



ESRF

## Experiment title:

Detection of iron-ligand vibrations in the  
themally induced high-spin low-spin transition of  
single-crystalline Fe(tpa)(NCS)<sub>2</sub> by angular resol-  
ved nuclear resonant inelastic scattering

## Experiment

number:

CH-308

Beamline: <b>ID- 18</b>	Date of Experiment.: from: 18. 06. 1997 to: 22. 06. 1997	Date of Report: 15. 08. 1997
Shifts: <b>12</b>	Local contact(s): <b>Dr. Joachim Metge</b> <b>Dipl. Phvs. Hanne Grünsteudel</b>	<i>Received at ESRF</i> <b>29 AUG 1997</b>

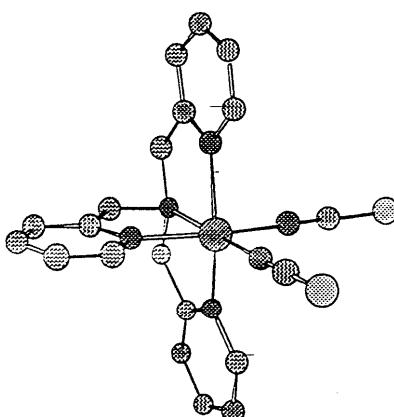
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## Report:

The complex [Fe(tpa)(NCS)<sub>2</sub>]·(tpa = tris(2-pyridylmethyl), Fig. 1) with non in the ferrous oxidation state exhibits a thermally induced “low-spin” ↔ “high spin” interconversion at a critical temperature T<sub>c</sub> 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. I:** [Fe(tpa)(NCS)<sub>2</sub>]

$[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  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  $[\text{Fe}(\text{tpa})(\text{NCS})_2]$ . 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  $[\text{Fe}(\text{tptMetame})]^{2+}$  or “tripod” ( $\text{tptMetame}$  = 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  $[\text{Fe}(\text{tpa})(\text{NCS})_2]$ . This confirms in an indirect way that the role of the NCS ligands in making spin-crossovers possible is not vital.

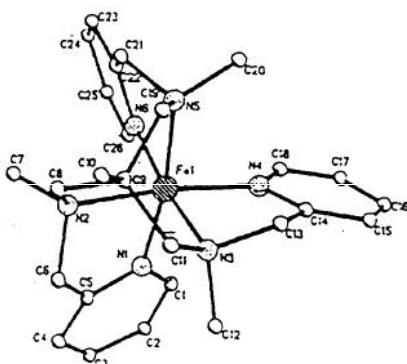


Fig. 2:  $[\text{Fe}(\text{tptMetame})]^{2+}$

[ 1 ] H. Paulsen, M. Grodzicki, H. Winkler and A.X. Trautwein, Density functional calculation of the vibrational spectra of the spin-crossover complex  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ , submitted to Chem.Phys.Letters.