X-ray absorption fine structure spectroscopy determination of the binding mechanism of tetrahedral anions to self assembled monolayers on mesoporous support

S. D. Kelly,[a] K. M. Kemner,[a] G. E. Fryxell,[b] J. Liu[b] and S. Mattigod[b]

[a]Argonne National Laboratory, Argonne, IL 60439, USA, and [b]Pacific Northwest National Laboratory, Richland, WA 99352, USA

X-ray absorption fine structure (XAFS) spectroscopy is used to investigate the chemical interaction between the end member [$Cu(NH_2)_6$] of self-assembled monolayers on mesoporous supports (SAMMS) and the tetrahedral anion SO_4. The local structure about Cu indicates monodentate bonding between the SO_4 anion and the SAMMS.

Keywords: SAMMS; actinides; environment.

1. Introduction

Waste management has become a primary concern at several U.S. Department of Energy (DOE) sites, where hazardous materials storage and contaminated areas need to be made safer for the environment. The development of many separation techniques and novel materials has benefited similar industrial environments, but a method is needed for separating anions from the remaining constituents in tanks of high-level waste. The flexibility of the design and chemistry of the ligand monolayers and the ceramic oxide supports of self-assembled monolayers on mesoporous supports (SAMMS) indicates that SAMMS can be tailored to separate specific contaminants. X-ray absorption fine structure (XAFS) spectroscopy is used to investigate the chemical interaction between the end member of the SAMMS [$Cu(NH_2)_6$] and SO_4 anions. In many waste materials, the SO_4 anion competes with other anions (such as $AsO_4$and CrO_4) for the available sorption sites on the SAMMS materials. Therefore, an understanding of the binding geometry of the SAMMS materials with SO_4 is needed to tailor the SAMMS materials to selectively trap contaminant anions. XAFS measurements of the SAMMS made at the Cu k-edges to determine the average local structure. Theoretical XAFS calculations using FEFF7 (Zabinsky *et al.*, 1995) indicate that mono-, bi-, and tridentate bonding between the tetrahedral anion and the SAMMS can be distinguished on the basis of local structure.

2. Methods

A complete description of the synthesis of the SAMMS sample is given elsewhere (Fryxell *et al.*, 1999). The SAMMS sample investigated in this study consists of Cu(II) ions bound to ethylenediamine (EDA) ligands that make up the monolayer on the mesoporous silica. With three EDA ligands, the Cu(II) ions form an octahedral complex, that provides ideal binding sites for tetrahedral anions. The SAMMS powder was added to a solution containing the tetrahedral anions, and then the liquid was pored off. The SAMMS sample investigated in this work is SAMMS + SO_4 indicating that SO_4, was introduced to the SAMMS.

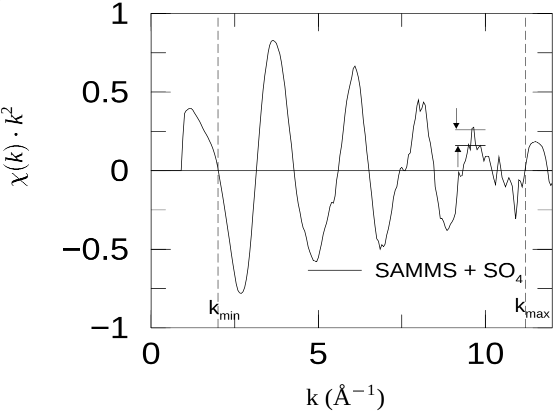

Figure 1
Example of Cu k-edge $\chi(k)\cdot k^2$ data taken at ~100 K on the SAMMS + SO_4 sample. The vertical lines represent the data range. The horizontal lines represent the peak-to-peak noise in the data.

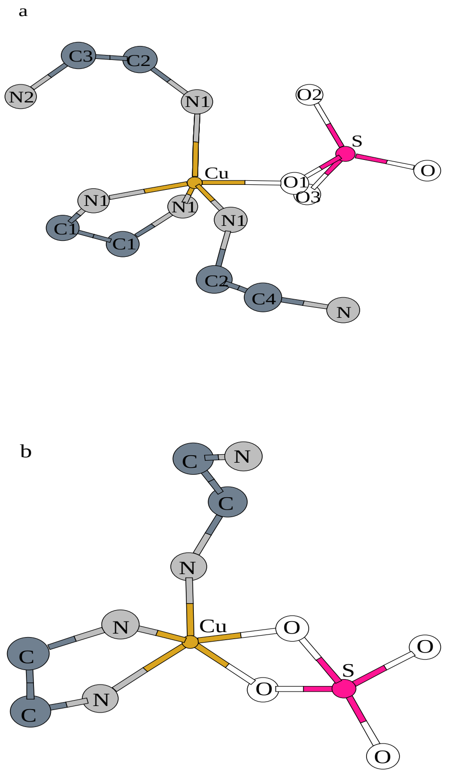

Figure 2
Two possible models for the structure about Cu in SAMMS + SO_4. (a) Monodentate bonding of the SO_4 anion, with one closed and two open NH_2-CH_2-CH_2-NH_2 chains bound to the Cu. (b) Bidentate bonding of the SO_4 anion, with one closed chain and one open chain bound to the Cu. The H atoms are not shown in the figure for simplicity.

The XAFS data were collected at the Materials Research Collaborative Access Team (MR-CAT) sector at the Advanced Photon Source (APS) and at the X23A2 beamline at the National Synchrotron Light Source (NSLS). The Cu K-edge data were collected at room temperature and at ∼100 K. The concentration of Cu in the SAMMS is approximately 6% by weight; therefore the measurements were made in the fluorescence mode. A Ni filter was used for the Cu k-edge XAFS measurements.

Table 1
Possible models for the SAMMS + SO_4 sample and goodness-of-fit parameters. Each model has either 5 or 6 O/N atoms about the Cu site. The open and closed chains are those at the end of the EDA ligand. The two most likely configurations on the basis of energy minimization (Fig 2a and b) are denoted with superscript a and b, respectively.

model	open chains	closed chains	$\mathcal{R}$	χ^2_ν	ν
monodentate	2	0	0.022	614	7
monodentate	2	1	0.024	800	5
^{a}monodentate	1	2	0.003	127	3
monodentate	1	3	0.010	594	3
monodentate	0	4	0.016	435	6
monodentate	0	5	0.015	488	6
bidentate	2	0	0.002	712	3
^{b}bidentate	1	1	0.002	6242	1
bidentate	1	2	0.002	5614	1
bidentate	0	3	0.008	769	4
bidentate	0	4	0.022	1176	4
tridentate	1	1	0.004	1164	6
tridentate	0	3	0.056	13021	2
tridentate	0	2	0.007	737	5
tridentate	1	0	0.002	606	5

For the experiments performed at the bending-magnet X23A2 beamline, a fixed-exit double-crystal silicon [220] monochromator was used to select the X-ray energy. The appropriate gas or gas mixture was used to achieve 10-15% absorption in the incident X-ray ion chamber and krypton gas was used in the fluorescence ion chamber. For the experiments performed at MR-CAT, the undulator gap was tapered (ΔE = 1 keV) and scanned, while a double-crystal silicon [111] monochromator was used to select the X-ray energy. Higher-order harmonics were removed with a harmonic rejection mirror. The incident X-ray ion chamber was filled with a nitrogen/helium (10/90) mixture, and the fluorescence ion chamber was filled with argon. Linearity tests (Kemner *et al.*, 1994) indicate less than 0.3% nonlinearity in the experimental setup for 50% attenuation of the incoming X-ray beam intensity.

The analysis software used in this study is part of the UWXAFS package (Stern *et al.*, 1995). Standard procedures were used to align the data and subtract the background. All of the measurements were made at least twice, and the resulting $\chi(k)$ data were averaged. Fig. 1 shows the averaged $\chi(k)$ data.

The value for $S_0^2 = 0.82 \pm 0.10$ was determined from a Cu_2O standard, to reduce the number of parameters determined in the fit.

3. Results and Discussion

Two of the lowest-energy configurations for the binding geometry of the $Cu(NH_2)_6$ end member of the SAMMS to a tetrahedral anion are shown in Fig. 2. The computer modeling is described elsewhere.(Fryxell *et al.*, 1999) As shown, the anion can displace an entire NH_2-CH_2-CH_2-NH_2 chain(s) and/or detach one end of a chain(s). From preliminary XAFS analysis of the first Cu shell, we determined that the Cu needs to be 5 or 6 coordinated with O/N. With this constraint, 15 different models (Table 1) have all combinations of the open and closed chain(s) with the SO_4 anion in mono-, bi-, or tridentate bonding to the Cu(II). An open chain is attached to the Cu at one point, and a closed chain is attached to the Cu at two points. Theoretical models of the Cu XAFS for all 15 models were calculated by using FEFF7 (Zabinsky *et al.*, 1995).

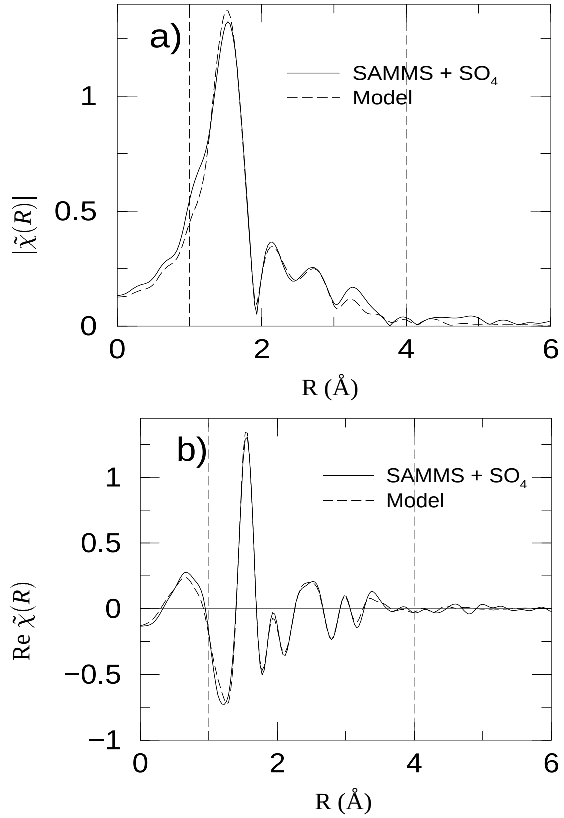

Figure 3
The Fourier transform of the Cu k-edge data from the SAMMS + SO_4 sample and the best-fit model. (a) The magnitude of the Fourier transform. (b) The real part of the Fourier transform. The dashed vertical lines represent the fit range.

Table 2
Best-fit results for the Cu k-edge data taken on the SAMMS + SO_4 sample at ∼ 100 K. The room-temperature data were fitted simultaneously. The thermal expansion coefficient was found to be consistent with zero. $\epsilon = 0.0 \pm 0.5\%$. $\Delta E_{0i} = 0 \pm 2$ eV for all paths. The fit parameters are listed in Table 3. The atom types are labeled in Fig. 2

Atom type	N_{degen}	R (Å)	σ^2 (Å^2)
Cu→O1	1	1.98 ± 0.02	0.004 ± 0.001
Cu→N1	4	2.02 ± 0.02	0.005 ± 0.001
Cu→H	8	2.35 ± 0.12	0.010 ± 0.032
Cu→C1	2	2.84 ± 0.08	0.004 ± 0.004
Cu→C2	2	3.09 ± 0.08	0.004 ± 0.004
Cu→S	1	3.15 ± 0.19	0.005 ± 0.013
Cu→O2	1	3.32 ± 0.38	0.003 ± 0.003
Cu→O3	1	3.39 ± 0.38	0.003 ± 0.003
Cu→C3	1	3.44 ± 0.88	0.004 ± 0.005
Cu→N2	1	4.20 ± 0.24	0.003 ± 0.005

Table 3

Parameters used to describe the model for the Cu k-edge data for the SAMMS + SO_4 sample. One overall energy shift was also determined in the fit. The room-temperature data and the ~100 K data were fitted simultaneously. An overall compression ϵ was determined for the room-temperature distances as compared to the ~100K distances. Total number of parameters is 18: ΔE_{0i}, ϵ, Δr_1 through Δr_{12}, $\theta_{\rm Debye}{}^1$, $\theta_{\rm Debye}{}^2$, $\theta_{\rm Debye}{}^3$ and σ^2.

Atom type	$N_{\rm degen}$	ΔR	σ^2
Cu→O1	1_s	Δr_1	$\theta_{\rm Debye}{}^1$
Cu→N1	4_s	Δr_1	$\theta_{\rm Debye}{}^1$
Cu→H1	8_s	Δr_2	σ^2
Cu→C1	2_s	Δr_3	$\theta_{\rm Debye}{}^2$
Cu→C2	2_s	Δr_3	$\theta_{\rm Debye}{}^2$
Cu→C1→N1	4_s	Δr_4	$\theta_{\rm Debye}{}^2$
Cu→C2→N1	4_s	Δr_5	$\theta_{\rm Debye}{}^2$
Cu→S	1_s	Δr_6	$\theta_{\rm Debye}{}^3$
Cu→O2	1_s	Δr_7	$\theta_{\rm Debye}{}^2$
Cu→O3	1_s	Δr_7	$\theta_{\rm Debye}{}^2$
Cu→N1→N1	2_s	Δr_8	$\theta_{\rm Debye}{}^2$
Cu→C3	1_s	Δr_9	$\theta_{\rm Debye}{}^2$
Cu→O1→N1	2_s	Δr_{10}	$\theta_{\rm Debye}{}^2$
Cu→O1→Cu→N1	2_s	Δr_{10}	$\theta_{\rm Debye}{}^2$
Cu→N2	1_s	Δr_{11}	$\theta_{\rm Debye}{}^2$
Cu→C4→N1	2_s	Δr_{12}	$\theta_{\rm Debye}{}^2$

Because each model includes many single- and multiple-scattering paths, several constraints were used to reduce the total number of fitted parameters. These constraints include one energy shift for the first O/N paths and another for all other paths; one σ^2 for the H paths; one σ^2 for the S path; one Debye temperature for all other paths that include C, N, and O atoms; and 5 to 9 ΔR_i values where several paths with the same scattering atom at approximately the same distance were constrained to have the same ΔR_i. Each model was simultaneously fitted to three average Cu K-edge data in R-space by using k-weighting values of 1, 2, and 3 in the Fourier transform of the data. With these constraints, a total of 10-17 parameters were determined in the fit to the data; the fit contains 18 independent points. The fit range in R-space is [1.0:4.0] Å. The data range in k-space is [2.0:11.0] Å^{-1}. The full width of the Hanning window sill d*k* was 2.0.

Table 1 lists the different SAMMS models and their goodness-of-fit parameters from a fit to the data taken on the SAMMS + SO_4 sample at ~100 K. The model for monodentate binding of the SO_4 anion gives a χ^2_ν value 3.4 times smaller than that of the next best model, where two standard deviations in χ^2_ν is 1.6 (Stern *et al.*, 1995). Therefore, this model is statistically better at describing the data than any of the other models. The best-fit model and data are shown in Fig. 3 and Table 2.

In conclusion, the XAFS analysis of the Cu k-edge data from the SAMMS + SO_4 sample indicates that the structure is best described by monodentate bonding of SO_4 anion to the Cu(II) bound to one closed and two open NH_2-CH_2-CH_2-NH_2 chains (see Fig. 2a). The confidence in model is based on three factors: (1) statistically the fit to the data is better than with any of the other models listed in Table 1, (2) the fit parameters are reasonable for this model, and (3) this model is one of the lowest-energy minimum configurations from theoretical molecular dynamic simulations.

XAFS spectroscopy can be used to determine mono-, bi-, or tridentate bonding between the end member of the SAMMS materials and tetrahedral anions. Future studies of the interaction between SAMMS and the contaminant anions AsO_4 and CrO_4 look promising.

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