

Characterization of Dinitrosyl Iron Complexes by X-ray Absorption Spectroscopy

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X-ray absorption spectroscopy is a powerful physical method to provide information about the electronic structure and differentiate various metalloproteins/metal complexes. The 1s to 3d transition observed in the metal K-edge absorption spectra, which is strongly perturbed by metal oxidation state, coordination geometry and ligand environment, determines the metal effective nuclear charge through the comparison of complexes with similar coordination environment. In order to delineate the electronic structure of {Fe(NO)₂} core within the dinitrosyl iron complex (DNIC), the X-ray absorption measurements on the Fe K-edge were carried out with synchrotron radiation at the 17C beam line.

The Fe K-edge spectra of a series of reference compounds [PPN][Fe^{III}(SPh)₄], [PPN]₂[Fe^{II}(SPh)₄], and [PPN][Fe^{III}(OPh)₄] are shown in Fig. 1. The pre-edge transition is due to the d-p mixing between Fe and ligand atoms in the distorted T_d local environment of the Fe center. [1] Taking the apparent peak position of pre-edge for comparisons, the energy of oxidized-form [Fe(SPh)₄][−] shifted from 7113.8 eV to 7112.5 eV ([Fe(SPh)₄]^{2−}) upon one-electron reduction of [Fe(SPh)₄][−]. Compared to the tetrahedral Fe(III) complex [Fe(SPh)₄][−], complex [Fe(OPh)₄][−] coordinated by the less covalent phenoxide ligands displaying a higher rising edge and pre-edge energy at 7114.2 eV may suggest the effective nuclear charge (Z_{eff}) of Fe in [Fe(OPh)₄][−] is higher than that of [Fe(SPh)₄][−]. We noticed that the metal K-edge absorptions are strongly perturbed by metal oxidation state, coordination geometry and ligand environment.[2] It is interesting to note that the pre-edge energy was known to correlate with metal oxidation state under the presence of the same coordination geometries and ligand types.[2]

Complexes [(NO)₂Fe(ONO)₂][−] (1), [(NO)₂Fe(OPh)₂][−] (2) and [(NO)₂Fe(OPh-F)₂][−] (5) coordinated by O-containing ligands display the higher pre-edge energies (7113.6, 7113.8 and 7113.7 eV) (Fig. 2a), compared to those of complexes [(NO)₂Fe(SET)₂][−] and [(NO)₂Fe(SPh)₂][−] (7113.5 and 7113.5 eV) (Fig. 2b). Accidentally, we noticed that the pre-edge energies of complexes [(NO)₂Fe(SET)₂][−], [(NO)₂Fe(μ-SET)₂][−] and [(NO)₂Fe(SPh)₂][−] (7113.5, 7113.8 and 7113.5 eV) lie between those of complexes [Fe(SPh)₄]^{2−} and [Fe(SPh)₄][−]. Also, complexes 1, 2 and 5 display the lower pre-edge energies (7113.6, 7113.8 and 7113.7 eV), compared to that of complex [Fe(OPh)₄][−]. We conclude that the {Fe(NO)₂}₉ DNICs featuring the pre-edge energy within the range of 7113.4–7113.8 eV may be adopted to probe

the formation of the monomeric DNICs containing the varieties of ligation modes and dimeric DNICs.

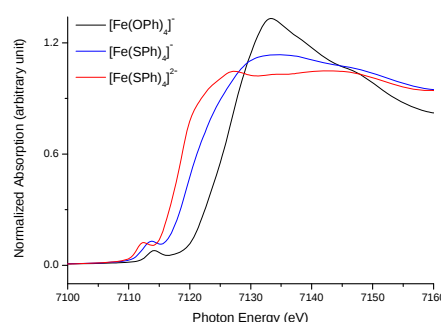


Fig. 1: Fe K-edge spectra of complexes [Fe(OPh)₄][−], [Fe(SPh)₄][−] and [Fe(SPh)₄]^{2−}

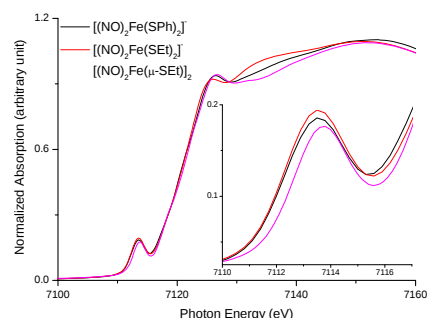
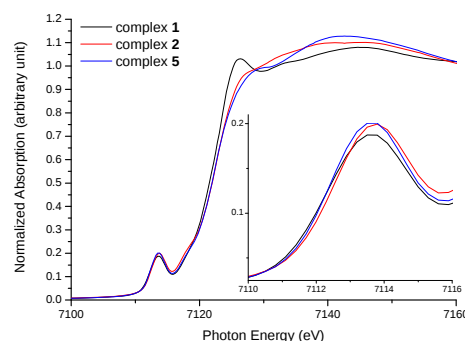


Fig. 2: (a) Fe K-edge spectra of complexes 1, 2 and 5, (b) Fe K-edge spectra of complexes [(NO)₂Fe(SPh)₂][−], [(NO)₂Fe(SET)₂][−], and [(NO)₂Fe(μ-SET)₂][−]

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