

LOCAL STRUCTURE AROUND CHROMIUM IONS IN AQUEOUS ACETATE SOLUTIONS

When metal ions are released into the environment, how do they interact with the world they find? In particular, how do aqueous metals adsorb on bacterial surfaces? Those are questions of great interest in environmental biogeochemistry. Studies carried out by researchers from Argonne National Laboratory and the University of Notre Dame using the MR-CAT 10-ID beamline at the APS provide an important first step toward understanding this process.

Contaminants such as chromium, cadmium, or uranium that leak into the environment generally become solvated in groundwater, increasing dramatically the contaminants' ability to move and spread. Along the way, these contaminants can meet various agents and surfaces, both mineralogical and biological, to which they can bind and that change their mobility. As a result, they stop somewhere and accumulate, which may or may not be desirable. Bacterial surfaces are rich in carboxyl functional groups COO^- , a radical that is typical of organic acids. The conditions under which significant adsorption/complexation can occur depend on the molecular binding mechanism. By beginning to understand how the metal behaves in the solution, and from there, how it binds to an acetate molecule (as a model of a carboxyl bond), science can explore important questions about metals in the environment.

To begin, the Argonne-Notre Dame team studied a model system of chromium salts dissolved in solution with and without an acetate ligand. They added acetic acid (CH_3COOH) to chromium solutions and observed how the metal behaves, i.e., whether or not it binds to the acetate. Acetic acid can bind to a metal in one of four ways: one is an electrostatic association that is not a strong bond, two are chemical bonds with a shared electron, and the fourth is a chemical bond in which two metal ions are bridged by the acetate group.

In the case of chromium ions, Cr^{3+} , three of them come together and form an aqueous trichromium acetate complex (Fig. 1) in which the acetate groups are in a bridging configuration between the chromium ions. The structure was derived by x-ray absorption fine structure (XAFS) spectroscopy as a function of pH, concentration, acetate-to-Cr ratio, and the age of the solution. The structure of hydrated Cr^{3+} ions was also obtained. Like most aqueous metals, the ions are not bare; they are surrounded by associated water molecules, called a hydration sphere. The first hydration sphere is the very inner circle of these hydrated molecules, which is quite structured. Going further out is another shell of more or less ordered waters—in this case, chromium, as a +3 ion, has a very strong interaction, and

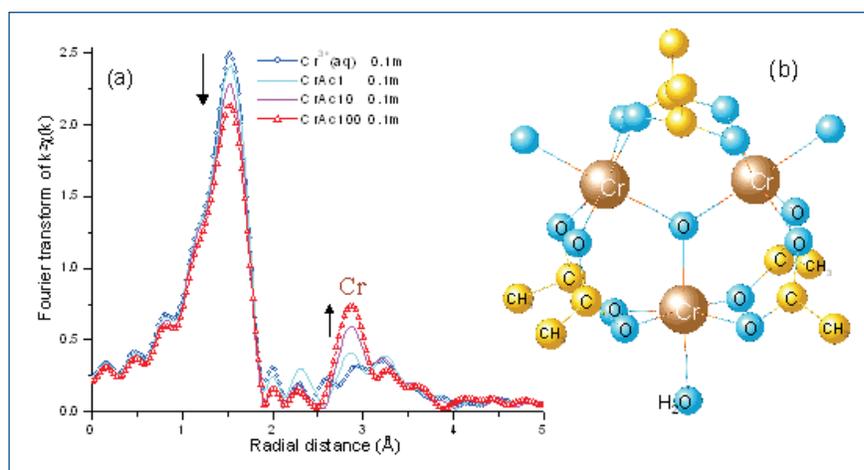


Fig. 1. (a) Results from EXAFS data for Cr acetate solutions; magnitude of the Fourier transform of $k^2 \chi(k)$. (b) Structure of the $\text{Cr}_3\text{O}(\text{CH}_3\text{COO})_6 \cdot 3\text{H}_2\text{O}$ solution complex

it is also able to order the second hydration sphere, forming a second shell of water molecules around the chromium ions.

This and other studies show that XAFS is an effective technique for investigating metal hydration and structure. Such information can also help in studies of the binding of dilute aqueous Cr to carboxyl ligands, as well as investigations of metal-metal interactions and polymerization in solution.

— David Appell

See: M.I. Boyanov^{1,2}, K.M. Kemner¹, T. Shibata², and B.A. Bunker², "Local Structure around Cr^{3+} Ions in Dilute Acetate and Perchlorate Aqueous Solutions," *J. Phys. Chem. A* **108**, 5131 (2004).

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M.B. acknowledges support from the Environmental Molecular Science Institute at University of Notre Dame (funded by NSF grant EAR-0221966), the United States Department of Energy, and the Bayer Corporation through a fellowship in environmental science. This work was supported in part by National Science Foundation grant EAR-0207169 and EAR-9905704, and the U.S. Department of Energy, Office of Science, Office of Biological and Environmental Research, Natural and Accelerated Bioremediation program. MR-CAT is supported by the U.S. Department of Energy under Contract No. DE-FG02-94-ER45525 and the member institutions. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.