

# XAFS Investigations of Hydrated Cr<sup>3+</sup> Ions and Their Complexation to Dissolved Acetate Groups

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## Introduction

We are using XAFS spectroscopy to investigate the atomic environment of aqueous Cr(III) ions, both hydrated and complexed to carboxyl ligands. Many structural studies applying various techniques point to the importance of knowing the geometry of hydrated cations [1, 2]. Aqueous metal adsorption to mineral and biological surfaces is also influenced by the solvated ion's form, size, and availability in solution, as well as by the geometry of the complex it forms with surface functional groups. Chromium itself has been identified as an important environmental contaminant.

X-ray and neutron scattering studies have found an octahedral hydration sphere for Cr(III), with a Cr–O distance of 1.97–1.98 Å [3–5]. Inner hydration molecules of chromium have unusually long residence times ( $\sim 10^6$  s) [6], suggesting that an outer hydration sphere distinct from bulk water could be formed. Evidence for this has been provided by neutron scattering [3], and other methods have also suggested the existence of an outer hydration sphere. The complexation of various metals to acetate groups in solution has been investigated by Fourier transform infrared (FTIR) spectroscopy [7]. The results show that aqueous metal-acetate complexes can be classified in four main groups: (a) ionic, (b) monodentate, (c) bidentate, and (d) bridging-bidentate (Fig. 1). In a separate FTIR study, Cr acetate complexes were found to be of the bridging-bidentate type (Fig. 1d) [8].

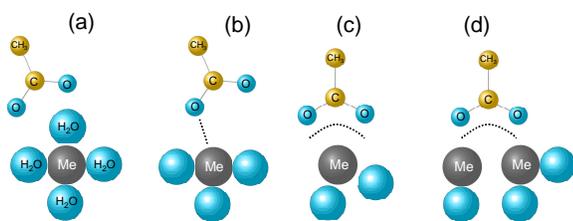


Fig. 1. Possible binding modes of an aqueous metal to an acetate ligand, as determined by FTIR: (a) ionic, (b) monodentate, (c) bidentate, (d) bridging-bidentate.

XAFS has been used previously to investigate Cr(III) hydration [9, 10]. Fourier transforms of the spectra show prominent features at  $\sim 3.3$  Å, suggesting ordering past the first hydration sphere. The origin of these features is under discussion. Some authors attribute them to contributions from second hydration shell molecules [9–11], while others suggest multiple scattering within the first hydration sphere as an explanation [12, 13]. We are attempting to provide new insight about these spectral features and the structure of hydrated Cr. Our study of Cr binding to acetate will test the FTIR binding mode assignment and will provide structural information about the Cr acetate aqueous complex.

## Methods and Materials

### Solution Preparation

Chromium perchlorate and chromium acetate solutions, prepared from distilled deionized water (18 MΩ) and the corresponding salts obtained from Sigma-Aldrich and Alfa-Aesar, were used without further purification. Concentrations ranged from 0.05 M to 0.2 M. Acetic acid was added to the Cr acetate solutions to study the shift in equilibrium between hydrated and acetate-complexed ions toward the complexed species. The water was boiled for at least 20 min to remove CO<sub>2</sub>. The pH was adjusted when necessary with NaOH.

### Synchrotron Measurements

The XAFS experiments were carried out at the MRCAT beamline [14]. The beamline undulator was tapered, and the incident energy was scanned near the Cr K-edge by using the Si(111) reflection of the double-crystal monochromator in quick-scanning mode. Harmonic rejection was achieved by reflection from a Rh-coated mirror. The beam was defined as 0.7 mm by 0.7 mm. During measurements the solutions were kept in drilled Plexiglas slides sealed with Kapton film windows. Spectra were recorded in fluorescence mode by using a Stern-Heald detector. Energy calibration was continuously monitored during data collection by using a Cr<sub>2</sub>O<sub>3</sub> standard placed above the beam and in front of the defining slits [15].

Raw data from the beamline were aligned on the energy axis by the reference data; background was subtracted by using AUTOBK [16]. The background removal parameters were varied to identify the most consistent procedure.

## Results

### XANES

Figure 2 shows normalized XANES scans and their energy derivatives for hydrated Cr and Cr bound to acetate. Differences between the two are clear. The sharp white line at 6009 eV and the step-like feature at 6015 eV in the hydrated Cr spectrum are reduced to a broad peak in the Cr acetate solution. The derivative spectrum also shows a shift in the inflection point and other differences.

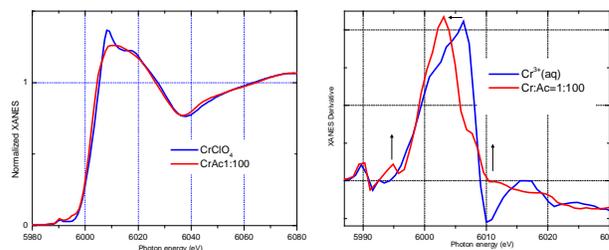


Fig. 2. (a) Normalized XANES scans and (b) energy derivatives of XANES scans from the Cr perchlorate solution and from the Cr acetate solution to which acetic acid has been added.

### EXAFS Spectroscopy

Figure 3 compares the Fourier transform of EXAFS data for samples containing hydrated Cr or Cr bound to acetate. We observe a reduction in first shell peak amplitude (at  $\sim 1.5$  Å) when acetate is available to bind Cr. The structure at about 3.2 Å and higher is similar in the two samples, but a prominent peak develops at about 2.9 Å when acetate is available to bind Cr.

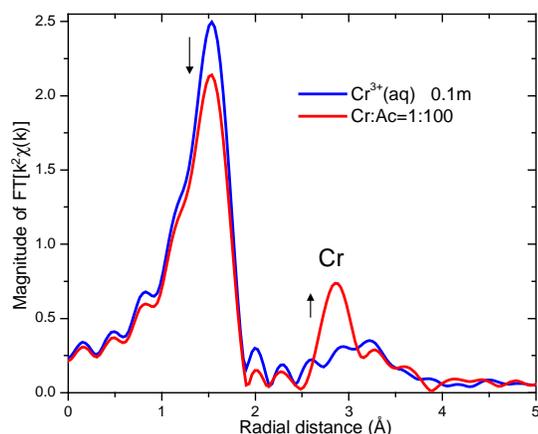


Fig. 3. Magnitude of the Fourier transform of EXAFS data for samples containing hydrated Cr or Cr bound to acetate.

### Discussion

The XANES part of the spectrum is sensitive to the local potential around the absorbing atom [17]. The large differences between spectra where Cr is only hydrated versus where acetate is available to bind the metal (Fig. 2) indicate that the local environment around Cr is changed significantly. The observed XANES changes for Cr are larger than those due to bidentate acetate binding of Cd and Pb [18, 19]. This observation can be interpreted as a qualitative indication that the larger changes in local atomic potential occur because another Cr atom is in the vicinity of the central Cr.

The qualitative conclusion above is supported by the EXAFS data. The reduction in first-shell amplitude in Fig. 3 can be rationalized by increased disorder due to penetration of the acetate group in the first hydration shell in order to bind the Cr in an inner-sphere complex. The prominent peak at  $\sim 2.9$  Å can be tentatively assigned to another Cr atom in the vicinity of the central Cr atom. The similarity of features at  $\sim 3.2$  Å and higher distances indicates that the contributions responsible for these features are present both for hydrated Cr and for Cr bound to acetate.

Detailed numerical modeling of the spectra using FEFF8 [20] is under way to determine the origin of the features and provide numerical data about the structure, such as distances, coordination numbers, and disorder.

### Acknowledgements

M.B. acknowledges support from the Environmental Molecular Science Institute at University of Notre Dame (funded by NSF grant EAR-0221966), the U.S. Department of Energy (DOE), and the Bayer Corporation through a fellowship in environmental science. Help in beamline setup from the staff of MRCAT is greatly appreciated, as is use of the laboratory of J. Fein. This work was supported in part by National Science Foundation grants EAR-0207169 and EAR-9905704 and by the

DOE Office of Science, Office of Biological and Environmental Research, Natural and Accelerated Bioremediation Program. MRCAT is supported by DOE under Contract DE-FG02-94-ER45525 and by the member institutions. Use of the APS was supported by the DOE Office of Science, Office of Basic Energy Sciences, under Contract W-31-109-Eng-38.

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