

Anion binding in self-assembled monolayers in mesoporous supports (SAMMS)

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Abstract

The binding of various anions to cationic transition metal complexes lining the pores of mesoporous silica is characterized and correlated to anion basicity.

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By lining the pore surfaces of mesoporous silica with self-assembled monolayers of organosilanes terminated with chemically selective ligands, a powerful new class of heavy metal sorbents has been realized, called self-assembled monolayers on mesoporous supports (SAMMS) [1–18]. When this interfacial functionality is composed of cationic transition metal complexes, a valuable new class of anion exchange material came into being [19]. Yoshitake and co-workers, have extended this concept to include other transition metal cations in similar cationic complexes inside mesoporous silica [20–23]. Other amine-based ligands (including polymer-based systems) were also explored, and the highest binding capacity was found with the diethylenetriamine ligand [20]. This synthetic strategy allows the chemist to easily modify both the metal center and ligand field, thereby tailoring chemical selectivity at multiple levels. For example, octahedral *tris*(ethylenediamine) complexes have 3 exofacial protons capable of hydrogen bonding with tetrahedral oxometallate anions (stereochemical selectivity). Copper(II) is known to have a very high affinity for amine ligands, however being a d^9 species it tends to undergo Jahn–Teller distortion to alleviate orbital degener-

acy, distorting its geometry away from an ideal octahedral coordination sphere. Thus, a monolayer interface composed of a copper(II) ethylenediamine (Cu-EDA) complexes has a firmly bound metal center, but the third EDA ligand is readily displaced by an incoming anion [24]. If the copper-anion salt is soluble (e.g. copper(II)sulfate), then this ligand displacement is reversible, and the anion can be displaced from the metal center. If the copper-anion salt is not soluble however, then the anion is effectively sequestered when bound to the metal center (solubility selectivity) [19]. This latter case pertains to anions such as chromate and arsenate, both of which are of significant environmental concern. Loading capacity for chromate anion was found to be 130 mg (or 1.12 mmol) chromate per gram of Cu-EDA SAMMS. Similar loading capacity is observed for arsenate anion (140 mg/g or 1.0 mmol/g). Given the 3:1 stoichiometry of the initially Cu(II)EDA complex, this correlates quite well with the initial silane population density on the mesoporous silica, suggesting that the majority of the Cu(II) binding sites are effectively utilized.

Detailed EXAFS studies revealed that the anion binds directly to the metal center in a monodentate fashion in these complexes, and in the process two of the coordinating N atoms are displaced from the Cu ion's coordination sphere [24]. Ultimately, this produces a trigonal bipyramidal complex, as shown in Fig. 1.

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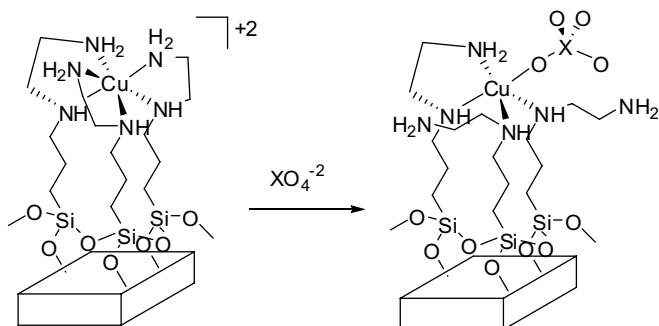


Fig. 1. Reaction of monolayer bound Cu(EDA)₃ with an oxometallate anion.

These cationic nanoporous sorbent materials might also be useful for sequestering other anions as well. For example, nanomaterials coated with Cu-EDA monolayers have also been used to bind the pertechnetate anion [25]. However, in some cases it can be expensive (or difficult) to determine the saturation binding capacities of these sorbent materials with certain anions. It would be useful to have a model that would allow simple prediction of this useful parameter for comparison or planning purposes. This communication summarizes our preliminary results related to this goal.

The Cu-EDA SAMMS were made as previously described [19]. Briefly, this involved taking a suspension of mesoporous silica (in this case MCM-41) in toluene, hydrating it with 2 monolayer equivalents of water, then treating it with 1 monolayer equivalent of (2'-aminoethyl)-3-aminopropyl trimethoxysilane ("EDA-silane"). This mixture was then held at reflux for 6 h, and then the methanol and water were distilled off, and then the EDA SAMMS were collected by filtration and washed with 2-propanol. The EDA SAMMS were then metallated by stirring them with an aqueous solution of CuCl₂ (excess) for an hour, then filtering and washing the product with water, then 2-propanol. The product was then air-dried to give the Cu-EDA SAMMS as a free-flowing Carolina blue powder.

All adsorption experiments were conducted using samples of groundwater (pH 8.3) spiked with sodium salts of appropriate anion. The initial concentrations ranged from 1 to 2 mmol/L. A solution to solid ratio of 10,000 ml/g was used in these experiments, and following a 24 h contact, the solution was separated from solids and the residual concentrations were measured (see Table 1). The

Table 1
Divalent oxyanion adsorption by Cu-EDA SAMMS (pK_b values are calculated from pK_a values from Ref. [27])

Anion	Max Ads (mmol/g CuEDA SAMMS)	Basicity index (pK_b)
HAsO ₄ ²⁻	1.02	7.04
CrO ₄ ²⁻	1.14	7.49
MoO ₄ ²⁻	0.76	9.76
SeO ₄ ²⁻	0.56	12.3

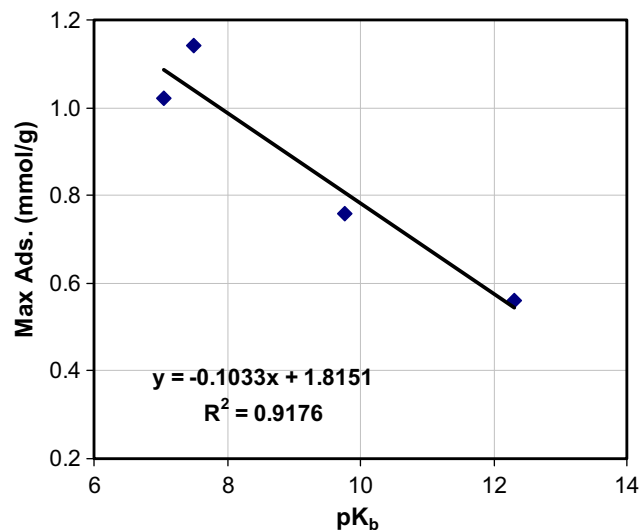


Fig. 2. Correlation of saturation binding capacity with pK_b [27].

anion loading on the Cu-EDA SAMMS was calculated using the differences in the initial and final concentrations and the solution to solid ratio.

Experiments using arsenate and chromate revealed saturation binding capacities close to the stoichiometrically predicted capacity [19]. However, when we started looking at other anion systems (e.g. molybdate, selenate, etc.), we found anion binding capacities that were notably lower than simple stoichiometry would predict. In an effort to better understand this interfacial adduct formation, we looked at this chemistry more closely and found that the binding capacities correlated well with anion basicity (see Fig. 2).

The binding of heavy metal cations to thiol-SAMMS was found to correlate nicely with the Misono softness parameter [11]. In thiol-SAMMS, the correlation was found to be between milli-equivalents of heavy metal per gram sorbent, and not milli-moles heavy metal per grams of sorbent, suggesting that charge accumulation at the interface was an important consideration in the heavy metal/thiol system. The observation that anion binding correlates to milli-moles of analyte per gram of sorbent suggests that this is a simple equilibrium process, and that charging issues are not as important here. This conclusion seems logical in light of the fact that anion binding in this system is a charge *quenching* process (in contrast to the charge *accumulation* in the heavy metal/thiol system described above).

Using this correlation, and the published pK_b values for pertechnetate (13.7), tungstate (10.3) and vanadate (6.22) anions [26] suggest that Cu-EDA SAMMS would have saturation binding capacities of 0.40, 0.75, and 1.17 mmol/g for pertechnetate, tungstate, and vanadate anions respectively.

In this case we have fixed the identity of the acid and varied the identity of the base. Obviously one could reverse this approach and fix the identity of the base and vary the

identity of the acid site, either by varying the metal center or the ligand field. This approach would allow one to characterize the binding chemistry of various sorbent materials, allowing systematic comparisons to be made.

In summary, Cu-EDA SAMMS has been found to be an effective anion sorbent material. The anion binds directly to the metal center, displacing a portion of the amine ligand field, resulting in a trigonal bipyramidal complex. Saturation binding capacity has been found to correlate to the anion basicity (pK_b), allowing for useful predictions to be made for other anion systems. This simple model is anticipated to be applicable to other nanoporous sorbent materials based on cationic transition metal complexes.

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