

**Experiment title:**

Detection of iron-ligand vibrations in the thermally induced high-spin low-spin transition of single-crystalline $\text{Fe}(\text{tpa})(\text{NCS})_2$ by angular resolved nuclear resonant inelastic scattering

Experiment number:

CH-308

Beamline:

ID- 18

Date of Experiment.:

from: 18. 06. 1997 to: 22. 06. 1997

Date of Report:

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Shifts:

12

Local contact(s):

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*Received at ESRF***29 AOUT 1997****Names and affiliations of-applicants (*indicates experimentalists):**

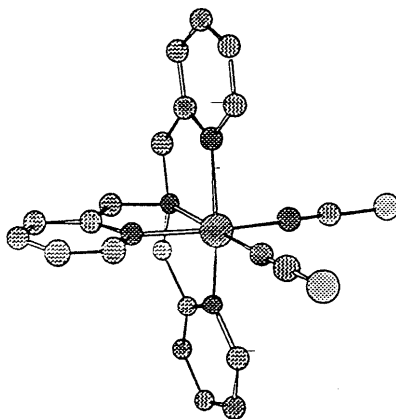
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Report:

The complex $[\text{Fe}(\text{tpa})(\text{NCS})_2]$ (tpa = tris(2-pyridylmethyl), Fig. 1) with non in the ferrous oxidation state exhibits a thermally induced “low-spin” \leftrightarrow “high spin” interconversion at a critical temperature T_c around 105 K. The transition is suggested to be entropically driven in the manner that the intramolecular vibrations in the high-spin state are softened and give thus rise to a higher vibrational entropy. The mode softening has been proven already in a previous experiment (CH 114) by nuclear resonant inelastic scattering (NIS) using a polycrystalline sample.

Molecular_orbital (MO) calculations have been carried out for the similar complex

**Fig. 1:** $[\text{Fe}(\text{tpa})(\text{NCS})_2]$

[Fe(phen)₂(NCS)₂] to understand the softening. The relevant normal modes involve partly the NCS nitrogens and partly- the aromatic nitrogens [1] In order to study their respective contributions in detail we have attempted to perform angular resolved MS measurements with single crystals of [Fe(tpa)(NCS)₂]. During the measurements it turned out, however, that the energy calibration was unstable so that the very difficult task of working out the differences in the phonon excitation spectrum as a function of the direction of the incoming beam could not be accomplished. After completion of the experiments it was found that the reason for our problems was a broken spring in the bearing of high-resolution monochromator. Thus a repetition of the series of measurements is inevitable.

In order to make reasonable use of the allocated beam time we have studied another spin-crossover complex, the so-called [Fe(tptMetame)]²⁺ or “tripod” (tptMetame = 1,1,1-Tris((N-(2-pyridyl)methyl)-N-methylamino)methyl)ethane), Fig. 2) which lacks the NCS ligands. It shows also a mode softening in connection with the spin-state interconversion. This is seen from the shift of a prominent peak on the energy-rich side of the scattering spectrum by approximately 10 meV similar to the observation in [Fe(tpa)(NCS)₂]. This confirms in an indirect way that the role of the NCS ligands in making spin-crossovers possible is not vital.

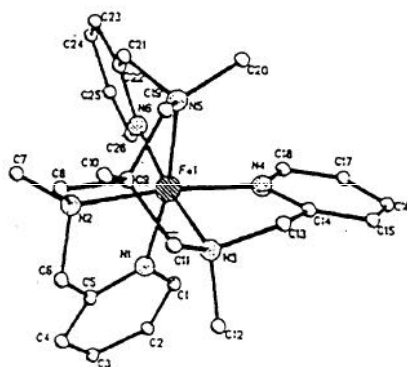


Fig. 2: [Fe(tptMetame)]²⁺

[1] H. Paulsen, M. Grodzicki, H. Winkler and A.X. Trautwein, Density functional calculation of the vibrational spectra of the spin-crossover complex [Fe(phen)₂(NCS)₂], submitted to Chem.Phys.Letters.