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EXAFS Study of the Nature of Zinc Complexation Sites in Humic Substances as a Function of Zn Concentration

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Abstract: Humic substances are known to play a key role in the immobilisation of metals in soils. The main complexing ligands that are supposed to interact with metals are carboxylic and phenolic. The complexation mechanism of zinc by two natural humic acids (T and F) was studied by EXAFS spectroscopy at the Zn-K edge over a wide range of zinc concentration. The ligation mechanism of Zn was found to vary with the metal concentration and the nature of the humic acid. As Zn concentration is raised, the amplitude of EXAFS spectra decreases, which is interpreted as an increased distribution of ligand sites. At low Zn concentration (300-5000 mg/Kg), zinc forms inner sphere complexes in octahedral coordination for T humic acid, and in octahedral and tetrahedral coordinations for F humic acid. At intermediate Zn concentration (32 g/Kg), a large number of different sites are observed and only octahedral coordination is detected. At high Zn concentration (500 g/Kg), most Zn forms outer sphere complexes. The difference of complexation mechanisms between humic acids F and T can be related to differences in their structure as indicated by ^{13}C -NMR spectroscopy.

1. INTRODUCTION

Soils are the most significant sink for trace elements released in the environment. It is now widely admitted that the toxicity of metals depends not only on their total concentration, but mainly on their chemical form, *i.e.* their speciation. Humic substances (HS) possess a polyfunctional (with O, N, and S-containing groups), polyelectrolytic and hydrophilic character, and the capacity to form intermolecular associations, and to change their spatial conformation [2]. Due to these characteristics, they can form stable complexes with metals. Despite the sustained interest of this topic for many years, much remains unknown regarding mechanistic aspects of the complexation. Several models have been proposed, including the formation of inner and outer sphere complexes [1]. In the present study, the complexation mechanism of Zn as a function of the metal concentration was investigated in two humic acids (HA) differing by the nature and/or proportion of their functional groups. Because of its versatile structural chemistry, Zn is a very good candidate for probing the different functional groups of HS that are likely to complex metals.

2. EXPERIMENTAL

Two HA were studied, one originating from a french soil [5], (T), and a reference material supplied by Fluka. They were extracted following the standardized International Humic Substances Society recipe [6]. ^{13}C -NMR analysis showed that the two HA are structurally different: T HA contains predominantly aromatic, and F HA aliphatic functional groups. Zn complexation was carried out at pH 5 by placing the humic acid in a dialysis membrane (Spectrapor 6 for PM 1000), $\text{Zn}(\text{NO}_3)_2$ being in the external solution. The system was stirred for 24 hours, and the absence of aqueous Zn at the end of the reaction was verified by ICP-AES. Zn-HA complexes were then freeze-dried for EXAFS experiments. EXAFS measurements were performed on the CRG/IF beamline ID32 bending magnet at the European Synchrotron Radiation Facility (ESRF) in Grenoble. Zn K-edge spectra for diluted samples were recorded at room temperature in fluorescence detection mode using a 5-element Ge detector having a total counting rate of 350 000 ph/s. For each sample 3-6 scans were collected and averaged. EXAFS spectra for concentrated HA and references were measured in transmission mode. Interatomic distances and coordination numbers (CN) were calculated by using experimental phase shift and amplitude functions extracted from ZnO [7] (Tab. I).

3. RESULTS AND DISCUSSION

3.1. Reference Compounds

The sensitivity of the method to different coordination chemistries will be exemplified with anhydrous Zn acetate, where Zn is 4-fold coordinated ($^{\text{IV}}\text{Zn}$) to four monodentate carboxyls ($d(\text{Zn-O})=1.973$ and 1.992 Å) [8], and aqueous Zn^{2+} , where it is fully solvated by six water molecules, $d(\text{Zn-O})=2.08$ - 2.17 Å [9]. These differences of site geometry are visualized on radial structure functions (RSFs) by a shift and change in amplitude of first RSFs peaks (Fig.1). Zn-O distances and CN determined by least squares fitting are in good agreement with cristallographic values (Tab. I). A systematic structural analysis of Zn organic and

coordination complexes contained in the Cambridge Structural Database showed that $\langle d(\text{IVZn-O}) \rangle \sim 1.9 \text{ \AA}$ and $\langle d(\text{VI Zn-O}) \rangle \sim 2.1 \text{ \AA}$. It is concluded from this analysis of reference compounds that the coordination site of Zn can be confidently inferred from bond length determination.

Table I: EXAFS and XRD structural parameter

	atomic pair	XRD		EXAFS				
		R (Å)	N	R (Å)	N	$\Delta\sigma$ (Å)	ΔE (eV)	weighted distance (Å)
sample								
Reference: ZnO	Zn-O	1.973	3	1.98	4	0	0	1.98
	Zn-O	1.992	1					
Anhydrous Zn acetate	Zn-O	1.949	1	1.97	4	0.01	0.64	1.97
monoclinic	Zn-O	1.952	1					
	Zn-O	1.96	1					
	Zn-O	1.965	1					
Zn in aqueous solution	Zn-H ₂ O	2.08-2.17	6	2.07	4.2	0	0	2.11
				2.2	2	0		
HA T 200 mg/Kg Zn	Zn-O			2.03	3	0	0	2.07
	Zn-O			2.17	1.4	0	0	
HA T 500 mg/Kg Zn	Zn-O			2.05	3.1	0	0	2.06
	Zn-O			2.15	0.5	0	0	
HA T 5000 mg/Kg Zn	Zn-O			2.02	2.4	0	0	2.06
	Zn-O			2.17	1	0	0	
HA T 32 g/Kg Zn	Zn-O			2.06	1.8	0.01	0	2.06
HA T 500 g/Kg Zn	Zn-O			2.04	3.5	0.01	0	2.08
	Zn-O			2.16	1.6	0.01	0	
HA F 1000 mg/Kg Zn	Zn-O			1.99	2.4	0	0	2.04
	Zn-O			2.10	1.8	0	0	
HA F 5000 mg/Kg Zn	Zn-O			1.98	2.3	0	0	2.03
	Zn-O			2.11	1.5	0	0	
HA F 500 g/Kg Zn	Zn-O			2.03	3.1	0.01	0	2.07
	Zn-O			2.16	1.6	0.01	0	

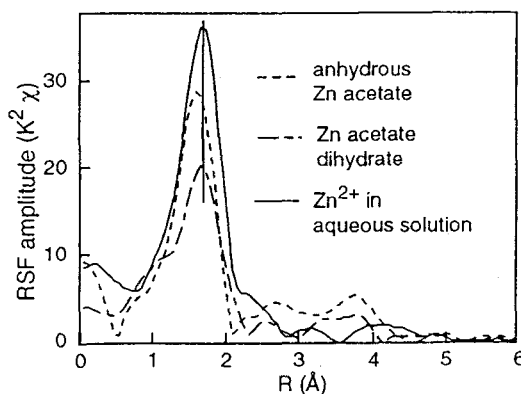


Figure 1: Comparaison of RSFs for Zn reference compounds.

3.2. Zn Complexed Humic Acids

Raw EXAFS spectra and RSFs for samples F and T as a function of Zn concentration are contrasted in Fig. 2, 3, 4 and 5. For sample T, Zn-O distances are typical of 6-fold coordination regardless of the complexation rate. As the Zn concentration is raised, the amplitude of the first three peaks markedly decreases, except for the most concentrated sample. This is expressed in Table I by an apparent decrease of CN with increasing metal concentration down to 1.8 for the 32 g/Kg sample. In the 300-500 mg/Kg concentration range, the RSFs amplitude was found to be notably higher than in most reference spectra. This indicates that Zn is bound to structurally similar complexing sites, and that individual Zn-O distances are coherent. The loss in amplitude when the Zn concentration is raised is interpreted by an increased distribution of complexing sites. As more Zn is

added, new types of ligands would participate in the complexation, in the reverse order of their affinity for the metal. However, the highest concentrated sample (500g/Kg Zn) does not follow this evolution. Its first RSF peak amplitude is very high, indicating that one Zn species predominates (Fig. 4). From comparison with aqueous Zn^{2+} (Fig. 6), it can be concluded that at high concentration, Zn forms predominantly an outer sphere complex. This interpretation is corroborated by cation exchange capacity (CEC) measurements. At pH 5, this capacity is between 175 to 260 meq of charge/100g [3], i.e., 57 to 85 g/Kg Zn^{2+} . Thus, at 500g/Kg Zn, only 10 to 20% of total Zn can be bound to functional groups, the remaining being weakly bound by an outer sphere complexation mechanism. The fact that the 500g/Kg sample has a slightly lower Zn-O amplitude than aqueous Zn^{2+} is probably due to the contribution of the minor inner sphere complexes, which represent 10 to 20% of total Zn. The presence of an outer sphere complex at high metal concentration (5 to 50 wt. % Fe^{3+}) was also observed by Mössbauer spectroscopy in Fe^{3+} -HA complexes [10].

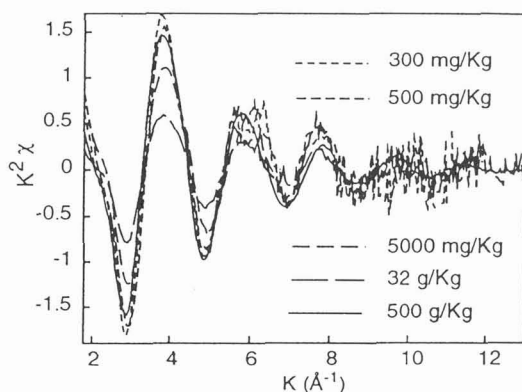


Figure 2: EXAFS spectra for Zn-T humic acid complexes at different Zn concentrations.

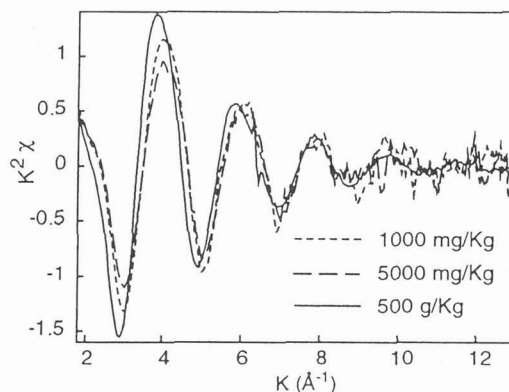


Figure 3: EXAFS spectra for Zn-F humic acid complexes at different Zn concentrations.

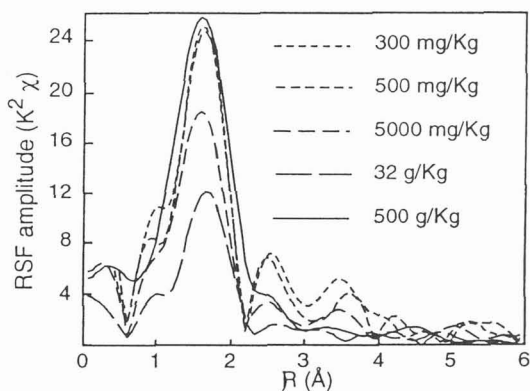


Figure 4: Comparison of RSFs for Zn-T humic acid complexes at different Zn concentrations.

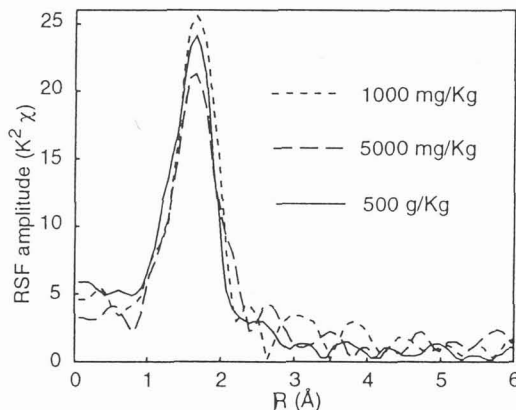


Figure 5: Comparison of RSFs for Zn-F humic acid complexes at different Zn concentrations.

The same amplitude evolution is observed for the F humic acid, but first shell Zn-O distances are shorter (Tab. I, Fig. 5). Values typically lie between 4-fold and 6-fold coordination. This suggests a mixture of the two coordinations, the former prevailing at lower concentration. This interpretation agrees with the ESR study by Senesi *et al.* [10] of Fe^{3+} -HA at low Fe concentration (2.8% Fe). They showed that part of the metal was bound to carboxylic and possibly phenolic groups as an inner sphere complex, in a tetrahedral and octahedral coordination. The present results show that tetrahedral configuration occurs only at very low Zn concentration. This 4-fold coordination is generally achieved by four monodentate carboxyl groups, as in anhydrous Zn acetate.

4. CONCLUSION

At low concentration, Zn forms inner sphere complexes being either solely 6-fold (T) or 6-fold and 4-fold (F) coordinated to O ligands. This difference in Zn site geometry observed for HA T and F can be related to their differences in structure as indicated by ^{13}C NMR spectroscopy. As Zn concentration is raised, the number of different ligand sites increases, the coordination being

exclusively octahedral. At very high metal concentrations, the major part of Zn (80-90%) is bound as an outer sphere complex. Therefore, this study demonstrates the existence of a plurality of binding sites in HA, and thus provides a structural support to the use of a continuum of thermodynamic stability constants to model solution complexation experiments [11].

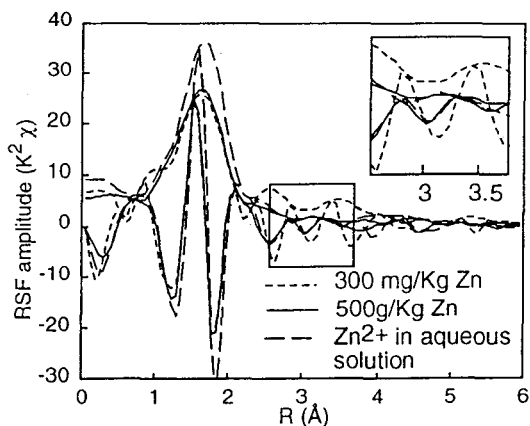


Figure 6: Comparison of RSFs for Zn-T humic acid complexes and Zn^{2+} in aqueous solutions.

Acknowledgments

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