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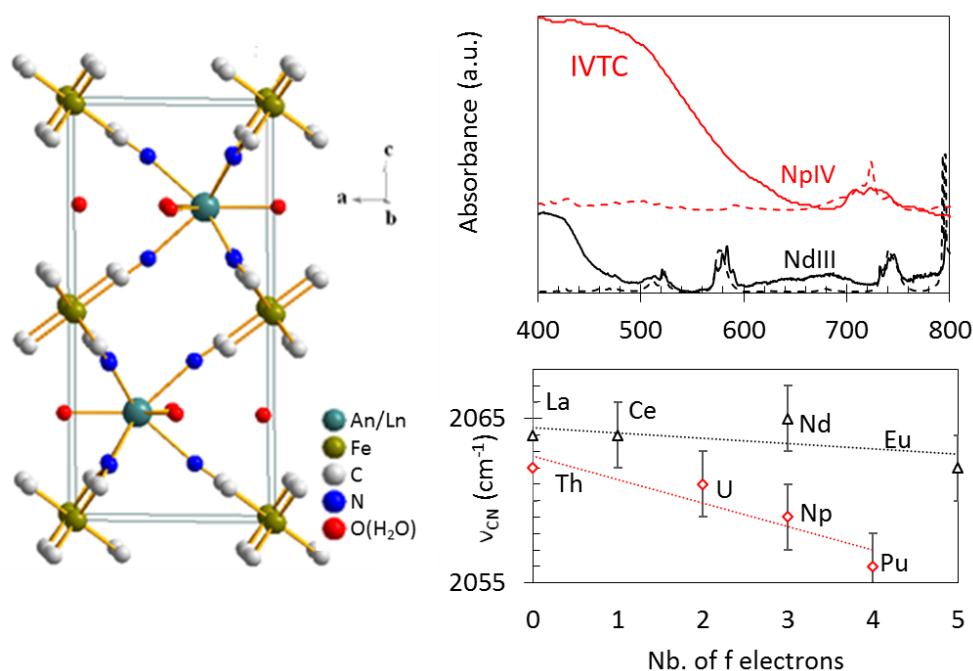
Electronic structure of f-element Prussian blue analogs by soft X-ray absorption spectroscopy

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Bimetallic cyanide molecular solids derived from prussian blue are well known as building blocks with long-range magnetic ordering [1,2]. Structurally speaking, these Prussian Blue Analogs (PBA) derivatives form cubic phases. For the trivalent lanthanides PBA, both hexagonal and orthorhombic phases have been described (Figure 1.a). In the case of tetravalent actinides analogs (Th to Pu), EXAFS and XRD have been used to describe the structure that is isomorphous to the early lanthanide (La-Nd) PBA [3, 4, 5]. The optical spectra of uranium, neptunium and plutonium compounds show intense intervalence charge transfer bands similar to the transition metal PBA (Figure 1b) and FTIR indicates a modification in the cyano bond elongation energies as a function of the actinide electronic configuration (Figure 1c).



Soft X-ray spectroscopy is then used to directly probe the valence molecular orbitals. It brings essential information about the cyano and iron molecular orbitals using complementary nitrogen and carbon K edges and iron L₃ edges.

Theoretical chemical calculations help to assign the NEXAFS spectral features to cast light on the actinide-cyano bonds nature [6]. Covalency versus ionicity, charge transfer and back-bonding effect are discussed for ferrocyanide compounds in the literature [7]. In light of the

References

- [1] O. Sato et al., *Inorg.Chem.* **38**, 4405, (1999)
- [2] S. Ferlay et al., *Inorg.Chem*, **38**, 229-234, (1999)
- [3] I. Bonnoure et al., *Can.J.Chem* 1305-1317, (2000)
- [4] G. Dupouy et al., *Eur. J. Inorg. Chem*, 1560–1569, (2011).
- [5] T. Dumas et al., *New J. Chem.*, **37**, 3003–3016, (2013).
- [6] T. Dumas et al., *PCCP.*, **18**, 2887–2895, (2016).
- [7] R.K.Hocking et al., *J.Am.Chem.Soc*, **128**, 10442-10451, (2006)
- [8] T. Dumas et al., *Chem. Commun.*, **54**, 12206–12209, (2013).