Bulk spin-crossover in the complex $[FeL(NCS)_2]$ of a novel tris(pyridyl)ethane-derived N_4-ligand— A look beneath the surface

Dennis Wiedemann and Andreas Grohmann*

Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 135, 10623 Berlin, Germany

Additional Figures

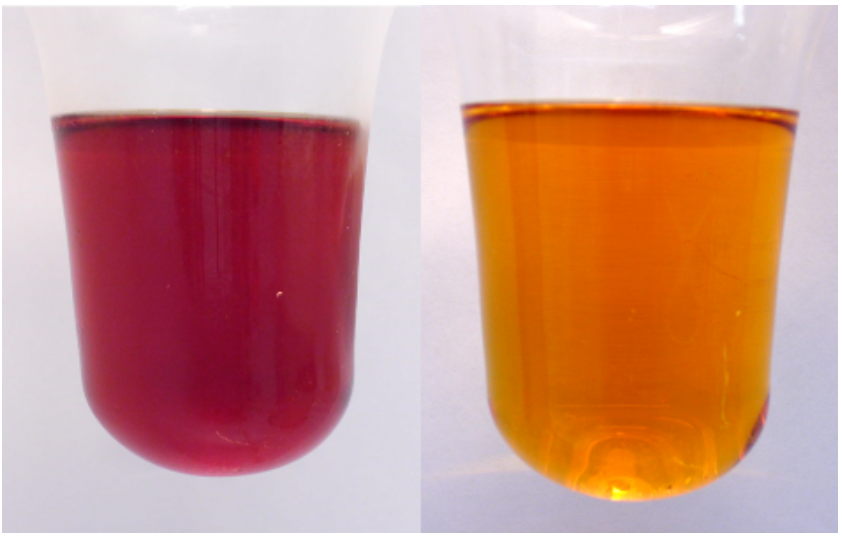

Fig. S1. Solution of $[FeL(NCS)_2]$ (**1**) in acetone just above the melting point (left) and at room temperature (right).

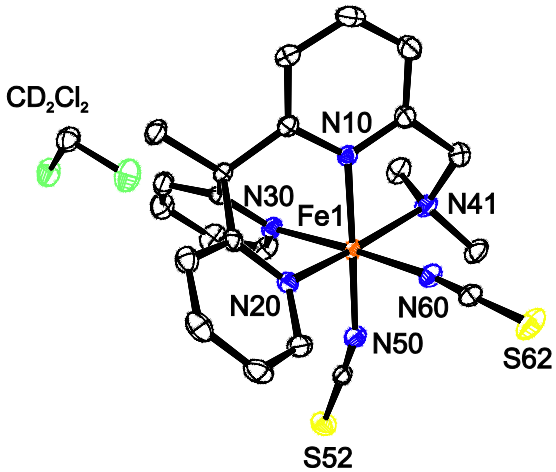

Fig. S2. ORTEP plot of **1** · CD_2Cl_2 at 150 K (ellipsoids of 50 % probability, hydrogen atoms omitted for clarity).

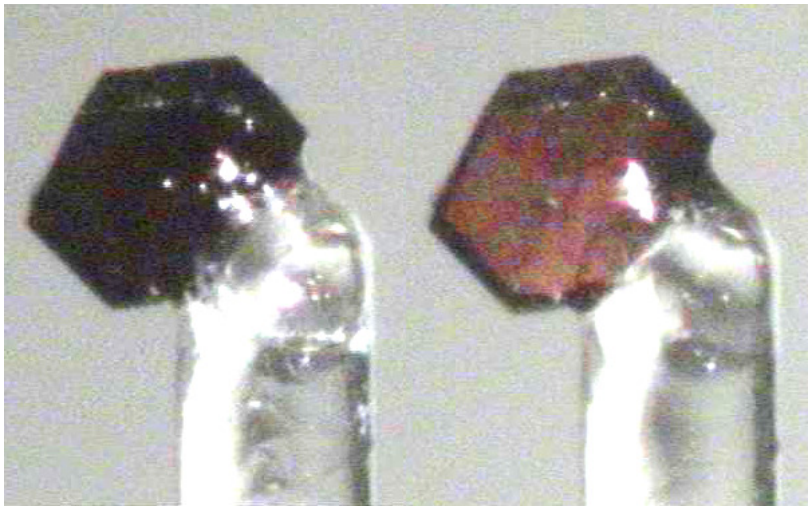

Fig. S3. Crystal of $[FeL(NCS)_2] \cdot CHCl_3$ (**1a**) at 150 K (left) and 300 K (right).

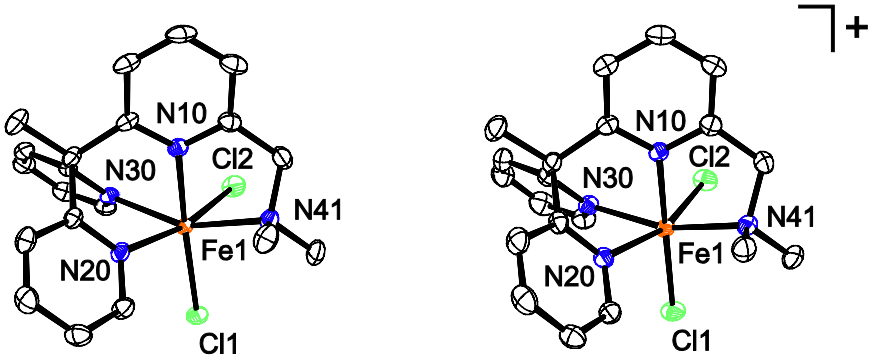

Fig. S4. ORTEP plots of $[FeCl_2L] \cdot CH_3OH$ (**2** · CH_3OH, left) and $[FeCl_2L]PF_6$ (**3**, right) at 150 K (ellipsoids of 50 % probability, solvent molecule, anion and hydrogen atoms omitted for clarity).

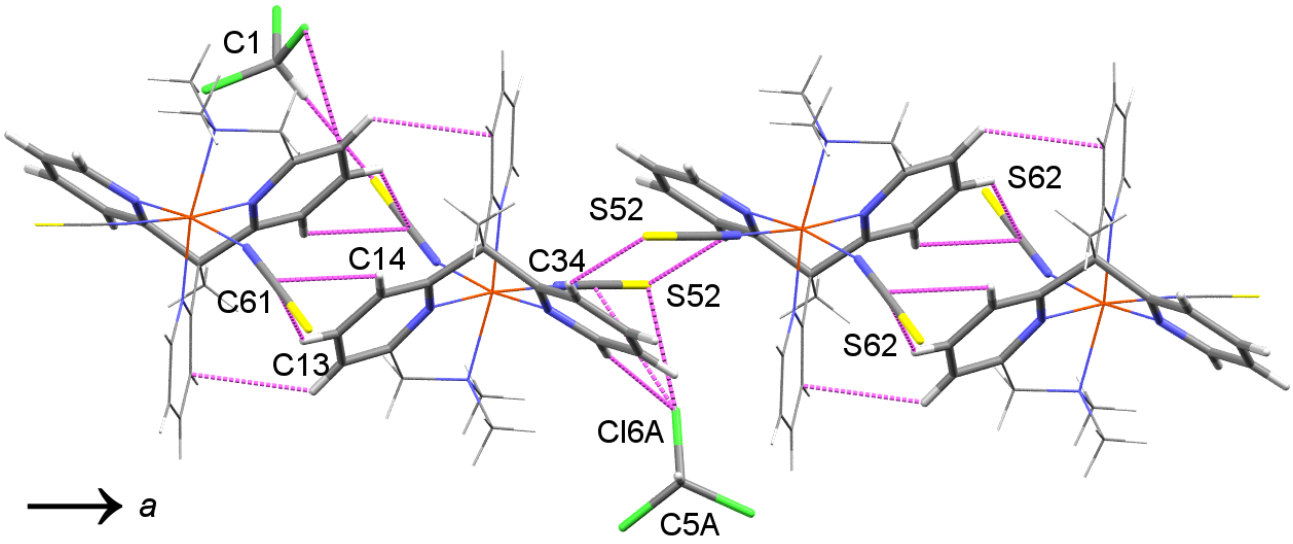

Fig. S5. MERCURY plot of structure detail in **1b** at 150 K: complex chain along [100] with two chloroform molecules (stick model, contacts as pink dashed lines, π stacking rings and thiocyanato ligands highlighted).

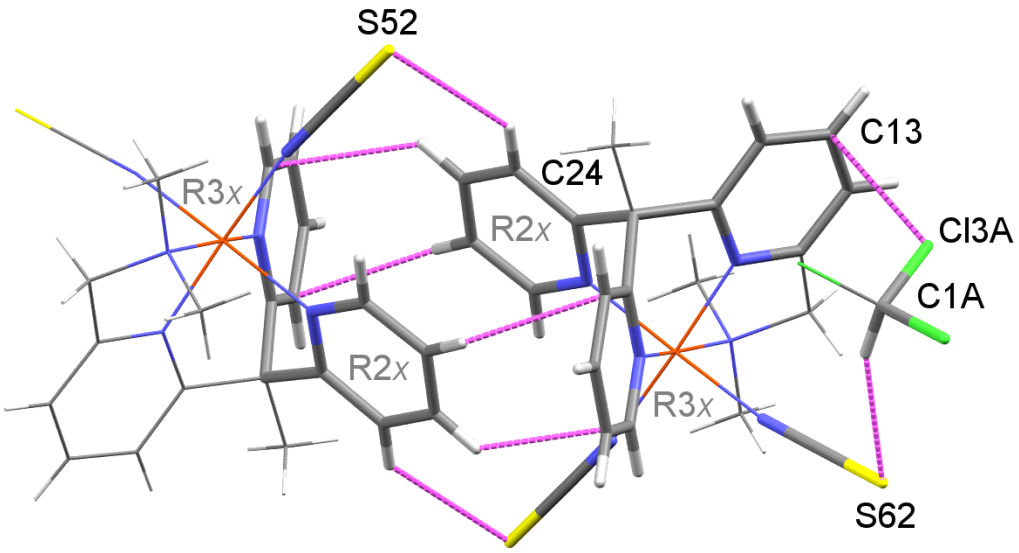

Fig. S6. MERCURY plot of structure detail in **1a** at 150 K: complex dimer with chloroform molecule (stick model, contacts as pink dashed lines, interacting parts highlighted).

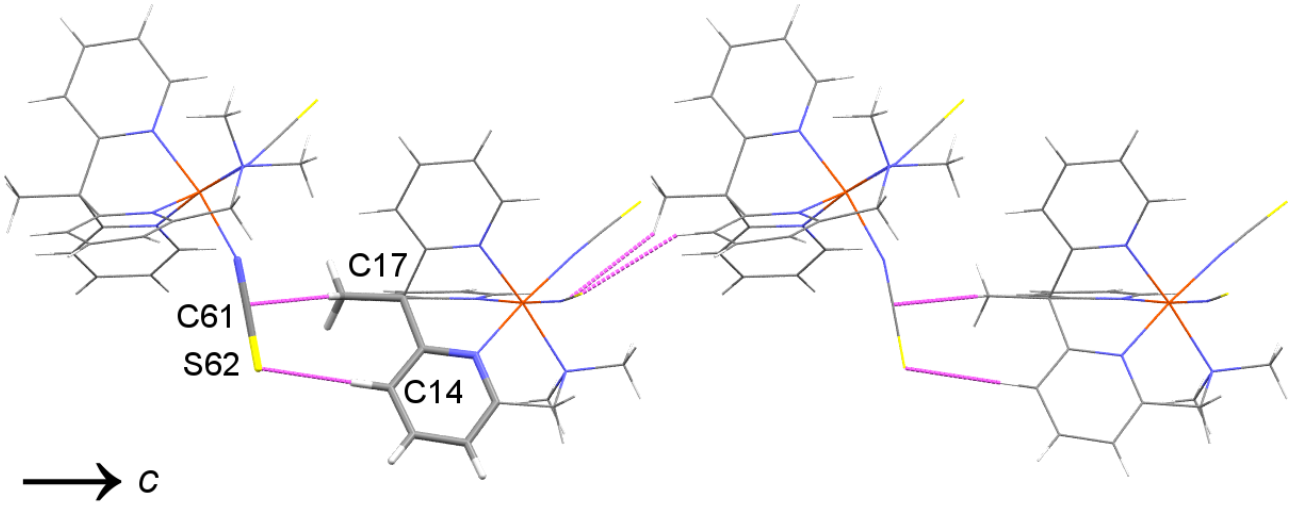

Fig. S7. MERCURY plot of structure detail in **1a** at 150 K: zigzag chain along [001] internally interacting *via* thiocyanato ligands (stick model, contacts as pink dashed lines, interacting parts highlighted).

Analysis of the Thermal-Expansion Tensor of 1a

$$x = p_0 + p_1 \cdot T$$

Table S1. Polynomial fit parameters for **1a** (thermal regime).

x	p_0	$p_1/10^{-3}$ K^{-1}
a/Å	18.052320	0.690928
b/Å	9.192367	0.762668
c/Å	16.167410	1.837536
β/°	105.433341	−3.794358
V/Å^3	2584.622000	672.095600

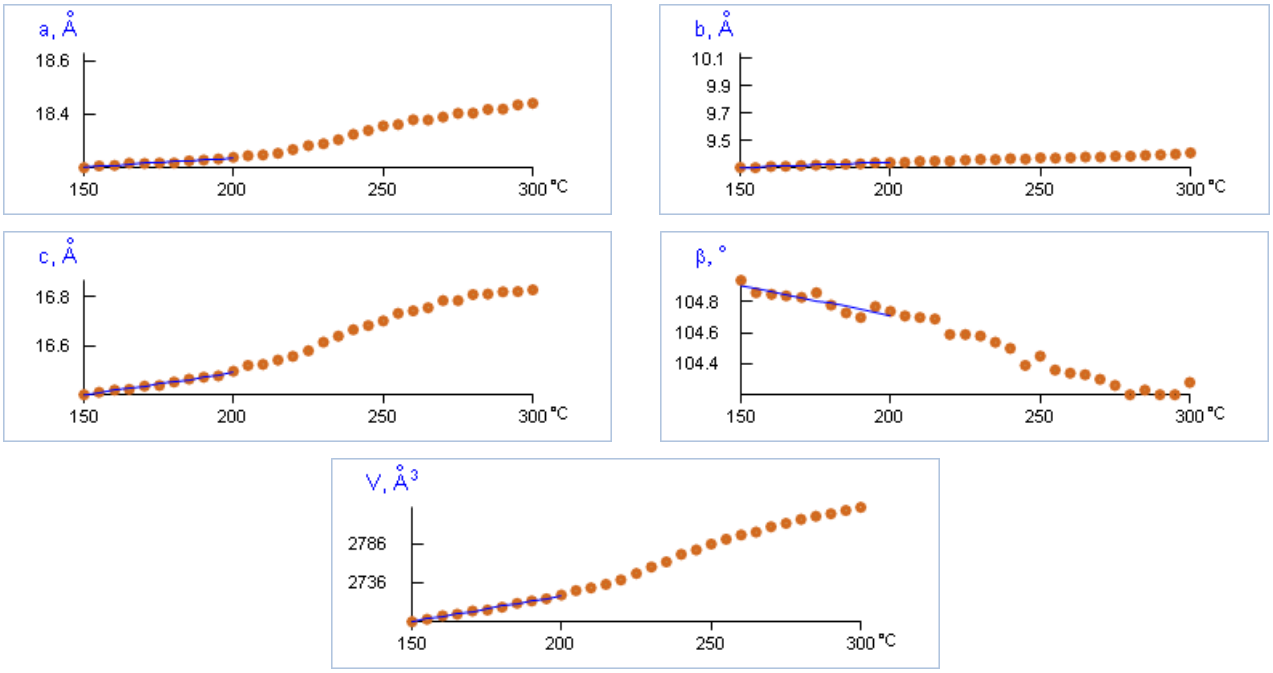

Fig. S8. Plots of cell constants and volume *vs.* temperature (in K) with polynomial fits for **1a** (thermal regime).

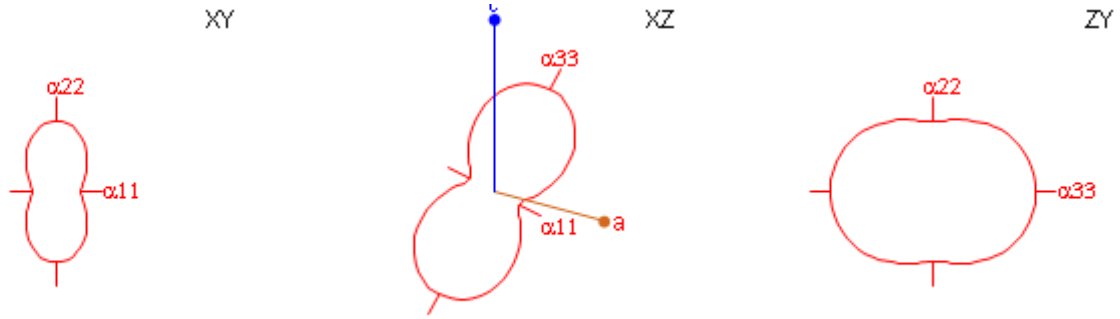

Fig. S9. Plots of slice planes through the isosurface representation of α for **1a** (thermal regime).

$$x = p_0 + p_1 \cdot T + p_2 \cdot T^2 + p_3 \cdot T^3$$

Table S2. Polynomial fit parameters for **1a** (SCO regime).

x	p_0	$p_1/10^{-3}$ K^{-1}	$p_2/10^{-6}$ K^{-2}	$p_3/10^{-9}$ K^{-3}
a/Å	20.431040	−35.511980	171.737300	−254.781600
b/Å	9.249759	0.507555	0	0
c/Å	13.915800	18.530860	−28.751820	0
β/°	124.372062	−220.841267	832.772191	−1077.474933
V/Å^3	1976.989000	5166.064000	−7732.078000	0

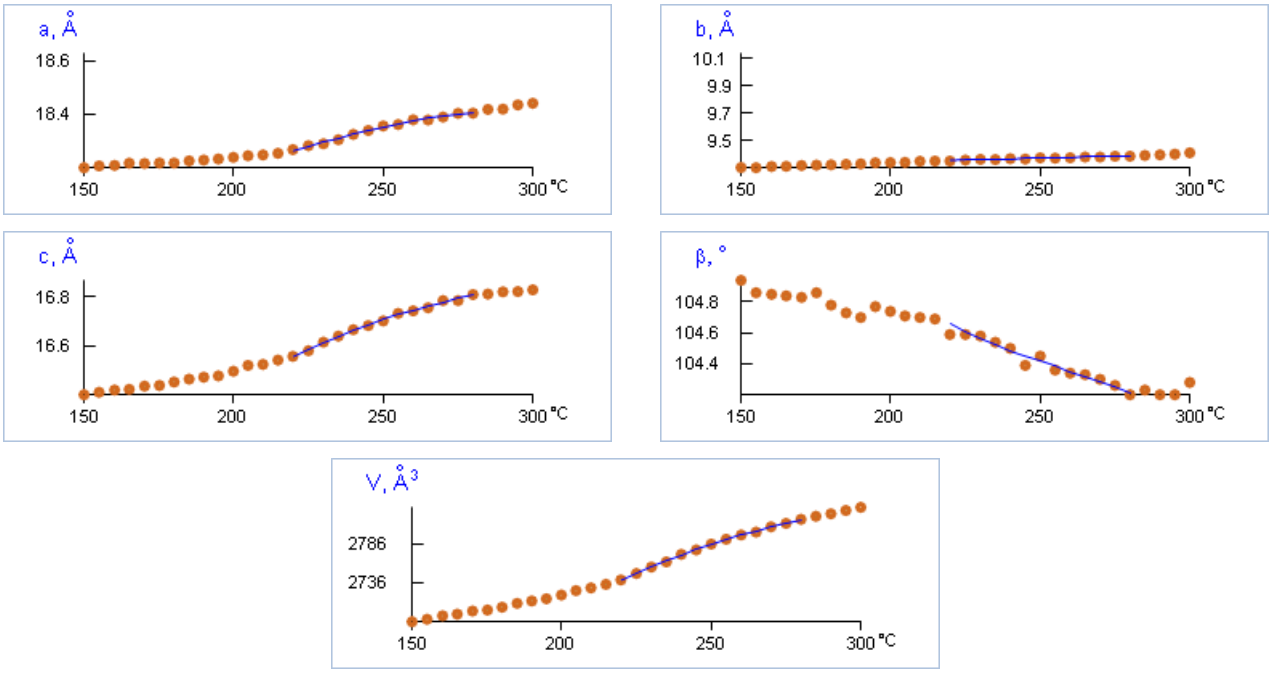

Fig. S10. Plots of cell constants and volume *vs.* temperature (in K) with polynomial fits for **1a** (SCO regime).

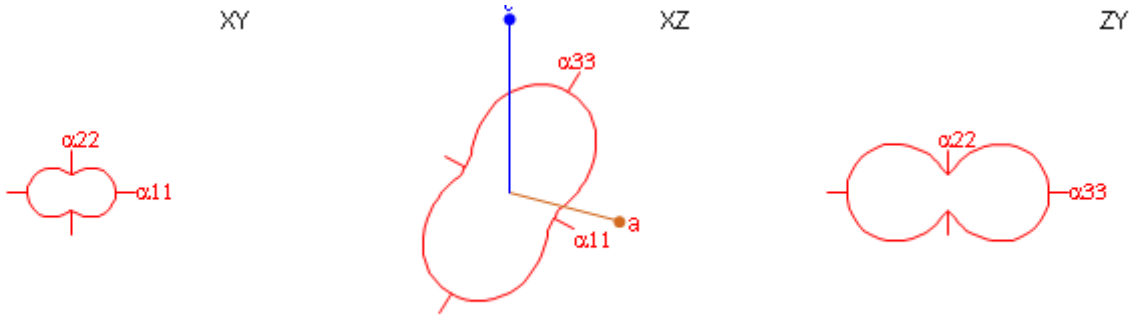

Fig. S11. Plots of slice planes through the isosurface representation of α for **1a** (SCO regime).

Analysis of the Thermal-Expansion Tensor of 1b

$$x = p_0 + p_1 \cdot T$$

Table S3. Polynomial fit parameters for **1b** (thermal regime).

x	p_0	$p_1/10^{-3}$ K^{-1}
a/Å	13.704340	0.548125
b/Å	15.309980	1.122647
c/Å	14.270460	1.656687
β/°	92.059393	−3.525024
V/Å^3	2990.535000	710.340500

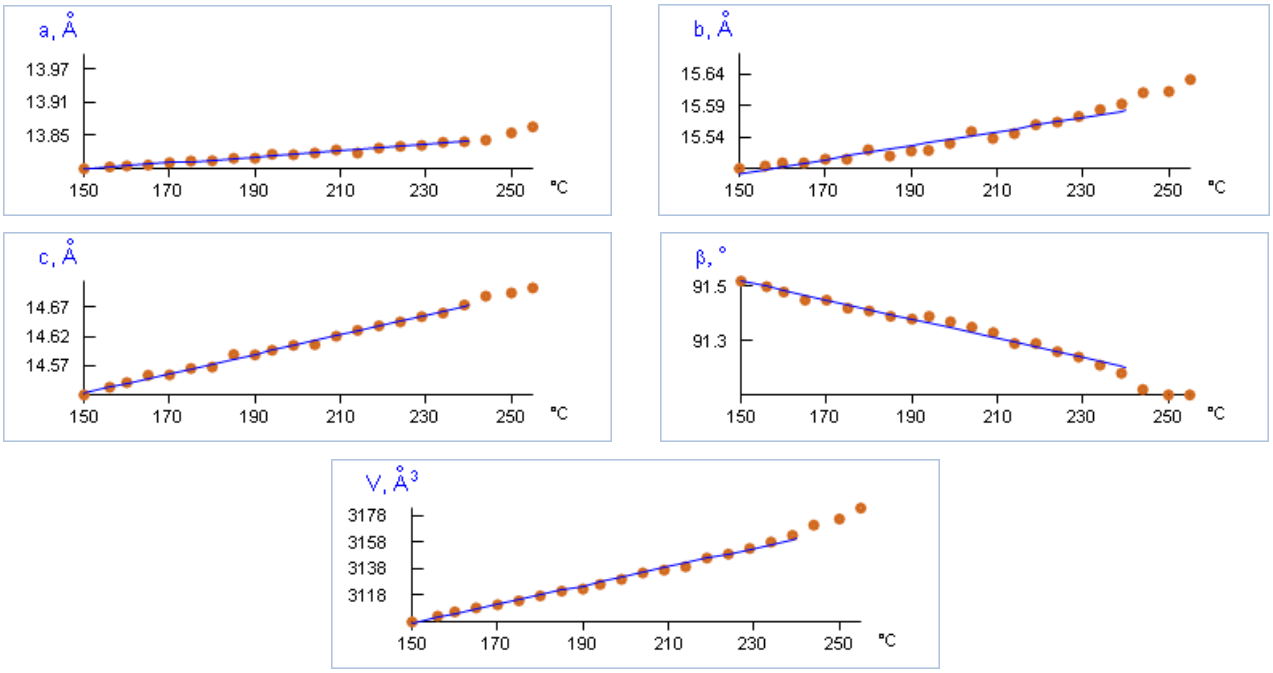

Fig. S12. Plots of cell constants and volume *vs.* temperature (in K) with polynomial fits for **1b** (thermal regime).

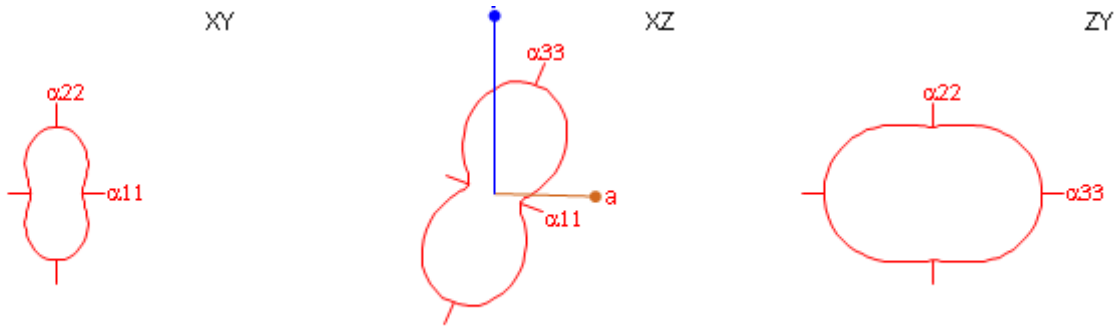

Fig. S13. Plots of slice planes through the isosurface representation of α for **1b** (thermal regime).