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FIRST COORDINATION SPHERE AND SPIN-STATE IN SPIN CROSS-OVER IRON AND COBALT COMPLEXES

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RESUME

Nous étudions par spectroscopie d'absorption des rayons X les transitions de spin de complexes du cobalt(II), du fer (II) et du fer(III). La contraction de la première sphère de coordination lors du passage haut-spin $\rightarrow$ bas-spin est mesurée par EXAFS pour tous les complexes. Le XANES des complexes du fer met en évidence les variations de structure électronique lors de la transition. La variation d'ordre local est confrontée aux résultats d'autres techniques pour discuter le caractère coopératif du phénomène.

ABSTRACT

We study by X-Ray absorption spectroscopy the spin crossover for Co(II), Fe(II) and Fe(III) complexes. EXAFS allows to measure the first coordination sphere contraction through the thermally induced high-spin $\rightarrow$ low-spin transition for all the complexes. The XANES of the iron spectra is modified with the changes in the electronic structure during the transition. The modification of the short range order is compared to the results of other techniques to discuss the cooperative character of the phenomenon.

INTRODUCTION

The complexes of transition metal ions belonging to d4-d7 electronic configurations can exist under high-spin and low-spin forms. In the few cases where the mean pairing energy $\bar{P}$ is of the same order of magnitude as the molecular orbital splitting (Δ_o in the case of an octahedral complex), a thermally induced transition can occur from high spin to low spin state when decreasing the temperature. The condition can be expressed as $|\Delta_o - \bar{P}| \sim kT$. A lot of synthetic, experimental and theoretical work has been performed to obtain new materials (1-6), to fully characterize the transition and to understand its real nature, local or more or less cooperative.

The spin crossover (with a ΔS change in spin) is associated with abrupt or smooth changes in magnetic, spectroscopic and structural properties. Available X-Ray diffraction data display a contraction $\Delta \bar{R}$ of the mean coordination radius upon transition from high to low-spin state. This evolution mainly depends on the spin variation ΔS , on the nature of the first neighbours (for example for oxygen (O), nitrogen (N), and phosphorus (P), $\Delta \bar{R}(\text{O}) < \Delta \bar{R}(\text{N}) < \Delta \bar{R}(\text{P})$), and on steric factors.

The abrupt or smooth character of the spin transition seems to depend on the existence of a concomitant crystallographic phase transition (1) with a modification ΔV of the cell volume upon the transition. We undertook this study (1) to put in evidence by EXAFS the $\Delta \bar{R}$ variation during the spin transition and to measure it in complexes where no single crystals can be obtained; (2) to characterize by XANES the electronic structural change, other things being equal (number of electrons, oxidation state, nature of the neighbours) in view of a better understanding of the XANES of coordination complexes.

EXAFS OF COBALT (II) COMPLEXES

The compounds are of the general type $\text{Co}(\text{H}_2\text{fsa}_2\text{en})\text{L}_2$, where $\text{H}_4\text{fsa}_2\text{en}$ is the bichelating Schiff base N,N' -ethylene bis (3-carboxy salicylaldehyde) (Fig.1).

Fig.1: $\text{Co}(\text{H}_2\text{fsa}_2\text{en})\text{L}_2$

Fig.2

The complexes for which $\text{L}=\text{H}_2\text{O}$ (4), and $\text{L}=\text{pyridine}$ (3), exhibit $\Delta S = 1$, $S=3/2 \longleftrightarrow S=1/2$ spin interconversions. These transitions are the most abrupt ones ever observed for cobalt (II) complexes. The $\chi_M \cdot T$ vs T plot (χ_M is the molar magnetic susceptibility) for $\text{Co}(\text{H}_2\text{fsa}_2\text{en})(\text{H}_2\text{O})_2$ is given in Fig. 2.

Up to now, it has been impossible to grow crystals of these compounds; so, we turned to EXAFS to obtain structural informations. The analysis of the spectra recorded at room temperature and at 40K allows us to evaluate the modification of the cobalt(II) local environment upon the high-spin $\longleftrightarrow$ low-spin conversion (5). For comparison, we also studied the compound for which $\text{L}=3\text{-methylpyridine}$ (3-Mepy) (6), which retains the high-spin form in the whole temperature range, and cobalt (II) and (III) compounds whose crystallographic structures are known (5).

The spectra are analysed by using the tabulated phase parameters of Teo and Lee (7) and Beni and Lee criterion (8). The EXAFS $k \cdot X(k)$ vs k spectra and the corresponding Fourier transforms for the $\text{L} = \text{H}_2\text{O}$ complex at 295 and 40K are given in Fig. 3.

The values of the mean metal-ligand bond distances found for model compounds are in good agreement with crystallographic data, within experimental error ($\pm 0.02 \text{ \AA}$).

For both spin crossover compounds, $\Delta \bar{R}$ is found to be $0.09 \text{ \AA}$ for a complete spin conversion (Table I).

TABLE I : EXAFS results for Cobalt complexes

L	$\bar{R}(295\text{K})/\text{\AA}$	$\bar{R}(40\text{K})/\text{\AA}$	$\Delta \bar{R}/\text{\AA} \text{ (a)}$
H_2O	1.96	1.88	0.09
py	1.98	1.89	0.09
3-Mepy	2.04	2.06	No

(a) calculated for 100% conversion

The respective variation of axial and equatorial bond lengths cannot be distinguished. However, owing to the difference in the population of the $d(x^2-y^2)$ orbital between the high spin and low spin forms (the population of the dz^2 orbital being unchanged), $\Delta \bar{R}$ (eq) is expected to be much larger than $\Delta \bar{R}$ (ax).

Fig.3:EXAFS and Fourier transform of $\text{Co}(\text{H}_2\text{fesa}_2\text{en})(\text{H}_2\text{O})_2$

EXAFS OF IRON COMPLEXES

We choose here tris(diethyldithiocarbamate) $\text{Fe}(\text{III})$, $\text{Fe}(\text{dtc})_3$, the structure of which is known at low and room temperature (9), even if the transition ($S = 5/2 \longleftrightarrow S = 1/2; \Delta S = 2$) is incomplete (10-11), and cis bis (o-phenantroline) bis (thiocyanato) $\text{Fe}(\text{II})$, $\text{Fe}(\text{phen})_2(\text{NCS})_2$, for which single crystal X-Ray diffraction data are lacking and an abrupt and complete transition occurs ($S = 2 \longleftrightarrow S = 0; \Delta S = 2$) (12-14).

We used tabulated phases and amplitudes of Teo and Lee (7). For $\text{Fe}(\text{dtc})_3$, the results differ slightly from crystallographic ones at both temperatures, due probably to the non transferability of Fe-S amplitude and phase parameters. An extraction of amplitudes and phases from the structural data at low temperature (low spin form) to find from them the distances in the room temperature form, which is a mixture of low and high-spin forms is underway. Nevertheless the variation $\Delta \bar{R}$ of the mean coordination sphere is practically the same by EXAFS and by diffraction ($\Delta \bar{R} = 0.05 \text{ \AA}$, i.e. $\Delta \bar{R} = 0.10 \text{ \AA}$ for a complete transition. The results are gathered in Table II.

TABLE II : EXAFS results for Iron complexes

COMPOUND	Temp. / K	R / Å	$\Delta \bar{R} / \text{\AA}$ (a)	$\sigma^2 / \text{\AA}^2$ (b)	r% (c)
$\text{Fe}(\text{III})(\text{dtc})_3$	290	2.30	0.10	0.002	0.6
	30	2.25		0.010	3.0
$\text{Fe}(\text{II})(\text{phen})_2(\text{NCS})_2$	290	2.15	0.24	0.007	1.8
	30	1.91		0.012	2.4

(a) Calculated for 100% conversion; (b) Debye-Waller factor;
(c) Fit agreement factor

For $\text{Fe}(\text{phen})_2(\text{NCS})_2$, the results are in Table II and in Fig. 4. The contraction $\Delta \bar{R} = 0.024 \text{ \AA}$, determined for the first time, is striking. It is in line with the abrupt character of the transition, with the important variation of the IR spectrum (stretching Fe-N or N-C) (12), Mössbauer spectra (14). This steepness implies a large value of the change in molecular vibrational entropy ΔS (vib mol).

Fig. 4

On the other hand, X-Ray powder diffraction results show little three-dimensional changes during the crossover (14). Comparison between short and long range order measurements clearly demonstrates, therefore, that an important $\Delta \bar{R}$ and intramolecular rearrangement does not imply a large variation of ΔV . This result points out the complementarity between short range and long range order techniques for a full characterization of the structural phenomenon and the determination of the respective influences of singlet-triplet energy gap and of cooperativity.

An other point of interest is the increase of the Debye-Waller factor in the low-spin form, observable also in the Fe(II) compound. Although the thermal part is decreasing with temperature, the overall increase is an indice of enhanced static disorder in the first coordination sphere.

The comparison of the results of Co(II), Fe(II) and Fe(III) complexes is not easy since the coordination spheres CoN4O2 , FeN6 and FeS6 are different. Nevertheless, for the two compounds with t_{2g} full orbitals in the low spin form, in CoN4O2 ($\Delta S = 1$), the mean contraction ($\Delta \bar{R} = 0.09 \text{ \AA}$) is less than the half of the one in FeN6 ($\Delta S = 2$; $\Delta \bar{R} = 0.24 \text{ \AA}$, which is consistent with the half spin number change and with the presence of two oxygen ligands instead of nitrogen ones. In spite of their half ΔS , the spin crossover Co(II) entities have a $\Delta \bar{R}$ comparable in magnitude to the one of Fe(III)S6 , which can be explained by the presence of an unpaired electron in the t_{2g} orbital of the Fe(III) species and to the soft character of sulfur in the dithiocarbamate ligands, without d- π^* interactions, which generally increase the $\Delta \bar{R}$ (1).

XANES OF IRON COMPLEXES

The XANES of both complexes at 300K and 30K is shown in Fig. 5. The energies of the transitions are given in Table III.

TABLE III : XANES Energies (a)

COMPOUND	Temp. /K	ENERGY / eV $\rightarrow$					
Fe(III)(dtc)_3	290	7106.8	7113.4	7119.0	7122	7136	
	30	7107.8	7112.4	7117.6	7123	7138	
						7128	7142
$\text{Fe(II)(phen)}_2(\text{NCS})_2$	290	7106.2	7110.5	7115	7121	7130	7137
	30	7106.6	7111.4	7114.6	7121.6	7130	
					7117.4	7126.3	7137

(a) Calibrated at the first maximum of the derivative of the metallic iron spectrum (7111.2 eV)

Fig.5: XANES spectra and second derivative of Fe(dtc)_3 and $\text{Fe(phen)}_2(\text{NCS})_2$

As expected, the most spectacular evolution is for the Fe(II) complex, but close examination of the second derivatives indicates important changes in both compounds. The main conclusions obtained from XANES are the following:

(i) new transitions appear in both spectra at low T. In particular, transitions in the edge of low spin species, which exist also in low spin ferro and ferricyanides, are probably attributable to spin allowed electronic transitions towards the states derived from the higher terms available in the strong-field

case, ($^2A_{2g}$, $^2T_{2g}$), ($^2T_{2g}$, 2E_g), ($^2A_{2g}$, 2E_g) for Fe(III), and two $^4T_{1g}$ for Fe(II) using formulations derived from Oh point group; an exact formulation would have to take into account departures from octahedral symmetry).

(ii) other transitions are shifted, in particular the preedge one which corresponds to a transition towards the higher eg orbitals in the low-spin case and the one at the top of the edge: the phenomenon is real but difficult to characterize quantitatively in Fe(dtc)₃, given the soft Fe-S6 coordination sphere and the small $\Delta\bar{R}$; the trend is clearly demonstrated in Fe(phen)₂(NCS)₂: disappearance of the white line at low temperature related to the first coordination sphere distortion, shift to higher energy of the top of the edge correlated to the contraction of the Fe-N distances.

Quantitative interpretation and safe attribution of the observed transitions imply more experimental and theoretical work (molecular orbital approach for preedge and edge, multiple scattering for edge and post-edge) and we are engaged in such a way.

CONCLUSION

Spin crossover is a remarkable thermally induced transition phenomenon present in some rare transition metal complexes which can exhibit bistability. The search of such bistable systems is one of the challenges in the development of molecular electronics devices. We tried to show that X-Ray absorption spectroscopy can be useful in this area: on the one hand, X-Ray absorption can help to understand what is going on in the spin transition and can be used as an efficient tool to characterize quantitatively structural short range order evolutions with EXAFS and to put in evidence electronic and stereochemical changes with XANES.

On the other hand, study of well-known characterized spin crossover complexes can give new insights to better understand the XANES part of the spectrum in the "simple" case when the oxydation state of the central ion and the nature of the ligands remain unchanged.

EXPERIMENTAL SECTION.

The experimental data were recorded at LURE, on EXAFS I spectrometer with channel-cut monochromators (Si 220, 2mm entrance slit for EXAFS and Si 400, 0.5mm entrance slit for XANES), with a storage ring energy of 1.72 GeV and an intensity of 100-250 mA.

EXAFS data processing used classical plane wave single electron single scattering analysis, with use of Beni and Lee criterion for Co(II) complexes (8), and filtered multiple shells fit in the k-space for Fe complexes. Samples were well pounded microcrystalline powders of calculated thickness. The temperature was fixed by an home-made Helium flow cryostat.

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