Coordination Chemistry and Photochemistry

Thermally and optically induced spin transition effect on the structure of iron(II) polymeric complexes

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Polymeric iron(II) complexes of the composition $Fe(atrz)_3A_2$, where atrz = 4-amino-1,2,4-triazole, A = anions, have been synthesized and characterized. The compounds exhibit an abrupt thermally driven spin transition (S=0 - S=2) at temperatures varying from 175 K to 400 K depend on composition. XAFS measurements were performed at the VEPP-3 storage ring at the Budker Institute of Nuclear Physics in Novosibirsk. In all studied compounds the Fe-N and Fe-C interatomic distances increase upon the thermally induced transition to the high spin (HS) state by amounts from 0.12 Å to 0.24 Å. The existence of long-life optically excited metastable HS states was established for the $Fe(atrz)_3(ClO_4)_2$ at 4.2 K. The changes in structure upon the transition to a metastable HS state differ from those in the thermally induced spin transition.

Keywords: **X-ray absorption; structure of polymeric complexes, molecular magnets**

1. Introduction

Thermally induced spin transitions were discovered more than sixty years ago by Cambi & Szegö (1931) and studied in detail by König *et al.* (1991) and Gütlich *et al.* (1990;1994). An abrupt change in the population of electronic states and, correspondingly, of the spin state of the transition metal ion with the increase in temperature was revealed for the coordination compounds of 3d elements which have the molecular symmetry near O_h and the electronic configurations from d^4 to d^7. The metal-ligand bond lengths are larger in the high spin (HS) state than in the low spin (LS) state. This increase in bond length ranges from 0.1 Å to 0.25 Å for different compounds of Fe(II) (König, 1987).

At a low temperature transition metal ions spin state can be changed reversibly by irradiating light of a certain wavelength. This phenomenon was discovered by Decurtins *et al.* (1984) and termed light-induced excited spin state trapping (LIESST) (Decurtins *et al.*, 1984). The excited state can be maintained for a sufficiently long time (>100 hours) at temperatures below 40 K. Light-induced (HS) states were observed in a great number of Fe (II) spin crossover complexes (Gütlich *et al.*, 1994), but direct structural information about metastable HS states was not obtained.

At the Institute of Inorganic Chemistry of the Russian Academy of Sciences methods were developed for the synthesis of polynuclear compounds of Fe(II) of the composition FeL_3A_2, where L= ligands, A = anions (Lavrenova *et al.*,1986).

Complexes with the Br⁻ and diluted phases with the NO_3^- can

find application as materials for optical memory where information can be recorded, for example, with the help of local heating by several degrees (above 300 K) with a thin laser beam and stored at room temperature. Such a two-dimensional picture can be read and then erased by cooling.

Since no one has, so far, succeeded in obtaining well crystallized polymeric compounds of this type, EXAFS (Extended X-ray Absorption Fine Structure) spectroscopy gives almost the only possibility to characterize their structural parameters. The goal of the present work is to realize this possibility, try to reveal light-induced spin crossover of Fe (II) polymeric complexes and to perform direct structural study of light-induced HS states of solid Fe (II) complexes at the first time.

2. Experimental

Measurements of EXAFS and XANES spectra were performed using synchrotron radiation of the VEPP-3 storage ring at the Budker Institute of Nuclear Physics in Novosibirsk. FeK-, ZnK- and BrK- edge EXAFS and XANES spectra were measured at temperatures above and below the spin-transition for polymeric compounds Fe(II) of the composition $Fe(atrz)_3A_2$ (atrz is 4-amino-1,2,4-triazole, A is NO_3^-, BF_4^-, Br⁻, I⁻, ClO_4^-) and diluted phases of the composition $Fe_xZn_{1-x}(atrz)_3(NO_3)_2$. FeK EXAFS and XANES spectra of the polymeric spin-transition compounds of the composition $Fe(atrz)_3(NO_3)_2$, $Fe(atrz)_3SiF_6$, $Fe(atrz)_3(ClO_4)_2$ were measured at 300 K and at 4.2 K without an optical treatment of the samples and after their irradiation with a Hg green line 546 nm with different exposure times within 90 minutes. The spectra were obtained using fluorescence detection mode as well as transmission mode. The X-ray fluorescence intensity were measured by Xe-filled electroluminescent detector in a current mode.

Data processing was performed using the program package EXCURV92 (Binsted *et. al.*, 1991). The k^3- weighting was carried out for photoelectron wave vectors in the interval 3 Å⁻¹ - 13 Å⁻¹. The phase and amplitude characteristics were calculated in an X_α-DW approximation.

The magnetic properties of the samples were measured by Faraday method in the temperature range 78-400 K. In most cases, such compounds exhibit an abrupt reversible spin transition (S=0, S=2) with a wide hysteresis loop accompanied by a change in optical properties.

3. Results and inferences

3.1. Thermally induced spin transitions

The fitting model involved the following nitrogen and carbon atoms of the triazole ring: N^1 atoms, which are coordinated to the absorbing metal atom, N^2 atoms, which are coordinated to the neighboring metal atoms, and C^1 atoms, which are nearest to the absorbing metal atom. Only the interatomic distances Fe-N, Fe-C or Zn-N, Zn-C and angles between the triazole ring and Fe-N and Zn-N bonds were varied while the geometry of the triazole rings was treated as fixed using restrained refinement process. Multiple scattering processes were not taken into account as far as experimental data were Fourier filtered using R-space window with upper limit of about 3.5 Å. As a result of the performed fitting the angles between the triazole ring planes and the Fe-N and Zn-N bond directions did not exceed 3°. The procedure produced good convergence in all cases with the R-factor less than 5%, except for the FeK data for Zn-containing samples in the LS-state. The failure of the model with fixed triazole ring geometry in this latter case may be explained by deformational distortions of the triazole ring.

Table 1

The values of the distances between Fe and Zn atoms and the atoms of the triazole ring - R (±0.01 Å.). T is the temperature of EXAFS measurements.

| Compound	Spin state	T(K)	R(Å) Fe-N[1]	R(Å) Fe-N[2]	R(Å) Fe-C[1]
Fe(atrz)₃(ClO₄)₂	LS	78	1.98	2.99	2.96
	HS	300	2.16	3.16	3.14
Fe(atrz)₃Br₂•H₂O	LS	78	1.97	2.98	3.01
	HS	370	2.17	3.13	3.13
Fe(atrz)₃(BF₄)₂	LS	78	1.95	2.97	2.94
	HS	370	2.19	3.19	3.15
Fe(atrz)₃(NO₃)₂	LS	78	1.95	2.97	2.94
	HS	370	2.18	3.18	3.15
Fe(trz)₃(NO₃)₂	LS	78	1.95	2.98	2.95
	HS	370	2.18	3.19	3.15
Fe₀.₈Zn₀.₂(atrz)₃(NO₃)₂	LS	300	1.97		
	HS	370	2.18	3.16	3.13
Fe₀.₃₃Zn₀.₆₆(atrz)₃(NO₃)₂	LS	78	2.04		
	HS	300	2.18	3.18	3.18
	Spin state	T(K)	R(Å) Zn-N[1]	R(Å) Zn-N[2]	R(Å) Zn-C[1]
Fe₀.₈Zn₀.₂(atrz)₃(NO₃)₂	LS	300	2.13	3.12	3.09
	HS	370	2.14	3.14	3.11
Fe₀.₃₃Zn₀.₆₆(atrz)₃(NO₃)₂	LS	78	2.15	3.15	3.12
	HS	300	2.14	3.14	3.11

In all studied polynuclear compounds there is a considerable increase in the Fe-N distances upon the transition from the LS to the HS state, as observed earlier for mononuclear and polynuclear complexes (Bausk et al., 1994, 1995; Michalowicz et al., 1995; Chen et al., 1995; Erenburg et al., 1997; Garcia et al., 1997), while the Zn-N distances remain unchanged. The Fe-N and Fe-C interatomic distances in the region up to 3.5 Å were found to be changed by amounts from 0.12 Å to 0.24 Å (Table 1). The effect of Zn atoms in the chain structure as the Zn content increases results in deformations in the LS state and an increase in the Fe-N distances as compared with the initial complex.

The decrease of spin transition temperature for the complexes with variable anions NO₃⁻, BF₄⁻, Br⁻, I⁻, ClO₄⁻ and for Zn-diluted complexes was found to correlate with increase of the Fe-N distances and changes in bond covalency determined from the chemical shifts in Mössbauer spectra (Erenburg et al., 1997) and the analysis of relative intensities of FeLα and FeLβ X-ray fluorescence spectra (Bausk et al., 1994), as well as with shifts of diffusion reflection spectra frequencies. The decrease of Tc appears to be associated with the increase in the Fe-N distances which can be caused by a decreasing "chemical pressure" due to the anion-cation interaction.

3.2. Optically induced spin transitions

Since the rate constant of the low-temperature relaxation (tunneling) $K_{HL}(T{\rightarrow}0)$ exponentially increases with ΔE^0_{HL} and correlates with T_c (Gütlich et al., 1994), we have chosen for the experiments the polymeric complexes: Fe(atrz)₃(NO₃)₂ Fe(atrz)₃SiF₆ and Fe(atrz)₃(ClO₄)₂, with substantially different temperatures of the equilibrium spin transition (T↑,T↓): of (342K,310 K); (255 K,241 K) and (175 K,175 K), respectively.

The analysis of the data obtained by matching experimental Fourier transform magnitudes for the Fe(atrz)₃(ClO₄)₂ (Fig. 1) and their model calculation using EXCURV92 computation for two Fe-N shells revealed that the state of complexes after irradiation can not be treated as a mixture of LS and HS states characterized by equilibrium Fe-N intetratomic distances 1.98 Å and 2.16Å., respectively. Results of model calculations presented on the Fig. 2 show that valuable FT magnitude amplitude decrease as well as unexpected peaks splitting and shifts observed on the Fig. 1 appear only if Fe-N distance difference is more than 0.20 Å. It was found that the optical irradiation of this
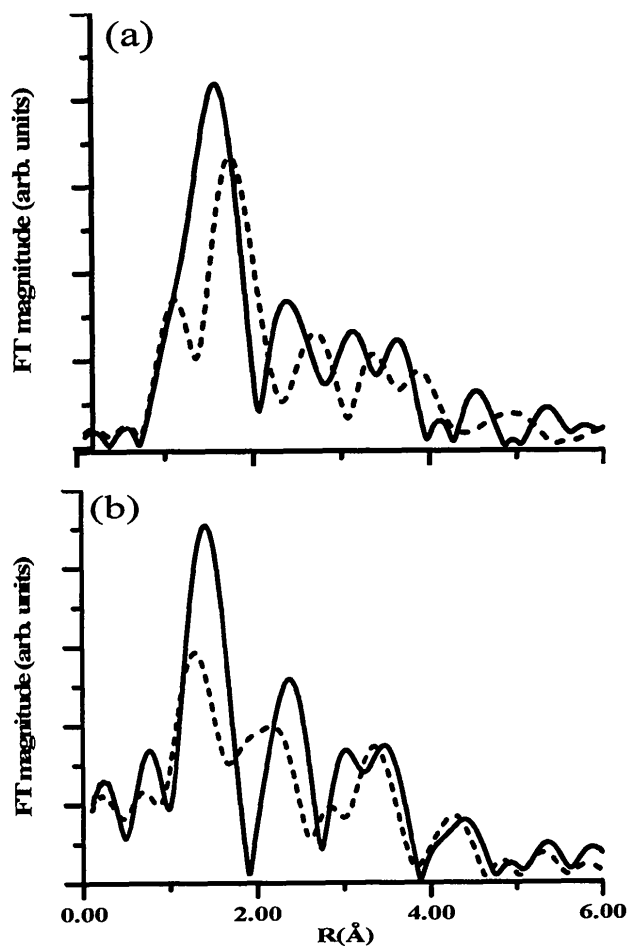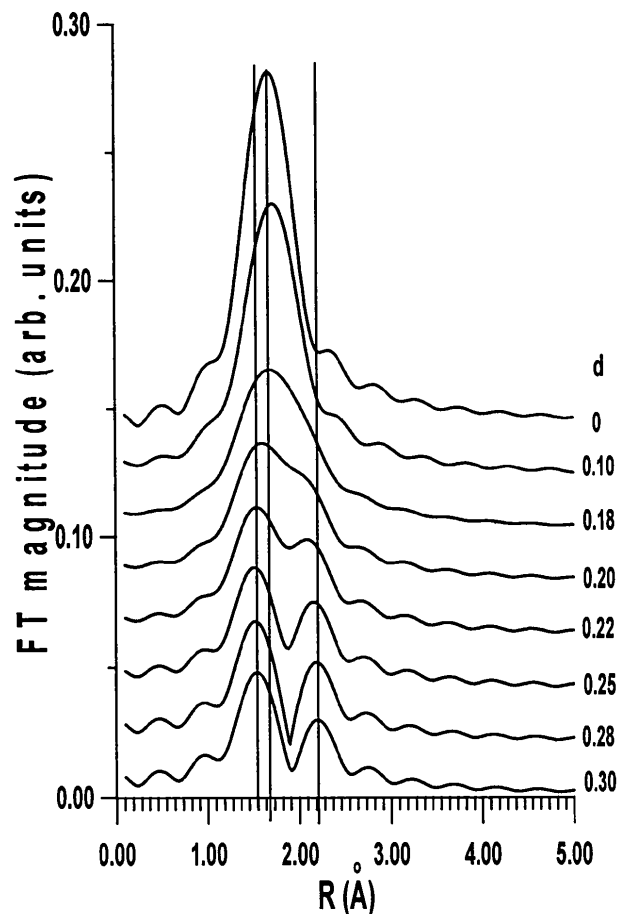

Figure 1

Fourier transform magnitude, obtained by treating the FeK EXAFS data for Fe(atrz)₃ (ClO₄)₂:

(a) - in the equilibrium states at 78 K (LS state, solid line) and at 300K (HS state, dashed line).

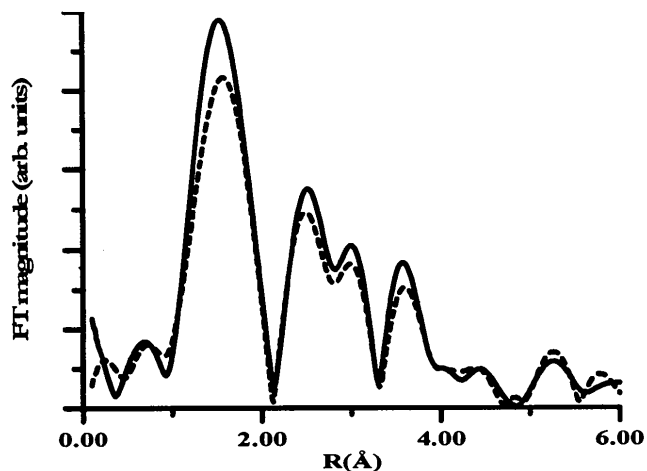(b) - at 4 K without an optical treatment (solid line) and after irradiation (dashed line).

compound causes transition of about a half of the all Fe atoms to the metastable HS state which is accompanied by the Fe-N distance increase up to 2.16 Å. At the same time it was found that Fe atoms remaining at the LS state are characterized by strong local surrounding geometry distortions and the average Fe-N distance decreases to 1.93 Å. Such types of distortions determined by mutual influence of HS and LS Fe atoms in polymeric chains can produce a resistance to completing the LS-HS transition.

Thus the process of a non-equilibrium light-induced transition to the HS state appears to be fundamentally different for molecular complexes with a weak bonding between molecules and the polymeric compounds with strong chemical bonds along the polymeric chains.

The long-life metastable HS state of the Fe(atrz)₃(NO₃)₂ and Fe(atrz)₃SiF₆ has not been found in any detectable amount after optical irradiation at 4.2 K may be because of their short time of life which are exponentially decreasing while the spin transition temperature increases. An amplitude changes obtained from FeK EXAFS data detected after optical irradiation (Fig. 3) can be explained by the chain geometry distortions caused by the HS states appearing and their following fast relaxation.

Figure 2
Results of the EXURV92 model calculation of FT magnitude demonstrating interference between two $\chi(k)$ sinusoidal terms forming by two Fe-N shells at various interatomic distances splitting d: 1st shell - R(Fe-N)= 2.00 Å; 2nd shell - R(Fe-N)= (2.00 +d) Å.

The structural changes upon the light-induced spin transition was detected by the direct method for the first time showing that EXAFS spectroscopy is powerful tool to study the LIEEST peculiarities in various compounds.

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Figure 3
Fourier transform magnitude, obtained by treating the FeK EXAFS data for Fe(atrz)₃ (NO₃)₂ at a temperature of 4.2 K : without an optical treatment (solid line) and after irradiation (dashed line).