

Biomimetic mono- and dinuclear Ni(I) and Ni(II) complexes studied by X-ray absorption and emission spectroscopy and quantum chemical calculations

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Abstract. Five biomimetic mono- or dinuclear nickel complexes featuring Ni(I) or Ni(II) sites were studied by X-ray absorption and emission spectroscopy and DFT calculations. Ni K-edge XANES spectra and K β main and satellite emission lines were collected on powder samples. The pre-edge absorption transitions (core-to-valence excitation) and K $\beta_{2,5}$ emission transitions (valence-to-core decay) were calculated using DFT (TPSSH/TZVP) on crystal structures. This yielded theoretical ctv and vtc spectra in near-quantitative agreement with the experiment, showing the adequacy of the DFT approach for electronic structure description, emphasizing the sensitivity of the XAS/XES spectra for ligation/redox changes at nickel, and revealing the configuration of unoccupied and occupied valence levels, as well as the spin-coupling modes in the dinuclear complexes. XAS/XES-DFT is valuable for molecular and electronic structure analysis of synthetic complexes and of nickel centers in H₂ or CO_x converting metalloenzymes.

1. Introduction

Nickel ions play important roles in many biological enzymes involved in small molecule activation catalysis. Prominent examples are hydrogen-converting nickel-iron hydrogenases and acetyl-CoA synthase (ACS) and carbon monoxide dehydrogenase (CODH) involved in carbon oxide (CO_x) chemistry [1-2]. These enzymes integrate mono- or dinuclear nickel centers in mixed ligand environments, combining H, C, N, or O ligands from hydride groups, CO/CO₂ or water species, and amino acids with S ligands from cysteine residues or metal-bridging sulfido groups. ACS, for example, holds a dinickel center, in which one Ni ion is ligated by two nitrogen ligands from the protein backbone and by two cysteine thiolate groups, which bridge between the two Ni ions. The nickel centers in the proteins often undergo redox changes in the catalytic cycle, so that, e.g., Ni(I) and Ni(II) species are formed. However, the redox and spin state of the nickel sites, as well as the detailed metal ligation environment may not always be accessible by protein crystallography and many spectroscopic methods. Knowing these properties is essential for unraveling the reaction mechanisms.

Synthetic model chemistry has been extensively used to mimic the metal coordinations and valence states in the proteins, aiming at a better understanding of their reactivity. In the present study, five crystallographically characterized mono- or dinuclear complexes containing formal Ni(I) or Ni(II) sites were studied (figure 1), with metal coordinations including either only nitrogen donors or additional S/O/H ligands, thus resembling the biological centers. X-ray absorption and emission spectroscopy (XAS/XES) is a tool, by which all oxidation and spin states of metal centers, as well as



their molecular and electronic configurations can be studied in proteins and synthetic systems. In particular the pre-edge absorption region of the K-edge, reflecting resonant core-level (1s) electron excitation into unoccupied valence orbitals (core-to-valence transitions, ctv), and the K β emission region, due to electronic 3p \rightarrow 1s decay (K β main lines, K $\beta_{1,3}$ and K β') or decay from occupied valence levels in the K $\beta_{2,5}$ region (valence-to-core transitions, vtc), bear valuable information on the electronic structure [3-7]. The respective absorption or emission features can be calculated using density functional theory (DFT), for electronic transition assignment and generation of model structures. Here, we used Ni K-edge XAS and K β emission spectroscopy and DFT calculation of the ctv and vtc spectral features to access the electronic structures of the nickel complexes.

2. Materials and Methods

Nickel complexes were synthesized as previously described [8-12] and powder samples were prepared by grinding with boron nitride (1:10 w/w). XAS/XES experiments were carried out at beamline ID26 of the ESRF (Grenoble, France) using a Si[311] double-crystal monochromator for excitation energy tuning and a vertical-plane Rowland spectrometer with 5 Si[551] analyzer crystals and an avalanche photodiode detector for narrow-band emission detection and a scintillation detector for total-fluorescence detection. Samples were held in a liquid-He cryostat at 20 K. Single-point DFT calculations on crystal structures of the complexes were performed with the program package ORCA [13] (TPSSh exchange-correlation functional, triple-zeta-valence-plus-polarization basis set). Calculated spectra were 183 eV shifted on the energy axis and stick spectra broadened by Gaussians (ctv, FWHM 1.2 eV) or Lorentzians (vtc, FWHM 3.0 eV) for comparison with experimental data.

3. Results

Figure 1 shows the crystal structures of the studied nickel complexes **1** (L(^tBu)Ni^IOEt₂ (L(^tBu/Me) = [HC(C(^tBu/Me)NC₆H₃(ⁱPr)₂)₂] [8]), **2** (L(^tBu)Ni^{II}SEt [9]), **3** ([L(^tBu)Ni^I]₂N₂ [8, 10]), **4** (PYR)Ni^{II}HNi^I (PYR²⁻ = [{NC(Me)C(H)C(Me)-NC₆H₃(ⁱPr)₂]₂(C₅H₃N)²⁻ [11]), and **5** ([L(Me)Ni^{II}H]₂ [11, 12]). Both mononuclear Ni complexes show a planar-trigonal coordination site with a bidentate β -diketiminate ligand (“nacnac”) and respective third O/S ligand, resembling the distal nickel ion in the ACS protein. **1** is a Ni(I) S = 1/2 (d⁹) system and **2** contains a high-spin (d⁸) Ni(II) ion. The dinuclear complexes represent increasing oxidation states. Complex **3** comprises a bridging N₂ ligand and two weakly coupled Ni(I) centers (each S = 1/2). **4** has a distorted trigonal Ni(I) site and a square-planar Ni(II) site, the hydride is bound only to the Ni(II), and the complex shows a doublet state with a low-spin Ni(II). **5** shows two hydride bridges and presumably antiferromagnetically coupled high-spin Ni(II) centers.

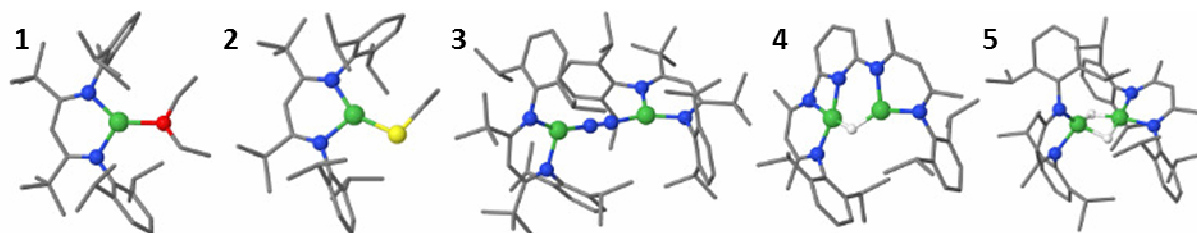


Figure 1. Crystal structure of complex **1**, **2**, **3**, **4**, and **5** [8-12]. Color code: Ni, green; N, blue; O, red; S, yellow; C, grey; H, white. The Ni ions and their first-sphere ligands are highlighted as spheres, non-bridging hydrogen atoms are omitted for clarity.

Ni K-edge XAS and K β XES spectra of the complexes are shown in figure 2. The overall shape changes in the XANES reflect the varying first-sphere coordination geometries of the nickel centers, featuring distorted 3- or 4-coordinated Ni sites, which cause pronounced 1s \rightarrow 4p transition features around 8337 eV in particular in **3** and **5**. The pre-edge absorption was relatively weak in all complexes, showing a single resolved feature around 8330-8332 eV. The K β main line emission was broad and rather similar for all complexes, showing only small variations, in response to the

Ni(I)/Ni(II) and ligand variations, in the intensity ratio of the $K\beta_{1,3}$ (~8265 eV) and unresolved $K\beta'$ (~8255 eV) spin-polarization features. The isolated ctv excitation transitions (figure 2C) varied mostly in their center energy, with **1** and **3** containing Ni(I) showing a ~1 eV lower ctv maximum than **2** containing Ni(II). **4** with a Ni(I)Ni(II) site showed a ctv feature at low energies, whereas **5** with a Ni(II)Ni(II) center showed a ~0.5 eV up-shifted feature. Pronounced variations in the $K\beta_{2,5}$ emission line shapes reflected the N/S/O/H ligand variations in the five complexes (figure 2D).

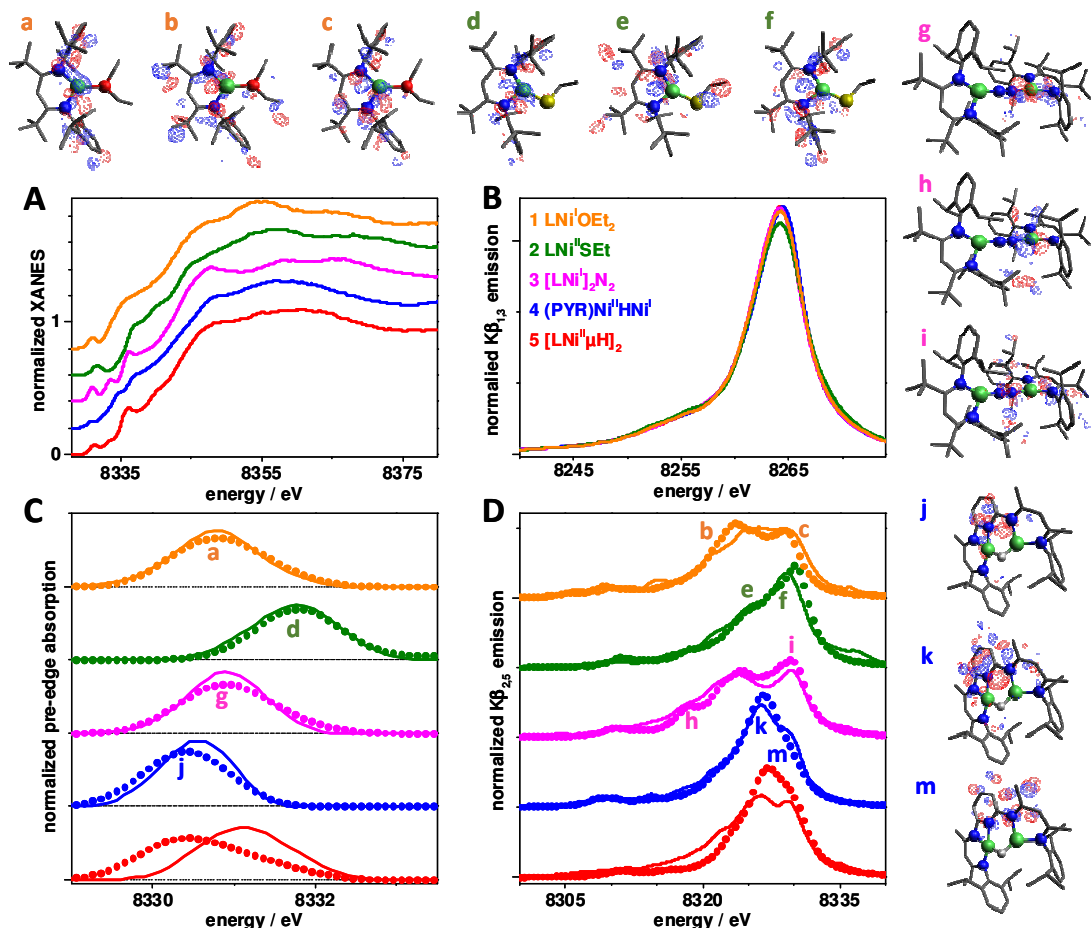


Figure 2. XAS/XES spectra of five nickel complexes. (A) Ni XANES spectra, (B) $K\beta$ main line ($K\beta_{1,3}$, $K\beta'$) emission spectra, (C) core-to-valence (pre-edge) absorption spectra, (D) valence-to-core ($K\beta_{2,5}$) emission spectra. Emission spectra were non-resonantly excited at 8800 eV; $K\beta$ main lines and DFT-calculated (dots) and experimental (lines) ctv and vtc spectra after background removal were normalized to unity area. Structures labelled a-m show metal- or ligand-centered molecular orbitals corresponding to the most intense excitation or decay transitions in the respective ctv or vtc regions.

The DFT-calculated and experimental ctv and vtc spectra are compared in figure 2 (C and D). We used the valence, spin, and multiplicity assignments from earlier studies [8-12] or alternative spin multiplicities ($M = 2S+1$) in the calculations. For complexes **1-4**, the calculated spectra essentially reproduced the single resolved ctv feature as well as the pronounced transition intensity and energy variations in the vtc spectra for $M = 2$ (**1**), $M = 3$ (**2**), $M = 3$ (**3**), and $M = 2$ (**4**) states, confirming the earlier spin state assignments such as the weak coupling of the two Ni(I) centers in **3** and the $S = 1/2$ Ni(I) and low-spin Ni(II) sites in **4**. Using ferromagnetic coupling of the two high-spin Ni(II) ions in **5** yielded ctv and vtc spectra, which clearly deviated from the experimental data, thereby supporting the alternative antiferromagnetic coupling assignment based on magnetic moment data [10, 12]. Further calculations on **5** will be reported in a forthcoming publication.

4. Discussion

We report XAS/XES spectra for five structurally characterized nickel complexes in the solid state, which mimic biological nickel centers [8-12]. The XANES spectral shape is pronouncedly affected by the first-sphere ligation variations causing altered 3d/4p mixing. However, The K β main line emission is rather insensitive to the Ni(I)/Ni(II) and ligand variations in the Ni complexes, presumably due to core-hole lifetime spectral broadening leading to unresolved spin-polarization features and few unpaired Fe(d) spins in the closed-shell systems, in contrast to earlier first-row transition metals [3-7].

The ctv (pre-edge absorption) and vtc (K $\beta_{2,5}$) emission features clearly are more sensitive to the relatively moderate ligation and valence state variations in the complexes. DFT at the TPSSh/TZVP level reproduced the experimental ctv and vtc spectra near-quantitatively, thus facilitating electronic transition and molecular orbital (MO) configuration assignment. The energy shifts of the ctv features are explained by energy variations of unoccupied valence MOs and the peak features of the vtc spectra reflect decay contributions from occupied valence MOs dominated by the respective ligand species. Our results confirm the coordination geometries and spin states of the nickel sites as deduced from earlier studies by other methods [8-12]. The results emphasize the sensitivity and selectivity of the XAS/XES-DFT approach for detection of metal ligation variations such as O/S exchange and metal-hydride bond formation [4-5], as well as specific spin state assignment even for multinuclear metal centers. This approach is highly valuable for investigations of nickel complexes in proteins and expected to provide new insights into their unique mechanisms of small molecule catalysis.

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