Supplementary Material (ESI) for New Journal of Chemistry

The crystallographic phase transition for a ferric thiosemicarbazone spin crossover complex studied by X-Ray powder diffraction.

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Supplementary Data

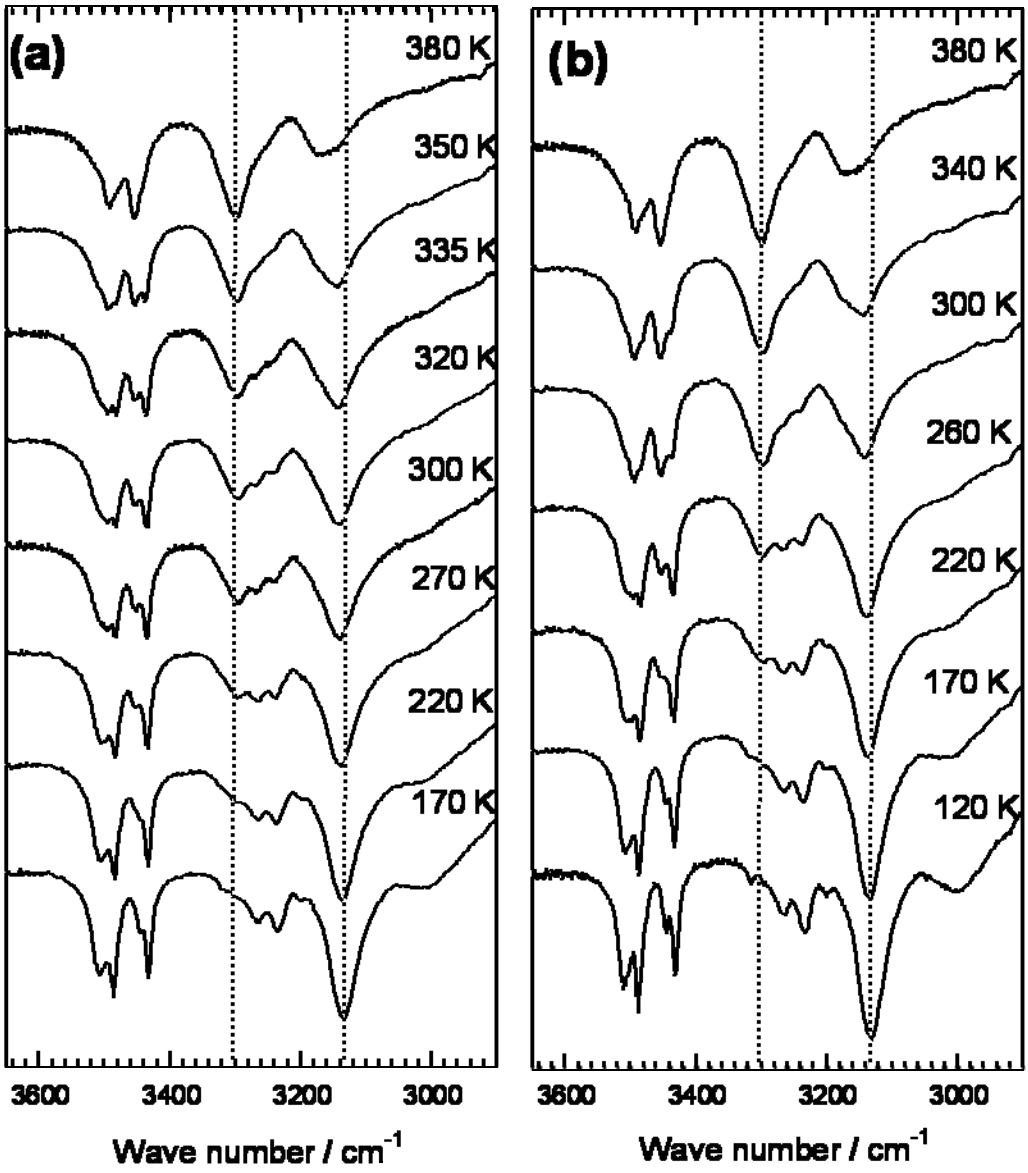

Figure S1 : IR spectra of compound $Li[Fe(5BrThsa)_2].H_2O$ in Heating mode from 170 to 380 K (a) and in cooling mode from 380 to 120 K (b) (From Ref. S1).

Dotted lines are only guides for eyes.

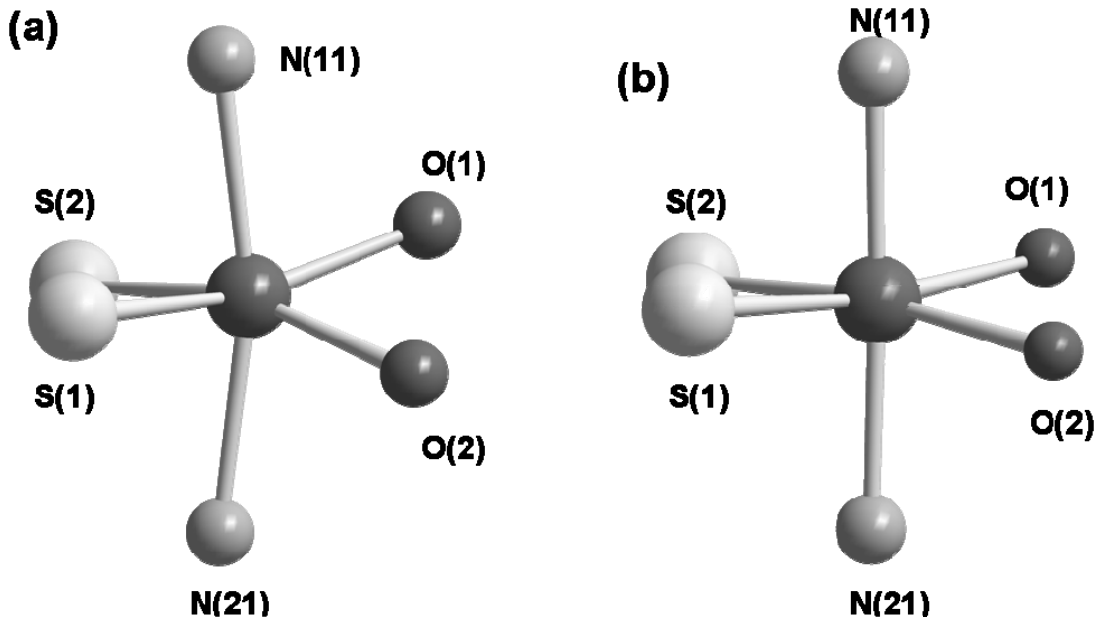

Figure S2 : Distortion of $[FeN_2O_2S_2]$ core in HS (a) and LS (b) phases.

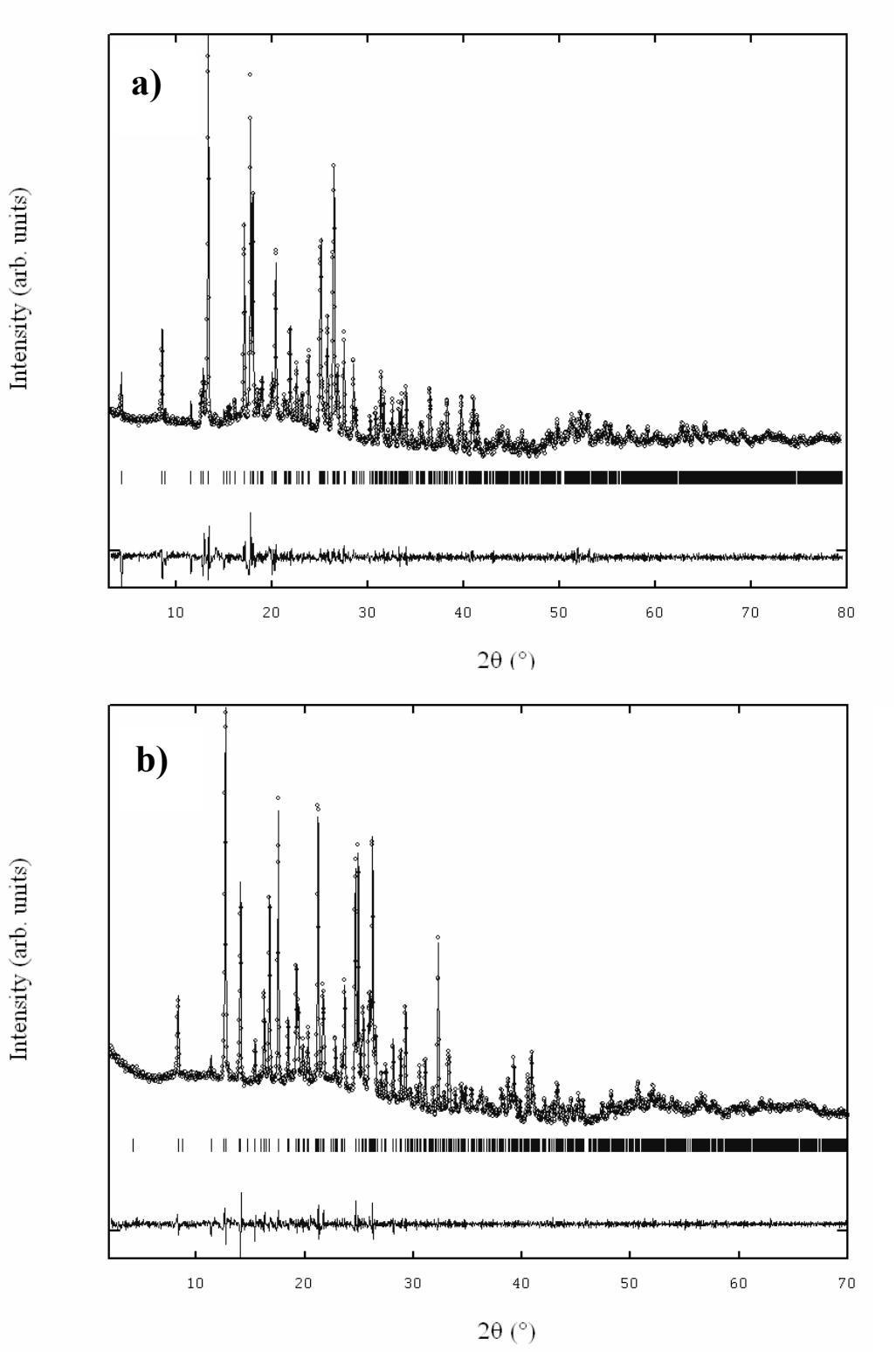

Figure S3 : Structureless whole pattern profile refinements for the LS phase (a) and the HS phase (b).

Table S1. Selected angles of LS and HS ferric thiosemicarbazone complexes. Labels are given in agreement with those used for $Li[Fe(5BrThsa)_2].H_2O$.

Compounds	$Cs[Fe(Thsa)_2]$ Ref. S2	$NH_4[Fe(5BrThsa)_2]$ Ref. S3	$NH_4[Fe(5ClThsa)_2]$ Ref. S4	$K[Fe(3,5Cl_2Thsa)_2]$,$1.5H_2O$. Ref. S5 Site Fe1	$K[Fe(3,5Cl_2Thsa)_2]$,$1.5H_2O$ Ref. S5 Site Fe2
T/K	298 K	300 K	135 K	103 K	103 K
Spin State	HS	LS	LS	LS	Almost LS
O(1)FeO(2)	84.3(5)	86.4(3)	87.3	86.6(6)	87.1(5)
O(1)FeS(2)	90.9(4)	-	89.6	91.8(7)	92.4(4)
O(1)FeN(11)	86.8(5)	89.7(3)	88.9	91.8(7)	90.3(6)
O(1)FeN(21)	109.8(5)	93.3(3)	93.4	89.6(6)	90.5(6)
O(2)FeS(1)	89.4(4)	89.9(2)	86.6	91.3(5)	93.1(5)
O(2)FeN(11)	108.0(5)	-	93.4	89.2(7)	90.8(6)
O(2)FeN(21)	85.6(5)	-	88.9	94.6(7)	90.7(6)
S(1)FeS(2)	100.3(2)	93.8(1)	93.5	90.3(2)	88.0(2)
S(1)FeN(11)	78.4(4)	85.8(2)	86.0	83.9(6)	83.7(5)
S(1)FeN(21)	87.2(4)	91.4(2)	91.7	94.9(5)	95.5(5)
S(2)FeN(11)	89.9(4)	-	91.7	91.4(4)	94.9(5)
S(2)FeN(21)	78.9(4)	-	86.0	84.9(5)	83.6(5)
O(1)FeS(1)	161.3(4)	176.2(2)	176.8	175.2(5)	174.0(5)
O(2)FeS(2)	161.2(4)	-	176.8	178.4(4)	174.2(4)
N(11)FeN(21)	159.9(5)	175.9(3)	176.8	176.1(8)	178.3(6)

Table S2. Cell parameters reported in literature for ferric substituted salicylaldehyde-thiosemicarbazone complexes

Compounds	$Cs[Fe(Thsa)_2]$ Ref S2	$Cs[Fe(Thsa)_2]$ Ref S2	$NH_4[Fe(5BrThsa)_2]$ Tabular crystals Ref. S3	$NH_4[Fe(5BrThsa)_2]$ Mica-Like crystals Ref. S3	$NH_4[Fe(5ClThsa)_2]$ Ref. S4	$NH_4[Fe(5ClThsa)_2]$ Ref. S4	$K[Fe(3,5Cl_2Thsa)_2]$,$1.5H_2O$ Ref S5	$K[Fe(3,5Cl_2Thsa)_2]$,$1.5H_2O$ Ref S5	$NH_4[Fe(3,5Cl_2Thsa)_2]$,$1.5H_2O$ Ref S6	$NH_4[Fe(3,5Cl_2Thsa)_2]$,$1.5H_2O$ Ref S6
T/K	103 K	298 K	300 K	300 K	135 K	298 K	103 K	298 K	103 K	298 K
System	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	Pna21	Pna21	Pnca	Pnca	Pbcn	Pbcn	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/a$
a (Å)	15.161(3)	15.285(3)	21.179(2)	20.837(8)	20.186(9)	20.348(9)	20.090(7)	20.221(8)	20.203(7)	20.273(7)
b (Å)	13.340(3)	13.402(4)	11.755(7)	11.761(7)	11.729(8)	11.791(5)	26.996(10)	27.210(9)	27.117(9)	27.437(9)
c (Å)	9.394(7)	9.449(8)	8.560(5)	8.619(6)	8.490(10)	8.548(4)	8.865(4)	8.916(5)	8.705(4)	8.852(5)
β(°)	-	-	-	-	-	-	98.37	98.08	99.05(9)	98.80(8)
V ($Å^3$)	1900	1936	2131.1	2112.2	2010.1	2050.9	4666	4857	4710	4866

References of Supplementary Data

S1. S. Floquet, Ph.D. Thesis, University Paris Sud, 2001.

S2. N. A. Ryabova, V. I. Ponomarev, V. V. Zelentsov and L. O. Atovmyan, *Sov. Phys. Crystallogr. (Engl. Transl.)*, 1981, **26**, 53-57.

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S6. N. A. Ryabova, V. I. Ponomarev, V. V. Zelentsov and L. O. Atovmyan, *Sov. Phys. Crystallogr. (Engl. Transl.)*, 1982, **27**, 46-52.