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XPS(ESCA) Characterization of Spin-State Crossover in an Iron(II) Mixed Complex

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High spin–low spin transformation of transition metal complexes is known to result in dramatic changes in the electronic structure, bonding relations (bond distances, covalency *etc.*) and even in chemical reactions of the system. Magnetic susceptibility measurement is the basic method for the detection of spin crossover but several other procedures (*e.g.* Mössbauer, EPR and NMR spectroscopy *etc.*) also reflect its effect in a system.

X-ray photoelectron spectroscopy (XPS, ESCA) was shown to be sensitive to changes in the electron structure of transition metal complexes [1, 2] reflecting *e.g.* the effect of mixed complex formation [3], H-bond formation [4], binding isomerism [5], outer sphere coordination *etc.* The XP(ESCA) spectra of high spin and low spin complexes containing the same central atom were also shown to be significantly different [6, 7]. The study of the temperature dependence of XPS patterns in systems known from magnetic measurements to show spin crossover nevertheless resulted very seldom in the ESCA characterization of the different spin states [8]. Most of the model systems investigated so far proved to be sensitive to the X-ray radiation in the course of the XPS measurement [9]. Thus no reproducible XPS patterns could be attained for the spin state isomers.

One of us (K.B.) together with Furlani and Mattogno found recently [10] that the bis(*o*-phenanthroline) dithiocyanato iron(II) mixed complex (showing a spin state crossover at 174 K) is completely stable to X-ray radiation during the measurement. Crossing the magnetic transformation temperature in either direction several times well reproducible XP spectral patterns and electron binding energy values could be determined for both spin states. The data could be used also for the calculation of the net atomic charges on the central and donor atoms of the complex reflecting the covalency changes due to the spin crossover.

The 4,7-dimethyl derivative of *o*-phenanthroline forms with thiocyanate and iron(II) ions a mixed complex of analogous composition but showing a magnetic transition temperature $T_C = 115.3$ K instead of the $T_C = 174$ K of the *o*-phenanthroline complex [11, 12]. To determine the reason of this dramatic difference in the T_C values, namely to find out whether the steric effect of the electron density changing effect of the methyl substituents dominate in their influence on the value of T_C, the XP spectra of the bis(4,7-dimethyl-*o*-phenanthroline) dithiocyanato iron(II) mixed complex were recorded at room temperature and liquid nitrogen temperature. The XPS patterns and the electron binding energies (e.b.e.) were compared with those of the analogous *o*-phenanthroline complex. The results of these investigations are presented in the following.

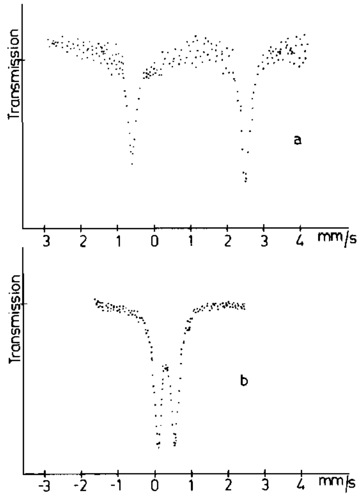

Fig. 1. The Mössbauer spectra of the bis(4,7-dimethyl-*o*-phenantroline)dithiocyanato iron(II) mixed complex measured (a) at room temperature and (b) at liquid nitrogen temperature.

Experimental

The bis(4,7-dimethyl-*o*-phenantrolin) dithiocyanato iron(II) mixed complex [Fe(4,7-diMe-*o*-phen)$_2$(NCS)$_2$] was prepared according to a published procedure [11, 12]. Its composition was checked by elemental analysis. Fe content: 10.1%; N content: 2.35%. The corresponding calculated values are: Fe 9.95%; N 2.37%.

The magnetic transformation temperature was determined by a Gouy balance and found to be 115 ± 1.5 K. (The value published by König *et al.* [11, 12] was 115.3 K). The Mössbauer spectra of the high spin and low spin isomers were determined by measurements made at room and liquid nitrogen temperature, respectively, on our apparatus cited in [13]. The spectra are shown in Fig. 1. The Mössbauer para-

TABLE I. XPS Electron Binding Energies (eV) of the High Spin and Low Spin Isomers of Bis(4,7-dimethyl-*o*-phenanthroline) dithiocyanato Iron(II) Complex (I) and the Analogous *o*-phenantroline Complex(II).[a]

Orbitals	I		II	
	High spin	Low spin	High spin	Low spin
Fe $2p_{3/2}$	709.3	708.6	709.2	708.3
Fe $2p_{1/2}$	722.9	722.5	722.6	721.3
Fe 3p	52.5	51.9	–	–
N 1s	399.1[b]	399.3[b]	NCS *o*-phen	NCS *o*-phen
			397.9 399.0	398.0 399.5
S 2p	162.1	161.9	162.1	162.1

[a] Reference C 1s = 285.0 eV. [b] Composite bands.

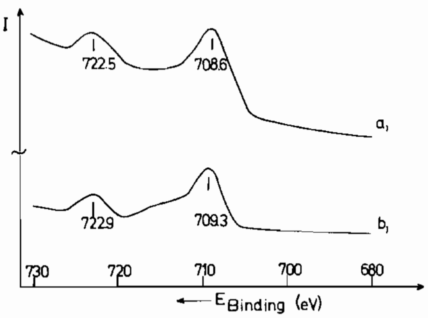

Fig. 2. The Fe 2p ESCA spectra of the bis(4,7-dimethyl-*o*-phenantroline)dithiocyanato iron(II) mixed complex measured (a) at liquid nitrogen temperature and (b) at room temperature.

meters: *isomer shift*: high spin form 0.96 ± 0.05 mm/s, low spin form 0.30 ± 0.05 mm/s; *quadrupole splitting*: high spin form 3.00 ± 0.05 mm/s; low spin form 0.50 ± 0.05 mm/s.

The XP spectra were recorded on a McPherson ESCA apparatus equipped with a variable temperature sample holder. The spectrum of the high spin isomer was determined at room temperature, that of the low spin at liquid nitrogen temperature (Fig. 2). Spin state changes were accomplished by crossing the transsformation temperature several times in either direction. The resulting XP spectra for both spin states were found to be completely reproducible indicating no X-ray damage during the measurement.

Results and Discussion

The electron binding energies (e.b.e.) of the dimethyl phenantroline thiocyanate mixed complex are presented together with those of the analogous phenantroline complex in Table I. Typical spectra of the Fe 2p lines of the former complex in high spin and low spin form, respectively, are shown in Fig. 2.

The spin crossover is primarily reflected by the significant change in the shape of the Fe 2p lines. The XP spectrum of the high spin isomer shows an unresolved satellite structure with rather broad Fe 2p peaks. In the low spin spectra those peaks are narrow and completely free of satellite structure. On the whole the Fe 2p spectra are very similar (almost identical) to those of the phenantroline complex measured earlier by Burger *et al.* [10]. The separation of the Fe $2p_{3/2}$ and $2p_{1/2}$ lines seem also to decrease due to the high spin → low spin transformation. In contrast the separation of the N 1s lines belonging to NCS^- and dimethyl *o*-phenantroline, respectively, is smaller than in the analogous *o*-phenantroline complex. This made their deconvolution impossible. Anyhow, the composite N 1s line of the low spin spectrum is significantly broader than that in the high spin spectrum. This indicates that the spin crossover has not equal effect on the e.b.e. value of the NCS^- and on that of the phenanthroline N atoms.

The excellent reproducibility of the XPS parameter, being ±0.15 eV even after crossing several times the magnetic transition temperature, allowed the determination of the effect of spin crossover on the e.b.e values of iron central atom and nitrogen donor atoms. Thus not only the disappearance of the satellite structure but a significant decrease in the e.b.e. values of the Fe orbitals and a small increase in the e.b.e. of the N 1s orbital indicated the high spin → low spin transformation. The S 2p e.b.e. values remained unchanged during the spin crossover.

The observed e.b.e. shifts reflect clearly the changes in the ionicity of the coordinative Fe–N bonds caused by the spin state change, the high spin isomer being closer to ionic structure (more positive Fe central atom with higher Fe e.b.e. values and more negative N donors with lower N 1s e.b.e.) and the low spin isomer closer to covalent structure (with the opposite trend of the e.b.e. values).

In spite of the great difference between the magnetic transition temperatures of the two complexes discussed the e.b.e. values of their corresponding orbitals were found to be almost equal. Their differences are not greater than the experimental error.

This surprising phenomenon strongly supports the assumption that solid state effects *e.g.* that of the crystal structure or lattice parameters dominate in the effect of substituents on the spin crossover temperature, the electron density on the donor atoms influenced by the substituents on the ligand has a secondary effect. Thus the methyl substituents of *o*-phenantroline seem to change the magnetic transition temperature of the complex by their steric effect which changes the lattice parameters and not by their effect on the electron densities.

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