EXAFS applications in coordination chemistry

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This chapter describes the applications of EXAFS spectroscopy for structural characterization and chemical speciation of metal complexes with small ligands in solution, and in microcrystalline or amorphous solids. A few EXAFS studies have been presented showing that the structures of chemical species in solution are not necessarily the same as in the crystalline state. Examples of solvated species include those of alkaline-earth metals, the halides, transition metals, lanthanides and actinides. Other structural or spectroscopic methods such as wide-angle X-ray scattering (WAXS) and NMR combined with EXAFS, extending the data analysis to the XANES region, as well as combination of K edge and L edges, can improve structural models. EXAFS analysis of multiple elements within the same structure, sometimes in combination with X-ray powder diffraction data, can provide 3D information, including absorber–ligand bond angles. The possibility of using EXAFS spectroscopy for analyzing a mixture of species is also discussed. Future applications will exploit very high brilliance X-ray lasers and will include monitoring reaction dynamics in real time and the rapid acquisition of high-quality high-density data sets of time-evolving systems.

1. Introduction

EXAFS spectroscopy is a key technique in defining the local structure, including that around metal ions in solution and in amorphous solids. Several reviews have addressed general applications of EXAFS in coordination chemistry (Garino et al., 2014; Levina et al., 2005; Muñoz-Páez & Marcos, 2013; Ohtaki, 1999; Penner-Hahn, 1999; Szabó et al., 2006). The present review focuses on metal complexes with small ligands in solution, with a few examples of microcrystalline or amorphous solids.

The EXAFS method has several unique strengths. It is element-specific and phase-independent: it has equal applicability to amorphous or crystalline solids, to liquids and solutions, and to gases. The phase and amplitude of EXAFS yield the elemental identity of ligand donor atoms and absorber–ligand distances. Linearly bridging groups such as $\text{C=N}$ can focus photoelectron back-scatter, providing metrics as far away as 5 Å. The application of multiple-scattering EXAFS analysis to known rigid ligand systems, such as porphyrins, can also provide absorber–scatterer angles (Levina et al., 2005). Below, we highlight the strengths of EXAFS spectroscopy in understanding the nature of metal complexes. Certain limitations of the EXAFS method are discussed in Section 6.
2. Complexes in crystals and solution

2.1. Lead(II)–penicillamine

A metal complex with strongly coordinated ligands does not always crystallize into the dominant solution structure. For example, with d-penicillamine (3,3’-dimethylcysteine; H₂Pen), lead(II) crystallizes as the 1:1 Pb(S₂N₂O-Pen) complex even when a combination of Pb L₃-edge EXAFS and ³⁵⁷Pb NMR shows that two 1:2 [Pb(S₂N₂O-Pen)(S-H₂Pen)]ⁿ⁻¹ (n = 0, 1) species with PbS₂NO coordination prevail in solution, with average Pb–2S and Pb–2(N/O) distances of 2.64 ± 0.04 and 2.45 ± 0.04 Å, respectively (Freeman et al., 1974; Schell et al., 2012; Sisombath et al., 2014). This result highlights that the same system can be examined in solution, powder and crystalline states to explore solution equilibria and phase-related structural differences. This particular strength of EXAFS is now widely exploited to probe catalysts in operando (Bordiga et al., 2013; Weiher et al., 2005).

2.2. Copper(II) hydration

Despite nearly 70 years of study, the structure of dissolved d⁰[Cu(aq)]²⁺ remains under active investigation, with a focus on the axial Jahn–Teller (JT) distortion. At the time of writing, the Cambridge Crystal Structure Database included 20 [Cu(aq)]²⁺ structures, including 17 [Cu(H₂O)₆]²⁺ structures, two [Cu(H₂O)₅]²⁺ structures and one [Cu(H₂O)₄]²⁺ structure (Dudev et al., 2006). Among the first-row transition-metal aqua ions, only copper(II) shows such structural variability, and has a similar heterogeneity in other ligand systems (Gray et al., 2000). Crystalline [Cu(H₂O)₆][ClO₄]₂ displays the standard JT-distorted octahedron, but [Cu(H₂O)₅][BrO₃]₂ does not [six Cu–O distances of 2.079 (4) Å], while crystalline [Cu(H₂O)₅](SiF₆) includes both regular and JT-distorted octahedral structures in a 1:3 ratio (Blackburn et al., 1991; Cotton et al., 1993; Gallucci & Gerkin, 1989; Ray et al., 1973).

With such heterogeneity of copper(II), the crystal structures cannot support inferences of solution structure.

Cu K-edge EXAFS of dissolved copper(II) complexes typically cannot resolve the five- and six-coordinate ligand alternatives because the axial ligands are weakly bound, distant and subject to rapid exchange (Helm & Merbach, 2005). EXAFS studies on [Cu(aq)]²⁺ in water have generally converged to a structural consensus describing a Jahn–Teller axially elongated octahedron with four Cu–Oₐx distance of 1.95 ± 0.01 Å and two Cu–Oₐeq distances of 2.29 ± 0.03 Å (D’Angelo et al., 1997; Persson et al., 2002; Tajiri & Wakita, 1986). Persson and coworkers combined Cu K-edge EXAFS (k ≈ 12 Å⁻¹) with WAXS data and excluded the elongated square-pyramidal model on the grounds that the fitted single axial bond included an excessively small mean displacement (σ²; Persson et al., 2002).

Cu K-edge EXAFS to k = 18 Å⁻¹ was attained with an aqueous copper(II) solution prepared using ultralow-zinc CuO (Frank et al., 2015). Analysis resolved two different axial Cu–O distances, Cu–Oₐx₁ = 2.19 ± 0.01 Å and Cu–Oₐx₂ = 2.33 ± 0.01 Å, along with four Cu–Oₑq distances of 1.97 ± 0.01 Å. This model was extended with MINUIT XANES (MXAN) analysis (Benfatto et al., 2005), yielding a C₄₄ axially elongated square-pyramidal [Cu(H₂O)₄]²⁺ structure (Fig. 1), with four Cu–Oₑq distances of 1.97 ± 0.02 Å, one Cu–Oₐx distance of 2.09 ± 0.03 Å and a nonbonded water molecule with a Cu–O distance of 3.0 ± 0.1 Å.

2.3. Thiocyanate: an ambidentate ligand

Ambidentate ligands can bind at either or both of two internal sites and include cyanide (CN⁻; C, N), cyanate (OCN⁻; N, O), thiocyanate (SCN⁻; N, S), nitrite (NO₂⁻; N, O) and sulfite (SO₃²⁻; S, O). Cadmium(II) can bind to either end of the thiocyanate ion. Crystalline octahedral Cd(SCN)₂

Figure 1

Left: Fourier-filtered K-edge EXAFS spectrum of copper(II) in 1 M HClO₄ (circles). Fits: JT octahedral, blue; elongated square pyramidal, green; elongated square pyramidal including a distant sixth oxygen scatterer, red. The vertical dotted line shows the k = 13.4 Å⁻¹ zinc cutoff. Inset: the best fit is unique only above k = 13 Å⁻¹. Right: the [Cu(H₂O)₅]²⁺ structural model (Frank et al., 2015).
Table 1
Coordination chemistry of the cuprous halides.
The typical Cu–X distance (R) error is ±0.03 Å (Persson et al., 1991).

<table>
<thead>
<tr>
<th></th>
<th>Chloride R (Å)</th>
<th>Bromide  R (Å)</th>
<th>Iodide  R (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>CuCl₂⁺</td>
<td>CuBr₃⁺</td>
<td>CuI₂⁺</td>
</tr>
<tr>
<td>DMSO</td>
<td>CuCl₂⁺</td>
<td>(CuBr₃⁺ and Cu₂Br₄⁻)§</td>
<td>CuI₂⁺</td>
</tr>
<tr>
<td>Pyridine</td>
<td>CuCl₂⁺</td>
<td>CuBr(py)⁻††</td>
<td>CuI₀</td>
</tr>
<tr>
<td>H₂O (excess Cl⁻)</td>
<td>CuCl₂⁻</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

† Copper concentration (C₉₋) = 88 M. †† Cu₉₋ = 0.01 Å. § Cu₉₋ = 0.006 Å. † Cu₉₋ = 0.002 Å. 

3.2. Copper(I) solvation

Cu K-edge EXAFS spectra are typically limited to k ≤ 13.4 Å⁻¹ because of spurious intensity at the Zn K edge imposed by trace zinc impurities. EXAFS analyses of Cu⁺X (X = Cl⁻, Br⁻, I⁻) in acetonitrile, DMSO, pyridine (py) or aqueous solution with added excess halide salts showed dimerization dependent both on concentration and halide size (Table 1). Linear [CuCl₂]⁻ and planar [CuCl₂]²⁻ complexes are formed in non-aqueous and aqueous solutions, respectively (Persson et al., 1991). In aqueous solution at high temperature (100–325°C), [CuCl₂]³⁻ with a Cu–Cl distance of 2.13 ± 0.01 Å dominates in excess chloride (Fulton et al., 2000). Double-bridged [CuₓX₄]²⁻ (X = Br⁻, I⁻) complexes are observed in DMSO solutions, while [CuₓI₂]⁻ dominates in concentrated copper(I) acetonitrile solution (Persson et al., 1991).

3.3. Lead(II) hydration

Studies of the solvation of lead(II) in water and several organic solvents further highlight the utility of EXAFS. Combined with XAS, EXAFS revealed six Pb–O distances of 2.54 ± 0.01 Å for [Pb(aq)]²⁺ in dilute acid solution (Persson et al., 2011). The fitted σ² = 0.027 ± 0.001 Å², indicating a large distribution of Pb–O distances (±0.16 Å), follows a theoretical prediction that electron density in anti-bonding lead 6s/ligand np molecular orbitals produces a distorted hemidirected structure and a spatial gap in the coordination sphere (Shimon-Ilvny et al., 1998; Walsh & Watson, 2005). However, when dissolved in 1,1,3,3-tetramethyleurea (TMU), a space-demanding ligand, the lead(II) ion organizes with six Pb–O distances of 2.517 ± 0.007 Å, now...
with a fitted \( \sigma^2 \) of 0.009 \pm 0.001 Å^2, indicating only a \( \pm 0.09 \) Å spread in Pb–O distances and implying a symmetrical holodirected coordination induced by increased ligand–ligand interactions in a [Pb(TMU)_6]^{2+} complex.

### 3.4. Actinide(III) hydration and ionic radii

The +3 oxidation state is most common for the heavier actinides, while the lighter actinide(III) ions are redox-unstable. The reported \([\text{An(aq)}]\)^{3+} crystal structures, \( [\text{M(H}_2\text{O})_6][\text{CF}_2\text{SO}_4]_3 \) (M = U to Cm, Cf), all show tricapped trigonal prismatic hydration (Apostolidis et al., 2010; Lindqvist-Reis et al., 2007; Matonic et al., 2001; Skanthakumar et al., 2007). EXAFS analyses of aqueous solutions reveal that the An–O distance shortens from 2.54 \pm 0.02 Å for uranium(III) to 2.42 \pm 0.01 Å for californium(III), consistent with ionic contraction across the actinide series (Brendebach et al., 2009; David et al., 1998; Galbis et al., 2010). This occurred without any specific trend in the coordination number (CN), which varies between eight and ten (Antonio & Soderholm, 2006). Analysis of a good-quality \((k = 2\text{–}16 \text{ Å}^{-1})\) \(L_2\)-edge EXAFS spectrum for an acidic aqueous (III) solution resolved two distances: six (\(\text{CN–O}_\text{prism}\) distances of 2.470 \pm 0.006 Å and three (\(\text{CN–O}_\text{cap}\) distances of 2.63 \pm 0.02 Å (Skanthakumar et al., 2007), while for californium(III) neither a square antiprism (CN = 8) nor a tricapped trigonal prism (CN = 9) model could be ruled out (Galbis et al., 2010). \textit{Ab initio} Monte Carlo quantum-mechanical models indicated that the EXAFS computed from a BP86 DFT (Rotzinger, 2005) simulation best reproduced the experimental EXAFS spectrum (CN \(\approx 8\) and \(R = 2.43\) Å), implying eight first-shell water molecules for dissolved [Cl(aq)]^{3+} (Galbis et al., 2010). Assessing EXAFS in a more limited \(k\) range (2–10.3 Å\(^{-1}\)), D’Angelo and coworkers found no decrease in coordination number in the actinide(III) series from uranium(III) to californium(III), and also found that dissolved [Cl(aq)]^{3+} is tricapped trigonal prismatic. They estimated the ionic radii of the dissolved uranium(III) to californium(III) ions in the actinide series by analyzing previously reported EXAFS spectra using a single-shell model for An–O with fixed CN = 9, finding a contraction from 2.527 \pm 0.009 to 2.422 \pm 0.007 Å (\(\Delta = 0.1\) Å; D’Angelo et al., 2013). The actinide(III) ionic radii in aqueous solution, obtained by subtracting the Shannon radius of a coordinated O atom (1.350 Å; David et al., 2001), are longer than the actinide(III) crystal structure radii but are similar to the lanthanide(III) counterparts.

### 3.5. Hydrated neptunium ions in different oxidation states

The systematic changes in the coordination environment of aqueous neptunium ions \((^{239}\text{NP}; t_{1/2} = 2.14 \times 10^6 \text{ years})\) in 1.0 M HClO\(_4\) solution were investigated using EXAFS as the oxidation state of neptunium was varied in \textit{vitro} using an X-ray spectroelectrochemical cell (Antonio et al., 2001). \([\text{Np}^{\text{III}}(\text{H}_2\text{O})_6]^{3+}\) and \([\text{Np}^{\text{IV}}(\text{H}_2\text{O})_6]^{4+}\) ions were produced with mean Np–O distances of 2.48 \pm 0.02 and 2.37 \pm 0.02 Å, respectively. Further oxidation yielded the \textit{trans-dioxo-neptunyl} species \([\text{NpV}_2\text{O}_7(\text{H}_2\text{O})_3]^{4+}\) and \([\text{NpV}_3\text{O}_8(\text{H}_2\text{O})_3]^{5+}\) with Np–O\(_\text{ax}\) bond lengths of 1.80 \pm 0.02 and 1.73 \pm 0.02 Å and average equatorial Np–O\(_\text{eq}\)(H\(_2\text{O}\)) bond distances of 2.44 \pm 0.03 and 2.36 \pm 0.03 Å, respectively. Each pair of hydrated species, \([\text{Np}^{\text{III}}] \rightarrow \text{Np}^{\text{IV}}\) and \([\text{Np}^{\text{IV}}] \rightarrow \text{Np}^{\text{V}}\), exhibited contraction of the bond distances with increasing oxidation state.

However, the above results are somewhat parameter-dependent. An independent analysis of high-quality \((k \approx 19.5 \text{ Å}^{-1})\) \(L_3\)-edge EXAFS spectra of hydrated neptunium(IV), neptunium(V), and neptunium(VI) ions in 1.0 M HClO\(_4\) proposed \([\text{Np}^{\text{IV}}(\text{H}_2\text{O})_6]^{4+}\) species (mean Np–O distance of 2.40 \pm 0.01 Å, CN = 10.4 \pm 1 \text{ with amplitude reduction factor } S_0^2 \approx 0.9 \text{ or CN = 9.7 \pm 1 with } S_0^2 \approx 1.0; \text{Ikeda-Ohno et al., 2008}). The EXAFS spectra of neptunium(IV) and neptunium(VI) were fitted with \([\text{NpV}_2\text{O}_7(\text{H}_2\text{O})_5]^{4+}\) and \([\text{NpV}_3\text{O}_8(\text{H}_2\text{O})_3]^{5+}\) models with Np–O\(_\text{ax}\) bond distances of 1.84 \pm 0.01 and 1.76 \pm 0.01 Å and with average Np–O\(_\text{eq}\)(H\(_2\text{O}\)) bond lengths of 2.49 \pm 0.01 and 2.42 \pm 0.01 Å, respectively, all of which are nominally longer than in the above 2001 study. This average Np–O\(_\text{eq}\)(H\(_2\text{O}\)) distance of 2.49 \pm 0.01 Å is intermediate between the bond lengths of 2.46 or 2.55 Å for five or six equatorial water ligands, respectively, from crystal structures with [NpO\(_2\)(aq)]^{+} ions. Therefore, the authors suggested that both [NpIV\(_2\text{O}_7(\text{H}_2\text{O})_5]^{4+}\) and [NpV\(_3\text{O}_8(\text{H}_2\text{O})_3]^{5+}\) are present in aqueous solution (Ikeda-Ohno et al., 2008). Comparing bond distances for solvated species with those in crystal structures is generally more reliable in order to obtain coordination numbers (especially at high CN) than a value from EXAFS model refinement, which is affected by additional uncertainty from an assumed amplitude reduction factor \(S_0^2\); see Section 3.8.

Another EXAFS study of hydrated neptunium(IV) ions proposed \([\text{NpIV}(\text{H}_2\text{O})_6]^{4+}\) complexes (Np–O distance of 2.40 \pm 0.01 Å, \(S_0^2 = 0.9; \text{Allen et al., 1997})\), which can be compared with the EXAFS models for hydrated uranium(IV): \([\text{U}^{\text{IV}}(\text{H}_2\text{O})_8]^{4+}\) \((U–O = 2.41 \pm 0.02 Å, S_0^2 = 1.0; \text{Hennig et al., 2007})\) or \([\text{U}^{\text{IV}}(\text{H}_2\text{O})_10]^{4+}\) \((U–O = 2.42 \pm 0.01 Å, S_0^2 = 1.0; \text{Moll et al., 1999})\).

### 3.6. Halide-ion hydration

The low energy of the F K-edge, 696.7 eV, presently fore-stalls aqueous-phase EXAFS analysis. A K-edge EXAFS study of aqueous Cl\_\text{aq}, limited to \(k = 8 \text{ Å}^{-1}\) due to a multi-electron excitation at 8.1 Å\(^{-1}\), revealed a shell of 6.4 hydrogen-bonded water molecules with a mean Cl–H distance of 2.23 \pm 0.04 Å and Cl⋯Cl–O distance of 3.14 \pm 0.02 Å, and a Cl–H–O angle of 156\(^\circ\) (Fulton & Balasubramanian, 2010), consistent with previous neutron diffraction metrics of Cl–H = 2.28 \pm 0.03 Å and Cl⋯O = 3.1 \pm 0.1 Å (Powell et al., 1993).

Combined Br K-edge EXAFS analysis and Monte Carlo simulation revealed an asymmetrical shell of 6.0 \pm 0.5 water molecules at a mean Br⋯O distance of 3.44 \pm 0.07 Å (Merkling et al., 2003), which is in good agreement with the previously found solvation shell (seven Br⋯O distances of 3.4 Å) using X-ray anomalous scattering (Ramos et al., 2000). Concurrent iodine multiple-edge \((K, L_1, L_3)\) EXAFS analysis
Table 2. EXAFS fitting parameters for halide hydration.

<table>
<thead>
<tr>
<th>Halide</th>
<th>CN</th>
<th>X−−H (Å)</th>
<th>X−−O (Å)</th>
<th>X−−H−O (°)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl−</td>
<td>6.4t</td>
<td>2.23 (4)†</td>
<td>3.14 (2)</td>
<td>156</td>
<td>Fulton &amp; Balasubramanian (2010)</td>
</tr>
<tr>
<td></td>
<td>6.4 (1.0)‡</td>
<td>3.11 (3)</td>
<td>3.05 (4)</td>
<td>Tongarra et al. (2010)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.0†</td>
<td>2.18 (2)</td>
<td>3.15 (2)</td>
<td>166 (2)</td>
<td>Antalek et al. (2016)</td>
</tr>
<tr>
<td>Br−</td>
<td>6.9</td>
<td>2.09 (2)</td>
<td>3.29 (3)</td>
<td>166 (4)</td>
<td>D’Angelo et al. (1994)</td>
</tr>
<tr>
<td></td>
<td>5.1 (5)</td>
<td>3.29 (4)</td>
<td>3.14 (5)</td>
<td>Simonet et al. (2002)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.0 (5)</td>
<td>3.44 (7)</td>
<td>3.04 (7)</td>
<td>Merkling et al. (2003)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>10.7</td>
<td>3.33 (3)</td>
<td>3.50 (4)</td>
<td>Filipponi et al. (2003)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8 (1)§</td>
<td>2.48 (2)</td>
<td>3.40 (2)</td>
<td>159 (2)</td>
<td>Feiters et al. (2005)</td>
</tr>
<tr>
<td>I−</td>
<td>6.3 (9)</td>
<td>2.65 (3)</td>
<td>3.50 (2)</td>
<td>148</td>
<td>Fulton et al. (2010)</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>2.56 (3)</td>
<td>3.50 (3)</td>
<td>159 (2)</td>
<td>Antalek et al. (2016)</td>
</tr>
<tr>
<td></td>
<td>8 (1)§</td>
<td>2.67 (2)</td>
<td>3.59 (2)</td>
<td>159 (2)</td>
<td>Antalek et al. (2016)</td>
</tr>
</tbody>
</table>

*Fixed value from aqueous and crystalline standards (Dang et al., 2006). † Uncertainties in the last digit are given parenthetically. § Refined EXAFS parameters: four Cl–O distances of 2.91 (1) Å, three Cl–O distances of 3.11 (1) Å, ten Br–O distances of 3.26 (3) Å, and nine I–O distances of 3.50 (3) Å. * Refined EXAFS distance of 3.34 (3) Å.

revealed an asymmetric solvation shell of 6.3 water molecules with a mean I−–H distance of 2.65 ± 0.03 Å and I−–O distance of 3.50 ± 0.02 Å, corresponding to an I–H–O angle of 148° (Fulton et al., 2010).

EXAFS combined with MXAN produced 3D solvation models for aquatic Cl−, Br− and I− (Antalek et al., 2016). Bromide and iodide exhibited globally symmetric solvation spheres, while chloride uniquely required a second shell with seven Cl−–H–O distances of 4.14 Å. EXAFS fitting parameters for halide hydration are given in Table 2.

3.7. Metal ions in ionic liquids

EXAFS investigations of metal complexes in ionic liquids have been reviewed (Estager et al., 2014; Hardacre, 2005). M(BF4)2·6H2O (M = Co²⁺, Cu²⁺) salts dissolved in [EMIm][BF4] (EMIm = 1-ethyl-3-methylimidazolium) produce unusual tetrahedral M(H2O)4¹⁻ aqua ions (Takao et al., 2012). Likewise, tetrahedral [CuCl4]²⁻ complexes form when dissolving anhydrous CuCl2 in [EMIm][Cl] (Li et al., 2010). Copper(II) and nickel(II) hydrates dissolved in [M2Im][Cl] (Cl2Im = 1-hexyl-3-methylimidazolium) were found to form [CuCl5]− and [NiCl5]− complexes, governed by the large size of the [Cl2Im⁺] cation, while in [EMIm][SCN] solvent [Cu(NCS)2(SCN)]⁻ is formed. Chromium(III) chloride hydrate forms [CrCl3(H2O)2]²⁻ and [Cr(NCS)3]³⁻ complexes in the ionic liquids [C6MIm][Cl] and [EMIm][SCN], respectively (Hartley et al., 2014).

3.8. Impact of multi-electron excitations on defining the solvation shell

Multi-electron excitations can impact EXAFS fits, influencing coordination numbers and bond distances. For example, the L3-edge EXAFS spectra of light lanthanide(III) complexes exhibit double-electron excitations (2p4d→5d²) in the k range 5–7 Å⁻¹ (Solera et al., 1995). For lanthanide ions and third-row transition metals, the short core-hole lifetime of high-energy K-edge EXAFS broadens double-electron features into negligible intensity. The long k range available from lanthanide K-edge EXAFS can compensate for the loss of information from spectral broadening and larger core-hole width (Γ) relative to the L edges (D’Angelo et al., 2008).

Multi-electron excitations are also prominent in the Ca K-edge EXAFS of calcium(II) aqueous solutions at k = 2.7, 3.7 and 10.3 Å⁻¹, which correspond to [1s3p], [1s3s] and [1s2p] double-electron excitations, respectively (Fulton et al., 2003), and in yttrium(III) K-edge EXAFS (Chaboy et al., 2001; Diaz-Moreno et al., 2000). In a background-correction procedure relying on the Z-dependent similarity of the multi-electron background, the Ar K-edge XAS was used to remove the multi-electron features of dissolved [Ca(aq)]²⁺, finding (7.2 ± 1.2) Ca–O, Ca–H and Ca–Br coordination numbers of 10.3 ± 0.1 Å⁻¹ and 2.43 ± 0.01 Å, while back-scattering from 16 Ca⋅⋅⋅H distances of 2.97 ± 0.02 Å (Fulton et al., 2003). Alternatively, double-electron excitations can be fitted rather than omitted, as in analysis of the K-edge EXAFS of dissolved [Ca(aq)]²⁺ (eight Ca–O distances of 2.42 Å in a disordered shell and Ca⋅⋅⋅H = 3.10 Å; D’Angelo et al., 2004).

The double-electron excitations [1s4s], [1s3d] and [1s3p] were observed in the K-edge EXAFS of aqueous strontium(II). EXAFS analysis using an atomic background model to account for these transitions yielded a solvation sphere with (7.3 ± 0.5) Sr–O distances of 2.643 ± 0.002 Å, while ignoring this model produced underestimated coordination numbers: 6.3 Sr–O distances at 2.62 Å (D’Angelo, Nolting et al., 1996) and (7.2 ± 0.5) Sr–O at 2.62 ± 0.03 Å (Plund et al., 1994).

For dissolved [Ba(aq)]²⁺, disregarding the respective L3-edge and L1-edge [2p4d→5d⁷] and [2s4d→6p5d⁵] double-electron excitations yielded RBa−O = 2.780 ± 0.003 Å and systematically underestimated the Ba–O coordination number, i.e., CN_{Ba−O} = 6.9 rather than 7.8 ± 0.3 (D’Angelo, Pavel et al., 1996). However, it is not clear why the same corrected EXAFS method produced a higher hydration number of 10.3 ± 0.1 for the smaller strontium(II) cation. Combined EXAFS and WAXS results suggested the same hydration number of 8.1 ± 0.3 for both metal ions, with R_{Sr−O} = 2.63 ± 0.02 Å and R_{Ba−O} = 2.81 ± 0.03 Å (Persson et al., 1995).

4. Multiple-edge XAS

Structural information can be extended when more than one element in a structure is susceptible to EXAFS analysis, because internal distances can be derived from independent absorbers. In some cases, intramolecular angles become available (Section 4.4).

4.1. Mixed-metal periodates

K-edge EXAFS and X-ray powder diffraction were combined to structurally characterize several microcrystalline M'[MIO₄]ₓ·xH₂O complexes (M' = Na⁺–Cs⁺, NH₄⁺ and MIV = Ni, Pb, Sn, Ge, Mn; Levenson, 1997). Sodium persulfate (Na₂S₂O₈) oxidation of dissolved Na₂SO₄ plus Na₂H₂IO₆ produced solid Na₂[Ni(IO₄)₂], for which Na and I K-edge EXAFS
spectra were collected. X-ray powder diffraction data showed that Na[NiO₆] belongs to space group P312 with layered edge-sharing NiO₆ and IO₆ octahedra and intercalated sodium ions. EXAFS analyses (fixed coordination numbers) yielded an Ni–O distance of 1.863 ± 0.002 Å, an I–O distance of 1.868 ± 0.001 Å and an Ni–I distance of 2.85–2.86 Å (Currie et al., 1994). The refined Ni⋯Ni distance of 4.969 ± 0.005 Å closely matched the unit-cell edge a from powder diffraction.

4.2. Platinum–thallium cyanogen complexes

Cyanogen as a ligand can promote M₁–CN–M₂ electronic delocalization (Giorgetti et al., 1997). [Pt(CN)]⁵⁻ and [Tl(CN)]⁴⁻ (n = 2–4) combine to form hetero-dimetallic [(NC)₂Pt–Tl(CN)₃]⁺⁻ (n = 0–3) complexes in solution. Pt and Tl L₃-edge EXAFS, vibrational and multinuclear (¹⁹⁵Pt, ²⁰⁵Tl) spectra were collected. X-ray powder diffraction data showed the local structure around platinum and thallium (Jalilehvand et al., 2001). Multi-scattering from the five linear axial and equatorial Pt–C–N bonds, but not from the four bent (149°) equatorial Pt–C–N units and short Pt–Tl distances (2.60–2.64 Å).

Slow evaporation of an acidic (HClO₄) [(NC)₂Pt–Tl(CN)]⁻ solution produced polycrystalline TlPt(CN)₃. X-ray powder diffraction revealed both proximate Pt–Tl = 2.627 ± 0.002 Å and TlPt(CN)₃ units forming linear –NC–Pt–Tl–NC–Pt–Tl–chains. Pt and Tl L₃-edge EXAFS analyses indicated extensive multiple scattering from the five linear axial and equatorial Pt–C–N bonds, but not from the four bent (149°) equatorial Tl–N–C bonds. The equatorial and axial Tl–N distances refined independently to 2.50 ± 0.01 and 2.31 ± 0.03 Å, respectively (Jalilehvand, Eriksson et al., 2001).

The complex [(NC)₂Pt–Tl(O–DMSO)]⁺, derived from mixing K₂[Pt(CN)]₃·3H₂O and [Tl(DMSO)]₃[ClO₄]₃ in dimethylsulfoxide, was studied using Pt and Tl L₃-edge EXAFS, multinuclear NMR and DFT calculations. The unoccupied sixth coordination site of platinum generated a slightly longer Pt–Tl bond with a distance of 2.67 ± 0.01 Å, with a mean Tl–O distance of 2.282 ± 0.002 Å and a Tl–O–S angle of 120°. The metal–metal bond has been described as a Pt(5dₓ²)²→Tl(6s)⁰ donation (Purgel et al., 2011).

4.3. Actinide(IV) hexacyanoferrates

The advantages and limitations of multiple-edge EXAFS spectroscopy were analyzed in applications to mixed-metal iron(II)/cobalt(II)/nickel(II) hexacyanoferrates (Giorgetti & Berrettoni, 2008). Micromicrocrystalline AnIV[Fe(CN)]₆·xH₂O complexes, in the hexagonal space group P6₃/m (An = Th, Np, Pu), were studied using Fe K-edge and An L₃-edge EXAFS and X-ray powder diffraction. The iron EXAFS Fourier transforms showed enhanced multiple scattering focused along the linear Fe–C–N segments within the [Fe(CN)]₆ units (Dumas et al., 2013). Cyanogen bridges connect An(IV) to [Fe(CN)]₆, producing [An(NC)₆(H₂O)]₃ tripped trigonal prisms with three equatorial water ligands. The An–N–C angle varies between 155° and 165°, reducing the multiple scattering along this path and damping the corresponding An L₃-edge EXAFS Fourier transform feature. The mean An–N distance decreases from 2.58 ± 0.03 Å for thorium(IV) to 2.45 ± 0.01 Å for neptunium(IV) to 2.42 ± 0.01 Å for plutonium(IV), reflecting the ‘actinide contraction’. The average An–H₂O distance (which is shorter than the An–N distance) follows the same trend. However, the EXAFS model fitting was performed over the range k = 0–12 Å⁻¹, thus mistakenly including the XANES region (k < ~2 Å⁻¹), wherein the short wavelength of the photoelectron due to its low kinetic energy (5–150 eV) makes multiple-scattering events between neighbour atoms dominant over single scattering.

4.4. Grignard reagent CH₃MgBr

The Grignard reagent CH₃MgBr in di-n-butylether solution was examined by measuring both Mg and Br K-edge EXAFS
spectra using a UHV-compatible cell for liquid samples (Abraham et al., 1996). The independent Mg·⋯Mg and Br·⋯Br distances allowed calculation of the internal angles within the dimeric species (Fig. 2). The bromide L\textsubscript{3}-edge at 1550 eV limited the Mg EXAFS oscillation to $k = 8\ \text{Å}^{-1}$.

4.5. Amorphous solid Cd(HCys)$_2$·H$_2$O

The Cd K-edge EXAFS spectrum of the white precipitate formed when Cd(OAc)$_2$ is added to twofold cysteine (H$_2$Cys) in aqueous solution consistently yielded a Cd–S distance of 2.52 ± 0.02 Å in either CdS or CdS$_2$O coordination models. The CdS$_2$O model, with a Cd–O distance of 2.27 ± 0.04 Å consistent with crystalline CdS$_2$O compounds (Cd–O$_{\text{ave}}$ = 2.240 Å), proved superior when compared against the Cd L\textsubscript{3}-edge XANES spectra of Cd(HCys)$_2$·H$_2$O and crystalline Cd$^{II}$S$_n$(N/O), thiolate complexes (Jalilehvand et al., 2009).

5. Mixed species in solution and evolving factor analysis (EFA)

XAS spectra follow Beer’s law, so that the EXAFS of mixtures are a linear sum of the EXAFS of the components. If the component EXAFS oscillations are sufficiently different, the number of species can be estimated using EFA, an application of principal component analysis (PCA). The approach requires multiple XAS spectra of a chemical system evolving with change in conditions, such as pH or ligand concentration, and typically requires the XAS of the beginning and end states of the evolving chemical system. The empirical orthogonal factors (EOF) of significant intensity can reveal the number of interacting chemical species. A plot of EOF intensities versus, for example, ligand concentration reveals speciation. Under some conditions, binding constants can be derived and complex systems can be fully specified (Conti et al., 2010; Gampp et al., 1985; Garrido et al., 2008; Maeder, 1987; Rossberg et al., 2003).

Speciation of a mixture can also be achieved by linear combination of the experimental EXAFS spectra of the individual components, if they are known, as for example for molybdenum(V) complexes in aqueous HCl (Jalilehvand et al., 2007). If unknown, the EXAFS of a specific component can be calculated from a model, as was performed in the study of mercury(II) complexation with cysteine and its derivatives; see Fig. 3 (Jalilehvand et al., 2006, 2013).

6. Limitations of EXAFS

6.1. Uncertainties

In EXAFS spectroscopy the sensitivity to back-scattering atoms is limited to ~5 Å, because the EXAFS amplitude reduces with $1/R^2$ and also with high mean displacement ($\sigma^2$) of nonbonded absorber–scatterer pairs at distance R, especially in solution. Therefore, EXAFS analysis may be of limited utility in defining the structure of a loosely bound second hydration shell (Ohtaki & Radnai, 1993), as shown for cobalt(II), nickel(II) and zinc(II) in aqueous solution (D’Angelo et al., 2002). Exceptions include the well defined second hydration shells for the [Cr(H$_2$O)$_6$]$^{3+}$ complex ion and its chloroqua cognates, [CrCl$_n$(H$_2$O)$_{6-n}$]$^{(3-n)+}$ (n = 1–3) (Díaz-Moreno et al., 1996; Munoz-Paez & Marcos, 1992), as well as for the [Cu(NH$_3$)$_3$]$^{3+}$ complex ion (Frank et al., 2008).

Several examples in this chapter relate the EXAFS uncertainty (±20%) in coordination number and its correlation to the amplitude reduction factor, $S_0^2$, describing inelastic losses due to multi-electron excitations (Bauer & Bertagnolli, 2007).

6.2. The need for complementary physical methods

EXAFS analysis cannot distinguish between back-scattering atoms of adjacent Z, for example (N, O) or (S, Cl). However, additional information supplied by complementary techniques, including multinuclear NMR and UV–visible spectroscopy, can allow detailed speciation and structural characterization. For example, combined results from $^{13}$C, $^{207}$Pb NMR, UV–Vis spectroscopy and electrospray ionization mass spectrometry (ESI-MS) were required to unveil co-existing dithiolate [Pb(S,N,O,Cys)(S-HCys)]$^{2-}$, [Pb(S,N-Cys)$_2$]$^{2-}$ and trithiolate [Pb(S,N-Cys)(S-HCys)$_2$]$^{3-}$, [Pb(S-HCys)$_3$]$^{3-}$ (minor) complexes in lead(II)–cysteine solutions (Jalilehvand et al., 2015). As the Pb–S distances, 2.65 ± 0.03 Å, did not differ significantly in the above three- or four-coordinated lead(II) complexes, and separation of the O/N EXAFS contributions in the presence of heavy back-scatterers such as S was difficult, the information from complementary spectroscopic methods was essential in identifying the chemical species in solution.

Figure 3
Fitting the experimental EXAFS spectrum of a mercury(II)–cysteine solution ($C_{\text{Hg}}$ = 0.083 M, C$_{\text{Hg(Cys)}}$ = 0.334 M, pH 9.1) to linear combinations of the simulated EXAFS oscillations for Hg(S,N,Cys)$_3$ (14%); Hg–S = 2.34 Å), Hg(S-Cys)$_3$ (40%); Hg–S = 2.44 Å) and Hg(S-Cys)$_4$ (46%; Hg–S = 2.52 Å) (Warner & Jalilehvand, 2016).
7. Future perspectives

The advantages conferred by EXAFS studies in providing structural metrics for almost any element (except the lightest) in virtually any phase (solid, liquid, gas, crystalline, amorphous or glassy) are now very well established. Future prospects include in situ/in operando and flow methods to understand reaction mechanisms and enzymatic structure/functions. The recent combination of EXAFS and MXAN makes use of information in the entire XAS spectrum to yield fully three-dimensional structures. These can be combined with DFT calculations to understand edge features in terms of electronic states and illuminate the fundamentals of structure and mechanism in terms of those states. The recent appearance of extreme high-brilliance, femtosecond pulse-width X-ray lasers holds out the promise of single-shot XAS spectroscopy and EXAFS structural resolution of nanosecond structural intermediates.

References


