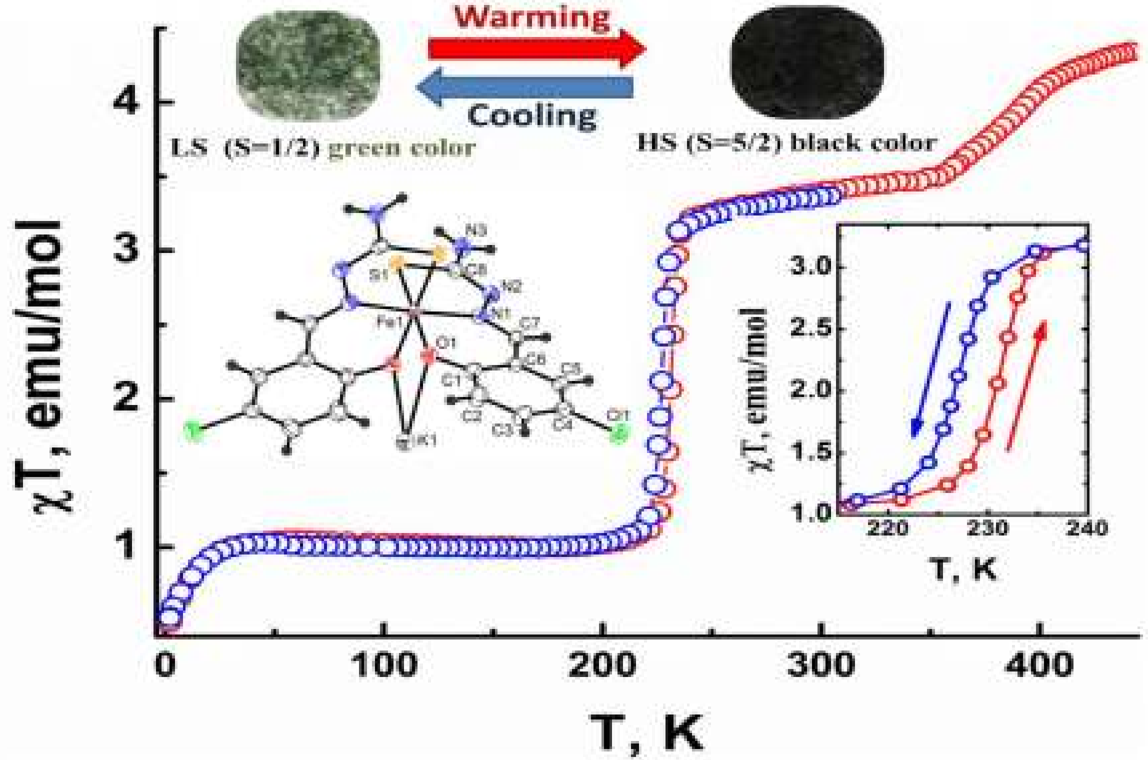
X International Voevodsky Conference
“Physics and Chemistry of Elementary Chemical Processes”
(VVV-2022)

Anionic spin-crossover complex of Fe(III) with space symmetry transition and thermal hysteresis around room temperature

Nataliya G. Spitsyna, Maxim A. Blagov

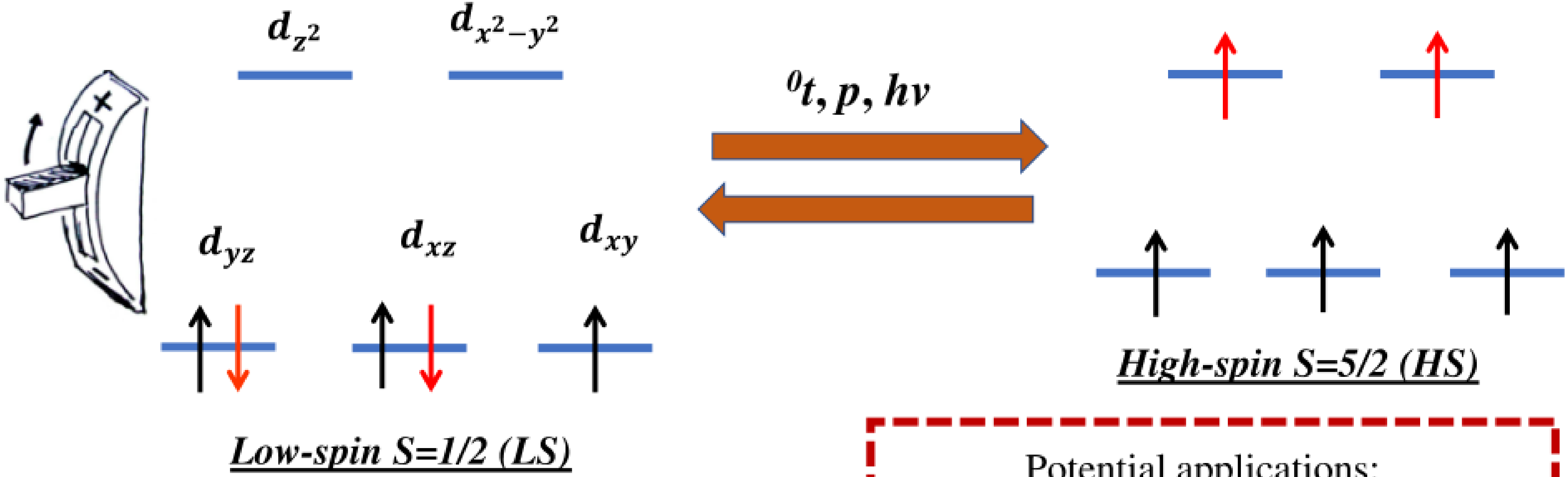
Institute of Problems of Chemical Physics, RAS, Semenov av. 1, 142432, Chernogolovka, Russia

* *E-mail: spitsina@icp.ac.ru*



Novosibirsk – 0.5-0.9 Sep. 2022

Spin Crossover Fe(III) with the d^5electronic configuration

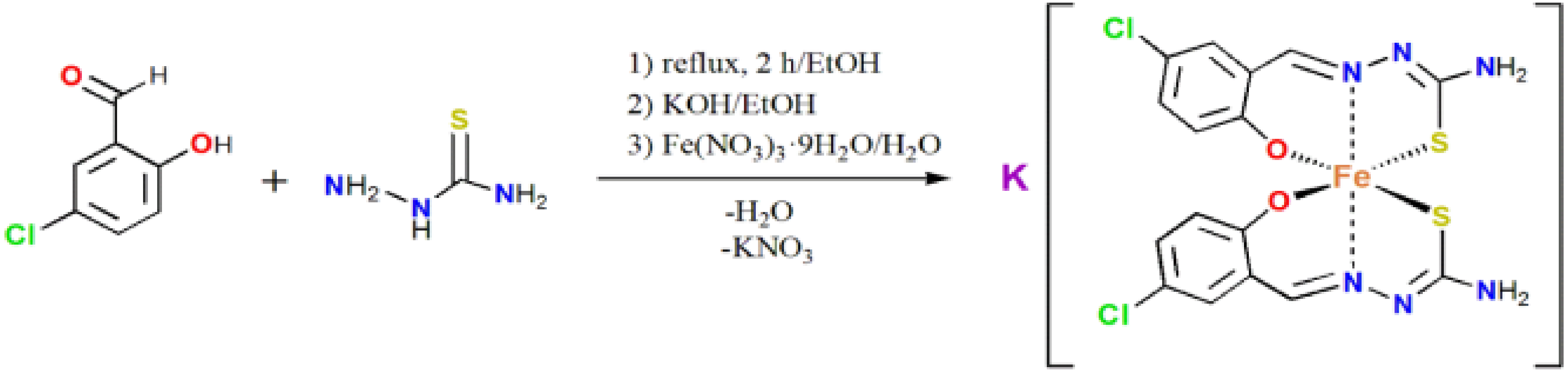


- Reversible SCO: S=1/2↔S=5/2;
- Changes in crystal structure: Fe-ligand bonds get elongation by ~10-15% (relative to the *LS* state).

Potential applications:

- Molecular switches;
- Data storage media;
- Nanoscale electronic devices;
- Biomimetic soft actuators.

Scheme of synthesis of the complex K[Fe(5Cl-thsa)$_2$]



A polycrystalline powder of K[Fe(5-Cl-thsa)$_2$] (**1**) was isolated.

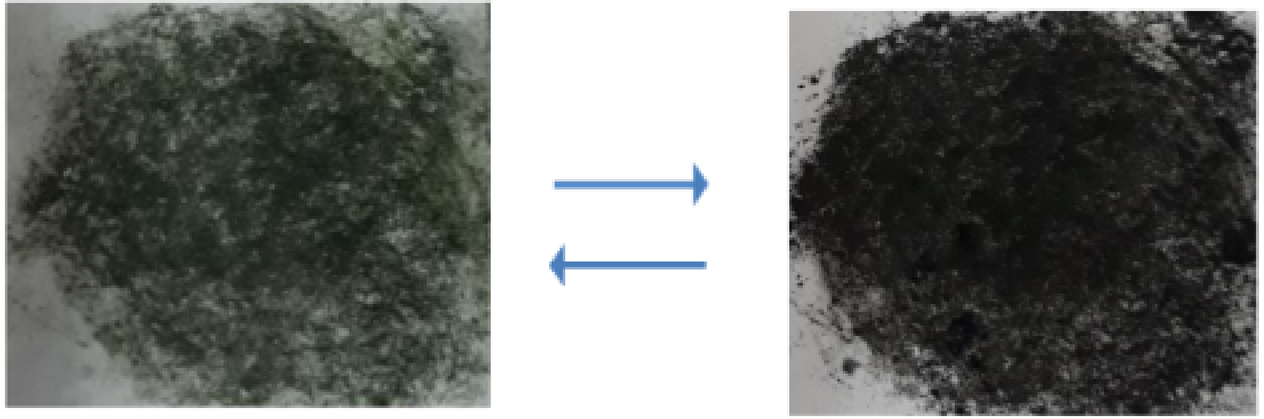


Photo of the thermochromism for the polycrystalline sample of **1** was green color (*LS*, S=1/2) at 77K, and black color *(HS*, S=5/2) at 300K.

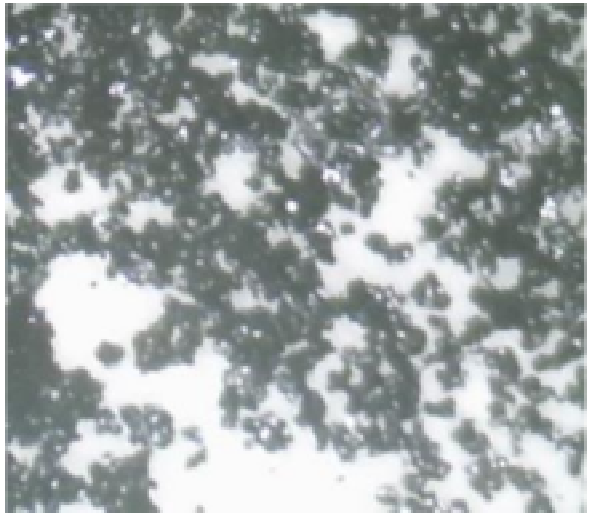
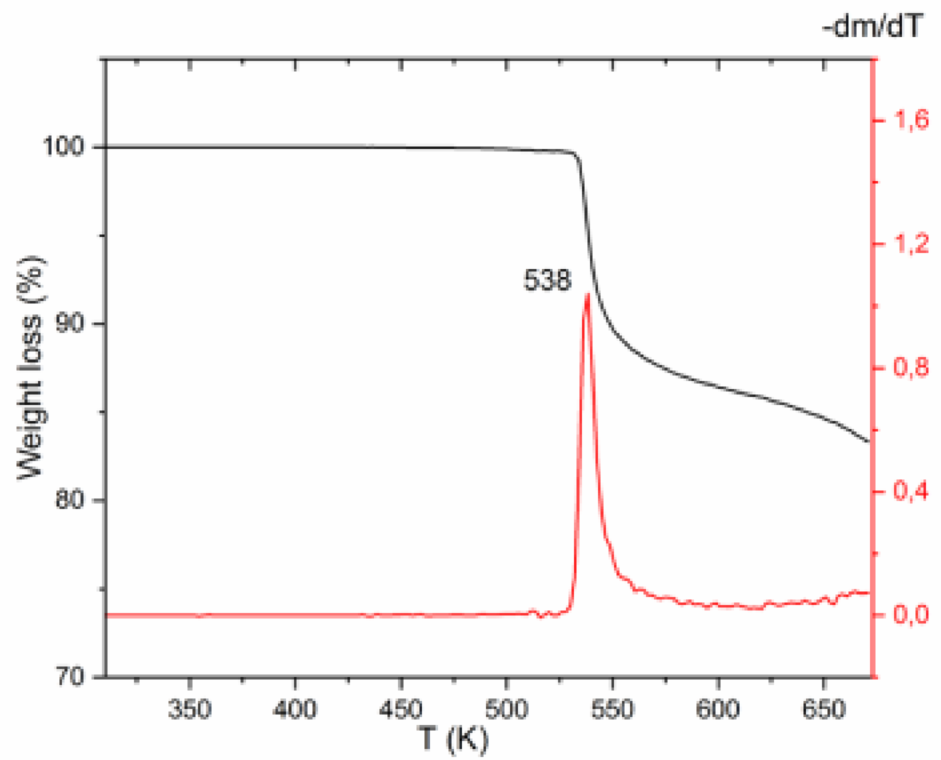
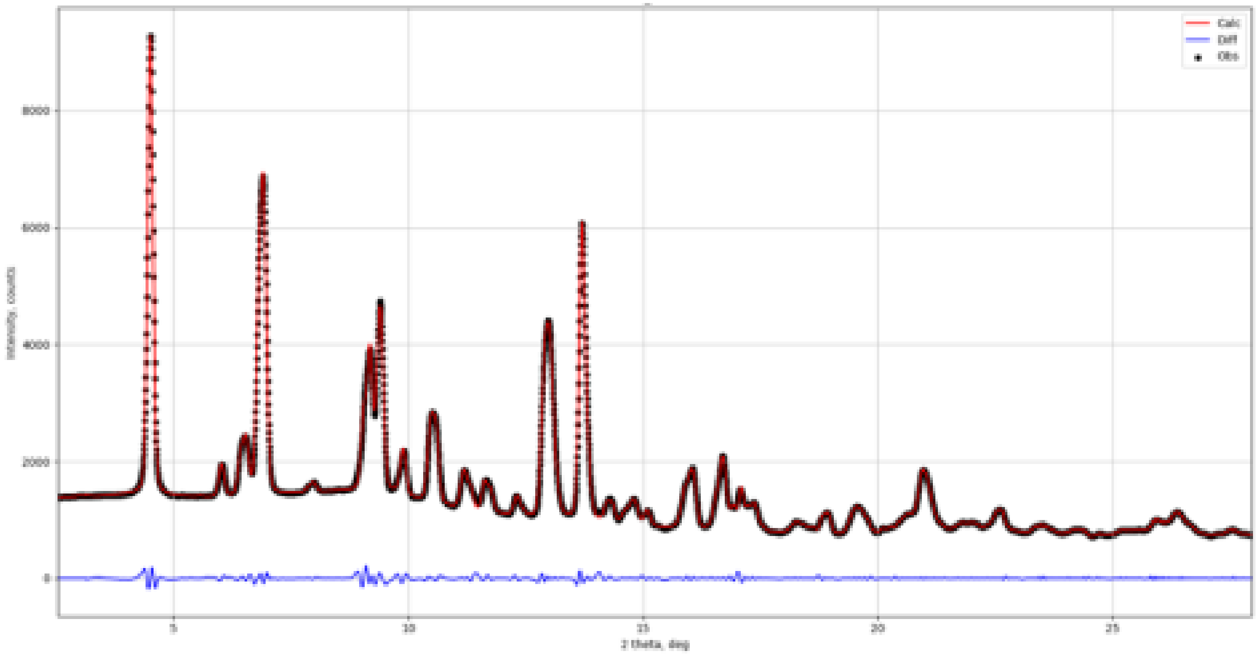


Photo of the polycrystalline sample of K[Fe(5Cl-thsa)$_2$].

Characterization of K[Fe(5Cl-thsa)₂] salt



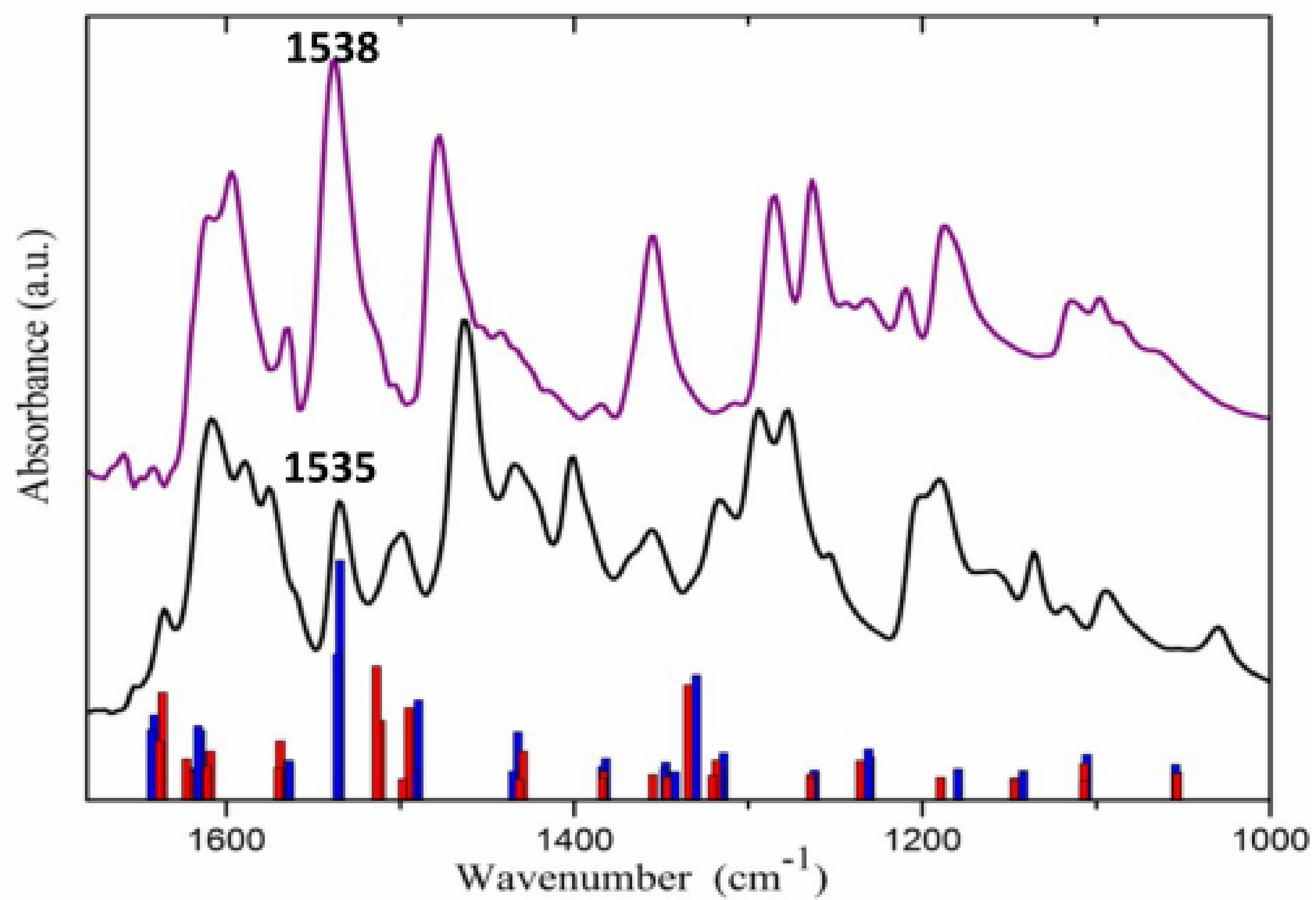
The thermogravimetric analysis for K[Fe(5Cl-thsa)2] was performed using a NETZSCH STA 409 C Luxx thermal analyzer. Sample weight - 8.366 mg, atm.- argon, flow rate V= 12 ml/min, temperature range- 27 - 700 °C, heating rate 10 °C/min.



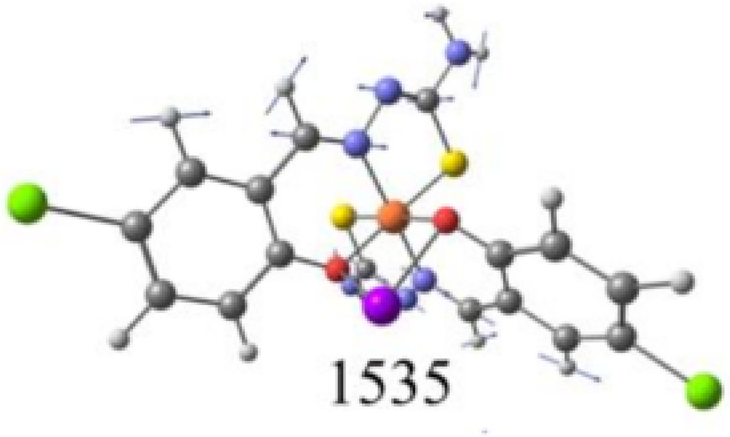
Powder X-ray diffraction pattern of K[Fe(5Cl-thsa)$_2$] taken at room temperature (black dots) and LeBail method refinement of *XRPD* data (red line) for orthorhombic P$_{bcn}$ structure. The bottom line is the difference plot.

Elemental analysis. Anal. Calcd (%) for K[Fe(5-Cl-thsa)$_2$], $C_{16}H_{12}Cl_2FeKN_6O_2S_2$ (550.28 g·mol^{-1}): C, 34.92; H, 2.20; N, 15.27; S, 11.63. Found: C, 34.99; H, 2.57; N, 15.24; S, 11.28 %. The electron-probe X-ray microanalysis afforded the elements ratio is Fe:K:S=1:1:2. The complex is soluble in water, ethanol, acetonitrile and DMF.

IR Spectroscopic studies

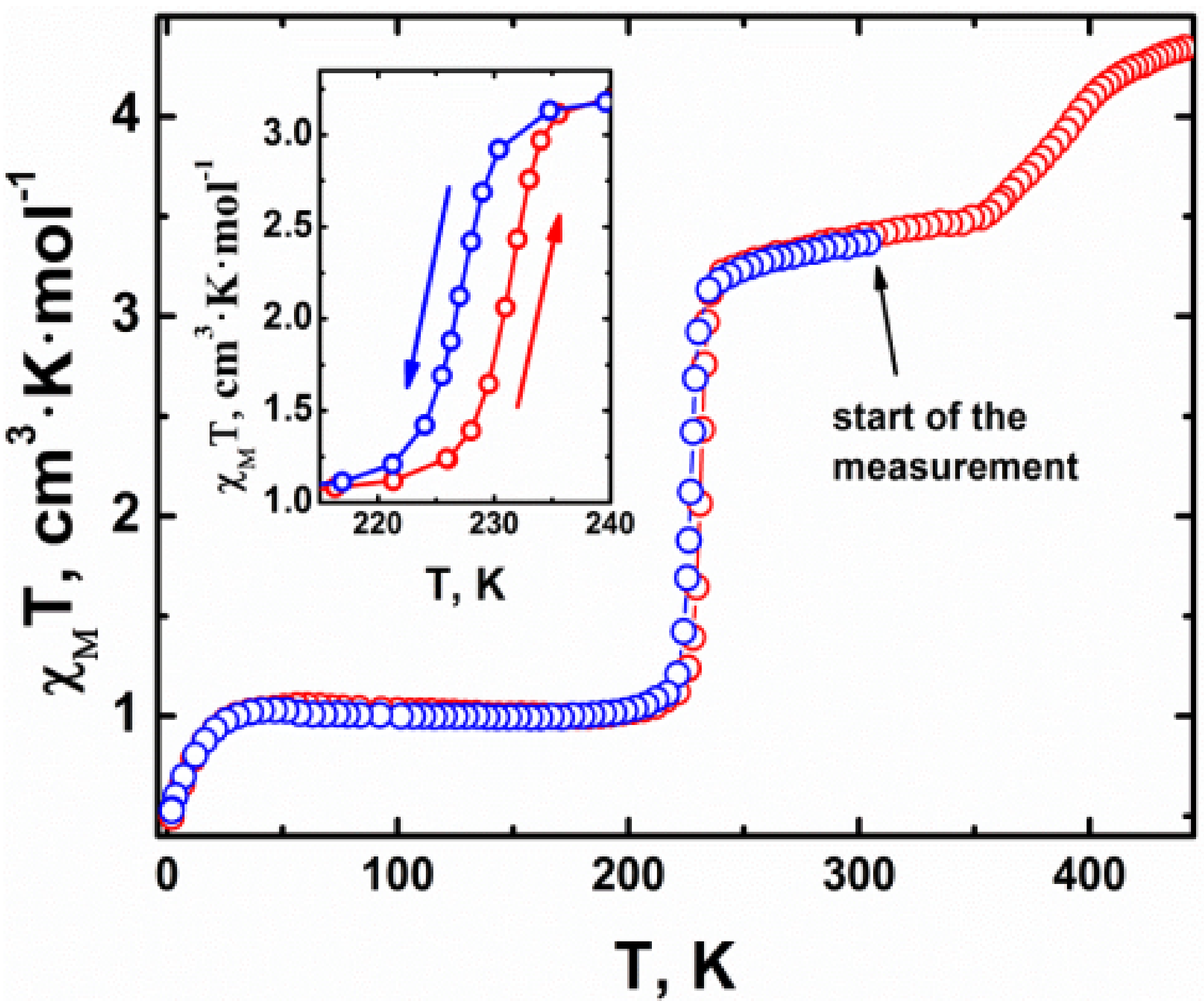


Experimental ***ATR FT-IR*** absorption spectra for the H_2-5Clthsa (violet line) and the K[Fe(5Cl-thsa)$_2$] (black line) at T=298K, in the range 1600–1000 cm-1. *IR* vibration frequencies calculated by DFT are given as bars at the bottom part of the Figure for K[Fe(5Cl-thsa)$_2$] in the HS (red) and LS (blue) states. The B3LYP* functional with the 6-31G(d,p) basis set was used.



- According to the calculated geometry of the cation and the IR spectrum, salt **1** is in the LS state
- The intense band (arrow) at 1535 cm-1 (C=Nim– stretching vibrations) shows the existence of a magnetically active ion configuration at 298K ***LS***, while according to the magnetic data, **γ_{HS} is 78%.**

Bulk magnetic properties



Temperature dependences of $\chi_M T$ product in the heating (red circles) and cooling (blue circles) modes. The scan rate is 2 K/min.

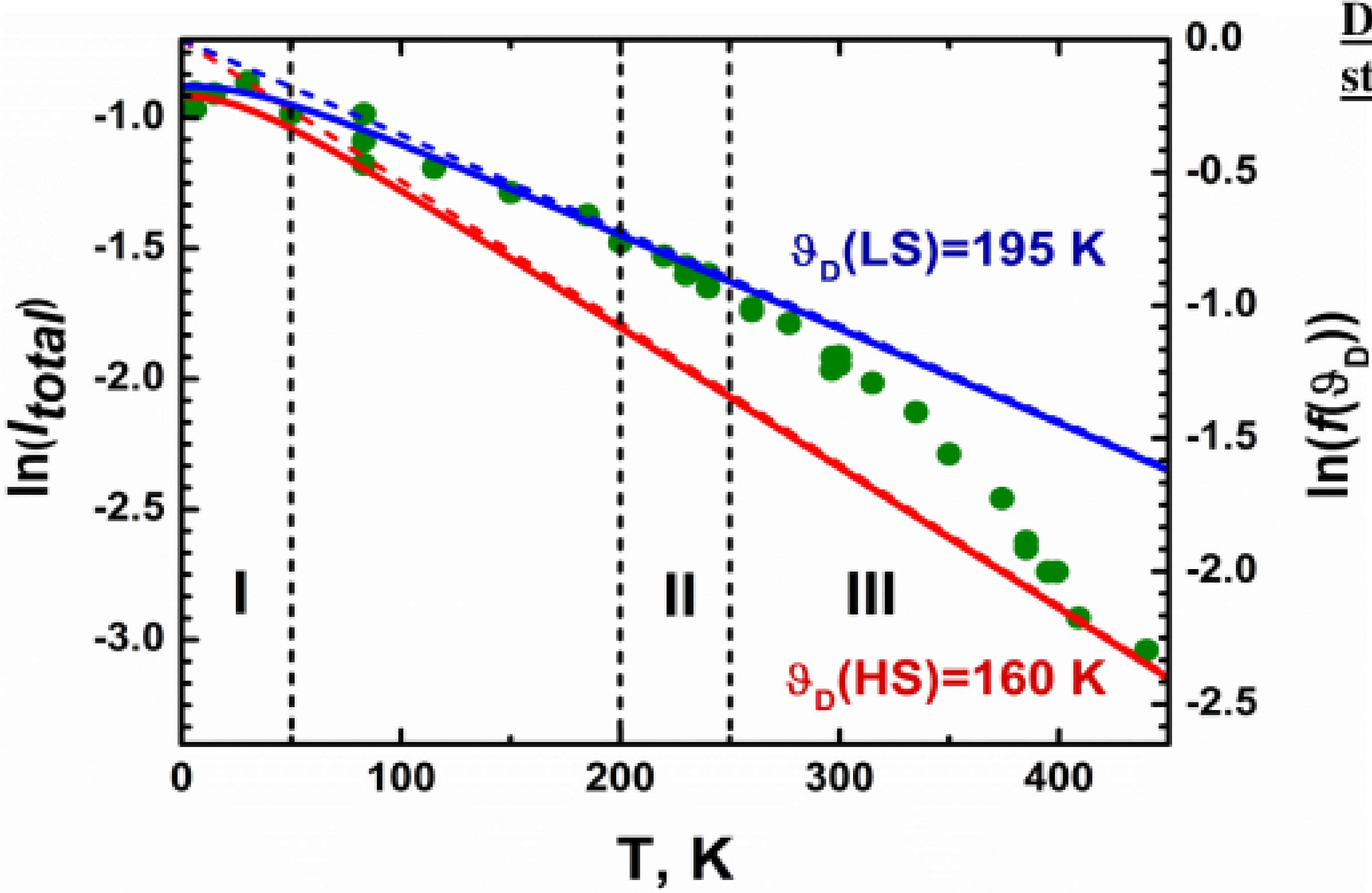
- The magnetic susceptibility for the **K[Fe(5Cl-thsa)$_2$]** salt has a complex temperature dependence. It can be interpreted as a three-step SCO from 96% of LS at 2K to 100% of *HS* fraction at 440K.
- The effective half-transition temperatures for **1** are T1/2↓=228 K and T1/2↑=232 K (T1/2=½·(T1/2↑+T1/2↓)=230K);
- A hysteresis of magnetic response with a maximum width of ~ 6 K is observed in a temperature range of 215-235K.

☐ First step – the conversion of residual HS fraction from 4% to 17%. (In the temperature range of 2- 50K)

☐ Second step – an abrupt spin transition increase in γ_{HS} from 17% to 74%. (In the temperature range of 200 - 250K, $\Delta\gamma_{HS}$ =57%)

☐ Third step– increase in γ_{HS} to essentially 100% ($\Delta\gamma_{HS}$ =26%) between 250 - 440K

^{57}Fe Mössbauer spectroscopy of K[Fe(5Cl-thsa)$_2$]



Temperature dependences of the total spectrum intensity *ln(Itotal)* logatithm and the logarithm of the Mössbauer effect probability *ln(f)*.

Solid lines - dependences for specific values of the Debye temperature $\ln(I_{\text{total}}(T)) = -\frac{3E_R^3}{k_B\vartheta_D^3}\int_0^{\vartheta_D} x\cdot \mathrm{cth}\left(\frac{x}{2T}\right)\mathrm{d}x + \ cons$), dashed lines - the classical approximation (T >> ϑ_D).

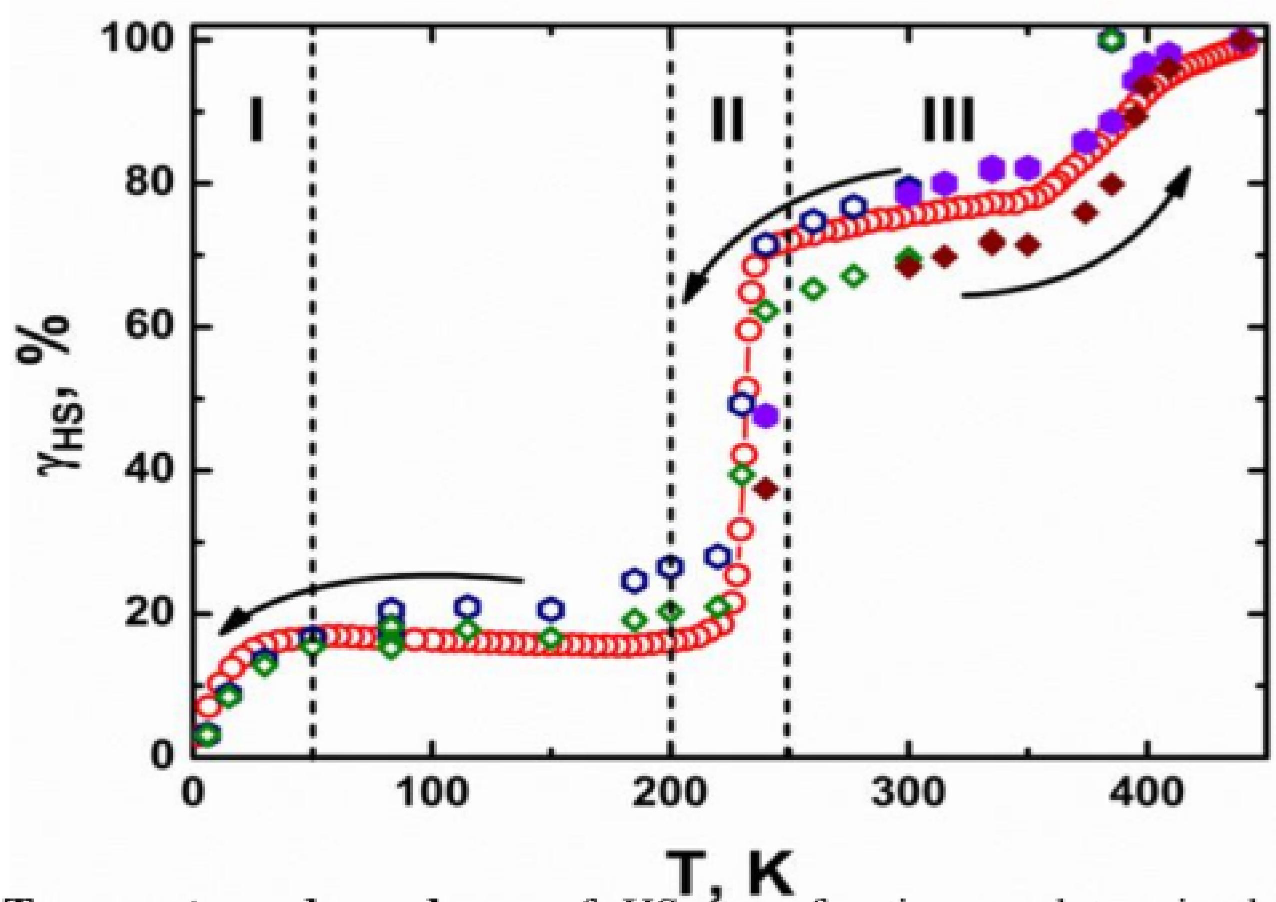
Determination of the Debye temperatures for the *HS* and
states of a magnetically active anion Fe(III)

- Debye temperatures (ϑ_D) for *LS* and *HS* complex were obtained from the Mössbauer data with the aim of the precise calculations of γ_{HS} values at different temperatures which corresponds to all steps of SCO from only *LS* state up to only HS state:

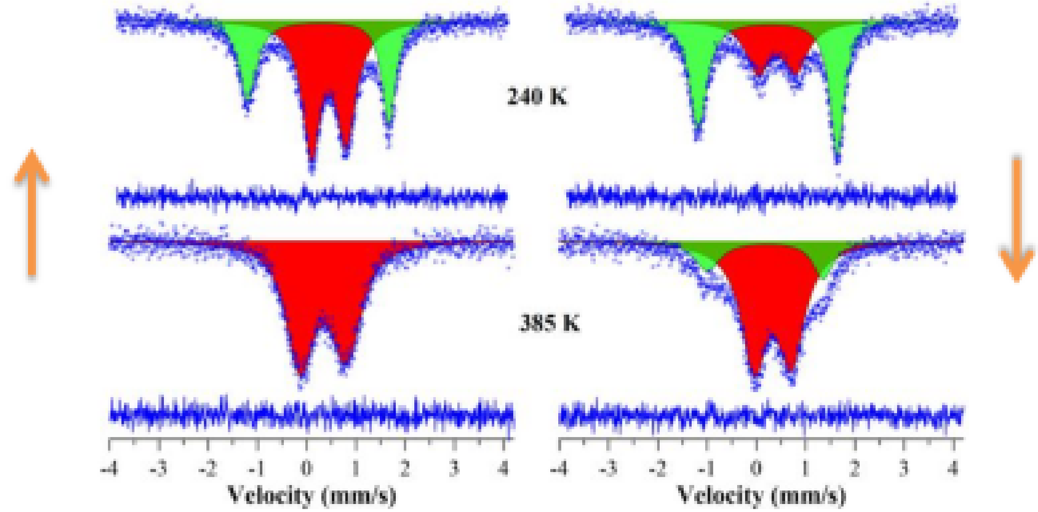
$$\gamma_{HS}=\frac{I_{HS}(T)\cdot f_{LS}(T)}{I_{HS}(T)\cdot f_{LS}(T)+(100-I_{HS}(T))\cdot f_{HS}(T)}\cdot 100\%$$

- The transition from the *LS* Debye temperature to the *HS* Debye temperature begins only at stage **III** at 250K, when the proportion of the *HS* fraction reaches 78%, and ends at 400K, when the content of the *HS* fraction is 90% - the "delay" effect.

^{57}Fe Mössbauer spectroscopy



Temperature dependence of *HS* state fraction as determined from Mössbauer experiment before (rhombuses)/after (hexagons) correction with Debye temperature and *DC* magnetic measurements (red circles) data of K[Fe(5Cl-thsa)$_2$] major polymorph. Empty blue hexagons/green rhombuses correspond to cooling mode, and violet hexagons/brown rhombuses correspond to heating mode.

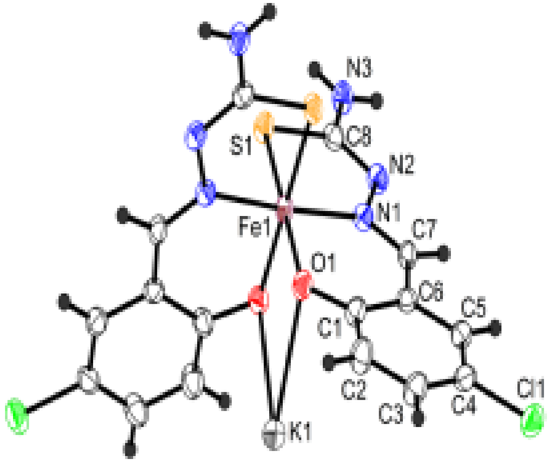


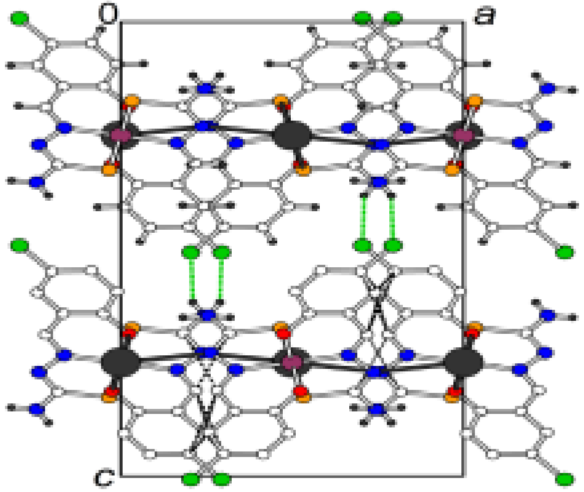
Mössbauer spectra of major polymorph K[Fe(5Cl-thsa)$_2$] taken at various temperatures.

- Mössbauer data almost perfectly match with SQUID data.
- Mössbauer data after correction for ϑ_D become closer to magnetic data at high temperature range (225-440K) but at low temperature range (50-225 K) match worse.
- *HS* fraction at 240K is either ~ 49% or ~ 71% as obtained in the heating and cooling modes, respectively. At 385K, the *HS* fractions are 88% and ~ 100% upon heating and cooling respectively.

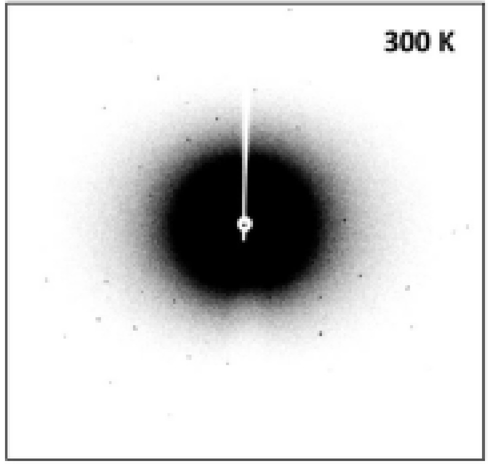
X-ray Crystallography of K[Fe(5Cl-thsa)$_2$]

Minor polymorph with ordered potassium cations





The molecular and crustal structure of 1.



Single-crystal synchrotron X-ray diffraction studies of K[Fe(5Cl-thsa)$_2$] at 100K, 250K and 300K revealed the same orthorhombic *Pbcn* space group. According to *PXRD*, it is absent in the main phase. Dimensions of the found single crystal (mm): 0.05×0.03×0.02.

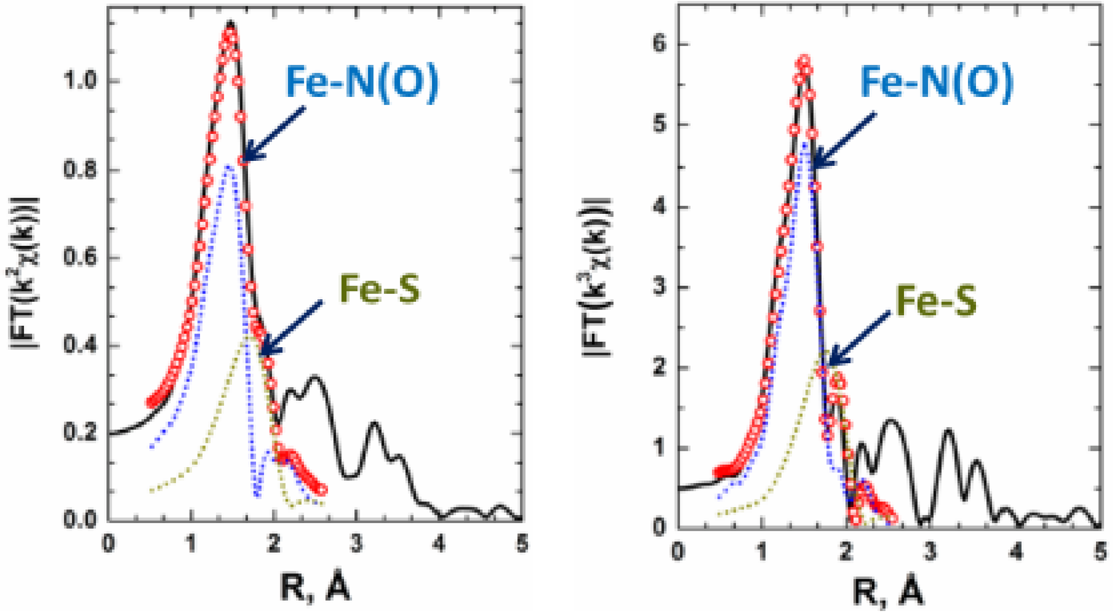
Major polymorph with disordered potassium cations

?

The experimental powder pattern was successfully indexed assuming an orthorhombic lattice (with systematic absences conforming with the *Pbcn* space group) to yield the following parameters (the values in brackets correspond to analogous parameters from the single-crystal experiment at the same temperature of 100 K):

$$a = \mathbf{11{,}4131} (11{,}615)\ \text{Å};$$
$$b = \mathbf{8{,}7513}\ (8{,}3480)\ \text{Å};$$
$$c = \mathbf{20{,}2123}\ (20{,}763)\ \text{Å};$$
$$V = \mathbf{2018{,}8}\ (2013{,}2)\ \text{Å}^3.$$

Synchrotron-based *EXAFS* investigation



Fourier transforms of the Fe K-edge *EXAFS* spectrum of K[Fe(5Cl-thsa)$_2$], corresponding to two different weighting schemes $k^2\chi(k)$ (left) and $k^3\chi(k)$ (right) giving rise to varied relative intensities of the Fe-N(O) and Fe-S components: experimental data (black lines), total theoretical best-fit (red circles), Fe-N(O) component (blue circles), Fe-S component (swamp-green circles).

Best-fit local-structure parameters around Fe atoms in K[Fe(5Cl-thsa)2] according to *EXAFS* at 300 K.

Path	Coordination number N	Interatomic dist. R, Å	Debye-Waller factor σ^2, Å^2	ΔE, eV	R_f
Fe-N(O)	4	1.95	0.0079	-6.6	0.010
Fe-S	2	2.28	0.0169		

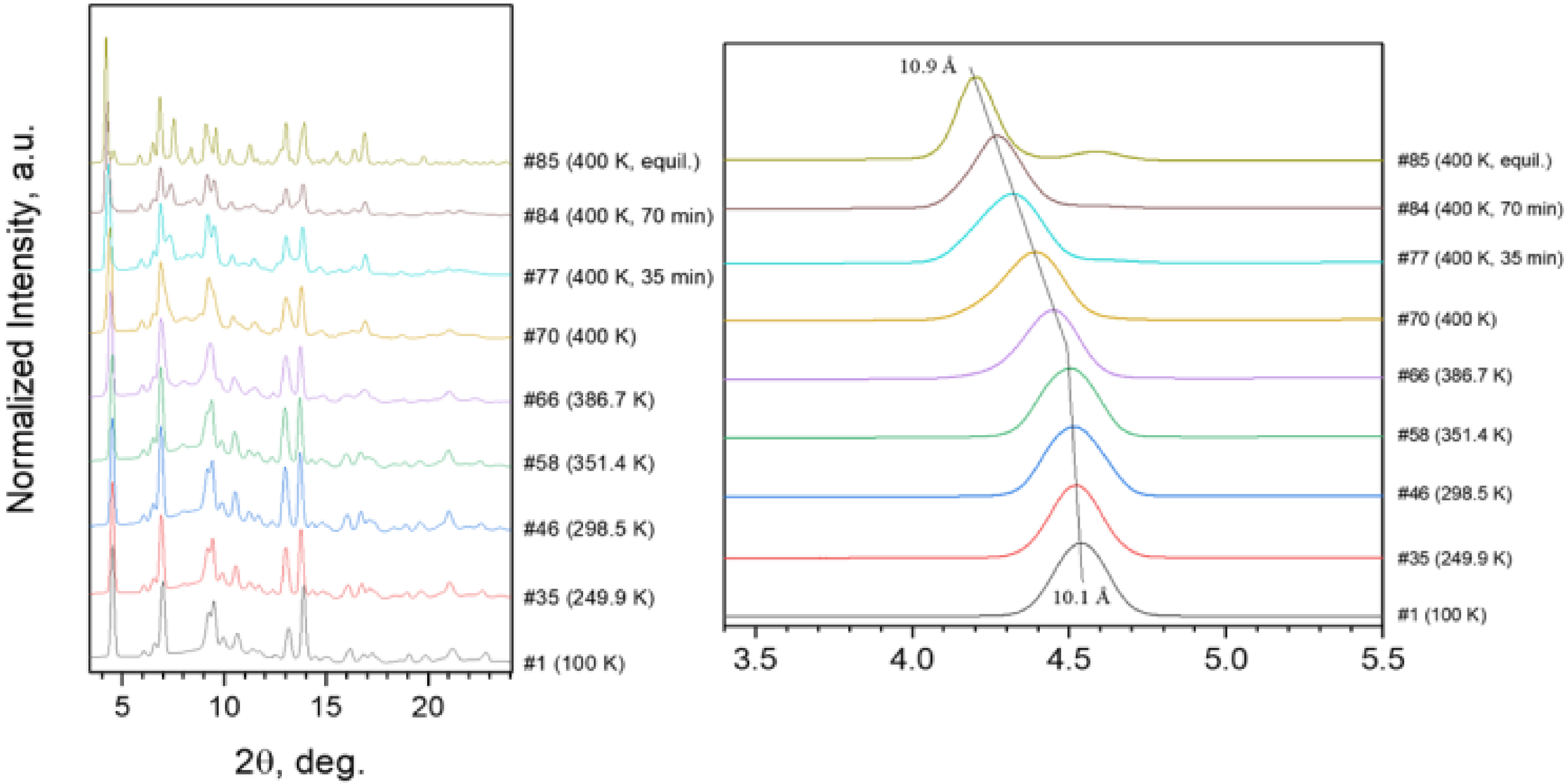
Fitting ranges: k=2.5…15.0 Å-1, R=1.1…2.2 Å.

- The bond lengths of the coordination octahedron for both polymorphs are identical and corresponds LS structure:

  - ***X-ray*** *l*(Fe-O)=1,953(2)Å, *l*(Fe-N)=1,951(2)Å, *l*(Fe-S)=2,2390(7)Å;
  - ***EXAFS*** *l*(Fe-O/N)=1,95 Å, *l*(Fe-S)=2,28 Å (Δ≤0,041Å).

- There is an effect of structural *«laggin»* for the main polymorph (powder), since at room temperature the proportion of the HS fraction is 75%.

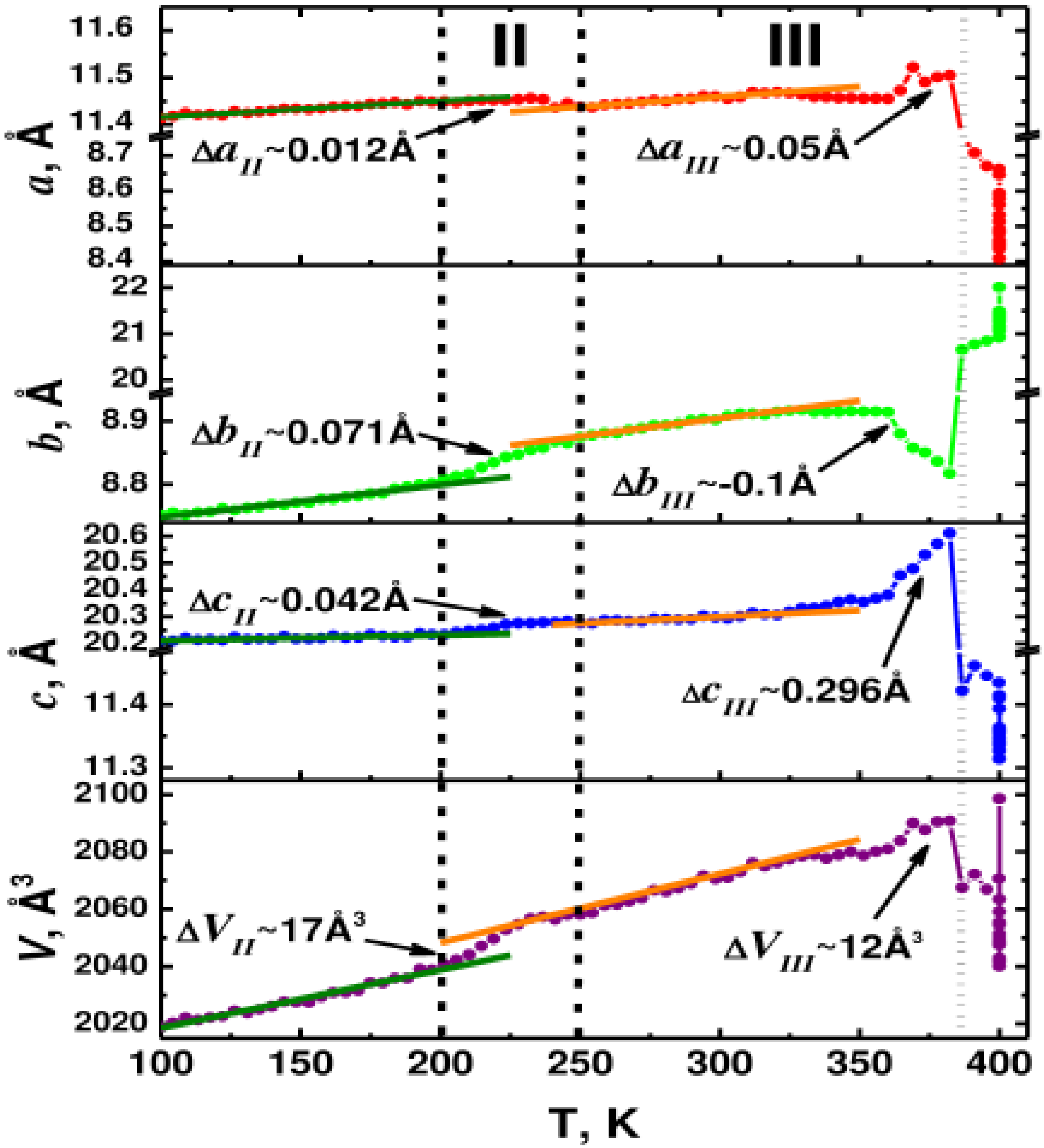
Synchrotron-based *XRPD* investigation



Powder diffraction patterns at various temperatures for K[Fe(5Cl-thsa)$_2$] (λ=0.8000 Å).

The right panel shows the change in temperature of the first low-angle peak corresponding to the interplanar spacing of the layered structure. The general structure of peaks experiences only minute changes on going from 100K (pattern #1) up to 386.7 K (pattern #66).

Synchrotron-based *XRPD* investigation



The changes of unit cell parameters *a*, *b*, *c* and *V* (based on *XRPD*) data in the temperature range 100-400 K for K[Fe(5Cl-thsa)$_2$] salt.

Roman numerals II (γ_{HS} from 17% to 75%, Δ γ_{HS}=58%) and III (γ_{HC} 75 to 100%, Δ γHS=25%) indicate the SCO step numbers according to magnetic measurements.

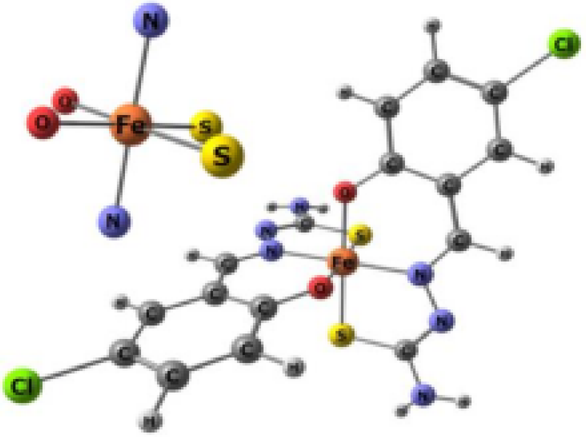
The short dashed lines (---) mark borders of the distinct SCO steps. The dotted line (···) at ~387 K indicates the *orthorhombic-to-monoclinic* structural phase transition with a symmetry lowering from orthorhombic to monoclinic (*Pbcn→P21/n*) space group .

Note that the Y-axes for *a*, *b*, and *c* parameters contain breaks.

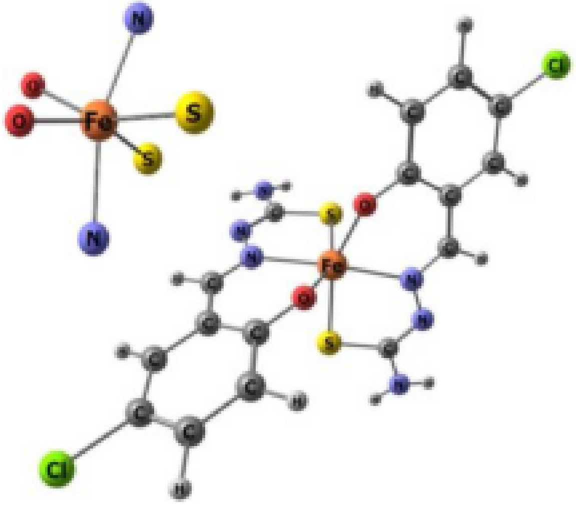
Theoretical calculations

no.	Functional	Type	HF, %	Spin state	E_{el}, a.u.	E_{ZPV}, a.u.	E_0, a.u.	ΔE_0(HS-LS), kJ/mol
1	OLYP	GGA	—	HS	-4676.896743	0.267317	-4676.629426	6.34
				LS	-4676.901767	0.269926	-4676.631841	
2	OPBE			HS	-4676.519302	0.269249	-4676.250053	25.78
				LS	-4676.531937	0.272064	-4676.259873	
3	TPSS	mGGA		HS	-4677.2150951	0.267466	-4676.9476291	85.67
				LS	-4677.2503820	0.270123	-4676.9802590	
4	TPSSh	GH-mGGA	10	HS	-4677.020263	0.271916	-4676.748347	44.40
				LS	-4677.039775	0.274515	-4676.76526	
5	PBE0-15	GH-GGA	15	HS	-4674.5620255	0.271981	-4674.2900445	18.97
				LS	-4674.571944	0.274673	-4674.2972710	
6	B3LYP*		15	HS	-4675.6142460	0.270846	-4675.3434000	20.07
				LS	-4675.6244784	0.273434	-4675.3510444	
7	B3LYP		20	HS	-4676.9703525	0.272984	-4676.6973685	-2.04
				LS	-4676.9720982	0.275505	-4676.6965932	
8	PBE0		25	HS	-4674.6515481	0.276317	-4674.3752311	-20.36
				LS	-4674.6464029	0.278928	-4674.3674749	

The OLYP, OPBE, B3LYP* and PBE0-15 functionals tested in DFT calculations confirm the feasibility of the SCO transition. A parametrization of the B3LYP functional was carried out in order to determine the optimal proportion of the Hartree-Fock exchange.
Optimization and calculation of frequencies: 6-31G(d,p);
Calculation of electronic energy E_{el}: 6-311+G(2df,2p);
Quantum Chemistry Package: Gaussian 09.

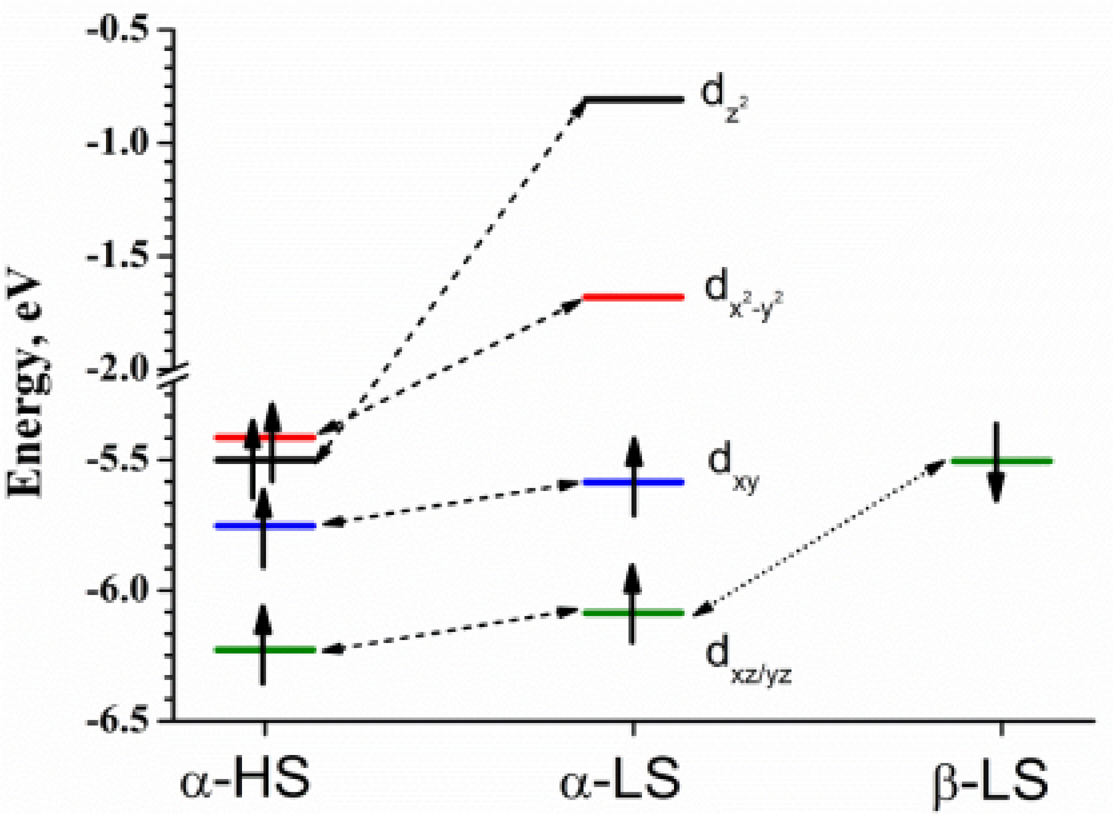


***LS*, S=1/2**

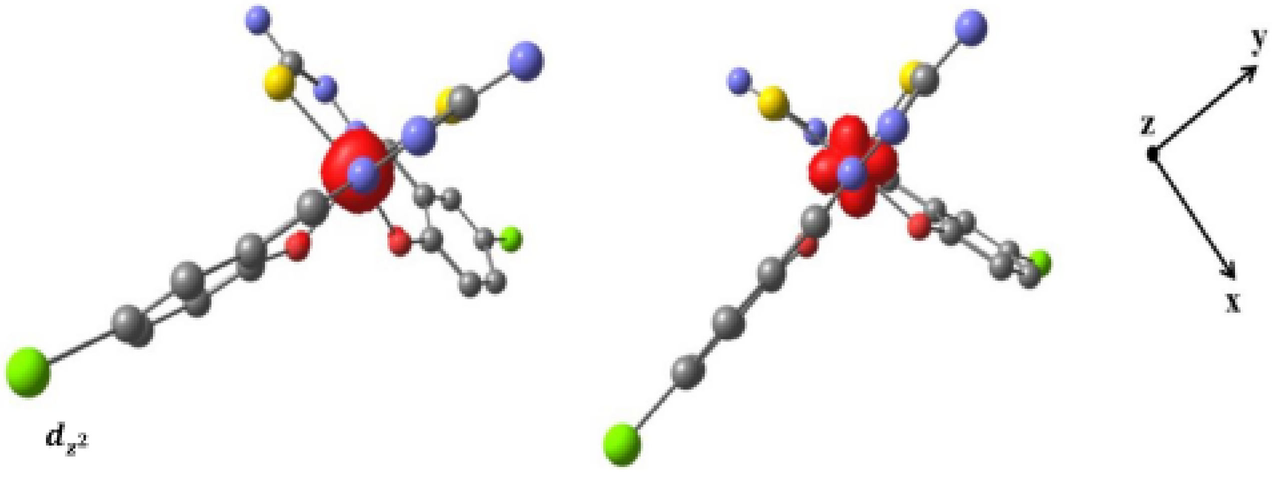


***HS*, S=5/2**

Theoretical calculations



The energy level diagram
of molecular orbitals with a predominant iron *d* orbitals contribution for the *HS* and *LS* states of the K[Fe(5Cl-thsa)$_2$] complex. Note that the Y-axis contains break. (B3LYP*/6-31G(d,p)).



Estimated spin density distribution
for *HS* (left) and *LS* (right) structures of K[Fe(5Cl-thsa)$_2$].

DFT calculations highlight the special role played by σ-bonding between the Nim ligand sites and the d_{z^2} orbital of the iron atom, which is consistent with the maximum relative elongation of the Fe-Nim bonds for all thsa-based complexes.

Concluding remarks :

- ✓ 2D heterometallic polymer **$\mathbf{K[Fe(5Cl\text{-}thsa)_2]}$** (**1**) has been synthesized and thoroughly characterized. The existence of two polymorphs for **1**, with ordered and disordered potassium cations, was found. According to the *PXRD*, only “trace” amounts of a polymorph with an ordered **K** cation are present in the main phase. The formation of a poorly crystallizing basic polymorph explains why it is difficult to obtain single crystals for thsa- complexes. The established structure of $K[Fe(5Cl\text{-}thsa)_2]$ on a single crystal is the 4-th one in CCDC since the 1970s, when these complexes were discovered.
- ✓ DC magnetization, Mössbauer measurements consistently indicate that the second major polymorph with potassium cations disordered over a few crystallographic sites undergoes a complicated three-step cooperative spin-crossover transition in a temperature range 2-440 K involving the following steps: I (2-50 K, gradual increase in the HS fraction), II (200-250 K, an abrupt increase in the HS fraction), III (250-440 K, gradual increase in the HS fraction to 100%). The SCO curve has a half transition temperature T1/2=230 K and a hysteresis loop with a width of 6 K.

Concluding remarks:

✓ According to EXAFS, Mössbauer- and IR- spectroscopy data SCO for the dominant polymorph is quite peculiar. The effect of "structural delay" of the rearrangement of the LS into the HS state is shown. Indeed, the increase in the HS concentration by 57% at the second step does not result in the expected significant increase in the iron(III)-ligand bond lengths. In addition, the final step of the spin conversion (ΔγHS=26%) is associated with a structural phase transition with a symmetry lowering from orthorhombic (*Pbcn*) to monoclinic (*P21/n*) space group.

✓ These results provide a new platform for understanding the multistep SCO character in the Fe(III) thsa-complexes and related compounds. The features of the electronic structure are established.

We thank:

Yan V. Zubavichus, Vladimir A. Lazarenko, Roman D. Svetogorov – the **SRF SKIF Boreskov IC SB RAS and NRC “Kurchatov institute”** for carrying out structural measurement at synchrotron *X-ray* structural analysis beamline.

Alexander N. Vasiliev, Olga Maximova, Vyacheslav S. Rusakov, Sergey A. Yaroslavtsev – **Lomonosov Moscow State University Faculty of Physics** for the *dc* – magnetometry measurements and Mossbauer spectral investigations.

IPCP RAS – Vladimir B. Krapivin, Maxim A. Blagov performed DFT calculations; – Vera P. Lodygina, Anatolii S. Lobach measured and contributed to analyses IR and TGA data.

This work was partially done with using of the Computational and Analytical Center for Collective Use of the **IPCP RAS** tool base. (State task, state registration No. AAAA-A19-119092390079-8)

THANK YOU FOR ATTENTION!!