# X-ray Absorption Spectroscopy of Aqueous Aluminum-Organic Complexes

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Aqueous-phase X-ray absorption near-edge structure (XANES) spectra were collected on dissolved Al complexes with organic ligands, including desferrioxamine B, EDTA, acetohydroxamate, malate, oxalate, and salicylate. Spectral interpretations were made using the density functional theory-based modeling package StoBe. The goals of this work were to study the geometric and electronic structural characteristics of these complexes relative to  $Al(H_2O)_6^{3+}$  and to examine the utility of the aqueous Al XANES technique as a tool for probing Al speciation and structure. In the case of EDTA, aqueous Fourier-transform infrared spectroscopy was also used to corroborate the structures of the  $Al(EDTA)^{-}$  and  $AlOH(EDTA)^{2-}$  complexes. Synthetic XANES spectra calculated with StoBe reproduced the observed spectral differences between  $Al(H_2O)_6^{3+}$ , Al(dfoB)<sup>+</sup>, and Al(EDTA)<sup>-</sup>. The narrower XANES feature observed for Al(dfoB)<sup>+</sup> relative to Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> can be attributed to a weaker splitting of the Al 3p - O 2p interactions in the former, while Al(EDTA)<sup>-</sup> exhibits split Al 3p – ligand interactions that likely result from the mixed O/N coordination. In complexes with mixed aqua/organic-oxygen ligation (Al-acetohydroxamate, Al-malate, Al-oxalate, and Al-salicylate), spectra exhibit linear, systematic changes in peak width as a function of H<sub>2</sub>O to organic ligand ratio in the Al coordination sphere. These results highlight the sensitivity of the aqueous Al K-edge XANES spectrum to coordination environment and demonstrate its utility as an experimental probe for future studies of Al speciation in complex solutions.

### Introduction

The aqueous chemistry of aluminum is of critical interest in the geologic and environmental sciences. In the aqueous phase, Al may be present in a variety of species depending on solution composition, confounding its behavior in the environment. The free Al<sup>3+</sup> ion strongly binds to water in solution, forming a series of monomeric and polymeric hydrolysis products depending on pH,<sup>1</sup> but equally important in natural aquatic environments are the various complexes formed with organic and inorganic ligands, such as fluoride, sulfate, silicate, small organic acids (e.g., acetate, oxalate, and citrate), and organic macromolecules such as humic substances.<sup>2–4</sup> These ligand complexes control Al dissolution kinetics, solubility, and mobility, thereby affecting mineral weathering and diagenetic processes.<sup>4-6</sup> The toxicity of Al to plants and fish is also dependent on speciation, which is important in regions of high dissolved Al content resulting from acid mine drainage and acid deposition.<sup>7–10</sup>

For these reasons, there has been a great deal of interest in understanding the chemistry of aqueous Al, including its speciation (i.e., the relative abundance and stoichiometries of Al-ligand complexes in solution) and the chemical and electronic structure of individual Al species, the latter being necessary for understanding and predicting chemical behavior. Numerous analytical techniques have been applied to the study of Al speciation,<sup>11,12</sup> with vibrational and nuclear magnetic resonance (NMR) spectroscopies proving particularly useful in resolving both aqueous speciation and structure. Many of these techniques

are used to study Al complexes from the perspective of the ligand, particularly when a ligand of interest is highly sensitive to a given spectroscopic method. Infrared and Raman spectroscopies have been used to study Al complexes with small organic acids and humic substances,<sup>13–17</sup> and Raman spectroscopy has also been applied to the study of aqua-Al complexes and their hydration structures.<sup>18–20</sup> Though useful, these techniques are limited to complexes that contain IR- and Ramanactive vibrational modes. <sup>17</sup>O, <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P, and <sup>19</sup>F NMR have also been effective in elucidating structural details of Al complexes from the ligand perspective<sup>21–28</sup> but are limited to a subset of ligands that contain NMR-active nuclei sensitive to Al complexation.

In general, a more complete understanding of metal-ligand structure can often be gained by combining ligand-based methods with complementary, element-specific techniques that probe the metal. <sup>27</sup>Al-NMR spectroscopy has been widely used to study Al solution complexes, often in combination with ligand-targeted NMR spectroscopy, vibrational spectroscopy, and molecular modeling. The <sup>27</sup>Al-NMR method has been applied with varying success to virtually all classes of aqueous Al complexes, including monomeric hydrolysis species,<sup>29-31</sup> polymers,<sup>32,33</sup> inorganic complexes (e.g., sulfate and fluoride),<sup>21,34</sup> and organic complexes (e.g., lactate, 35,36 oxalate, 37 citrate, 35,38 salicylate,<sup>36</sup> amino acids,<sup>22</sup> and EDTA<sup>35,39,40</sup>). However, the method is limited due to the high sensitivity of the quadrupolar <sup>27</sup>Al nucleus to electric field gradients that may arise from geometric distortions and mixed ligation in the Al coordination sphere. This effect can cause substantial peak broadening in the <sup>27</sup>Al-NMR spectrum, limiting one's ability to study or even detect many environmentally relevant Al complexes.

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Another promising element-specific technique is Al K-edge X-ray absorption near-edge structure (XANES) spectroscopy. Aledge XANES has been used extensively to study the structure of Al in solid phases, but due to the relatively short penetration depth of X-rays in air at the Al K-edge (~1550 eV), the experiments are typically done under vacuum. Attempts have been made to overcome this experimental complexity by designing sample chambers and solution cells that minimize beam attenuation, and Al-edge XANES has now been applied to the study of dissolvedphase Al.<sup>41–45</sup> Matsuo and co-workers, using a thin solution cell for collection of transmission-mode spectra, have applied the Al XANES technique in combination with discrete variational  $X\alpha$  (DV- $X\alpha$ ) calculations to study aqueous Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> and Alethylenediaminetetraacetate (Al(EDTA)<sup>-</sup>).41,42 Discrete variational X $\alpha$  (DV-X $\alpha$ ) calculations were run for spectral interpretation, and on the basis of these results, the authors proposed a distorted 6-coordinate geometry for  $Al(H_2O)_6^{3+}$  and a 5-coordinate geometry for Al(EDTA)<sup>-</sup>. The Al XANES technique was also used by Matsuo et al. to track the structural transformation of Al during polymerization and precipitation of gibbsite from Al(OH)<sub>4</sub><sup>-</sup> on pH reduction, illustrating its potential for monitoring chemical changes in real-time.<sup>45</sup> In a recent report,<sup>44</sup> we presented a detailed analysis of the aqueous  $Al(H_2O)_6^{3+}$  fluorescence-mode XANES spectrum and its structural implications using density functional theory (DFT) based XANES modeling, illustrating that the combined experimental and modeling approach is effective in elucidating the electronic structure of the complex. We provided a modified interpretation of the XANES spectrum, arguing that it is in fact consistent with the highly symmetric octahedral structure proposed on the basis of ab initio geometry optimizations reported in the literature.

In this work, we extend the use of the Al K-edge XANES technique to the study of mixed-ligand aqueous Al species, including organic complexes with oxalate, salicylate, malate, acetohydroxamate (aHA), desferrioxamine B (dfoB), and EDTA. Oxalate, salicylate, and malate are typical examples of the small carboxylic acids abundant in natural waters and are representative of the metal-binding functional groups in humic substances.46 Desferrioxamine B, a trihydroxamate siderophore secreted by microbes for acquiring Fe, is also abundant in many soils,47 and aHA is often used as a simpler structural analogue in chemical studies of dfoB.48,49 These particular organic acids were chosen not only for their environmental relevance, but also to systematically study the effects of mixed aqua-organic oxygen ligation on the aqueous Al XANES spectrum in systems with relatively straightforward aqueous speciation. The comparison shows a clear, predictable narrowing trend in the Al XANES spectrum as water molecules are replaced by organic oxygen ligands in the Al coordination sphere. We also revisit the Al(EDTA)<sup>-</sup> spectrum previously described by Matsuo,<sup>42</sup> extending the study of this system to include the AlOH(EDTA)<sup>2-</sup> complex dominant at higher pH. On the basis of aqueous Fourier-transform infrared (FTIR) spectra and DFT-based XANES calculations, an octahedral-hexadentate structure is proposed for Al(EDTA)<sup>-</sup>, consistent with the literature consensus. A similar octahedral structure is predicted for AlOH-(EDTA)<sup>2-</sup>, with one acetate ligand displaced by a hydroxyl. This work provides new insights on the geometric and electronic structures of some geochemically relevant aqueous Al complexes, while further demonstrating the utility of the XANES technique as an additional tool for elucidating the speciation and structure of aqueous-phase Al.

## **Materials and Methods**

Materials and Sample Preparation. Reagent-grade chemicals, including aluminum chloride hexahydrate (AlCl<sub>3</sub>•6H<sub>2</sub>O), hydrochloric acid (HCl), sodium hydroxide (NaOH), malic acid disodium salt (Na2·malate), oxalic acid disodium salt (Na2· oxalate), salicylic acid monosodium salt (NaH·salicylate), acetohydroxamic acid (aHA), desferrioxamine B mesylate (dfoB), and ethylenediaminetetraacetic acid disodium salt (Na2·EDTA) were purchased from Sigma-Aldrich. Aluminum chloride and organic acid 100 mM stock solutions were prepared in plastic bottles using deionized water (Milli-Q, 18 M $\Omega$ resistivity). Organic stock solutions were prepared 1-2 days in advance to allow complete dissolution. Aluminum-organic solutions were prepared by addition of stock solutions to deionized water, followed by slow NaOH addition to yield the desired Al concentration (20 mM), Al-organic ratio, and pH. This procedure ensured that the majority of the Al was in an organic-complexed form before base addition. A pH of 4.0 was chosen to maximize ligand complexation while preventing Al polymer formation and precipitation. Higher pH Al-EDTA solutions were prepared in the same manner, with higher EDTA to Al solution ratios to ensure complete complexation. After the mixing and base addition steps, solutions were analyzed by spectroscopy within the same day. pH values were measured using an Orion model 525A pH meter with Orion PerpHecT ROSS Model 8203 and Orion 9107BN pH electrodes following a three-point calibration with buffers at pH 4.0, 7.0, and 10.0.

**XANES Spectroscopy.** X-ray absorption spectra were collected in the modified Soft X-ray Endstation for Environmental Research (SXEER-2)<sup>43,44</sup> on the Molecular Environmental Sciences (MES) beamline 11.0.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory (Berkeley, CA). Fluorescence-mode X-ray absorption spectra were collected on liquid samples in a 1 atm He environment using either a GaAsP photodiode or a photomultiplier tube outfitted with a phosphor scintillator. Two types of solution cells were used in the experiments: a Plexiglas solution cell fitted with a 100 nm thick Si<sub>3</sub>N<sub>4</sub> window and a vertically aligned plastic beverage straw, plugged at the bottom with Teflon tape and with a small rectangular slit cut into the side. The liquid sample was retained in the straw by surface tension, allowing the X-ray beam to contact the air—water interface at the rectangular slit.

XANES spectra were collected between 1550 and 1600 eV, with step sizes of 0.2 eV in the edge region between 1560 and 1573 and 0.5 eV below and above the edge. Baseline correction and normalization were performed by fitting straight lines to the spectra well below and above the edge, then rescaling the spectra by zeroing the line slopes and setting pre-edge and postedge line intercepts to 0 and 1, respectively. In some of the overlay graphs, spectra were slightly rescaled based on peak height to compare spectral shapes in the XANES region. Energy calibration was performed periodically by collecting a spectrum on a single-crystal corundum sample and shifting the first XANES transition to 1567.5 eV, as described in ref 44. Normalization and calibration were performed using WinXAS<sup>50</sup> and Microsoft Excel.

**Infrared Spectroscopy.** Aqueous FTIR spectra were collected in attenuated total reflection (ATR) mode using a Bruker IFS 66v/S spectrometer, equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector, with an aperture setting of 4 mm. The sample spectra were collected on a ZnSe trough-style ATR crystal, housed in a Spectra-Tech ATR unit. IR spectra were obtained from an average of 5000 interferometer scans. Spectra of clean (Milli-Q) water were collected before

and after sample collection for use in subtraction of ZnSe features and the water feature near  $1640 \text{ cm}^{-1}$ .

Calculation of X-ray Absorption Spectra. X-ray absorption transition energies and oscillator strengths were calculated with density functional theory, implemented in the StoBe software package<sup>51</sup> using the gradient corrected exchange functional of Becke52 and correlation functional of Perdew.53 In StoBe, X-ray absorption transition energies and probabilities (oscillator strengths) are calculated using the transition-potential method.<sup>54</sup> In this method, initial and final states are calculated using the same potential; one that corresponds to a "transition state" in which the  $\alpha$ -1s orbital is assigned an electron occupation of one-half. This procedure accounts for the majority of the relaxation energy on core excitation, while simplifying the calculation of transition energies and intensities.<sup>54,55</sup> The DFT level of theory implemented in StoBe, an improvement over the traditional X $\alpha$ -multiple scattering method with a "muffintin" potential,<sup>54,56</sup> has been used to accurately describe XANES spectra at the O K-edge of water and ice (refs 57-59 and references therein), the C, N, and O K-edges of numerous organic molecules (refs 49, 60-64 and references therein), the Fe L<sub>2</sub>/L<sub>3</sub> edges of a ferrocene-labeled peptide,<sup>63</sup> and recently the Al K-edge of  $Al(H_2O)_6^{3+}$  in our previous report,<sup>44</sup> to name a few examples. Advances in theoretical XANES modeling continue to be made, with real-space multiple scattering and time-dependent density functional theory (TDDFT) methods being active areas of research (e.g., refs 65-67 and references therein). StoBe was chosen in our work, however, as it is a fast, relatively simple, well-established, commercially available, and easily accessible molecular orbital-based method for semiquantitatively understanding orbital contributions involved in XANES transitions.

Although the raw transition energies and intensities were much more important in our interpretations of the experimental XANES spectra, synthetic spectra were also generated from the calculated transitions to qualitatively assess agreement between theory and experiment. These synthetic spectra can be generated within StoBe by assigning Gaussian peaks to each of the calculated transitions, with peak areas fixed by the oscillator strength. In StoBe, the widths of the Gaussian peaks are assigned according to a continuous, piecewise linear function of energy defined by four variables,  $E_1$ ,  $E_2$ ,  $w_1$ , and  $w_2$ . Specifically, a constant width of  $w_1$  is assigned below energy  $E_1$ , a constant width of  $w_2$  is assigned above energy  $E_2$ , and the width is varied linearly between energies  $E_1$  and  $E_2$ . These width and energy parameters are typically chosen by the user to obtain a good fit with an experimental spectrum. Increasing the peak width with energy in this fashion accounts for two effects: the decrease in lifetime of the excited state (and hence wider peak) with increasing energy above the ionization potential, and the way in which StoBe handles continuum-state transitions above the ionization potential. These transitions are approximated in StoBe by addition of a large, secondary basis set of diffuse orbitals, such that the continuum is represented by a large but limited series of discrete transitions. In order to represent the postedge continuum in the spectra, these transitions require larger peak widths than those representing the sharp bound state transitions closer to the absorption edge. Although we do not necessarily expect the increase in peak width to be piecewise linear, the technique is a simple way to fit a synthetic spectrum with very few parameters. The method has also proven adequate in several previous studies (58 and references therein). Finally, the StoBe program also calculates three-dimensional (3D) electron densities for each molecular orbital (viewed using the program Molden<sup>68</sup>), useful in qualitatively assessing the atomic orbital contributions involved in bonding.

Calculations were run using the IGLO-III basis set<sup>69</sup> on Al and DZVP basis set<sup>70</sup> on the ligands (C, H, O, and N). For most of the complexes we studied, use of the IGLO-III basis set on all elements would have exceeded the maximum number of orbital Gaussians allowed in StoBe (version 1.0 for Microsoft Windows), and in our previous study the IGLO-III/DZVP combination performed well.44 The ionization potential (IP) was recalculated as the difference in total energy between structures with Al  $\alpha$ -1s orbital occupations of 1 and 0. This new value was typically lower than the IP calculated for the half-corehole complex by 2.6-2.8 eV, depending on the complex. An initial energy calibration was performed by shifting the half-corehole IP and transition energies downward by this amount. Comparison with experimental spectra required an upward reshifting of the transitions by 4.0-4.5 eV, depending on the complex. In our previous study, this shift was found to vary with the basis set of the absorbing element.<sup>44</sup> In this study, as in the previous, the absolute value of this shift is not of critical importance.

Speciation Calculations. The aHA acid dissociation constant and stability constants for the Al-aHA system (T = 25 °C, ionic strength ( $\mu$ ) = 0.2 M) were taken from Farkas et al.,<sup>71</sup> and stability constants (not including acid dissociation constants) for the Al-malate system (T = 37 °C, ionic strength ( $\mu$ ) = 0.15 M) were taken from Venturini-Soriano and Berthon.<sup>72</sup> Stability constants for all other species, including the malic acid dissociation constants, were collected from the Martell and Smith database<sup>73</sup> and represent values at T = 25 °C and varying  $\mu$ . Stability constants were included for Al dimer and trimer species but not for Al<sub>13</sub> or Al solids. As necessary, stability constants were converted to overall formation constants ( $\beta$ ) and extrapolated to zero ionic strength using activity coefficients calculated with the Davies equation. The formation constant values used are given in the Supporting Information. Speciation calculations were performed with ionic strength corrections (Davies equation) using Visual MINTEQ version 2.50,74 a Microsoft Windows version of MINTEQA2 version 4.0.75 The pH 4 results (Table 1) were obtained by maintaining charge balance in the calculation and iteratively adjusting the Na<sup>+</sup> concentration until a pH of 4.0 was calculated. This procedure closely mimicked the experimental procedure, which involved NaOH addition with no attempts to fix ionic strength. In all cases, the calculated Na<sup>+</sup> content was similar to the amount of NaOH required in the experiments to reach pH 4.

#### **Results and Discussion**

The XANES spectra of the aqueous Al-organic solutions studied are shown in Figure 1, along with aqueous AlCl<sub>3</sub> solutions at low and high pH (Figure 1f,g). The energy of the first Al XANES peak is a good indicator of coordination number for Al, and the peak at 1569.2 eV for 20 mM AlCl<sub>3</sub> at pH 3.6 (Figure 1f) is consistent with the 6-coordination of the  $Al(H_2O)_6^{3+}$  complex (Figure 2a), the dominant solution species at this pH.<sup>44</sup> For comparison, the spectrum of a 20 mM AlCl<sub>3</sub> solution adjusted to pH 12.3 is shown in Figure 1g. At this pH, the dominant species in solution is the tetrahedral  $Al(OH)_4^-$  complex (Figure 2b).<sup>30</sup> The complex exhibits a bound state transition at 1565.8 eV, consistent with 4-coordinate Al-containing minerals that exhibit this peak near 1566 eV.<sup>76,77</sup> With the exception of the high pH Al-EDTA solution (Figure 1c, discussed below), the peak energies for the Al-organic spectra are within 1569.1-1569.8 eV, just above that of the Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> complex. This is slightly above the

 TABLE 1: Chemical Speciation of the Al-Organic Solutions

 Used in the XANES Experiments<sup>a</sup>

	1		
20 mM AlCl <sub>3</sub> + 20 mM aHA, <sup>b</sup> pH 4.0 (18.4 mM Na <sup>+</sup> ) <sup>c</sup>			
	conc. (mM)	% Al	% aHA
Al <sup>3+</sup>	5.88	29.7%	
Al(OH) <sup>2+</sup>	0.18	0.9%	
$Al(aHA)^{2+}$	9.50	48.0%	47.5%
Al(aHA) <sup>+</sup>	4 09	20.7%	20.5%
$\Delta IOH(aHA)_{0}^{0}$	0.13	0.6%	0.6%
$H(aHA)^0$	2.01	0.0 %	10.0%
II(dIIA)	2.01		10.0 %
$20 \text{ mM AlCl}_3 + 60 \text{ mM aHA, pH } 4.0 (38.0 \text{ mM Na}^+)$			
	conc. (mM)	% Al	% aHA
$Al^{3+}$	0.14	0.7%	
Al(aHA) <sup>2+</sup>	2.95	14.7%	4.9%
$Al(aHA)_2^+$	15.54	77.7%	25.9%
$Al(aHA)_3^0$	0.86	4.3%	1.4%
AlOH(aHA) <sub>2</sub> <sup>0</sup>	0.51	2.5%	0.8%
H(aHA) <sup>0</sup>	22.39		37.3%
20 mM AlCl <sub>3</sub> + 20 mM Na <sub>2</sub> Malate, pH 4.0 (24.8 mM Na <sup>+</sup> )			
	conc. (mM)	% Al	% Mal <sup>b</sup>
Al <sup>3+</sup>	0.11	0.5%	
Al(Mal) <sup>+</sup>	0.23	1.1%	1.1%
AlOH(Mal) <sup>0</sup>	1.02	5.1%	51%
Al <sub>2</sub> OH(Mal) <sub>2</sub> <sup>-</sup>	0.10	1.0%	1.5%
$\Delta l_2(OH)_2(Mal)^{2+}$	0.10	2.4%	1.3%
$\Lambda_1(OH) (Mal)^+$	0.24	5.7%	2.80%
$A1_2(OII)_3(Wal)$	1.55	15.5%	2.070
$A1_2(OII)_3(Ivial)_2$	1.55	13.3%	10.60
Al <sub>3</sub> (OII) <sub>4</sub> (Wal) <sub>4</sub> $(Mal)_4$	0.55	1.9%	10.0%
$AI_4(OH)_5(IVIaI)_4$	5.05	00.0%	00.0%
H(Mal)	0.21		1.0%
20 mM AlCl <sub>3</sub> + 20 mM Na <sub>2</sub> Oxalate, pH 4.0 (3.2 mM Na <sup>+</sup> )			
	conc. (mM)	% Al	% Oxal <sup>b</sup>
Al <sup>3+</sup>	2.59	12.9%	
$Al(Oxal)^+$	11.43	57.1%	57.1%
$Al(Oxal)_2^{-}$	2.64	13.2%	26.4%
Al(Oxal) <sub>3</sub> <sup>3-</sup>	0.04	0.2%	0.5%
AlOH(Oxal) <sup>0</sup>	0.62	3.1%	3.1%
$Al_3(OH)_3(Oxal)_3^0$	0.84	12.5%	12.5%
20 mM AlCl <sub>3</sub> + 20 mM (NaH)Salicylate, pH 4.0 (18.6 mM Na <sup>+</sup> )			
	conc. (mM)	% Al	% Sal <sup>b</sup>
A1 <sup>3+</sup>	1.61	8.0%	
AIOH <sup>2+</sup>	0.05	0.3%	
Al(Sal) <sup>+</sup>	17.88	89.4%	89 4%
$\Delta I(Sal)$	0.31	1.6%	3.1%
$\Lambda_1(OH)$ (Sol) 0	0.51	0.6%	0.6%
$\mathbf{U}$ (Sol) <sup>0</sup>	0.00	0.0%	0.0%
$U(S_{0}1)^{-}$	0.10		0.3%
11(381)	1.27		0.3%
<sup>a</sup> Only species repre	senting more than	0.5% of total	Al or organic

<sup>*a*</sup> Only species representing more than 0.5% of total Al or organic are listed. <sup>*b*</sup> aHA = acetohydroxamic acid, Mal = malate, Oxal = oxalate, Sal = salicylate. <sup>*c*</sup> Amount of excess Na<sup>+</sup> added in the charge-balanced calculation to achieve a pH of 4.0.

observed range for octahedral coordination in Al-bearing solid phases but is still consistent with 6-fold coordination for these complexes.

Chemical speciation calculations were conducted to determine the relative abundance of various Al-organic complexes present for the solution conditions used in the XANES experiments. Species abundances are listed on a percentage basis in Table 1 for illustrative purposes, but it is important to note that our primary goal with these calculations was merely to assess which species are most likely in the majority. (Although inaccuracies in the reported stability constants for the Al-organic species



**Figure 1.** Al K-edge XANES spectra of aqueous AlCl<sub>3</sub> and Al–organic solutions. All spectra were collected on solutions containing 20 mM Al at pH 4.0, unless indicated otherwise in the legend. Where specified, ratios in the legend refer to the total Al to organic concentration ratio, not the stoichiometry of the dominant solution species.

considered would affect the detailed percentages given in Table 1, it is unlikely that the true dominant species are different from those indicated by the calculations.) Speciation results for each solution are discussed in more detail below. The configurations of some of the dominant solution complexes are illustrated in Figure 2, with hypothetical configurations shown for complexes with unknown or debatable structure, including the Al-malate and Al-salicylate complexes. The speciation results and XANES spectra for these solutions are described below, beginning with a discussion of the  $Al(dfoB)^+$  complex, in which the Al ion is fully complexed by organic O ligands (in this case, O from C=O and N-O groups). This is followed by results obtained for structures with more complex mixed-ligation. These include Al(EDTA)<sup>-</sup>, which involves complexation by organic O and N ligands, followed by cases involving sequential replacement of organic O ligands by OH<sup>-</sup> and H<sub>2</sub>O.

**Organic O Ligation:** Al–dfoB. Desferrioxamine B (dfoB) is a common, well-studied siderophore found in soils, which is known to form a strong, symmetric, hexadentate aqueous solution complex with Fe.<sup>61,78</sup> The binding constant for Al, although not as high as for Fe (log K = 24.14 for Al vs 30.6 for Fe(III)),<sup>73</sup> indicates that the Al–dfoB complex is quite strong. The speciation calculation for the 20 mM AlCl<sub>3</sub>, 20 mM dfoB solution at pH 4 indicates that 99.8% of the Al in solution is bound within the Al(dfoB)<sup>+</sup> species, with the terminal amine



**Figure 2.** Structures of the aqueous Al species dominant in solution under the conditions investigated in the XANES experiments. Only one ligand configuration is shown for each complex, although multiple configurations may exist for some species; for example, one of the two aHA ligands in  $Al(aHA)_2^+$  could be rotated to displace an axial water ligand. Two configurations are shown for  $Al(salicylate)^+$ , since the structure of this species is uncertain.

protonated below pH 9. We assume that the bonding geometry is similar to that of the Fe-complex, with bidentate chelation by all three of the hydroxamate ligands in the structure (Figure 2d), consistent with the DFT-optimized Al(dfoB)<sup>+</sup> structure of Domagal-Goldman et al.<sup>79</sup> This is also consistent with the bonding environment proposed for the Al(aHA)<sub>3</sub><sup>0</sup> complex on the basis of <sup>27</sup>Al-NMR spectroscopy (Figure 2c).<sup>71</sup>

The XANES spectrum of the 1:1 Al-dfoB solution (Figure 1a) exhibits a strong feature at 1569.8 eV, appearing much narrower in width than the  $Al(H_2O)_6^{3+}$  feature. Peak broadening in XANES spectra can often be attributed to transition splitting resulting from geometric distortions. However, our previous DFT calculations indicated that the broadness of the  $Al(H_2O)_6^{3+}$  spectrum is caused by the presence of multiple Al 3p - O 2s/p transitions, observed for both highly symmetric and distorted complexes.<sup>44</sup> The spectral differences observed for  $Al(H_2O)_6^{3+}$  and  $Al(dfoB)^+$  are therefore assumed to be due to the differences in ligands, rather than geometry effects.

Theoretical XANES spectral simulations were performed in StoBe using  $Al(aHA)_3^0$  as a model for the  $Al(dfoB)^+$  complex. The larger Al(dfoB)<sup>+</sup> structure could not be run in StoBe with the chosen basis sets due to size constraints, but the similarity in coordination environments between the two complexes makes  $Al(aHA)_3^0$  a very good model (Figure 2). To test exclusively for ligand effects, the structure of the coordination sphere was assigned the same highly symmetric geometry used in previous calculations on  $Al(H_2O)_6^{3+}$ , with Al–O bond lengths set to 1.90 Å and O-Al-O bond angles set to 90°.44 Bond lengths and angles within the acetohydroxamate ligand were assigned based on the DFT-optimized, hydroxyl deprotonated cis-aHA structure of Edwards et al.<sup>78,80</sup> After a 4.4 eV correction (similar to the 4.6 eV correction required for Al( $H_2O_{6}^{3+}$ ), the synthetic spectrum produced from the calculated XANES transitions closely reproduces the features observed in the  $Al(dfoB)^+$ spectrum (Figure 3). The results suggest that the sharp, narrow XANES feature primarily results from one set of three degenerate transitions, labeled "i." in the figure, exhibiting Al 3p - O2p antibonding character (orbital plot i. in Figure 3). A smaller contribution comes from transition set "ii.", which also exhibits Al 3p - O 2p antibonding character, but with apparently less electron density on the Al-bound ligands.

The Al(aHA)<sub>3</sub><sup>0</sup> calculation results differ markedly from those obtained previously for Al( $H_2O$ )<sub>6</sub><sup>3+,44</sup> Although some splitting



**Figure 3.** XANES spectrum of the Al(dfoB)<sup>+</sup> complex compared with StoBe calculation results for the structurally analogous Al(aHA)<sub>3</sub><sup>0</sup> complex. The black vertical lines represent energies of calculated Al 1s to valence orbital transitions (with line heights proportional to transition probability); the thick gray vertical line is the calculated ionization potential; and the synthetic spectrum calculated from the transitions (thin black curve) overlays the experimental spectrum (gray circles). Calculation results have been shifted +4.4 eV to achieve alignment with experiment. One representative electron density image is shown below the plot for each of the first two major transition clusters, indicated by roman numerals. The synthetic spectrum was generated using the following parameters (in eV):  $E_1 = 1573.7$ ,  $E_2 = 1581.7$ ,  $w_1 = 4.3$ ,  $w_2 = 10$ .

of the Al 3p – O 2p interaction is observed here for Al(aHA)<sub>3</sub><sup>0</sup>, the effect is not as strong as with Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>. Further, no significant Al 3p – O 2s contribution is observed for Al(aHA)<sub>3</sub><sup>0</sup>,

highlighting important differences in the electronic structures of the two complexes. The results for  $Al(aHA)_3^0$  may also be compared with the results of Domagal-Goldman et al., who assert based on natural bond orbital (NBO) calculations that the Al-O bonds within the Al(dfoB)<sup>+</sup> complex are exclusively ionic.79 Our calculation results are not consistent with this assertion, since the electron density images in Figure 3 do suggest some Al 3p - O 2p orbital interaction. However, these density plots are only a qualitative indicator of orbital interactions and cannot be used to accurately assess the degree of covalent bonding without further processing and validation. In addition, the experimental spectrum itself is not necessarily inconsistent with the idea that the Al-O bonds are ionic, since an Al 1s - 3p transition without significant electron sharing between atomic Al and O orbitals would also yield the single, narrow XANES feature observed. It is important to note that an energy-optimized  $Al(aHA)_3^0$  or  $Al(dfoB)^+$  structure might exhibit different bond lengths and angles than the idealized structure used here, which may have an influence on the XANES calculation results. However, given the degree to which the calculations reproduce the experimental spectrum, the idealized  $Al(aHA)_3^0$  structure used here is assumed to be sufficient for spectral interpretation.

Organic O/N Ligation: Al-EDTA. The XANES spectra collected on Al-EDTA solutions at pH 4.0 and 7.5 are shown in Figure 1, panels b and c, respectively. Speciation calculations indicate that the Al(EDTA)<sup>-</sup> and AlOH(EDTA)<sup>2-</sup> complexes are dominant in solution at these respective pH values (Figure S2, Supporting Information). To ensure complete complexation of Al, the solutions were prepared with greater proportions of EDTA (30-40 mM) relative to the 20 mM Al. The Al(EDTA)<sup>-</sup> XANES spectrum (Figure 1b) has a single peak centered at 1569.2 eV. It lacks the higher-energy shoulder present in the  $Al(H_2O)_6^{3+}$  spectrum (Figure 1f) but exhibits a slight shoulder at 1567 eV, between the 4- and 6-coordinate regions highlighted in the figure. The spectrum of the hydroxylated AlOH(EDTA)<sup>2-</sup> complex at pH 7.5 (Figure 1c) has a lower energy peak at 1568.3 eV, which either includes or replaces the 1567 eV shoulder observed for Al(EDTA)<sup>-</sup>. The emergence of these features between the 4- and 6-coordinate regions may be the result of N ligands bound directly to Al, or it may be due to geometric factors, indicating either a distorted 6-coordinate or possibly a 5-coordinate geometry for these structures.

The coordination geometry of the Al(EDTA)<sup>-</sup> complex has been a subject of debate in the literature. Proposed structures have included 7-fold coordination involving the six EDTA ligands and a water molecule,<sup>81</sup> 6-fold coordination involving either the six EDTA ligands or a combination of EDTA ligands and water molecules, 35,39,40,82,83 and a 5-coordinate structure involving four EDTA ligands and a water molecule.42 Of these possibilities, the strongest evidence is in support of the 6-coordinate, hexadentate structure (full coordination by the EDTA with no water ligands in the coordination sphere), which has been proposed based on <sup>27</sup>Al-NMR spectroscopy, <sup>39</sup> <sup>13</sup>C- and <sup>1</sup>H NMR spectroscopy,<sup>82</sup> and ab initio calculations.<sup>83</sup> The 5-coordinate structure proposed by Matsuo et al.<sup>42</sup> was based on Al-edge XANES spectroscopy, discrete variational Xa (DV-Xα) XANES modeling, and unpublished NMR data. However, their Al-EDTA spectrum differs from ours in important ways. First, their XANES spectrum more closely resembles the pH 7.5 AlOH(EDTA)<sup>2-</sup> spectrum (Figure 1c) than the Al(EDTA)<sup>-</sup> spectrum. Second, the peak-to-peak energy difference between Al-EDTA and  $Al(H_2O)_6^{3+}$  in their study appears to be approximately 3 eV, whereas our data indicate a difference of



**Figure 4.** ATR-FTIR spectra of 20 mM Na<sub>2</sub>EDTA (a-c) and 20 mM AlCl<sub>3</sub> + 20 mM Na<sub>2</sub>EDTA (d, e) solutions as a function of pH. The legends give the dominant aqueous species (discussed in the text and Supporting Information), along with solution pH in parentheses.

less than 1 eV for the pH 7.5 spectrum, suggesting a possible calibration error. Solution pH and calibration procedures were not reported in their study.

We used aqueous infrared spectroscopy to further verify the structures of the Al(EDTA)<sup>-</sup> and AlOH(EDTA)<sup>2-</sup> complexes. The asymmetric stretch of the carboxylate group,  $v_{as}$ , is highly sensitive to H-bonding, protonation state, and metal binding, and can be used to infer carboxylate binding modes in solids and solution.<sup>84-86</sup> This technique was used here to probe the EDTA acetate group interactions with Al. Infrared spectra were first collected on aqueous EDTA in the absence of Al, shown in Figure 4a-c. The pH 11.3 spectrum (Figure 4a) exhibits a single band at 1574 cm<sup>-1</sup> corresponding to the  $v_{as}$  of the free carboxylates in EDTA<sup>4-</sup>, the dominant solution species at this pH (Figure S1, Supporting Information). At pH 4.1 (Figure 4b), the H<sub>2</sub>EDTA<sup>2-</sup> species is dominant (Figure S1), and the  $v_{as}$  band increases to 1618 cm<sup>-1</sup> due to hydrogen bonding between the free carboxylates and the protons in the structure, which are believed to reside on the amine groups.<sup>87-89</sup> As the pH is lowered further and the EDTA acetate groups become protonated, the  $v_{as}$  band is replaced by a weaker carbonyl stretch at 1730 cm<sup>-1</sup> (pH 0.44, Figure 4c). These values are consistent with previous infrared results obtained for EDTA in D<sub>2</sub>O by Nakamoto, et al.<sup>86,88</sup>

The aqueous FTIR spectra collected on equimolar (20 mM) Al–EDTA solutions at pH 4.2 and 8.1 (Figure 4d,e) provide insight into the mode of acetate binding in the Al(EDTA)<sup>–</sup> and AlOH(EDTA)<sup>2–</sup> complexes. The Al(EDTA)<sup>–</sup> spectrum exhibits a single  $\nu_{as}$  band at 1654 cm<sup>–1</sup>, suggesting that all four of the EDTA acetate groups are tightly bound to the Al, consistent with the hexadentate binding mode previously proposed.<sup>39,82,83</sup> The 80 cm<sup>–1</sup> increase in  $\nu_{as}$  relative to EDTA<sup>4–</sup> is consistent with other general observations of metal binding by carboxylate in solution,<sup>90–92</sup> and the  $\nu_{as}$  value of 1654 cm<sup>-1</sup> is consistent with trivalent metal—acetate interactions previously observed in metal—EDTA solid salts.<sup>86,93</sup> The AIOH(EDTA)<sup>2–</sup> spectrum exhibits a  $\nu_{as}$  band at 1637 cm<sup>-1</sup>, which is still consistent with metal binding, but may be indicative of a slightly weaker Al—O(-C) bond. This spectrum also exhibits a distinct shoulder at 1592 cm<sup>-1</sup>, indicative of free or weakly H-bonded carboxylate. The ratios of the two peaks suggest that at most one of the four EDTA acetate groups is detached from the Al in this complex, presumably replaced by a hydroxyl group in the Al coordination sphere. The infrared spectroscopy results therefore suggest that both Al(EDTA)<sup>-</sup> and AlOH(EDTA)<sup>2–</sup> are 6-coordinate. The structures proposed based on the IR evidence are shown in Figures 2e and 2f.

For the XANES modeling of Al(EDTA)-, we used the aqueous-phase structure recently calculated by Coskuner and Jarvis,<sup>83</sup> which was optimized using DFT (PBE/cc-pVTZ level of theory) with the COSMO continuum solvation model. This structure has the geometry shown in Figure 2e, with bond lengths of 2.09 Å for Al-N, 1.88 Å for equatorial Al-O (i.e., those within the plane of the Al-N bonds) and 1.92 Å for axial Al-O. Results obtained using this structure are shown in Figure 5a, including the calculated XANES transitions and the synthetic spectrum (solid line), overlain with the experimental Al(EDTA)<sup>-</sup> spectrum from Figure 1b (gray circles). A synthetic spectrum was obtained that closely matched experiment after shifting the calculated transitions 4.0 eV, which is slightly less than the 4.4 eV shift required for the Al(aHA)<sub>3</sub><sup>0</sup>/Al(dfoB)<sup>+</sup> comparison. Strong transitions located near 1569 eV after correction reproduce the main Al(EDTA)<sup>-</sup> peak, and a significant transition near 1567 eV is present under the low-energy shoulder. All of these transitions exhibit Al 3p character and varying amounts of O 2p and N 2p character. The lower energy transition, labeled transition "i.", apparently contains slightly stronger N 2p components relative to transition set "ii." at higher energy, which exhibits more O 2p character. This suggests that the broadening of the spectrum and the appearance of the lower energy feature are the result of mixed N/O ligation.

To investigate distortion effects, StoBe calculations were also performed for an ideally symmetric Al(EDTA)<sup>-</sup> geometry (Figure 5b). The structure was assembled by shifting the Al and ligand positions to yield Al-O/Al-N bond lengths of 1.90 Å and bond angles of 90°, using the optimized structure as a starting point. This structure exhibits similar transitions near 1569 eV, but the lower energy transition decreases in intensity. This may suggest that distortion effects are controlling the XANES features for this complex, but it could equally be argued that optimum Al-O and Al-N bond lengths are the critical factor, as this procedure required a significant shortening of the Al-N bonds. Discussing ligand and distortion effects independently in this case may therefore not be practical. An attempt was also made to investigate AlOH(EDTA)<sup>2-</sup> with StoBe using an approximate geometry assembled from the optimized Al(EDTA)<sup>-</sup> structure. For this structure, one of the two axial carboxylates was moved out of the coordination sphere by rotating the acetate group 180° about the C-N bond, and an OH<sup>-</sup> group was added in its place at a distance of 1.7 Å, yielding a structure similar to the schematic in Figure 2f. XANES calculation results for this structure are shown in Figure 5c, shifted 4.0 eV for consistency with the Al(EDTA)<sup>-</sup> results. The results do contain some weak transitions in the lower energy region near 1568 eV, but they are not far enough above the noise level to clearly account for the lower energy of the main



Figure 5. StoBe results for Al(EDTA)<sup>-</sup> and AlOH(EDTA)<sup>2-</sup> complexes. (a) Calculated transitions (black vertical lines), ionization potential (gray line), and synthetic spectrum (black curve) obtained using the DFT-optimized Al(EDTA)<sup>-</sup> structure of Coskuner and Jarvis. The synthetic spectrum ( $E_1 = 1573.3$ ,  $E_2 = 1578.3$ ,  $w_1 = 3.4$ ,  $w_2 =$ 10) overlays the experimental Al(EDTA)<sup>-</sup> XANES spectrum (gray circles). Calculation results have been shifted +4.0 eV to achieve alignment with experiment. Representative electron density images are shown above the plot for the transition clusters indicated by roman numerals. (b) Calculated transitions and ionization potential for an Al(EDTA)<sup>-</sup> structure with a highly symmetric coordination sphere; Al-ligand bond lengths of 1.9 Å and bond angles of 90°. (c) Calculated transitions for an AlOH(EDTA)<sup>2-</sup> structure obtained via modification of the structure in (a) as discussed in the text. The calculated ionization potential occurs off the scale at 1558.6 eV. Results in (b) and (c) have also been shifted 4.0 eV for consistency.

peak in the AlOH(EDTA)<sup>2–</sup> spectrum. It is clear that this approximate, hypothetical structure does not capture the important features of the spectrum. A better analysis of this spectrum could likely be obtained in the future by calculating an optimized structure with inclusion of solvation waters.

Mixed Aqua/Organic Ligation: 1:3 Al–aHA and 1:1 Malate. In the 1:3 Al–aHA solution (20 mM AlCl<sub>3</sub>, 60 mM aHA, pH 4), only  $\sim 4\%$  of the Al<sup>3+</sup> is present in the Al(aHa)<sub>3</sub><sup>0</sup>

aqueous complex. The majority of the Al is in the  $Al(aHA)_2^+$ form (78% total  $Al^{3+}$ ), with a significant fraction also in the Al(aHA)<sup>2+</sup> form (15% total Al<sup>3+</sup>, Table 1). Speciation of the 1:1 Al-malate solution (20 mM AlCl<sub>3</sub>, 20 mM Na<sub>2</sub>malate, pH 4) is more complicated due to the presence of polymeric species. The calculation results suggest that this solution is dominated by complexes such as  $Al_4(OH)_5(malate)_4^-$ ,  $Al_2(OH)_3(malate)_2^-$ , and Al<sub>3</sub>(OH)<sub>4</sub>(malate)<sub>4</sub><sup>3-</sup>. The proportions listed in Table 1 are approximate at best, since the Al-malate stability constants used are only strictly valid at 37 °C.72 Regardless, we assume the results are accurate enough to suggest that the majority of the Al in solution is present in mixed H<sub>2</sub>O/OH/malate complexes. Chelation by the malate in such complexes presumably accounts for 2-3 of the 6 octahedral sites around the Al, with the remaining 3-4 sites occupied by H2O and OH-. A purely hypothetical example structure (not based on any theoretical or experimental evidence) is shown in Figure 2d for the Al<sub>2</sub>(OH)<sub>3</sub>(malate)<sub>2</sub><sup>-</sup> complex to illustrate what the ligand distribution might look like. One could also imagine a structure in which Al ions share OH<sup>-</sup> ligands, as in the Al dimer,  $Al_2OH_2(H_2O)_8^{4+}$ .

XANES spectra collected on the 1:3 Al-aHA and 1:1 Al-malate solutions are shown in Figure 1d. The overlay illustrates that the two spectra are nearly identical, despite differing organic ligands and complicated speciation. The spectra are similar to the Al-dfoB spectrum, exhibiting a single feature at 1569.8 eV, but are slightly wider. One common characteristic of these two solutions is the ratio of water to organic-O ligands in the inner coordination sphere of Al, which we suggest might be responsible for the similarity of the two spectra. In the 1:3 Al-aHA solution, the majority of the Al is bound to two oxygens from H<sub>2</sub>O and four from aHA. In the 1:1 Al-malate solution, the majority of the Al is also bound to approximately two (plus or minus one) oxygens from H<sub>2</sub>O, with the balance consisting of organic O and OH<sup>-</sup>. On the basis of this comparison, it is not yet clear if Al complexes containing varying proportions of organic O and OH<sup>-</sup> can be resolved.

Mixed Aqua/Organic Ligation: 1:1 Al-aHA, Al-Oxalate, and Al-Salicylate. In the equimolar Al-aHA, Al-oxalate, and Al-salicylate solutions, between 50 and 90% of the Al is present in 1:1 Al-organic complexes (Table 1). Smaller proportions of Al are also present as uncomplexed Al( $H_2O$ )<sub>6</sub><sup>3+</sup> and 1:2 Al-organic complexes. For the 1:1 Al-oxalate and Al-aHA complexes, shown schematically in Figures 1i and 1j, bidentate chelation is assumed. Bidentate chelation by aHA is likely, since this binding mode has been observed in the Al(aHA)<sub>3</sub><sup>0</sup> complex.<sup>71</sup> For oxalate, ab initio studies have demonstrated that the bidentate Al(oxalate)<sup>+</sup> species is more stable than possible monodentate forms above pH 3.94,95 Kubicki et al.94 argued on the basis of <sup>27</sup>Al chemical shift calculations that a monodentate form with a singly protonated oxalate would be more consistent with the <sup>27</sup>Al-NMR features observed by Thomas et al. on an equimolar Al-oxalate solution at pH 3.3.37 However, a protonated structure would be inconsistent with the pH titration results reported by Thomas et al. for the same system, which indicate that both protons are lost from oxalic acid on complexation with Al.<sup>37</sup> Further experimental evidence for the deprotonated bidentate complex was provided by Clausén et al., based on EXAFS experiments with Ga as an Al analogue and a comparison of FTIR results using Ga and Al at pH values below  $4.0^{15}$ 

For salicylate, there is disagreement in the literature as to whether the phenol group deprotonates at low pH on complexation with Al. The phenol-deprotonated bidentate Al(salicylate)<sup>+</sup> complex, shown in Figure 2k, has been argued based on <sup>27</sup>Al NMR<sup>36,96</sup> and <sup>13</sup>C NMR spectroscopy.<sup>23</sup> A monodentate, phenolprotonated Al(H•salicylate)<sup>2+</sup> complex, however, has been proposed as the dominant complex in low pH 1:1 Al–salicylate solutions on the basis of infrared and UV resonance Raman data collected at and below pH 3.8,<sup>16,97</sup> as well as a reinterpretation of the published <sup>27</sup>Al-NMR data collected at pH 3.3 on the basis of chemical shift calculations.<sup>16,94</sup> Potentiometry data on this system are more consistent with the Al(salicylate)<sup>+</sup> stoichiometry (e.g., ref 98), but Trout and Kubicki argue that the potentiometry analyses may not be applicable to the solution conditions used in their resonance Raman study and/or may contain inaccurate assumptions.<sup>16</sup>

For our particular set of solution conditions, some insight on the 1:1 complex stoichiometry may be gained from the observed changes in pH during solution preparation. The 20 mM 1:1 Al-salicylate solution was prepared by combining and diluting 100 mM stock AlCl<sub>3</sub> and Na-H-salicylate solutions, followed by slow adjustment to pH 4.0 with concentrated NaOH. This procedure was repeated to study the detailed pH changes as a function of NaOH addition (titration curve results are included in the Supporting Information). Before adjustment to pH 4.0, the pH of the 1:1 Al-salicylate solution had a measured value of 2.51, whereas the individual AlCl<sub>3</sub> and Na•H•salicylate stocks after dilution to 20 mM had pH values of 3.6 and 5.8, respectively, clearly indicating the liberation of protons on complex formation. Achieving a pH of 4.0 in the 1:1 solution required addition of NaOH to a final concentration of approximately 18.5 mM. Assuming that the 1:1 Al-salicylate complex is dominant at pH 4.0 as our speciation calculations suggest, these results are consistent with the liberation of one proton per complex, yielding the Al(salicylate)<sup>+</sup> stoichiometry. The close agreement between our pH titration curve and the theoretical curve predicted from speciation calculations (SI, Figure S3) suggests that our solution conditions are consistent with published stability constants from pH 2.5 to 4.0. Within this pH range, the 1:1 Al(salicylate)<sup>+</sup> always makes up a majority of the Al and salicylate in solution (SI, Figure S4), although this does not rule out the possibility that the remainder is present in a 1:1 Al(H•salicylate)<sup>2+</sup> complex not previously considered in formulation of the stability constants. We therefore assume, regardless of the arguments to the contrary based on NMR predictions,  $^{16,94}$  that the Al(salicylate)<sup>+</sup> complex is dominant in this pH regime. Because the IR and resonance Raman analyses suggest that the phenol is protonated in the complex, an alternate possibility to the bidentate structure (Figure 2k) is one in which an Al-bound water deprotonates and is potentially stabilized by H-bonding between the hydroxyl group and the protonated phenol (Figure 21). This alternate structure is referred to as the AlOH( $H \cdot salicylate$ )<sup>+</sup> species.

The XANES spectra for the three solutions (Figure 1e overlay) are very similar, exhibiting a shape intermediate between the broad, asymmetric spectrum of  $Al(H_2O)_6^{3+}$  and the narrower spectra of the organic complexes discussed above. In the case of aHA, this may be partly due to the fact that approximately half of the Al in solution is in fact a mixture of  $Al(H_2O)_6^{3+}$  and  $Al(aHA)_2^+$ . However, the  $Al(H_2O)_6^{3+}$  proportion in the Al–oxalate and Al–salicylate solutions is low enough that the 1:1 Al–organic complexes are the primary contributors.

The XANES spectra of the Al–organic complexes discussed thus far exhibit a clear, linear trend with substitution of  $H_2O$ for organic-O ligands in the Al coordination sphere. Specifically, as  $H_2O$  is replaced by organic-O, the low-energy peak and broad, high-energy shoulder characteristic of the Al( $H_2O$ )<sub>6</sub><sup>3+</sup> spectrum



**Figure 6.** XANES spectra for the low pH AlCl<sub>3</sub>, Al–aHA, and Al–dfoB solutions from Figure 1, overlaid for comparison. Descriptions in the legend refer to solution compositions, not the dominant species stoichiometries. The dominant species under the given solution conditions are discussed in the text and Table 1.

begin to merge, creating a narrower and more symmetric feature in the XANES region. This change with ligand substitution is more clearly observed in Figure 6. In this figure, the XANES results for the low pH AlCl<sub>3</sub>, Al-aHA, and Al-dfoB solutions are overlaid, effectively illustrating spectral change as a function of hydroxamate group substitution. Specifically, the high-energy shoulder between 1571 and 1575 eV decreases in intensity, and the main peak shifts up slightly to 1570 eV with the substitution of water ligands by hydroxamate. To a large degree, these observations are reproduced by the XANES modeling. Figure 7 shows the calculated electron transitions for  $Al(H_2O)_6^{3+}$ ,  $Al(aHA)^{2+}$ ,  $Al(aHA)_{2}^{+}$ , and  $Al(aHA)_{3}^{0}$ , compared with the experimental spectra from Figure 6. Identical coordination shell geometries were assigned to the four structures (Al-O = 1.9Å, O-Al-O angle = 90°). The Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> structure with 12 point-charge solvation waters in the second shell was used in the comparison, since this structure better reproduced the experimental spectrum (see Figure 5 in ref 44). In this structure, two point-charge water molecules were assigned to each water ligand in the complex in an H-bond accepting position.<sup>44</sup> In the  $Al(aHA)^{2+}$  and  $Al(aHA)_{2}^{+}$  structures, the second shell point charges were included for the remaining water ligands and removed for the water ligands replaced by aHA. Again, these structures do not reflect the changes in coordination geometry that likely occur with ligand exchange. Using these structures, it was difficult to generate synthetic spectra that adequately reproduced the experimental data, so synthetic spectra are not shown for comparison. From a qualitative perspective, however, the calculated transitions exhibit the types of changes observed in the experimental spectra; the Al 3p - O 2p interactions consolidate and move to lower energy, and the Al 3p - O 2sinteraction is gradually lost with exchange of H<sub>2</sub>O by aHA.

It is not clear if organic O and hydroxyl ligands are as easily resolved in the XANES spectrum. It was observed above that the 1:3 Al-aHA and 1:1 Al-malate solution spectra were very similar, despite the presence of hydroxyl groups in the dominant Al-malate complexes. Unfortunately, this observation makes it difficult to resolve which of the two Al-salicylate structures shown in Figure 2 is the true structure, based on XANES arguments. In other words, although it is tempting to argue that the bidentate structure is the most likely based on the spectral similarity between Al-salicylate, Al-aHA, and Al-oxalate, the Al-salicylate spectrum is not necessarily inconsistent with the monodentate AlOH(H•salicylate)<sup>+</sup> structure.



**Figure 7.** Electron transitions (thin vertical lines) and ionization potentials (thick gray vertical lines) for mixed aqua-organic Al complexes as a function of hydroxamate substitution, calculated using Stobe. Experimental XANES spectra from Figure 1 are shown for comparison, with solution conditions indicated in parentheses in the legend.

#### **Summary and Conclusions**

Al-edge X-ray absorption near-edge structure (XANES) spectra were collected on a series of Al-organic complexes to study the effects of coordination environment on the spectra. The purposes of these experiments were two-fold: (1) to reveal insights into the geometric and electronic structures of the specific complexes studied and (2) to illustrate more generally the utility of the XANES technique as a tool for studying dissolved Al speciation. The XANES spectra were interpreted using the DFT-based software package StoBe.

Synthetic spectra generated using StoBe reproduced the observed differences in XANES spectra between Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> and the hexadentate Al–organic complex Al(dfoB)<sup>+</sup>. The calculation results indicate that whereas the Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup> spectrum is influenced by multiple Al 3p – O 2s and 2p interactions, the Al(dfoB)<sup>+</sup> spectrum is dominated by a single Al 3p – O 2p transition. Calculated spectra also reproduced the XANES spectrum for the hexadentate Al(EDTA)<sup>-</sup> complex, which exhibited unique features attributable to the mixed O/N ligation within the coordination sphere. Infrared spectroscopy evidence was also presented that confirmed the hexadentate structure of the complex. StoBe calculation results were less successful in reproducing the AlOH(EDTA)<sup>2-</sup> features, which may have been due to the lack of a more appropriate, energy-optimized structure.

Spectra collected on mixed aqua-organic Al complexes exhibited highly systematic trends. It was observed that Al complexes involving different organic ligands (acetohydroxamate, malate, oxalate, and salicylate) yield very similar spectra

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when the ratios of organic O to H<sub>2</sub>O in the coordination sphere are similar. Further, the XANES spectra exhibit a steady narrowing of the near-edge feature on progressive replacement of H<sub>2</sub>O by organic O in the Al coordination sphere. This observation was qualitatively reproduced in spectral calculations on the Al-H<sub>2</sub>O-aHA system. Spectra collected on mixed complexes believed to contain OH<sup>-</sup> in the coordination sphere appeared similar to those that do not, suggesting that differences arising from OH<sup>-</sup> and organic-O may be difficult to resolve without further studies on structurally well-known complexes. Overall, these results demonstrate that the XANES technique has the sensitivity to resolve many structural aspects of aqueous Al complexes. Used in combination with <sup>27</sup>Al-NMR and other ligand-based spectroscopic methods, this technique represents a powerful tool in elucidating aqueous Al structure, and one that will see greater use in the future as synchrotron-based tools become more readily available and user-friendly.

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**Supporting Information Available:** Stability constants used in speciation calculations, concentration versus pH diagrams for the EDTA and Al–EDTA systems, and pH titration results and speciation diagram for the Al–salicylate system. This information is available free of charge via the Internet at http:// pubs.acs.org.

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