Electronic Supplementary Material (ESI) for Dalton Transactions

Thermally and photo-induced spin crossover behaviour in an Fe(II) imidazolylimine complex: $[FeL_3](ClO_4)_2$

John R. Thompson, Rosanna J. Archer, Chris S. Hawes, Alan Ferguson, Alain Wattiaux, Corine Mathonière, Rodolphe Clérac,* and Paul E. Kruger*

Electronic Supporting Information (ESI)

Fig. S1. Molecular structure and atomic numbering scheme for **L** at 113 K.

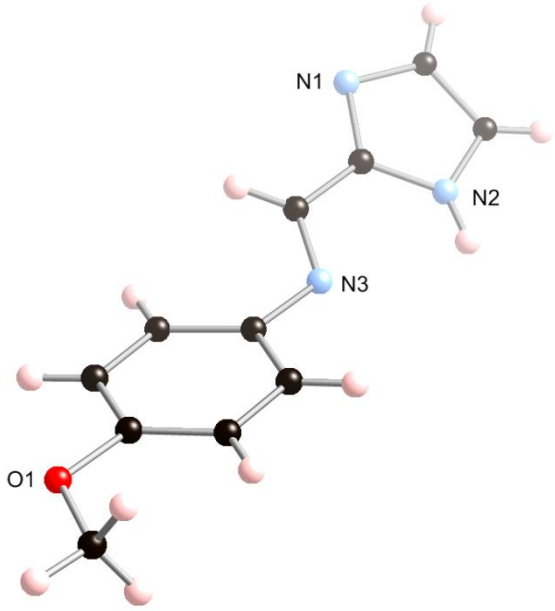


Table S1. X-ray crystallography data for **L** at 113 K

Temperature/ K	113(2)
Chemical formula	$C_{11}H_{11}N_3O$
Formula Mass	201.23
Crystal System	Orthorhombic
a/ Å	5.0830(2)
b/ Å	8.1957(4)
c/ Å	24.4759(12)
α/ °	90
β/ °	90
γ/ °	90
Unit cell volume/ Å^3	1019.64(8)
Space group	$P2_12_12_1$
Z	4
λ/Å	0.71073
μ/mm^{-1}	0.088
N_{obs}	17679
N_{unique}	1804
R_{int}	0.0457
$^aR_1$	0.0464
$^awR_2$	0.1212
Goodness of fit on F^2	1.148

^{a} $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$

Fig. S2. Molecular structure of **1** illustrating the intra-molecular C-H···π interaction between adjacent methoxy-benzene rings.

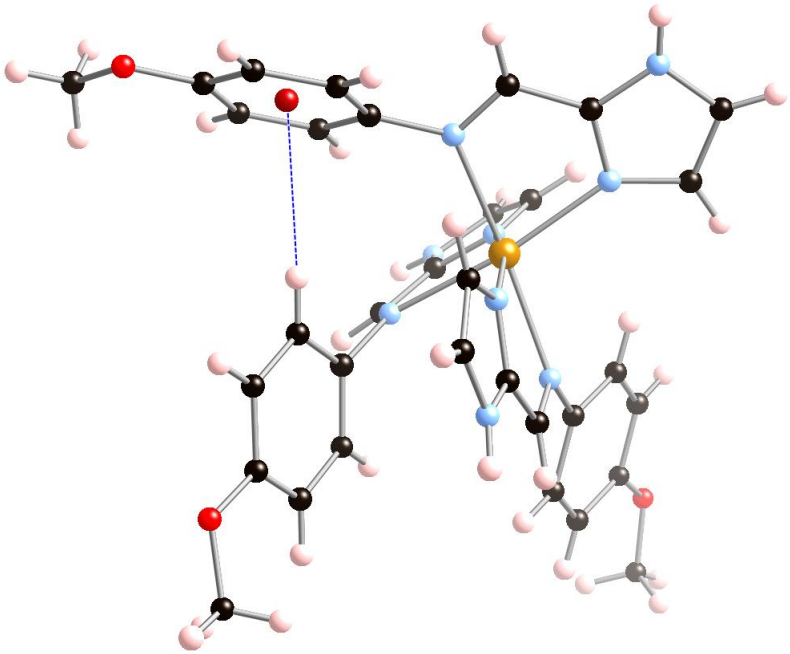


Table S2. Parameters of hydrogen bonding interactions within **L** (113 K) and **1** (116 K).

D–H…A	D–H/Å	*d*(H…A)/Å	*d*(D…A)/Å	<(DH…A)/°
L				
N2–H2…N1^{i}	0.86	2.07	2.887(3)	159
1				
N2–H2…O10^{ii}	0.86	2.23	3.056(5)	162
N2–H2…O11^{ii}	0.86	2.43	3.130(4)	138
N5–H5…O9^{iii}	0.86	2.22	2.961(4)	144
N8–H8…O4	0.86	2.12	2.922(4)	155

Symmetry codes: i = 1+x, y, z; ii = 2-x, -y, -z; iii = -1+x, y, z.

Fig. S3. Spin crossover induced octahedron distortion [1]:

The spin crossover from LS to HS state also corresponds to the deformation of the FeN_6 octahedron. Such a deformation of the FeN_6 octahedron is mostly evident from the variation of the N-Fe-N angles. A useful parameter to index the degree of distortion is Σ. The Σ parameter derives from the N-Fe-N angles as it is the sum of the deviations from 90° of the 12 *cis*-N-Fe-N angles in the coordination sphere. Σ is equal to 0 for an ideal octahedron and increases with the deformation. The variation at the spin crossover, ΔΣ, may appear between 30%-55% depending on complex.

The ΔΣ in the current example, **1**, at 116 and 292 K is *ca*. 35%, see Table S1.

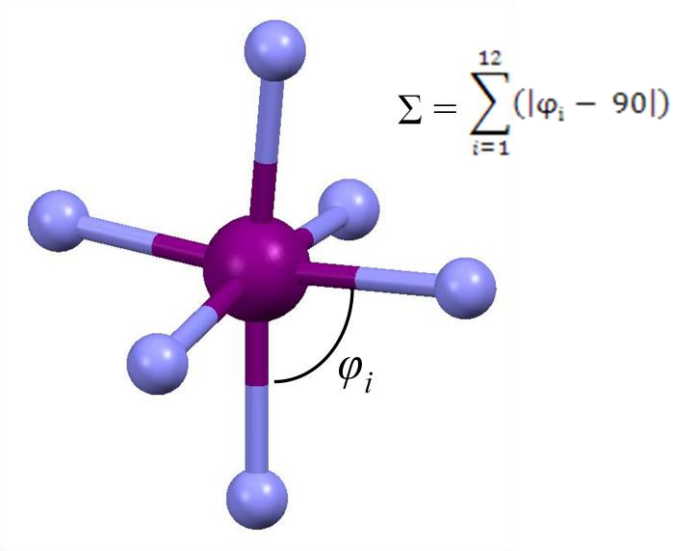


Table S3. Selected bond lengths for **1** at 116 and 292 K and the corresponding values of Σ as defined above.

T (K)	*Fe*−$N_{imidazole}$ (Å)		*Fe*−N_{imine} (Å)		*Σ*	*% Change*
116	N1	1.995	N3	2.051	73.3	
	N4	2.000	N6	2.067		
	N7	2.018	N9	2.078		34.8
292	N1	2.128	N3	2.250	98.8	
	N4	2.140	N6	2.231		
	N7	2.135	N9	2.266		

Fig. S4. The Mössbauer spectra recorded at 293 K (top) and 4.2 K (bottom).The deduced parameters from the simulations of the data are given in Tables S1 and S2.

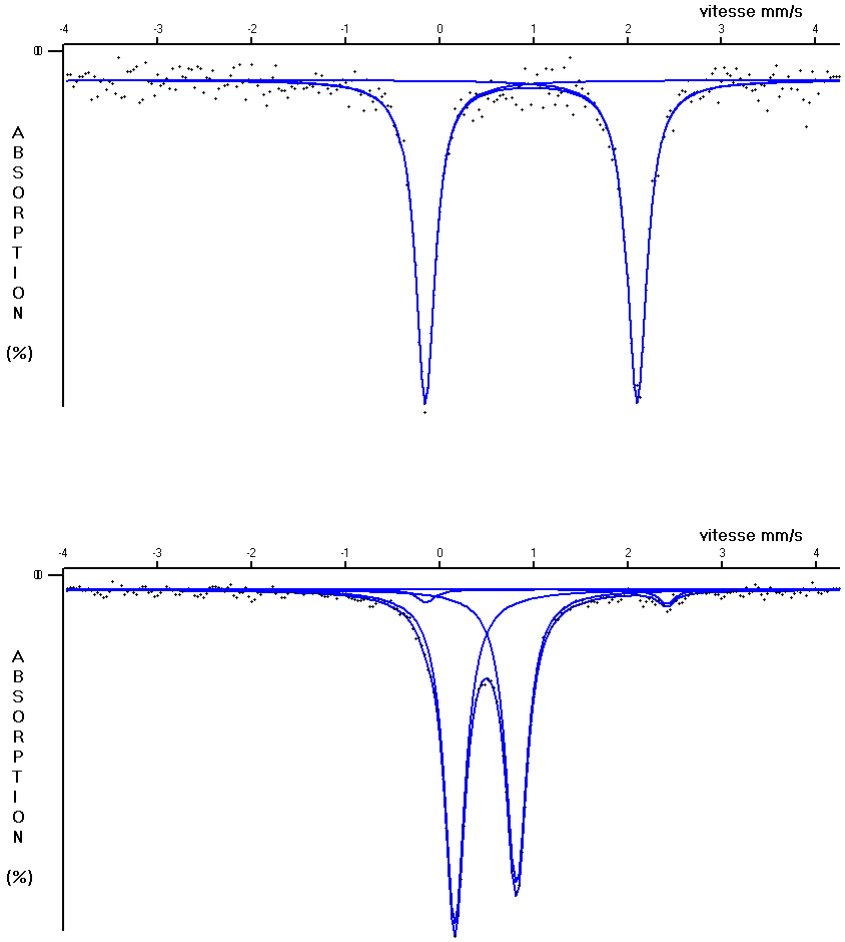


Table S4. Hyperfine parameters for **1** at 293 K

Site	δ (mm/s)	Γ (mm/s)	Δ (mm/s)	%	Site
1	0.96(2)	0.25(2)	2.26(2)	100	Fe^{2+} HS

Table S5. Hyperfine parameters for **1** at 4.2 K.

Site	δ (mm/s)	Γ (mm/s)	Δ (mm/s)	%	Site
1	1.1(1)	0.26(1)	2.5(1)	3	Fe^{2+} HS
2	0.47(1)	0.263(3)	0.66(1)	97	Fe^{2+} LS

Fig. S5. The first derivative of χT against the temperature, $d\chi T/dT$ *vs.* T, identifies $T_{1/2}$ = 158 K. Both heating and cooling modes give identical magnetic responses showing that the observed spin crossover is perfectly reversible.

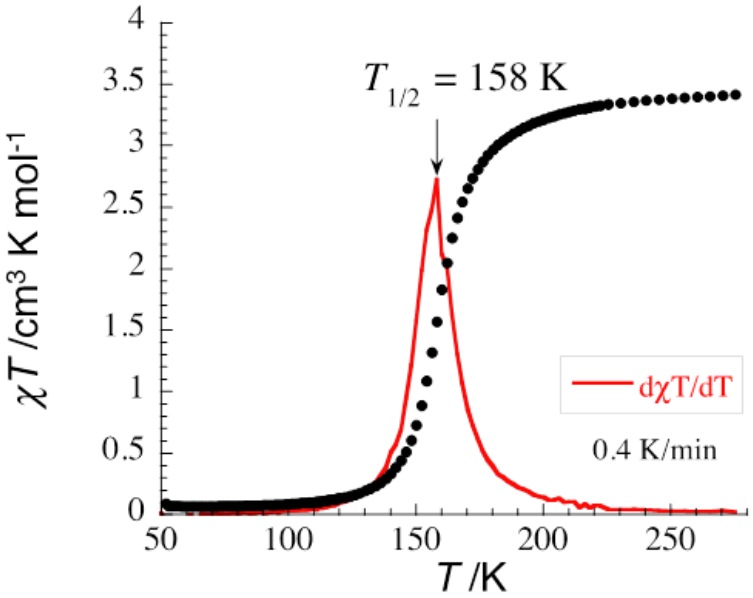
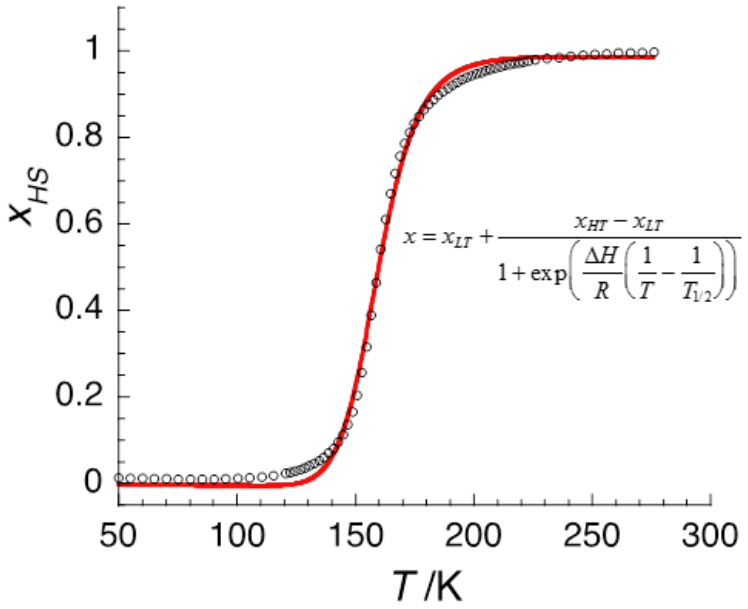


Fig. S6. The x_{HS} (= $\chi T/\chi T_{HT}$) *vs.* T data fit to the ideal solution model, Equation 1.



The best fit (red line and equation on the figure) was obtained with the following parameters: the enthalpy change ΔH associated with the spin-crossover phenomenon is equal to 24.7(1) kJ/mol, $T_{1/2}$ equal to 159(1) K, and the entropy changes calculated as $\Delta S = \Delta H / T_{1/2}$ = 155 J/K/mol.

Fig. S7 Reflectivity spectra at 10 K during a white light irradiation (0.05 mW/cm^2).

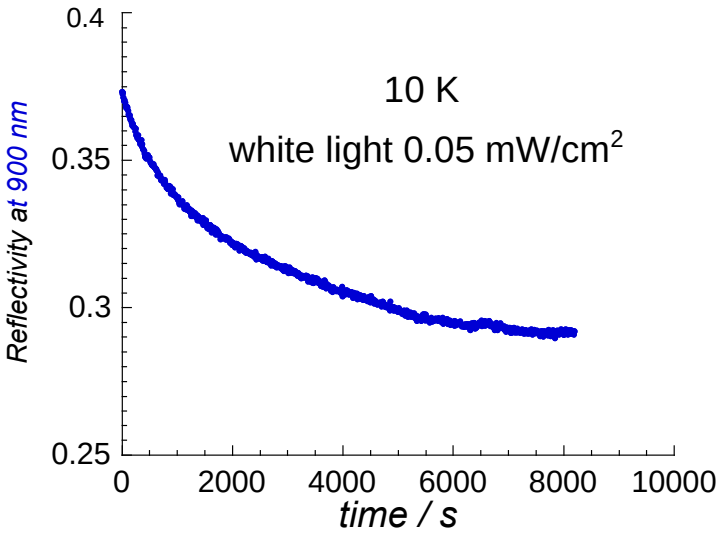
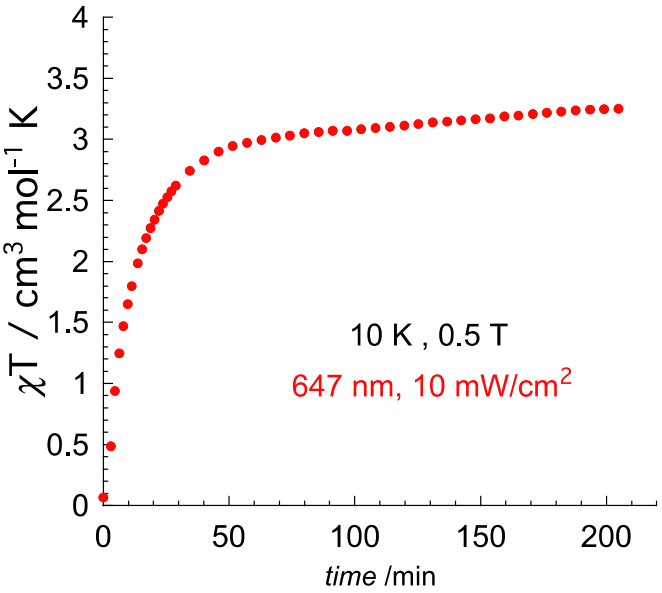


Fig. S8 The time dependence of the χT product at 10 K under 0.5 T, which starts at 0.17 cm^3.K/mol to around 3.35 cm^3.K/mol after 3.5 hours under a red light (647 nm) irradiation.



References:

[1] *Spin Crossover in Transition Metal Compounds II*, P. Guionneau, M. Marchivie, G. Bravic, J. F. Létard, D. Chasseau, *Top. Curr. Chem.*, **2004**, 234, 97.