

**Experiment title:**

The spectroscopic study of the atomic and electronic structure of binuclear Ni and Pd acetylacetonate complexes in solution

Experiment

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Report:

Determination of the atomic and electronic structure of mono- and binuclear metal (Ni and Pd) acetylacetonate complexes in solution was the main goal of this study. We focused on the generation of a highly stable M_2O_2 core which had been detected in our previous mass spectrometric studies. Ni K -edge and Pd L_3 -edge XAS spectroscopy were utilized for the characterization of electronic structure and local environment of the metal atoms. Measurements were performed at low temperature (25-30K) in cryostat both for the diluted solid samples (10 wt.% in microcrystalline cellulose) and for the frozen solutions in acetonitrile. Nickel and palladium acetylacetonates (acac) and their analogues with fluorinated ligands (trifluorinated – tfpd, hexafluorinated – hfpd) were used in the study.

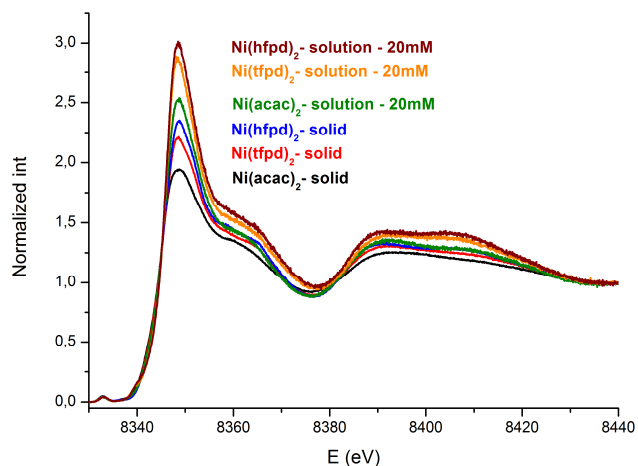


Figure 1. Ni K -edge XANES spectra of Ni(acac)₂, Ni(tfpd)₂, Ni(hfpd)₂ and their 20 mM solutions in acetonitrile.

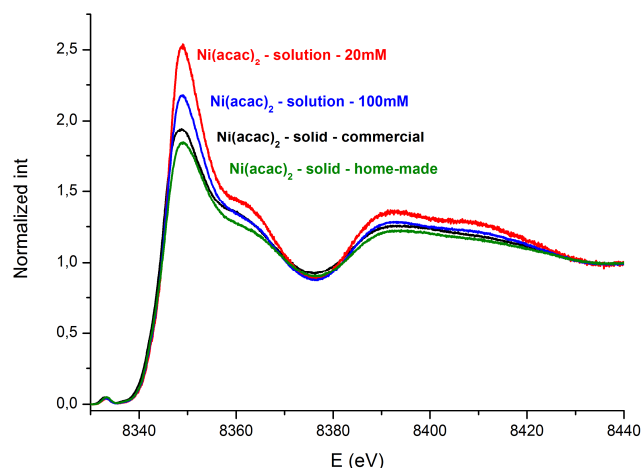


Figure 2. Ni K -edge XANES spectra of commercial Ni(acac)₂, home-made Ni(acac)₂ and 20 mM and 100 mM solutions of Ni(acac)₂ in acetonitrile.

Spectra were collected with the use of protection from radiation damage (short scans of different sample areas). The scan time for each point was about 20-30 seconds. All single-scan spectra for each sample were averaged. The resulting spectra were normalized to the edge jump.

The presence of intense undivided white lines (main absorption lines) in XANES spectra of all nickel compounds and their solutions clearly shows the octahedral coordination geometry of Ni^{2+} (Figure 1). The nature of the ligands has notable impact on the relative intensity of the main absorption line. For the solid samples the increase of the number of F-substituents leads to the growth of white line intensity. For solutions the same effect is observed, also the main absorption lines intensities are higher compared with those for the solid samples. In order to get additional information we compared spectra of commercial nickel acetylacetonate, home-made nickel acetylacetonate and two solutions of $\text{Ni}(\text{acac})_2$ in acetonitrile (diluted – 20 mM and concentrated – 100 mM). The differences in the absorption lines shapes were detected (Figure 2). Possibly, different water content in two solid samples obtained in different ways led to the slight variation in the Ni^{2+} coordination sphere. It should, however, be borne in mind that the small variations in spectral lines intensities may be caused by possible inaccuracy in the spectra normalization. For the solutions, the concentration effect can be explained by the presence of equilibrium between several forms of nickel acetylacetonate complexes in solution. Probably, the dissolution of solid trimeric nickel acetylacetonate in coordinating solvent (acetonitrile) led to the formation of the series of mononuclear and dinuclear complexes, and their concentrations depend on ratio between $\text{Ni}(\text{acac})_2$ and acetonitrile. This observation is in agreement with the results of our previous mass spectrometric studies. The same results were obtained for the fluorinated analogues of $\text{Ni}(\text{acac})_2$ except that their low solubility in acetonitrile significantly narrows the available concentration range.

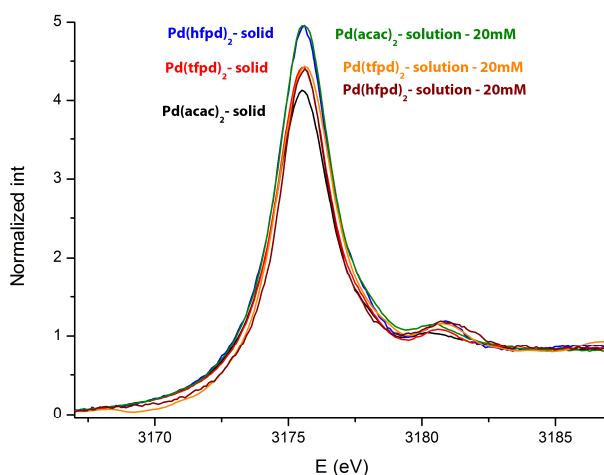


Figure 3. Pd L_3 -edge XANES spectra of $\text{Pd}(\text{acac})_2$, $\text{Pd}(\text{tfpd})_2$, $\text{Pd}(\text{hfpd})_2$ and their 20 mM solutions in acetonitrile.

EXAFS data were recorded as well for all described samples, but dimeric structures (with Ni..Ni scattering paths) were not reliably detected even in the solid $\text{Ni}(\text{acac})_2$ samples.

Pd L_3 -edge XANES measurements were performed in cryostat under vacuum conditions (10^{-6} mbar) in order to get rid of undesirable argon absorption lines. The spectra of the solid samples were recorded in a reliable manner. The white line intensity changing trends observed in the case of palladium compounds were similar to those for nickel compounds (Figure 3). For the solutions we failed to obtain reliable data due to the partial evaporation of frozen solvent under vacuum conditions.

In summary, we have observed the strong impact of the ligands nature on the intensity of the main absorption lines in the XANES spectra of nickel and palladium acetylacetonate complexes. The equilibrium between several forms of acetylacetonate complexes in solution was detected in the experiments with various solutions concentrations. The formation of binuclear acetylacetonate complexes in solutions as the result of partial dissociation can be proposed.