Accepted Manuscript

Title: Metal-Ion Complexation Effects in C 1s-NEXAFS Spectra of Carboxylic Acids – Evidence by Quantum Chemical Calculations

Authors: M.K. Armbruster, B. Schimmelpfennig, M. Plaschke, J. Rothe, M.A. Denecke, R. Klenze

PII: S0368-2048(08)00145-X
DOI: doi:10.1016/j.elspec.2008.10.007
Reference: ELSPEC 45599

To appear in: Journal of Electron Spectroscopy and Related Phenomena

Received date: 7-7-2008
Revised date: 31-10-2008
Accepted date: 31-10-2008


This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.
Metal-Ion Complexation Effects in C 1s-NEXAFS Spectra of Carboxylic Acids – Evidence by Quantum Chemical Calculations

M. K. Armbruster*, B. Schimmelpfennig, M. Plaschke, J. Rothe, M. A. Denecke, R. Klenze
Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgung, Postfach 3640, D-76021 Karlsruhe, Germany

* corresponding author:
M. K. Armbruster
Forschungszentrum Karlsruhe
Institut für Nukleare Entsorgung
Postfach 3640
D-76021 Karlsruhe
Germany

e-mail: markus.armbruster@ine.fzk.de
Phone +49-(0)7247-82-3486
Fax +49-(0)7247-82-3927

Abstract

Previous systematic C 1s-NEXAFS studies carried out for humic acid (HA) loaded with polyvalent metal cations (M\textsuperscript{n+}) reveal spectral features which were postulated to result from metal ion complexation: a strong decrease of the C 1s (COO\textsuperscript{-}) → π\textsuperscript{*}C=O transition intensity and the appearance of a new absorption feature at slightly lower energy adjacent to the carboxyl resonance. Although spectroscopic results for the M\textsuperscript{n+}-PAA (polyacrylic acid) system (selected as model for structurally ill-defined HA) reveal the same spectral features, evidence by an independent approach for interpretation of these features is desirable. It is well established that quantum chemical calculations are capable of reproducing transition features
in C 1s core excitation spectra of small organic molecules, e.g., acetate, which is chosen here as a fragment containing the complexing group to model the macromolecular HA and PAA systems. In this study, the RI-ADC(2) approach, as implemented in the TURBOMOLE program package, is applied to calculate vertical core excitation spectra of various metal acetates and the acetate anion. An energy shift (Δf) between the C 1s (COO') → π* C=O transition of the acetate anion and various metal cation acetates is established. Calculated shifts are very similar to the experimentally observed values for the energy difference between the C 1s (COO') → π* C=O peak and the absorption feature appearing after metal ion complexation in Mⁿ⁺-PAA/PAA. According to our computations, structural changes of the acetate complexes (e.g., the O-C-O bond angle) compared to the free acetate anion are predominantly responsible for the spectral changes observed upon metal ion complexation.

**Keywords:** C 1s-NEXAFS, metal ion complexation, quantum chemical calculation, acetate complexes, RI-ADC(2)

### 1. Introduction

Organic residues left over from biodegradation of living organisms possess chemically reactive sites which regulate transport and retention of nutrients or possible contaminants in aquifers, soils and sediments [1]. Especially the water soluble fractions of this natural organic matter (NOM) - mainly comprised of humic (HA) and fulvic acids - have been subject of intense research in the past, e.g. [2,3,4,5]. This research interest lies in possible risks posed by colloid sized organic acid macromolecules acting as carriers for toxic metal ions (Mⁿ⁺), e.g., actinide cations in the case of nuclear waste storage in geological formations [6]. HA is commonly characterized as colloid-sized polyfunctional biopolymer with high structural diversity depending on origin and formation history. So far, this diversity has been a limiting
factor in the search of a unified structural model for HA. HA exhibits a strong affinity for complexing polyvalent metal ions at pH conditions longing from slightly acidic to slightly alkaline. The role of proton-exchanging functional groups such as carboxylic or phenolic groups has been investigated by many researchers, in order to describe HA complexation behavior. Previous comparative EXAFS studies of HA and ion exchange resins point to carboxylate groups as the primary HA metal ion binding sites [7]. Characterization of the number and density of these proton-exchangeable groups is accessible by titration experiments. These values are correlated to the metal loading capacity - a key feature in the description of HA - according to the charge neutralization model [8]. However, the exact molecular structures of Mn⁺-HA complexes are generally unknown. Typical HA characteristics like the varying complexation strength (described in terms of stability or complexation constants) or quasi-irreversible reaction kinetics observed for certain HA fractions (sometimes associated with binding by ‘strong sites’) are not understandable in macroscopic HA descriptions based on bulk characterization techniques.

The nature of Mn⁺-HA complexes has been investigated by laser excitation luminescence spectroscopy, where predominantly trivalent actinides (e.g., Cm³⁺ [9]) or chemical homologue lanthanides (e.g., Eu³⁺ [10]) with high luminescence yields act as sensitive probes reflecting the local coordination environment. More recently, the usefulness of carbon K-edge (C 1s-level at ~285 eV) NEXAFS spectroscopy has been demonstrated for the investigation of Mn⁺-HA complexes - looking from the point of view of the organic ligand [11,12,13,14]. C 1s-NEXAFS spectromicroscopy with sub-µm lateral resolution for in-situ investigations of hydrated NOM samples is available at Scanning Transmission X-ray Microscopy (STXM) stations, e.g., at the NSLS (Brookhaven, NY), ALS (Berkeley, CA) and SLS (Villigen, Switzerland) synchrotron light sources [15,16,17]. Chemical speciation of NOM using C 1s-NEXAFS provides information of structural subunits based on characteristic spectral features due to C 1s → π*/σ* transition resonances, e.g., the carboxylic C 1s (COO⁻) → π⁺C=O
transition at ~288.4 eV [18]. A distinct complexation effect visible in C 1s-NEXAFS spectra of $M^{n+}$ loaded HA aggregates has been suggested by comparing results obtained for Aldrich HA with those for poly acrylic acid (PAA: [-CH$_2$-CH(COOH))$_n$]$_n$) [19]. PAA is a water soluble polymer with a high content of carboxyl functional groups attached to an aliphatic chain and has found widespread application to mimic HA in metal ion sorption studies ([20] and references therein). $M^{n+}$-PAA samples exhibit a strong decrease of the C 1s (COO$^-$) $\rightarrow$ $\pi^*$ transition intensity compared to that of Na(I)-PAA. This decrease is accompanied by the appearance of a new absorption feature at slightly lower energy adjacent to the carboxyl resonance. This behavior is similar to that observed for several HA / $M^{n+}$-HA samples, e.g., $M^{n+}$ = Zr$^{4+}$, Eu$^{3+}$ [19,21] (Zr$^{4+}$ is chosen as chemical homologue for tetravalent actinide ions [22]). Moreover, the extent of the decrease of the carboxyl resonance and corresponding increase of the shoulder at lower energy observed for $M^{n+}$-PAA has been shown to depend on the type of metal cation added to the PAA suspension [14]. To correctly interpret the observed metal ion complexation effect in the C 1s-NEXAFS, we perform ab initio calculations of the core excitation spectra.

Spectroscopic properties derived from quantum chemical calculations depend on the topology of a molecule, i.e., type of atoms, distances and angles between them. The knowledge of well-defined structural parameters allows the calculation of quantum mechanical wave functions, energy expectation values and response properties of molecular systems. Organic acids with comparably simple molecular structure can be successfully treated with moderate computational effort, as demonstrated for various substituted benzoic acids [23]. Both PAA and HA are organic macromolecules with an ill-defined (PAA) or even unknown (HA) molecular topology. Nevertheless, as mentioned above, carboxyl groups are known to be the primary complexing sites for metal cations in these organic substances. Therefore, in this study we consider three different hydrated mono acetate complexes of the trivalent cations La$^{3+}$, Eu$^{3+}$, Gd$^{3+}$ and Cm$^{3+}$, the tetravalent Zr$^{4+}$ and the uranyl [UO$_2$]$^{2+}$ cation as models for
the bonding environment in HA and PAA complexes. For these systems we calculate \textit{ab initio} the carboxylic C 1s (COO\(^{-}\)) \rightarrow \pi^{*}_{\text{C=O}} transition in the metal ion acetate complex and compare it to that for the free acetate ion. With these calculations we intend to provide theoretical evidence for the correct interpretation of the complexation effect in the core excitation spectra of the M\(^{n+}\)-PAA/HA suspensions. Only recently shifts in of C 1s (COO\(^{-}\)) \rightarrow \pi^{*}_{\text{C=O}} energy positions following interaction of acetate and formate with alkaline cations have been experimentally observed and calculated by density functional theory (DFT) based methods [24].

2. Sample preparation and STXM/NEXAFS measurements

Soft X-ray spectromicroscopy investigations are performed at the STXM endstation (X1A outboard STXM) at the National Synchrotron Light Source, Brookhaven, NY ([15,25,26] and references therein). Experimental details and details of the sample preparation in ‘wet-cells’ have been given elsewhere [27]. Stacks of images from sample regions are recorded as a function of incident photon energy E. For a review of the procedure for image stack data analysis and spectra normalization, see [19,26]. C 1s-NEXAFS spectra are extracted through the analysis of the absorption signal, \(\mu(E)\times d = \ln(I_0(E)/I(E))\), where \(d\) is the sample thickness, I and \(I_0\) the transmitted intensities derived from image regions containing carbonaceous material (I) and from image regions free of particles (I\(_0\)).

3. Experimental Results

The spectra of Aldrich HA and PAA are dominated by the C 1s (COO\(^{-}\)) \rightarrow \pi^{*}_{\text{C=O}} transition appearing as the most prominent resonance feature at \(\sim 288.4\) eV (feature C in Figs. 1, 2). Previous publications show that polyvalent metal ion complexation with these polymers induces a decrease of the carboxyl resonance intensity, while at the same time a shoulder
appears at slightly lower energy (~0.5 - 1 eV) adjacent to the carboxylic transition (feature B in Figs. 1, 2) [19]. In the case of PAA the extent of the intensity decrease varies for different metal cations. In the normalized C 1s-NEXAFS spectra of Na\(^{+}\)-, Eu\(^{3+}\)- and [UO\(_2\)]\(^{2+}\)-PAA the carboxylic peak C is observed to decrease and the shoulder B to increase in this order [14,20]. In case of Aldrich HA metal ion complexation induces a segregation of material with higher and lower optical density, corresponding to HA fractions with higher and lower affinity for metal cations [28]. Both fractions exhibit distinct spectral signatures. The Zr\(^{4+}\)-HA spectrum shown in Fig. 2 corresponds to the optically denser material [21] (feature A at ~285.0 eV in Zr\(^{4+}\)-HA is associated with aromatic C 1s (C-H) \(\rightarrow\) \(\pi^*\) transitions). Pure HA at pH 4.0 and Zr\(^{4+}\)-HA (Fig. 2) exhibit similar spectral changes observed for the PAA/ Zr\(^{4+}\)-PAA system.

- Fig. 1 and Fig. 2

4. Quantum chemical calculations

4.1 Theory

The calculations of the vertical C 1s (COO\(^-)\) \(\rightarrow\) \(\pi^*\) excitation energies and transition strengths were done within the second-order Algebraic Diagrammatic Construction (ADC(2)) [29]. The ADC method is a specific reformulation of the diagrammatic perturbation theory for the polarization propagator [30] and it combines diagonalization of a Hermitian secular matrix with Rayleigh-Schrödinger perturbation theory for the secular matrix elements. The ADC(2) implementation in the program package TURBOMOLE, which is used in this study, allows the calculation of core-excitation spectra of comparatively large molecules with adequate basis sets by means of the resolution-of-the-identity (RI) approximation for the two-electron integrals [31,32]. Implementation in the RICC2 module is based on synthesis of the
closely related ADC(2) approach, the approximate coupled-cluster singles-and-doubles model CC2 [33] and the iterative variant of the doubles correction to configuration interaction singles CIS(D∞) [34]. The formalism is based on the following time-dependent quasi-energy Langrangian

\[ L(\lambda_k, \lambda_\text{CI}, t) = \langle \Psi_0 | \hat{H}(t) - i \frac{\partial}{\partial t} | \Psi_0 \rangle + \sum_k \sum \lambda_k F_k \left[ \hat{H}(t) - i \frac{\partial}{\partial t} \right] (\lambda_k, t), \]

which is made up of the expectation value of the Schrödinger operator \( \hat{H} - i \frac{\partial}{\partial t} \) and contains the constraints \( F_k [\hat{H}(t) - i \partial / \partial t] \) for the wave function parameters \( \lambda_k \). This is a general approach to derive the expressions for response functions of interest for a given ground-state energy model \( \langle \Psi_0 \rangle \). By taking the derivatives of the Langrangian \( L(\lambda_k, \lambda_\text{CI}, t) \) with respect to the parameters \( \lambda_k \), one obtains the stability matrix, e.g., the electronic Jacobian:

\[ A_{\text{el}} = \left( \frac{d^2 L}{d \lambda_k d \lambda_\text{CI}} \right)_0. \]

The poles of the response functions and thus the excitation energies occur as the eigenvalues of the matrix \( A \). One can show that the ADC(2) secular matrix \( A^{ADC(2)} \) is simply the symmetric (real case) or Hermitian part (complex case) of the CIS(D∞) model:

\[ A^{ADC(2)} = \frac{1}{2} \left[ A^{CIS(D∞)} + \left( A^{CIS(D∞)} \right)^T \right] \]

Further details are given in [31]. From a physical point of view, the ADC(2) approach includes the core-hole relaxation and the response of the ionic core to the presence of an excited electron consistently through second order in electronic repulsion. Other approaches such as the static exchange [35] and the combination of DFT and the transition potential (DFT-TP) [36] neglect the second order polarization effect.

### 4.2 Geometry optimization of model systems
The theoretical structural parameters for the metal complexes and the free organic anion are obtained in the gas phase. This means that solvation effects are not taken into account. Computations are performed for three different structural arrangements of mono acetate complexes for $M^{n+} = Zr^{4+}$, La$^{3+}$, Eu$^{3+}$, Gd$^{3+}$ and Cm$^{3+}$: the 8-fold coordinated $[M(CH_3COO)_b(H_2O)_{6}]^{(n-1)+}$ with bidentate ($^b$) coordination of the CH$_3$COO$^-$ (Fig. 3a) and two different 9-fold coordinated $[M(CH_3COO)(H_2O)_7]^{(n-1)+}$, one with bidentate ($^b$) (Fig. 3b) and the second with monodentate ($^m$) (Fig. 3c) bonding of the acetate group. For the uranyl complexes we consider two different structures: $[UO_2(CH_3COO)(H_2O)_4]^+$ with bidentate ($^b$) (Fig. 4a) and monodentate ($^m$) (Fig. 4b) bonding of the acetate group. The geometrical parameters of the complexes and the CH$_3$COO$^-$ anion were optimized with the TURBOMOLE RI-DFT module using the BP86 exchange-correlation functional [37]. The coulomb integrals are approximated with the RI approach, in which specially optimized auxiliary basis sets are used [38]. For the elements H, C, O, Zr and La we use the def2-TZVPP basis [39] and for U the so called def-TZVPP basis set, which is a slightly modified form of the basis sets of Dolg et al [40]. For the elements Eu, Gd [41,42] and Cm [43,44] the specially designed basis sets for the ‘f-in-core pseudopotentials’ are used: for Eu and Gd the (7s6p5d)/[5s4p3d]/[31111/3111/311] and for Cm the (8s7p6d1f)/[5s4p4d1f]/[32111/3211/3111/1] basis set. The following effective core potentials (ECPs) of the Stuttgart-Cologne-Group [45] are applied for the inclusion of scalar relativistic effects: for Zr the ECP-28 (28 core electrons in the potential), for La the ECP-46, for U the ECP-60 and for Eu, Gd and Cm the f-in-core effective core potentials (ECP-52, ECP-53 and ECP-85, respectively). A closer look at the energies of the two 9-fold coordinated systems shows that lanthanides and Cm prefer bidentate bonding of the organic group. The energy differences between the structural isomers are rather small, however, 3.79, 3.37, 8.19 and 7.97 kJ/mol for Eu, Gd, La and Cm, respectively. Monodentate bonding is favored by 3.58 and 27.41 kJ/mol for uranyl and Zr, respectively. One must be careful with these energy differences, as the data
represents gas phase calculations. The calculated energy differences are too small to allow clear predictions about preferred bonding geometries.

During the geometrical parameter optimization of the monodentate complexes $[\text{M}(\text{CH}_3\text{COO})^m(\text{H}_2\text{O})_7]^{(n-1)^+}$ and $[\text{UO}_2(\text{CH}_3\text{COO})^m(\text{H}_2\text{O})_4]^+$ we observe an intramolecular protonation of the carboxyl group through a neighboring water ligand. This can be attributed to an effect of the non-existent water shell in the gas phase calculations. The resulting complexes are therefore labeled as $[\text{M}(\text{CH}_3\text{COOH})^m(\text{OH})(\text{H}_2\text{O})_6]^{(n-1)^+}$ and $[\text{UO}_2(\text{CH}_3\text{COOH})^m(\text{OH})(\text{H}_2\text{O})_3]^+$.

- Fig. 3 and Fig. 4

**4.3 Computation of transition energies**

The main focus of this study is on C 1s NEXAFS spectral changes in the energy range of the carboxyl transition in acetates following metal ion complexation. In the calculated C 1s core excitation spectra the carboxyl transition always exhibits the largest oscillator strength. Other transitions are around one order of magnitude weaker and will not be considered further. We compare the C 1s (COO$^-$) $\rightarrow$ $\pi^*_{C=O}$ transition energies of the metal mono acetate complexes with that of the corresponding free acetate anion. The calculated transition energies are not shifted to coincide with the experimental values, as we are not interested in absolute energy positions but in energy differences only. In the following this calculated difference in the C 1s (COO$^-$) $\rightarrow$ $\pi^*_{C=O}$ transition energies of the complex and the free anion will be referred to as the ‘complexation shift’, $\Delta f$.

Based on the geometrical parameters obtained by energy optimization of the metal acetates and the free acetate anion (cf. section 4.2), calculations of core excitation spectra are performed in two steps: in a first step a Hartree-Fock wave function is calculated for the different metal acetate complexes and in a second step the RI-ADC(2) calculation is
performed. The latter step requires further optimized auxiliary basis sets for the two-electron integrals [46]. All investigated complexes show qualitatively the same behavior, independent of the metal center and the coordination number. The metal complex C 1s (COO) → \( \pi^*_{\text{C}=\text{O}} \) transition lies at lower energies than the transition in the free anion (see Fig. 5 and Tab. 1). The values of \( \Delta f \) range from 0.44 eV for the uranyl complex \([\text{UO}_2(\text{CH}_3\text{COO})^b(H_2\text{O})_4]^+\) to 1.02 eV for \([\text{Zr(OOCH}_3)^b(H_2\text{O})_6]^{3+}\).

For consistency, two additional basis sets, cc-pwCVTZ and cc-pwCVQZ [47], which are especially constructed to accurately describe electron-electron correlation in combination with core excitations, are compared with the def2-TZVPP basis used for computation of \( \Delta f \) for \([\text{Eu(CH}_3\text{COO})^b(H_2\text{O})_7]^{2+}\) (Tab. 2). The differences in the shifts are small compared to the def2-TZVPP basis set results (0.01 eV to 0.04 eV) and negligible in comparison to the absolute values of \( \Delta f \) (0.44 to 1.02 eV). Therefore, the def2-TZVPP basis applied for the C and O atoms is adequate in this study of C 1s core excitations in the metal acetate complexes.

Generally, we obtain larger \( \Delta f \) values for the metal acetate complexes with bidentate bonding compared to monodentate bonding. The 8-fold and 9-fold coordinated Zr-complexes with bidentate bonding show the largest \( \Delta f \) values. The trivalent lanthanides and Cm(III) have - for a given structure model - very similar \( \Delta f \) values. The uranyl acetate complexes show a different behavior; \( \Delta f \) for the monodentate complex is larger compared to the bidentate system.

Fig. 6 shows \( \Delta f \) values for the metal complexes (diamonds) and those obtained for the hypothetical CH3COO\(^-\) anions (dash symbols) calculated using structural parameters which are set to the values of the corresponding metal ion complexes.

Comparison of both data sets (diamonds and dash symbols in Fig. 6) allows the discrimination of contributions to \( \Delta f \), which can be traced back to the complex geometry (i.e.,
The Δf values for the complexes are with one exception only slightly larger than those for the hypothetical acetate anions. This finding suggests that Δf is mainly determined by the geometrical change of the CH$_3$COO$^-$ structure upon complexation. Our computations exhibit a correlation between the O-C-O bond angle of the carboxyl group in the metal complexes and the Δf values (diamonds in Fig. 6 and Tab. 1). The Δf values are more sensitive to the O-C-O bond angle than C-C bond length, which contracts by roughly 10 pm; large energy shifts correspond to large deviations of the O-C-O angle from the angle in the free carboxyl anion (129.28°).

The metal acetates can be divided into three groups according to Δf value: Zr-acetates with bidentate bonding exhibit the largest shifts and smallest O-C-O bond angles, the lanthanide and actinide complexes with bidentate bonding are in the intermediate range and the monodentate complexes show the smallest Δf values and largest bond angles (diamonds in Fig. 6). Generally, we observe the largest change in Δf and smallest O-C-O bond angle for the bidentate systems, from 111° for [Zr(CH$_3$COO)$_b$(H$_2$O)$_6$]$^{3+}$ to 118° for [La(CH$_3$COO)$_b$(H$_2$O)$_7$]$^{2+}$. The bidentate uranyl complex [UO$_2$(CH$_3$COO)(H$_2$O)$_4$]$^{+}$ behaves differently; it shows the smallest shift (0.44 eV) of all metal acetates considered here. Additionally, the shift computed for the complex is smaller than that calculated for the hypothetical acetate anion with the same structure (diamond symbol in Fig. 6 below corresponding dash).

Our calculations reveal that the coordinating water molecules have a minor effect on the C 1s (COO$^-$) → π*$\text{C}=$O transition energy; the excitation energies of the 8- and 9-fold coordinated bidentate acetate complexes differ by only 0.05 eV. Detailed analysis of the molecular orbitals involved in the C 1s core excitation shows the electronic transition to be mainly localized on the carboxyl group, minor contributions from the metal cation and the water molecules. This corresponds well to the results in Fig. 6, where Δf values are shown to be determined by the
modified structural parameters of the acetate ion (dash symbols), with only minor contribution from the electronic structure of the metal center and a negligible effect from hydration.

The influence of a second water shell on $\Delta f$ is calculated for energetically optimized La complexes by comparing results for $[\text{La(CH}_3\text{COO})_3(\text{H}_2\text{O})_6]^{2+}$ ($\Delta f = 0.72$ eV) with water molecules in the first coordination sphere to that for $\{[\text{La(CH}_3\text{COO})_3(\text{H}_2\text{O})_6(\text{H}_2\text{O})_{20}]^{2+}$ ($\Delta f = 0.59$ eV) having an additional second shell of 20 water molecules which surround completely the inner complex. These two $\Delta f$ values differ by only 0.13 eV, indicating a relatively small influence of the second water shell.

- Fig. 5 and Fig. 6

5. Conclusion

Our quantum chemical calculations of geometrically optimized model metal acetate complexes and the energies of their C 1s (COO$^-$) $\rightarrow \pi^*_{\text{C-O}}$ transitions serve to understand the experimentally observed complexation effect in C 1s-NEXAFS spectra of carboxylic acids, including HA and PAA. For various metal cations the calculated spectra of acetate complexes show a complexation shift $\Delta f$ of the C 1s (COO$^-$) $\rightarrow \pi^*_{\text{C-O}}$ transition to lower energies compared to the free acetate anion. The computed $\Delta f$ values lie within the same range as experimentally determined values for the difference in energy between the C 1s (COO$^-$) $\rightarrow \pi^*_{\text{C-O}}$ peak and the new peak observed following complexation in C 1s NEXAFS spectra of PAA/M$^{n+}$-PAA systems. The computations reveal that structural modifications of the ligand following metal cation complexation determine the magnitude of $\Delta f$, with only small contributions affected by metal center electronic structure or hydration. Although the calculation of C 1s core excitation spectra of complex organic macromolecules (PAA or HA) is not yet possible with currently available quantum chemical methods, selected spectral features can be reproduced for structurally well-defined subunits. As calculated $\Delta f$ values for
metal ion acetates (in the range of 0.44 to 1.02 eV) correspond well to the experimental values obtained for PAA/M$^{n+}$-PAA (in the range of 0.5 to 1 eV) we conclude that our calculations of carboxyl transitions in metal acetates at the \textit{ab initio} level provide evidence for the correct interpretation of the experimentally observed C 1s NEXFAS absorption feature as a complexation effect in PAA and HA. The observed feature 0.5-1 eV below the carboxyl resonance of the organic acid can be attributed to an energy shifted $1s \rightarrow \pi^*_{\text{C=O}}$ transition in the M$^{n+}$/carboxylic acid complex. This implies that the decrease in organic acid carboxyl resonance intensity upon complexation with M$^{n+}$ occurs because this transition is split and a portion of the original intensity becomes associated with the new lower energy transition.

Our calculations show that the extent of the energy shift is primarily dependent on the binding mode of the carboxylate groups to the metal centers, bidentate versus monodentate, and on structural parameters of the ligand itself. More detailed investigation is required to ascertain if analysis of C 1s-NEXAFS can be applied to identify binding modes of carboxylate groups of complex organic molecules to metal cations.

**Acknowledgements**

We are grateful for beamtime allotment by BNL/NSLS. The experimental data was recorded using the X-1A STXM developed by the group of Janos Kirz and Chris Jacobsen at SUNY Stony Brook, with support from the Office of Biological and Environmental Research, U.S. DoE under contract DE-FG02-89ER60858, and the NSF under grant DBI-9605045. MP and JR thank Sue Wirick for technical assistance at the X1A beamline. MKA and BS thank the TURBOMOLE developers (especially Ch. Hättig) for constant support and giving access to the latest development versions.
References


[46] B. Schimmelpfennig, private communication

**Fig. 1:** Normalized experimental C 1s-NEXAFS spectra of Na-PAA and PAA complexed with Eu$^{3+}$ and UO$_2^{2+}$ (data taken from [20]).

**Fig. 2:** Normalized experimental C 1s-NEXAFS spectra of HA at pH 4 and Zr$^{4+}$-loaded HA and PAA at pH 4 (data taken from [21]).

**Fig. 3:** Energetically optimized structures (BP86/def2-TZVPP) of
(a) [La(CH$_3$COO)$_6$$(H_2O)_6$]$_2^{2+}$, (b) [La(CH$_3$COO)$_b$$(H_2O)_7$]$_2^{2+}$ and
(c) [La(CH$_3$COO)$_m$$(OH)(H_2O)_6$]$_2^{2+}$.

**Fig. 4:** Energetically optimized structures (BP86/TZVPP) of (a) [UO$_2$(CH$_3$COO)$_b$$(H_2O)_4$]$^+$ and (b) [UO$_2$(CH$_3$COO)$_m$$(OH)(H_2O)_3$]$^+$.  

**Fig. 5:** The C 1s (COO$^-$)$\rightarrow$$\pi$$^*$ transition energies in eV obtained for the different structures and metal cations under investigation. The numbers after the element symbols represent the coordination numbers; ($^b$) and ($^m$) correspond to the bi- and monodentate acetate bonding, respectively. The theoretically calculated excitation energies are not shifted to experimental values. All data are obtained with the RI-ADC(2) method.
**Fig. 6:** Complexation shift ($\Delta f$) in eV against the O-C-O angle in degree of the carboxyl group in the investigated metal complexes and free acetate anions. Diamonds correspond to the metal complexes and dashes to the free acetate anion, where the structural parameters are set to the values of the corresponding metal ion complexes.
**Table 1:** Geometrical parameters (BP86), transition energies and Δf values (RI-ADC(2)) of the acetate ion and the mono acetate complexes. All data are obtained with the def2-TZVPP basis set for C, O and H and the basis sets described in the text for the metal atoms. The (b) and (m) correspond to bi- and monodentate bonding of the acetate anion.

<table>
<thead>
<tr>
<th>System</th>
<th>d[C-M]/pm</th>
<th>&lt;[OCO]/°</th>
<th>d[C-C]/pm</th>
<th>f[1s→πC=O*]/eV</th>
<th>∆f/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃COO⁻</td>
<td>-</td>
<td>129.28</td>
<td>157.29</td>
<td>292.03</td>
<td>-</td>
</tr>
<tr>
<td>[Zr(CH₃COO)₆(H₂O)₆]³⁺</td>
<td>255.60</td>
<td>111.48</td>
<td>145.94</td>
<td>291.01</td>
<td>1.02</td>
</tr>
<tr>
<td>[Zr(CH₃COO)₆(H₂O)₇]³⁺</td>
<td>259.72</td>
<td>112.07</td>
<td>146.74</td>
<td>291.16</td>
<td>0.87</td>
</tr>
<tr>
<td>[Zr(CH₃COOH)₆(OH)(H₂O)₆]³⁺</td>
<td>322.18</td>
<td>120.58</td>
<td>147.43</td>
<td>291.44</td>
<td>0.59</td>
</tr>
<tr>
<td>[La(CH₃COO)₆(H₂O)₆]²⁺</td>
<td>283.47</td>
<td>117.66</td>
<td>148.93</td>
<td>291.31</td>
<td>0.72</td>
</tr>
<tr>
<td>[La(CH₃COO)₆(H₂O)₇]²⁺</td>
<td>288.08</td>
<td>118.00</td>
<td>149.39</td>
<td>291.36</td>
<td>0.67</td>
</tr>
<tr>
<td>[La(CH₃COOH)₆(OH)(H₂O)₆]²⁺</td>
<td>348.39</td>
<td>121.65</td>
<td>149.14</td>
<td>291.49</td>
<td>0.54</td>
</tr>
<tr>
<td>[Eu(CH₃COO)₆(H₂O)₆]²⁺</td>
<td>274.94</td>
<td>117.06</td>
<td>148.69</td>
<td>291.33</td>
<td>0.70</td>
</tr>
<tr>
<td>[Eu(CH₃COO)₆(H₂O)₇]²⁺</td>
<td>278.51</td>
<td>117.60</td>
<td>149.15</td>
<td>291.38</td>
<td>0.65</td>
</tr>
<tr>
<td>[Eu(CH₃COOH)₆(OH)(H₂O)₆]²⁺</td>
<td>338.88</td>
<td>121.68</td>
<td>149.04</td>
<td>291.50</td>
<td>0.53</td>
</tr>
<tr>
<td>[Gd(CH₃COO)₆(H₂O)₆]²⁺</td>
<td>274.11</td>
<td>117.00</td>
<td>148.64</td>
<td>291.33</td>
<td>0.70</td>
</tr>
<tr>
<td>[Gd(CH₃COO)₆(H₂O)₇]²⁺</td>
<td>277.79</td>
<td>117.56</td>
<td>149.14</td>
<td>291.38</td>
<td>0.65</td>
</tr>
<tr>
<td>[Gd(CH₃COOH)₆(OH)(H₂O)₆]²⁺</td>
<td>337.77</td>
<td>121.74</td>
<td>149.06</td>
<td>291.50</td>
<td>0.53</td>
</tr>
<tr>
<td>[UO₂(CH₃COO)₆(H₂O)₄]⁺</td>
<td>281.48</td>
<td>116.53</td>
<td>149.13</td>
<td>291.59</td>
<td>0.44</td>
</tr>
<tr>
<td>[UO₂(CH₃COOH)₆(OH)(H₂O)₅]⁺</td>
<td>342.03</td>
<td>122.46</td>
<td>149.40</td>
<td>291.51</td>
<td>0.52</td>
</tr>
<tr>
<td>[Cm(CH₃COO)₆(H₂O)₆]²⁺</td>
<td>278.83</td>
<td>117.47</td>
<td>148.76</td>
<td>291.34</td>
<td>0.69</td>
</tr>
<tr>
<td>[Cm(CH₃COO)₆(H₂O)₇]²⁺</td>
<td>282.91</td>
<td>117.97</td>
<td>149.23</td>
<td>291.39</td>
<td>0.64</td>
</tr>
<tr>
<td>[Cm(CH₃COOH)₆(OH)(H₂O)₆]²⁺</td>
<td>342.66</td>
<td>121.90</td>
<td>149.13</td>
<td>291.50</td>
<td>0.53</td>
</tr>
</tbody>
</table>
Table 2: Comparison of C 1s (COO\(^-\)) \(\rightarrow \pi^*_{C-O}\) transition energies using different basis sets for C and O for CH\(_3\)COO\(^-\) (first column) and [Eu(CH\(_3\)COO)\(^b\)(H\(_2\)O)\(^g\)]\(^{2+}\) (second column). For Eu (f-in-core ecp) and H the def-TZVPP and def2-TZVPP are used. All data are obtained with the RI-ADC(2)-Method on BP86 – geometries.

<table>
<thead>
<tr>
<th>Basis set (C,O)</th>
<th>(f_{Ac}[1s\rightarrow\pi_{C-O}^*]/\text{eV})</th>
<th>(f[1s\rightarrow\pi_{C-O}^*]/\text{eV})</th>
<th>(\Delta f/\text{eV})</th>
</tr>
</thead>
<tbody>
<tr>
<td>TZVPP</td>
<td>292.03</td>
<td>291.38</td>
<td>0.65</td>
</tr>
<tr>
<td>cc-pwCVTZ</td>
<td>291.86</td>
<td>291.20</td>
<td>0.66</td>
</tr>
<tr>
<td>cc-pwCVQZ</td>
<td>291.69</td>
<td>291.07</td>
<td>0.62</td>
</tr>
</tbody>
</table>
Fig. 1

Fig. 2
Fig. 5

Fig. 6