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XAFS Studies of Cobalt(II) Binding by Peat, Plant and Soil Derived Solid Humic Acids

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Beamlines: X11A, X18B and X23A2

Introduction: Humic acids (HAs) binding of nutrient and toxic metals affects their bioavailability and rates of release. Solid HAs are the predominant form in most sediments and soils. Carboxylate is their major binding group [1]. Recent isotherm studies of tight organic binding of metals by different soil- and peat-derived solid HAs indicate a common tightest organic binding site A, B or C for Cu(II), Fe(III), Mn(II) and Co(II) [2,3]. However, EXAFS data for Cu(II), Fe(III) and Mn(II) at 77K and different metal loading levels did not distinguish different binding sites for a given metal at different metal loading levels [2]. Labile cobalt(II) may form inner- or outer-sphere coordinated complexes. The XAFS work of Xia et al [4] raises two fundamental questions: 1) Can sites A and B for Co(II) binding by different HAs be distinguished structurally by XANES measurements? 2) Can inner-sphere binding of Co(II) be confirmed by EXAFS measurements at different temperatures? This paper reports XAFS data from 60 to 300 K for tight organic binding of Co(II) by several peat, plant and soil derived HA solids and gels. Cobalt(II) acetate tetrahydrate was used as a standard. The results are compared with data for binding of cobalt(II) by other humic substances [4].

Methods and Materials: X-ray absorption spectra were collected on Beam Lines X11A, X18B and X23A2 at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, Upton, NY. Each Beam Line has a double Si(III) crystal monochromator. Detuning the primary beam by 20-25% rejected higher harmonic reflections. The samples were mounted in Kapton tape either as freeze-dried Co(II)-loaded solids or as water-washed Co(II)-loaded HA gels. Solid cobalt(II) acetate tetrahydrate was used as the XAFS standard and cobalt foil was used for energy calibration. The pre-edge and near-edge regions of the data ($-30 \text{ eV} < E - E_K < 40 \text{ eV}$, $E_K = 7709 \text{ eV}$) were acquired with a 0.5 eV energy increment. The EXAFS data in the range $50 \text{ eV} < E - E_K < 1000 \text{ eV}$ were acquired with a 2 eV energy increment. Measurements were made at room temperature and temperatures down to 60 K. At least six measurements were averaged for the same sample to improve the signal to noise ratio. Small energy shifts between scans were corrected by aligning spectra with their absolute energies and interpolating to the same 0.25 eV increment grid before the averaging. Energy calibration and alignment was made with Co foil measured in transmission mode simultaneously with X-ray fluorescence spectral measurements with an Fe foil filter of all other samples.

Results: Cobalt(II) Acetate Tetrahydrate Standard. Carboxylate is the major HA-metal binding group under environmental conditions, as shown by FTIR spectra [2,5]. For this reason, we used solid cobalt(II) acetate tetrahydrate as the reference of the cobalt(II) oxidation state and to test the ability of Winafs 2.0 and FEFF7 software to model the EXAFS data.

Solid Cobalt(II) Acetate Tetrahydrate consists of monomers with two axial monodentate acetate groups and four equatorial aquo ligands. There are three inner-sphere Co-O lengths of 2.0974, 2.0979 and 2.1172 Å, and the Co-C(carboxylate carbon) distance is 3.03 Å [6]. The XANES spectra of Cobalt(II) Acetate Tetrahydrate at temperatures from 60 to 300 K have the expected 1s-3d pre-edge feature and are closely similar.

The first derivatives cross the zero line only once at $E - E_K < 40 \text{ eV}$ [4], indicating that XANES spectra (even at 60 K) do not detect the distorted inner coordination sphere of the standard. The EXAFS spectra of the standard at 77 and 300 K were fitted satisfactorily with $S_o^2 = 1$ (fixed), 6 first shell oxygens at Co-O = 2.08 Å and 2 second shell carbons at Co-C(carboxylate) at $3.03 \pm 0.01 \text{ Å}$. Thus, EXAFS data also do not reveal the inner-sphere distortion of Co(II) even at 60 K.

Examination of the first derivatives of the many XANES spectra of Co(II)-loaded HAs (Solids and Gels) and the Cobalt(II) Acetate Tetrahydrate standard in no case gave evidence of a distorted first coordination sphere. Water and carboxylate are weak field ligands and Co(II) (d^7) is not subject to Jahn-Teller distortion. Distorted first shell Co-HA coordination evidently requires donors other than water and carboxylate and rigid inner coordination sphere conformations.

The EXAFS data for HA-bound Co(II) show that the majority of the Co(II)-HAs investigated have 1–2 second shell C atoms associated with presumed monodentate carboxylate groups based on the Cobalt(II) Acetate Tetrahydrate structure [6]. The six Co-O vectors range from 2.05 - 2.08 Å and Co-C(carboxylate) = 2.87-2.93 Å. Others obtained similar results for IHSS fulvic and humic acids and for a Chelex-20 derived HA from a Wisconsin mineral soil [4].

The schematic view of Co(II) binding by a solid HA in Fig. 1 envisions the strongest organic binding site A [2,3] as

neutral, with two monodentate carboxylate ligands from different parts of the HA backbone resulting in formation of a chelate ring of unknown size. Weaker binding at site B involves monodentate carboxylate with five aquoligands completing the inner coordination sphere that separate the acetate counter-ion (we use cobalt(II) acetate as the metal source to favor ion-exchange binding through eq (1) based on stoichiometric binding of Ca(II) by HAs that is used to measure their carboxylate content and to buffer the system. The formation of some sort of chelate ring in binding structure A but not in structure B is consistent with the more negative entropy change in the first Co(II) binding step [2,3].

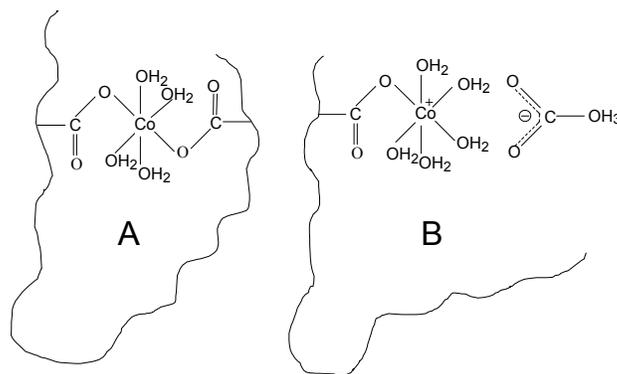
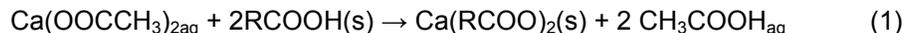


Figure 1 Schematic views of Co(II) binding sites A and B of solid humic acid IHA. Both involve monodentate carboxylate quite well separated along the HA backbone and six-coordinate cobalt(II) [4]. Site A is envisioned to have lower entropy than site B because of putative chelate ring formation. Site B forms when another HA-carboxylate group is too far away to interact with cobalt(II)

Conclusions: By examining a variety of HAs isolated from peat, plant and soil sources at temperatures down to 60 K, this work confirms that XANES measurements cannot distinguish between aquo and carboxylato ligands in the inner coordination sphere of Co(II) [4]. However, between 1 and 2 inner-sphere carboxylato ligands can be detected in all the peat, plant and soil derived HA samples investigated by EXAFS measurements, confirming inner-sphere coordination of HA-bound Co(II). The precision of C(carboxylate) detection is limited by the extent and quality of the data and the contribution from inner-sphere O to the FT peaks used to detect carbon. Putative chelate ring formation is consistent with a relatively negative entropy change in step A, the stronger organic Co(II) binding step.

References:

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