentration (microgram per milliliter) remaining in the solutions] have been routinely observed.[16] The metal loading is at least 1 order of magnitude higher than that obtained from high surface area conventional silica. Besides heavy metals, mesoporous silica has also been functionalized for binding transitional metals, using ethylenediamine and other molecules as the complexing agents.[18,19]

The design of mesoporous anion-binding materials has not been reported. Making anion-binding materials is more difficult because so many anions of concern are similar in size ($r = 2.3-2.5$ Å) and shape (e.g. tetrahedral). The choice of good anion selective ligands is very limited. One has to depend on the combined effect of charge, size, shape, acid–base interaction, solvation, and hydrogen bonding.[4,5]

In this paper, we report the synthesis and the use of metal-chelated ligands immobilized on mesoporous silica as an efficient anion binding material for both arsenate and chromate. By exploring the electrosteric charge matching and the solubility differences, nearly complete removal of arsenate and chromate has been achieved in the presence of competing anions for solutions containing up to 100 ppm toxic metal anions under a variety of experimental conditions. Good selectivity between chromate (or arsenate) and sulfate ions can be achieved at high anion concentrations. Anion loading is more than 120 mg (anion)/g of adsorption materials. The anion-loading capacity of this material is comparable (on a molar basis) to the heavy-metal-loading capacity achieved with the best cation sorbent materials (functionalized mesoporous silica) reported earlier,[16,17] when the stoichiometry of binding and the atomic/molecular weight of the target species are taken into consideration. This approach is especially promising considering the rich chemistry that can be explored with monolayers[20,21] and with mesoporous silica[15] and the possibility of designing better anion recognition ligands.[4,6]

Experiments and Modeling

Mesoporous silica materials were synthesized with cetyltrimethylammonium chloride/hydroxide as the surfactant, tetramethylammonium silicate, HiSil silica powders, sodium aluminate as the precursor, and mesitylene solutions as the pore expander.[10,16] The calcined mesoporous silica had a surface area of 900 m^2/g and nominal pore size of 60 Å, as determined by nitrogen adsorption and transmission electron microscopy (TEM). The mesoporous silica was functionalized with an ethylenediamine (EDA) terminated silane [1-(2 aminoethyl)-3-aminopropyl]trimethylsilane]. The procedures were described in ref 16. Mesoporous silica was first suspended in toluene and pretreated with approximately two monolayers' worth of water. This suspension was stirred vigorously for 1 h to distribute the water throughout the mesoporous matrix. The hydrated mixture was then treated with one monolayers' worth of [1-(2-aminoethyl)-3-aminopropyl]trimethoxysilane and heated to reflux for 6 h. At the end of the reflux period, the reflux condenser was removed, and replaced by a still head, and the methanol and water were removed, via azeotropic distillation. This last step drives the condensation equilibria of monolayer formation to completion and is critical to the preparation of high-quality monolayer coatings. Failure to perform this step results in EDA coatings with significant defects that can interfere with the desired chelation chemistry. After all of the methanol and water were removed, the mixture was allowed to cool, and the powders were collected by filtration, washed copiously with 2-propanol, and dried. ^{29}Si NMR revealed a high degree of silane cross-linking and a surface population of 4.9 silanes/nm^2, indicative of a well-behaved monolayer structure.

Incorporation of the Cu(II) ions was accomplished by stirring the functionalized silica prepared above in an aqueous solution of the appropriate metal salt (e.g. copper(II) chloride) for a few hours to produce Cu–EDA–Si. The metalized adduct was collected by filtration, washed with water and then 2-propanol, and dried.

The adsorption behavior toward chromate (CrO_4^{2-}) and arsenate ($A_SO_4^{3-}$) was studied in the presence of sulfate ions (SO_4^{2-}). Sulfate is a common competing anion and is very difficult to separate from chromate and arsenate due to the structural similarities. A sample of 0.1 or 0.02 g of M–EDA–Si powders was dispersed in 10 mL of solutions containing different concentrations of chromate (from K_2CrO_4), arsenate (from $Na_2HA_SO_4$), and sulfate (from Na_2SO_4). Therefore, the solution volume to the adsorbing materials ratio was either 100 or 500 mL/g. The solutions were shaken overnight (12 h) and then filtered through a 0.45 mm syringe filter to remove the sorbent materials. The as-prepared chromate and arsenate solutions usually had a pH value between 5 and 6. The removal of the anions reduced the pH by less than 1 unit. The remaining concentrations of arsenate, chromate, and sulfate were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) techniques after appropriate dilution.

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Table 1. Results of Chromate Adsorption by Cu−EDA−Si Materials

sol. vol/solid (mL/g)	CrO_4^{2-} (mg/L)		% Removal	specific adsorp. (mg/g)	K_d	SO_4^{2-} (mg/L)	
	initial	final				initial	final
100	1	<0.01	100	0.1	>100000	0	0
100	10	<0.01	100	1	>100000	0	0
100	100	<0.01	100	10	>100000	0	0
100	1	<0.01	100	0.1	>100000	150	0
100	10	<0.01	100	1	>100000	150	0
100	100	<0.01	100	10	>100000	150	0
100	500	12.1	97.6	48.8	4045	163	0
100	1000	13.3	98.7	98.7	7607	154	60
100	2000	1041	47.9	95.9	91	150	147
100	5858	4529	22.7	132	29	150	149
100	27	0.15	99.4	2.7	17342	1137	89
500	1	<0.01	100	0.1	>100000	175	0
500	10	0.03	99.7	1	151874	175	0
500	100	1.8	98.2	49.1	27345	175	8.39
500	405	161	40	122	757	151	110
500	500	245	51	127	522	163	159
500	924	686	26	119	173	154	155
500	27	0.80	97.1	13.1	16435	1137	843

Table 2. Results of Arsenate Adsorption by Cu−EDA−Si Materials

sol. vol/solid (mL/g)	AsO_4^{3-} (mg/L)		% Removal	specific adsorp. (mg/g)	K_d	SO_4^{2-} (mg/L)	
	initial	final				initial	final
100	1	0.03	98.5	0.1	4846	0	0
100	10	0.1	99.1	1.0	10746	0	0
100	100	1.4	98.6	9.9	7224	0	0
100	1	0.03	97	0.1	16587	150	0
100	10	0.2	98	1.0	29	150	0
100	100	1.7	98.2	9.8	5720	150	0
100	500	11.6	97.6	48.8	4045	150	1.3
100	1000	108	89	89.1	820	150	5.7
100	2000	584	71	142	242	150	68.6
100	4063	2875	29	119	41	150	95.2
100	14	1.35	90.4	1.27	937	1000	90.6
500	10	1	90.6	4.5	4946	150	1.9
500	100	18	82	40.5	2520	150	8.4
500	373	240	36	66.5	277	150	123
500	14	5.5	60.4	4.2	763.5	1000	963

Two emission lines were chosen for each element as a cross-check for spectral interference. The calibration standards were matrix-matched in water. Due to the high emission intensity of Cr, a radial view of the plasma was used. The detection limit of the ICP instrument is 10^{-3} mg/L. Ten times dilution was used for anion solutions ranging from 100 to 500 mg/L; 100 times dilution was used to anion solutions above 1000 mg/L. All adsorption tests and concentration measurements were done in duplicates, and only the average results are reported in this paper. The duplicate results were found to differ by less than 20%.

Computer modeling is used to obtain a better understanding of the anion-binding process because it is difficult to directly characterize the anion-ligand complex structure on the mesopore using commonly available spectroscopic techniques. The binding of anions involves second-neighbor interaction, rather than the nearest neighbor interaction, as in the case of cations. The molecular structure and electrostatic potential of the copper-chelated ligands and anion-bonded complexes were calculated using the PM3 and PM3 Hamiltonians,[22] as implemented in PCSpartan 5.1.[23] The PM3 Hamiltonian has been shown to provide accurate descriptions of the structural properties for both organic molecules[24] and transition-metal complexes.[25] The energy-optimized molecular structure was determined by force relaxation methods. The electrostatic potential was subsequently evaluated at the optimal geometry and mapped onto the three-dimensional isosurface defined by the 0.05 e/au^3 electron density probability. To provide a better qualitative estimate of the binding energetics in solution, we used experimental heats of formation wherever available. Relative energetics between anion binding species were estimated.

Results

The anion removal tests were performed with Cu−EDA−Si in aqueous solutions containing 1, 10, and 100 mg/L (ppm) chromate (or arsenate) with a solution (mL) to sorbent (g) ratio of 100. The results from the Cu−EDA−Si are shown in Table 1. In all the tests essentially 100% chromate was removed in a single treatment. The distribution coefficients were found to be significantly in excess of 100 000. Competition experiments with 150 mg/L sulfate demonstrated little effect on the binding behavior. Chromate concentrations in excess of 1000 mg/L began to saturate the binding sites. The maximum sorption capacity in this system is about 130 mg/g, or 1.12 mmol/g. At a much higher solution-to-sorbent ratio (500 mL/g), complete removal of chromate was observed for chromate levels up to 100 mg/L. Higher concentrations of chromate under these conditions resulted in saturation of the Cu−EDA binding sites.

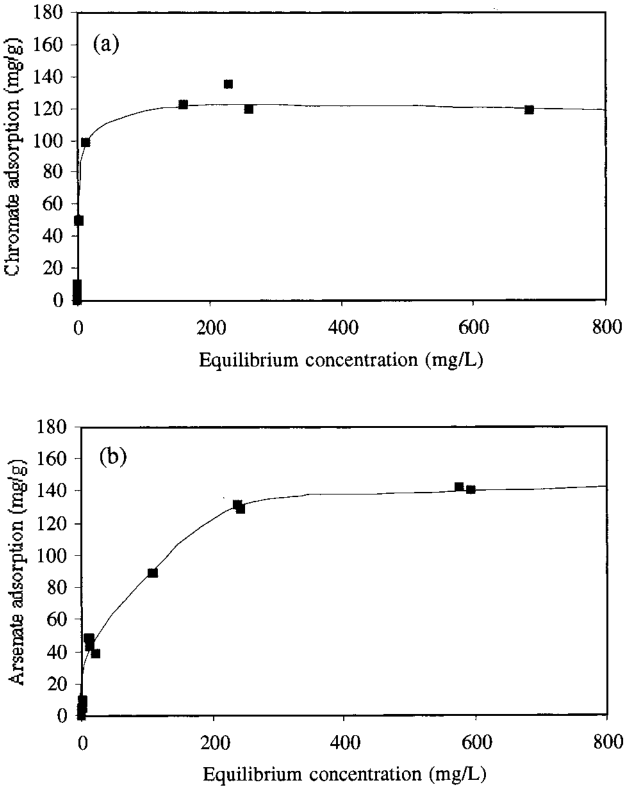

Figure 1. Adsorption isotherms of Cu−EDA−Si for chromate (a) and arsenate (b) in 150 mg/L Na_2SO_4 solutions.

Removal of arsenate was also found to be facile, as shown in Table 2. The maximum loading capacity is about 140 mg/g, or 1.00 mmol/g. The difference is that the residual concentrations of arsenate are all slightly higher than the chromate at low anion concentrations. This suggests that the binding affinity for chromate is greater than that of arsenate.

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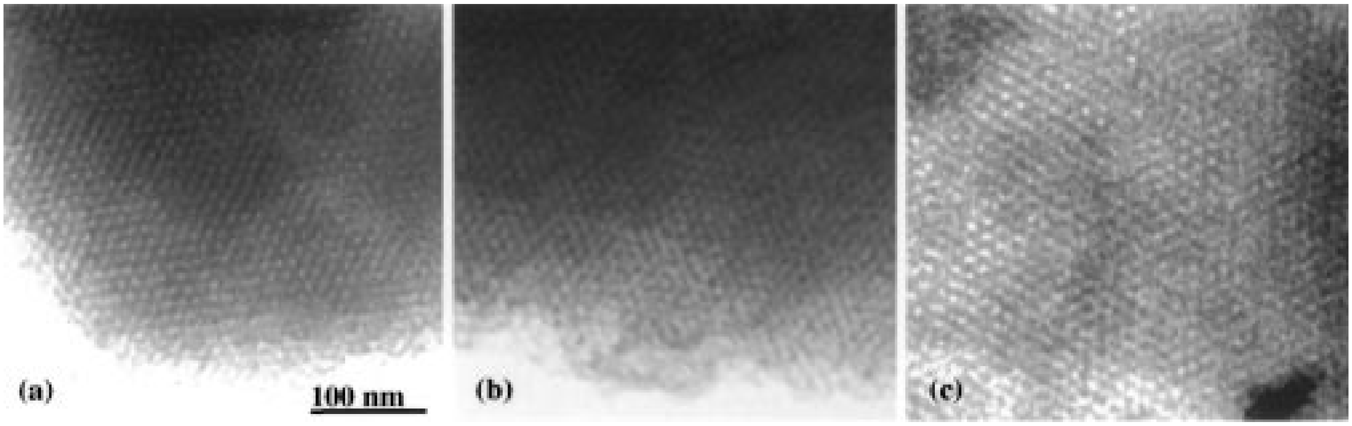

Figure 2. TEM images of Cu−EDA−Si after absorption tests: (a) Cu−EDA−Si tested in 10 mg/L chromate, (b) Cu−EDA−Si tested in 1000 mg/L chromate, and (c) Cu−EDA tested in 1000 mg/L arsenate.

The adsorption isotherms for chromate and arsenate are shown in parts a and b of Figure 1 respectively. For chromate, the initial adsorption curve is very steep until the maximum adsorption capacity is reached (130 mg/g) and the isotherm levels off quickly. For arsenate, the initial adsorption curve is not as steep as that of chromate. The maximum adsorption isotherm is gradually reached from 0 to 300 mg/L equilibrium concentrations. The loading density of the EDA silanes within the mesoporous silica was determined gravimetrically to be 3.3 mmol/g. Assuming a 3 to 1 stoichiometry in the Cu-(II) EDA complex, this gives a content of 1.1 mmol of Cu−EDA complex/g of sorbent material. This assumption is verified by energy-dispersive X-ray spectrascopic (EDX) compositional analysis, which gives a Cu(II) concentration of 1.0−1.4 mmol/g sorbent material. Therefore, the anion loading density of 1 mmol/g is in excellent agreement with the saturation capacities measured for both chromate and arsenate.

Ramana, and Sengupta reported a maximum specific adsorption of 40 mg of As/g of resin (or 74 mg of arsenate/g of resin) for the copper-chelated pyridyl and tertiary ammonium polymers.[8] Although Ramana and Sengupta's results were obtained under flow conditions and our results obtained under static conditions, the Cu−EDA mesoporous materials still compare favorably with the some of the best anion-exchange resins reported in the literature.

Cu−EDA−Si showed selectivity between chromate (or arsenate) and sulfate under high anion concentrations. When the chromate (or arsenate) concentration is low, there are insufficient chromate ions to cover the binding sites. Then there are vacancies in the monolayer interface that the sulfate anion can fill. However, as the concentration of chromate (or arsenate) increases and there is sufficient chromate to occupy all the binding sites, the sulfate ions will be displaced. For example, at a solution-to-sorbent ratio of 500 mL/g and 150 mg/L sulfate, all anions are adsorbed at chromate concentrations below 100 mg/L. When the chromate concentrations are increased to over 100 mg/L and the materials approach their saturation capacity, virtually no sulfate is adsorbed. This observation shows that the Cu−EDA−Si materials have a much higher affinity for chromate (or arsenate) than sulfate. This conclusion is also supported by the testing results at higher sulfate concentrations: at 1000 mg/L sulfate concentration the chromate concentration can be reduced from 27 to 0.8 mg/L.

For means of comparison, pure mesoporous silica and mesoporous silica functionalized with (aminopropyl)-silane (APS) were also tested for anion binding under similar experimental conditions. The adsorption of chromate and arsenate on these materials was negligible.

Figure 2a−c shows the TEM image of the samples with adsorbed chromate and arsenate. These TEM images correspond to 10 mg/L chromate, 1000 mg/L chromate, and 1000 mg/L arsenate solutions, with a solution-to-sorbent ratio of 100 (mL/g). The ordered mesoporous structures are still visible in all the samples. There is no evidence of massive precipitation of particles containing copper, chromium, or arsenic. EDX spectra were collected from the TEM samples and shown in Figure 3. Semiquantitative analysis was performed on these spectra. Although slight compositional variations were observed from one region to another, the trends are consistent with the results from other methods. The anion loading is about 20 mg/g for 100 mg/L chromate solution, 131 mg/g for 1000 mg/L chromate solution, and 153 mg/g for 1000 mg/L arsenate solution. The EDX results are in excellent agreement with those obtained from the wet chemical analysis.

Discussion

Ramana et al. studied the copper-chelated pyridyl and tertiary ammonium polymers for arsenate and selenite binding and suggested that preferred binding of these anions was due to the solubility difference between the cupric arsenate, cupric selenite, and other more soluble cupric salts (chloride and sulfate).[8] This is a reasonable explanation for the high anion-binding affinity of our Cu−EDA−Si materials. Because detailed structural information on the immobilized anion-ligand complex cannot be easily obtained from commonly available spectroscopic techniques, we used computer modeling to obtain a better understanding of the specific interaction of the anions and Cu−EDA−Si materials.

EDA is known to chelate to a wide assortment of transition metal cation and to have a high affinity for

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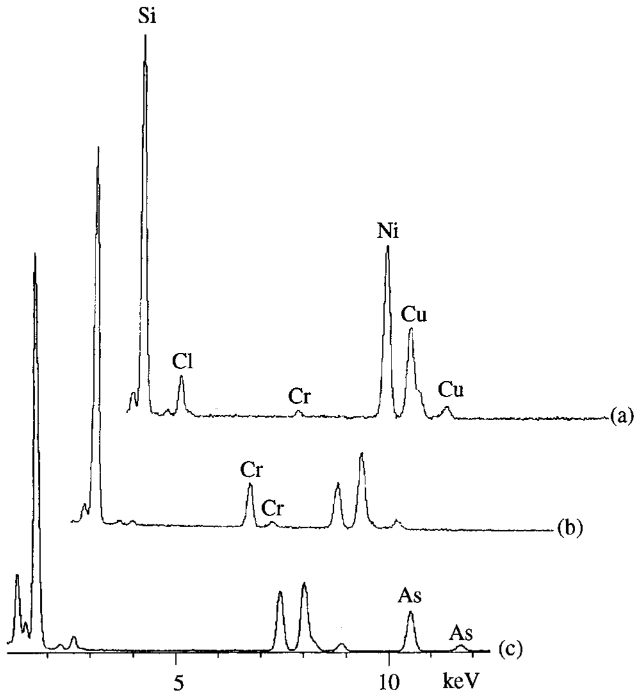

Figure 3. EDX spectra of Cu−EDA−Si samples after adsorption tests: (a) Cu−EDA−Si tested in 10 mg/L chromate, (b) Cu−EDA−Si tested in 1000 mg/L chromate, and (c) Cu−EDA tested in 1000 mg/L arsenate.

cupric ion to form a six-coordinated complex.[26,27] The log K_1 (association constant) for the ethylenediamine and Cu(II) in solution is 10.75, while log K_2 is 9.28.[28] A third ethylenediamine ligand can bind to the cupric ion if present in high enough concentration.[29] The third EDA ligand is known to be weakly held, and the log K_3 has been determined to be approximately −1.[30] Copper(II), being a d^9 species, undergoes Jahn−Teller distortion to alleviate the orbital degeneracy by lengthening the bonds to the two apical ligands.[28] While significant in complexes such as $Cu(H_2O)_6^{2+}$ and $Cu(NH_3)_4(H_2O)_2^{2+}$, this distortion is thought to be minimal in those complexes composed of chelating amines.[31]

When EDA ligands are bonded on a substrate, they are expected to behave differently. However, the molecules in the monolayer should not be regarded as rigid. Previous work also suggests[16] that at a surface coverage of 3.3 mmol/g the monolayer still contains structural defects. It has been widely recognized that the chain conformation in the monolayer can be significantly affected by the interaction with the solvent and solute.[32] Therefore, these molecules should have enough flexibility and freedom to coordinate with the metal cation. Because of the monolayer environment, the local concentration of EDA is quite high. The highly effective interfacial concentration of EDA is expected to facilitate the addition of the third EDA ligand. This will favor the highest possible coordination. Once the Cu(II) ion associates with the EDA ligand, it should be rapidly and tightly incorporated into the monolayer matrix.

On the basis of the above discussion, we believe that the octahedral coordination is a good starting point for the Cu−EDA complex on mesoporous silica. The Cu(EDA)$_3$ complex should be approximately octahedral, the first two EDA ligands being strongly bound and the third being still labile. The experimental results of the Cu to EDA ratio (about 1 to 3) also support this assumption. In the computer modeling, the cationic octahedral complex contains an electrophilic basket with C_3 symmetry that forms an ideal host for a tetrahedral anion. Once the anion is coordinated within the C_3 "basket," it "unlocks" the complex, releasing an EDA ligand, and binding directly to the cupric ion. The analogy of a lock and key is apropos; the adsorption of the anion is like the insertion of a key into its lock, while the displacement of the EDA ligand corresponds to the opening of the lock. In the case of sulfate, the corresponding copper sulfate is soluble; therefore, the sulfate ion can dissociate, and the unlocking process is reversible. Hence, sulfate can be displaced by an anion that binds more strongly. In the case of chromate (or arsenate), since the corresponding copper chromate (or arsenate) is insoluble (suggesting that dissociation of the

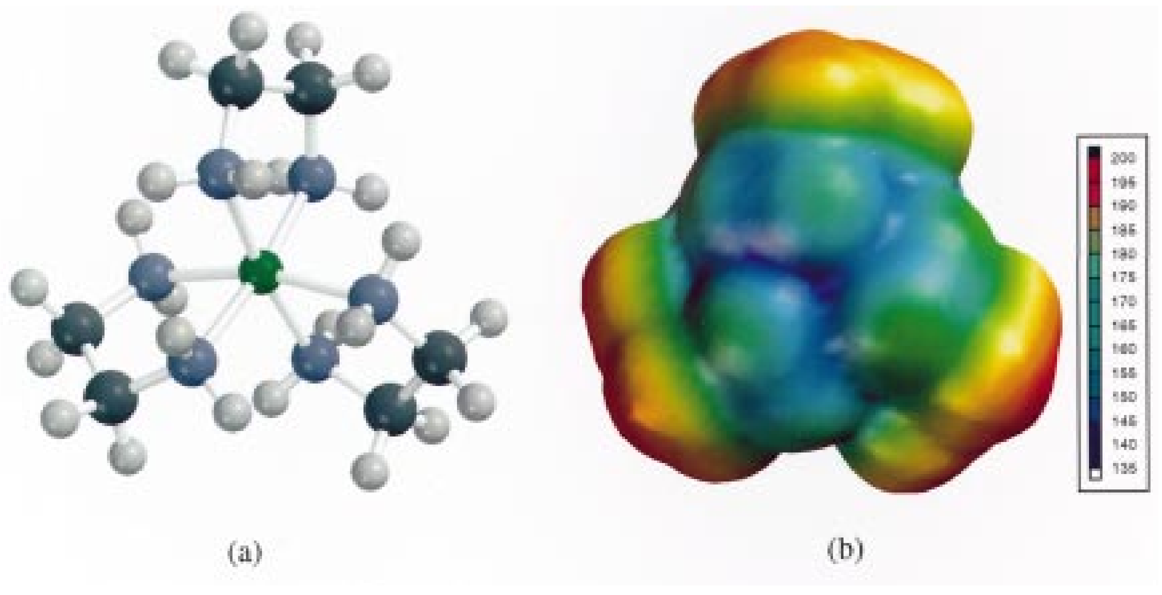

Figure 4. Molecular structure (a) and electrostatic potential (b) of the $[Cu(EDA)_3]^{2+}$ complex. The electrostatic potential (kcal/mol) is mapped onto the 0.05 e/au^3 electron density isosurface. Atom typing: Cu, green; N, blue; C, black; H, gray.

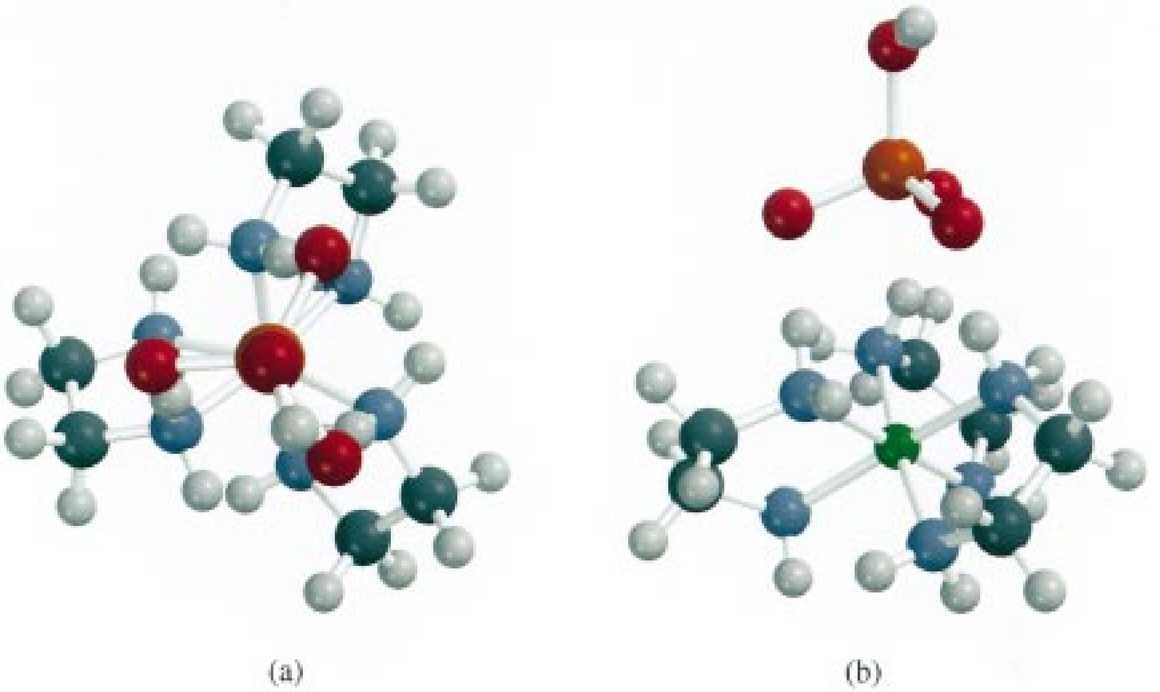

Figure 5. Two views of the proposed initial lock-and-key interaction of arsenate dianion ($HAsO_4^{2-}$) with the $Cu(EDA)_3^{2+}$ complex: (a) the C_3 axis of the anion basket; (b) a side perspective. Atom typing: Cu, green; As, large red; C, black; N, blue; O, smaller red; H, gray.

chromate anion is unlikely), it cannot easily be displaced.

To further elucidate this mechanism, we examined several key steps of the proposed lock and key model using electronic structure methods. Given the difficulty modeling the exact reaction mechanism for displacement of bound water in the reaction pathway, we chose to examine several proposed intermediates of the model. Figure 4 shows the stick-and-ball model and the isopotential surface of one cupric ion chelated with three EDA ligands to form the octahedral cage. The C_3 symmetry of the top surface is clearly visible. Figure 5 shows that the shape and the dimension of the positively charged Cu−EDA basket are such that they fit the negatively charged tetrahedral geometry of the anions very well. As the anion approaches, it begins to interact with the copper center. This interaction displaces one EDA ligand that is loosely bonded until a direct bond is formed between the cupric ion and the oxygen atoms in the anions. The final binding configuration with the displaced ligand is shown in Figure 6.

The divalent cations of nickel and cobalt have much higher log K_3 values for EDA than does copper (4.3 and 3.3, respectively[33]). This enhanced affinity suggests that displacement of the EDA ligand should be less favorable, thus these complexes should be less readily “unlocked." Preliminary testing with Ni−EDA−Si, and Co−EDA−Si has revealed K_d values of approximately 6000 for chromate anion and 200−600 for arsenate. The fact that these values are significantly better than “typical” (i.e., quaternary ammonium) anion-exchange resins supports the concept of the C_3 templating of the octahedral M−EDA complex to the tetrahedral oxyanion. In addition, the fact that these K_d values are lower than those determined for the Cu−EDA−Si system implies that chromate and arsenate do not, in fact, unlock the Co and Ni complexes.

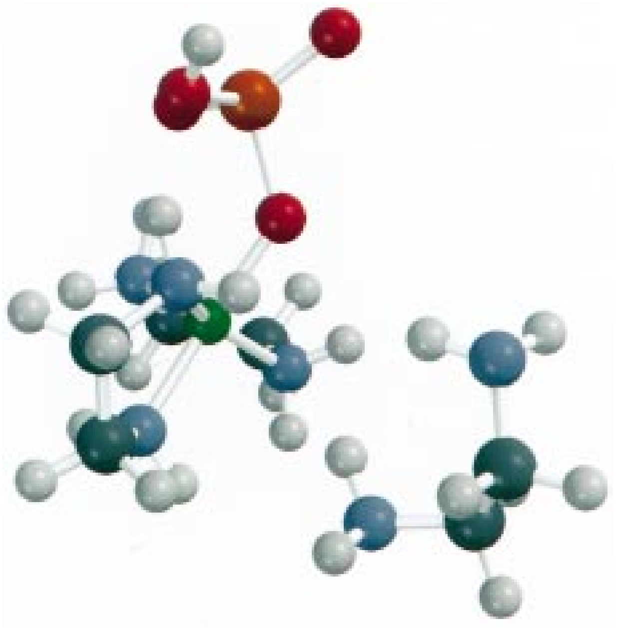

Figure 6. Formation of the $Cu(EDA)_3^{-}$ $HAsO_4$ complex with displacement of an EDA ligand. The distant EDA ligand is shown to the right. Atom typing: Cu, green; As, large red; C, black; N, blue; O, smaller red; H, gray.

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Conclusions

The synthesis of the M−EDA−Si materials is a simple, direct, and convergent synthesis. These nanocomposite materials are easily made from commercially available bulk materials. We suggest that the octahedral (or distorted octahedral) M(EDA)$_3$ complex is a stereospecific cationic template for those anions with C_3 symmetry. The anion-binding affinity involves a stepwise association of the tetrahedral oxyanion to the M−EDA complex (insertion of the key into the lock), followed by displacement of one of the EDA ligands by the anion (unlocking the complex). In this case, the selectivity appears to be dictated by the "solubility" of the M(EDA)$_2$−anion adduct (more accurately, the ability of the anion to dissociate from the adduct). Anions that can dissociate have a lower binding affinity and can be displaced, while those that cannot dissociate are irreversibly sequestered. Cu−EDA−Si materials are superior anion-binding materials. Complete oxyanion removal can be achieved over a wide concentration ranges. At low anion concentrations, all tetrahedral anions, including sulfates, adsorb. At higher concentrations, chromate and arsenate displace the more weakly bound sulfates. In addition, low concentrations of chromate and arsenate can be removed from higher concentrations of sulfates.

Similar techniques have been widely used to construct self-assembled monolayers with anion recognition cavitand receptors on flat substrates.[21] Considering the rich possibilities inherent in monolayer chemistry, the uniquely ordered porosity in mesoporous materials with controlled pore size and pore shape, and the availability of even larger pore size mesoporous materials,[13] we believe that there is great potential to design more sophisticated functionalized nanomaterials for use in molecular recognition.

Currently we have not directly verified the coordination chemistry and the lock-and-unlock mechanism. We hope to obtain further evidence from future work using extended X-ray adsorption fine structure (EXAFS) and other advanced spectroscopic techniques.

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