

# Applications of X-ray Absorption Spectroscopy in Coordination Chemistry

It is advantageous to use X-ray absorption spectroscopy to extract structural and electronic information from molecules of interest. The atom specific character of this spectroscopy may allow us to investigate selective information of certain atoms out of a complex system. It bears therefore a tremendous potential for the future nano- and biosciences. Here we will give some examples on the application in coordination chemistry.

## Atom Type

Since each atom has its own characteristic absorption edge, it is easy to tell which atom exists in the sample studied. For example, the absorption at 7112 eV of Fe is hardly mistaken as Ni or Cu at 8333 and 8979 eV, respectively. This could be very useful to identify the metal ion, which is responsible for the active site of a complicated system like an enzyme reaction in a biological system.

## Formal Oxidation State

It is known that the absorption edge would shift towards higher energy with the higher oxidation state. However, we should be careful about such statement, calibrations with the known oxidation state are needed and the closest possible geometric environment around the atom of interest should be kept in order to determine the formal oxidation state unambiguously. The various oxidation states of manganese are nicely displayed in Fig. 1. as the Mn K-edge XANES spectra, where the edge energies of Mn(0); Mn(II); Mn(III); Mn(IV) and Mn(VII) do follow the trend of having the highest energy in  $\text{KMnO}_4$  and the lowest in Mn foil.

Another example is the determination of the oxidation state of Ni ion in a series of Ni complexes with non-innocent ligand. Such non-innocent ligand (L) can be exhibited in various oxidation

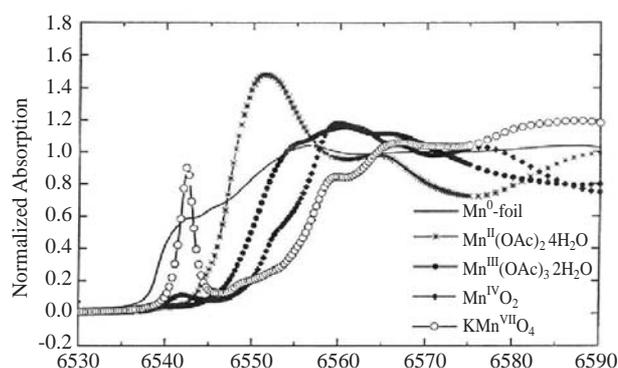


Fig. 1: Mn K-edge XANES spectra of a series of Mn compounds.

states such as  $L^0$ ;  $L^{1-}$ ; and  $L^{2-}$ , these will in turn affect the formal oxidation state of Ni atom. It is generally recognized that Ni(II) is the most stable species for square planar complexes. However, based on the Ni L-edge absorption spectra shown in Fig. 2, we can clearly say that in all these com-

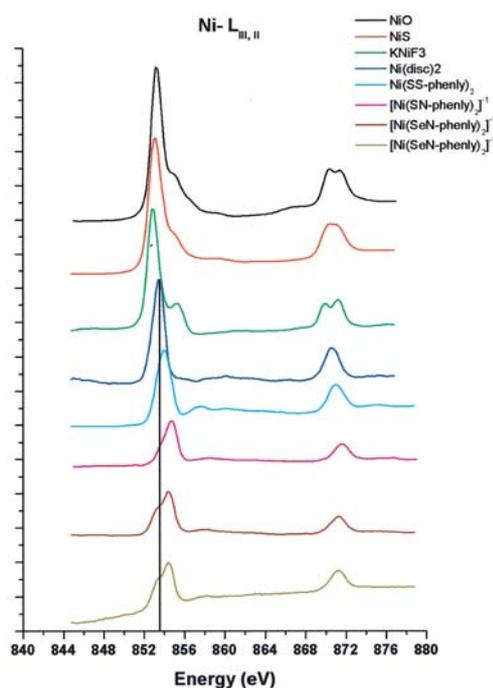


Fig. 2: Ni L-edge absorption spectra of various Ni complexes.

plexes, a mixed Ni(II) and Ni(III) oxidation states is found which is also further confirmed by ESR studies. This is an example that it will be hardly recognized without the evidence of X-ray absorption spectra. In the same token, NO ligand is interesting because of its existence of various forms such as  $\text{NO}^+$ , a nitrosyl group; NO, a free radical; and  $\text{NO}^-$ , a monoanion. The oxidation state of the metal ion will depend on the oxidation state of NO ligand, in order to sort out the formal oxidation state of metal ion and NO ligand correctly, X-ray absorption spectra of metal ion as well as N atom can be applied to achieve this.

The Fe K-edge absorption spectra of  $\text{Fe}(\text{NO})(\text{S}_2\text{CNR}_2)_2$  are shown in Fig. 3 together with other NO containing iron complexes. Here all the complexes have similar absorption as that of  $\text{Fe}(\text{NO})(\text{S}_2\text{CNR}_2)_2$ , where Fe is identified as Fe(I) and NO is  $\text{NO}^+$ . However, in  $\text{Fe}(\text{NO})_2\text{S}_5$ , Fe is still Fe(I) but both NO ligands are believed to be NO free radicals. In addition, the formal oxidation of NO can be probed with N K-edge absorption spectra.

### Spin Crossover System

The K-edge absorption at the near-edge range (XANES) is known to be sensitive to the coordination symmetry and the oxidation state of the target atom. Because metal L-edge absorption spectrum reflects the photoexcitation of electron from 2p to 3d orbitals, it is very sensitive to the electronic changes of the target atom, especially the changes involving the modification on the 3d

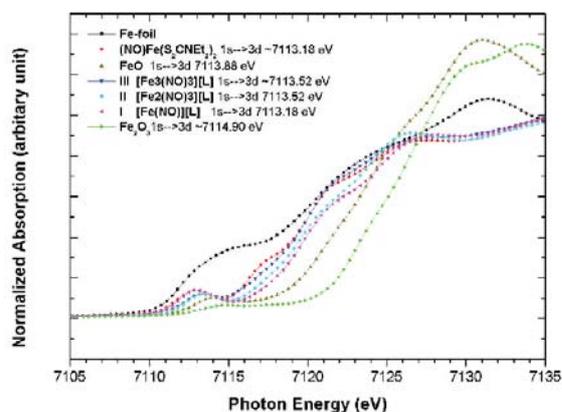


Fig. 3: Fe K-edge absorption spectra of  $\text{Fe}(\text{NO})$  containing complexes.

orbital populations such as the spin-crossover phenomenon. Therefore, the soft X-ray absorption spectroscopies (K- and L-edge) are ideal for the study of light induced excited spin state trapping (LIESST) in this iron(II) complex. This work presents the first example of applying the K- and L-edge absorption technique to examine the LIESST phenomenon.

The drastic change in spin states of Fe(II) complex gives rise to a high spin(HS) state with  $S=2$  and a low spin(LS) state with  $S=0$ . Fe K-edge spectra of a typical spin crossover complex,  $\text{Fe}(\text{phen})_2(\text{NCS})_2$ , are depicted in Fig. 4, where the distinct difference in the shape of the white line absorption part between HS and LS states (HS-1 & LS-1) are apparent. It is clear that Fe K-edge spectrum does reflect the changes of the population of the antibonding orbital of Fe-N due to the spin transition of the Fe(II) ion. In Fig. 3, the Fe L-edge absorption spectra of  $\text{Fe}(\text{phen})_2(\text{NCS})_2$  for HS-1 and LS-1 states are reproduced. As compared to Fe K-edge spectra, the Fe L-edge absorption spectra are even clearer by a significant shift in energy for HS-1 & LS-1 states. As noted, a shift

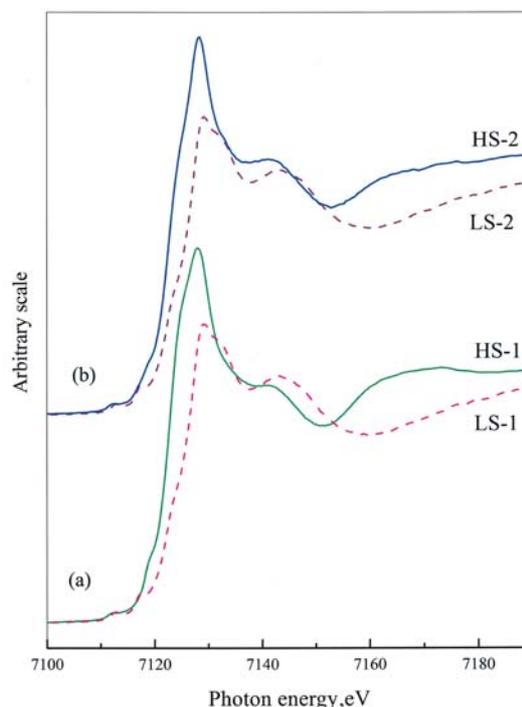


Fig. 4: Fe K-edge absorption spectra of  $\text{Fe}(\text{phen})_2(\text{NCS})_2$ : HS-1 and LS-1 are spectra taken at 300 K and 17 K respectively. HS-2 is the one after light excitation at 17 K, LS-2 is the one relaxed from HS-2 taken at 70 K.

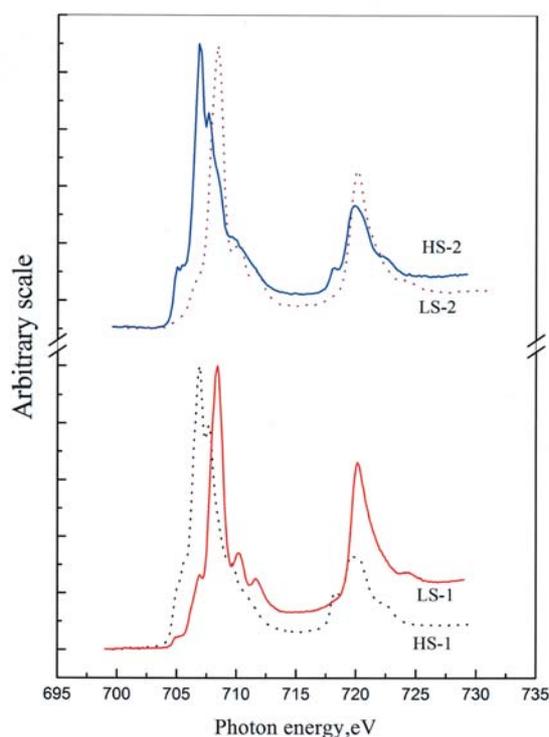


Fig. 5: Fe L-edge absorption spectra of  $\text{Fe}(\text{phen})_2(\text{NCS})_2$ : HS-1/LS-1 and HS-2/LS-2 are defined as in Fig. 4.

of 1.44 and 0.5 eV in Fe LIII and LII absorption edge toward high energies was detected by going from 300 (HS-1) to 77 K (LS-1).

The metal L-edge absorption spectra can be simulated with a multiplet calculation, which is based on the crystal field theory with e-e repulsion (B, C), crystal field strength (10Dq) and the spin-orbit coupling being taken into consideration. The comparison between experiment and theory by multiplet fitting indicates that 10 Dq is 2.13 and 0.91 eV for LS and HS state respectively, and metal to ligand charge transfer (MLCT) is important for the fine structure of the peak profile in both HS and LS states.

The difference in the L-edge absorption between HS-2 and HS-1 is mainly due to the temperature effect based on the crystal field multiplet simulation. LS-2 and LS-1 states are basically the same from our observation.

Light induced excited spin state trapping (LIESST) of this complex at 17 K is depicted in Figs. 4 and 5 with the one with (HS-2) and the other without (LS-1) the light excitation. This gives a clear demonstration of how valuable this technique is for such a study.

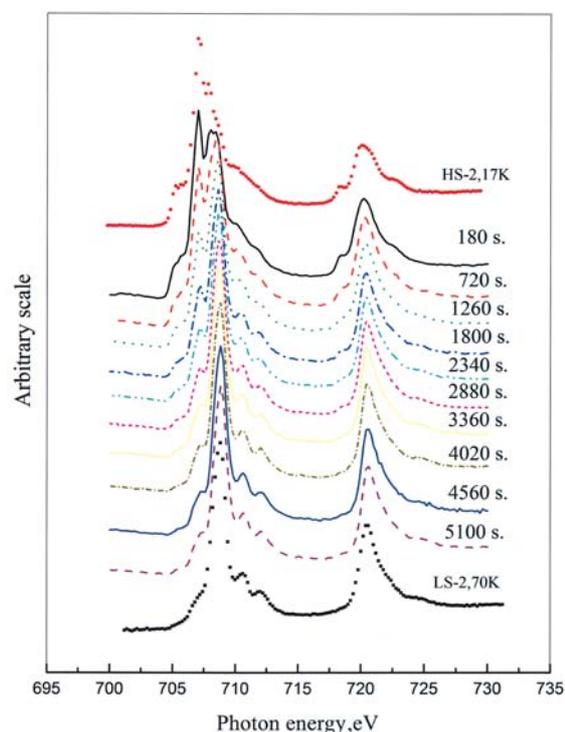


Fig. 6: Relaxation phenomenon monitored by the Fe L-edge absorption spectra.

The thermal relaxation from the metastable HS-2 state to the LS-2 state at 57 K is illustrated in Fig. 6, where a series of Fe L-edge absorption spectra is monitored at various time periods after the light-induced excitation has taken place. The typical spectra of the HS-1 and LS-1 states are also included to illustrate the change. It clearly depicts the change of spectra from a mainly HS state at 180 s after the excitation to a typical LS state at ~4000 s. after the excitation.

In addition, the bond distances of Fe-N in both spin states as well as the light induced excited spin state can be derived from EXAFS, the result is shown in Table 1 together with the corresponding distances obtained from the diffraction experiment. As noted, the Fe-N distances of HS-1 and LS-1 obtained from EXAFS are not significantly different from those obtained from single crystal diffraction data. According to the EXAFS data, distances of Fe-N in the HS-2 state are slightly shorter than those of HS-1, but significantly longer than those of the LS-1 state after the temperature effect is taken into account.

Table 1. Distances (Å) of Fe-N in the HS-1, LS-1 and HS-2 states.

	Fe-N1	Fe-N2	Fe-N2O
HS-1			
EXAFS(298K)	2.190(5)	2.132(5)	2.115(5)
XRD (298K)	2.214(8)	2.194(8)	2.070(9)
HS-2			
EXAFS(17K)	2.12(1)	2.06(1)	2.04(1)
XRD <sup>†</sup> (30K)	2.184(5)	2.177(5)	2.006(5)
LS-1			
EXAFS(17K)	1.979(5)	1.985(5)	1.943(5)
XRD (15K)	1.962(2)	1.967(3)	1.925(3)

†Guionneau et al., J Am Chem Soc 2002,124, 194-5.

[Co(bpy)<sub>3</sub>]<sup>2+</sup> is normally a HS species at the temperature range of 10 to 300 K, however, according to the theoretical prediction, it would display a thermally dependent gradual spin transition when it is encapsured in an oxalato framework, owing to the space confinement of the [LiCr(ox)<sub>3</sub>]<sup>2-</sup> framework. Indeed we did observe such spin transition using Co K-edge absorption spectroscopy, which is shown in Fig. 7.

In conclusion, X-ray absorption spectroscopy is an extremely useful tool not only on the characterization of molecular species but also on the investigation of materials.

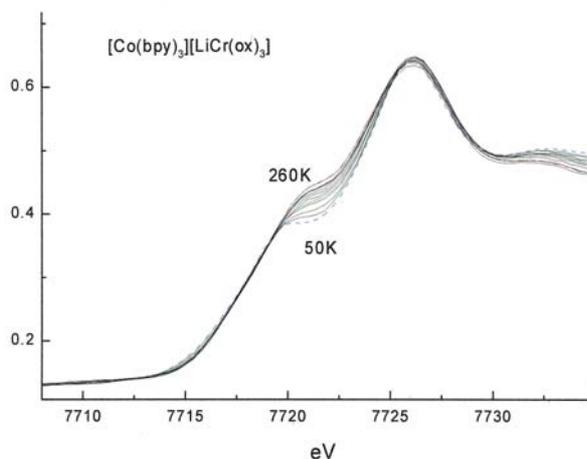


Fig. 7: Co K-edge absorption spectra of Co(bpy)<sub>3</sub><sup>2+</sup> in oxalato-framework.

### Beamlines:

17C1 W20/XAS beamline

20A1 High Energy SGM beamline

### Experimental Stations:

Photoabsorption end station

EXAFS end station

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