Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Material for:

Ligand effects in an Heteroleptic bis-Tridentate Iron (III) Spin Crossover Complex showing a Very High $T_{1/2}$ Value

Wasinee Phonsri,[a] Victor Martinez,[a] Guy N. L. Jameson,[b] Casey G. Davies,[b] Boujemaa Moubaraki,[a] and Keith S. Murray[a*]

[a]School of Chemistry Building 23 Monash University Clayton Victoria, 3800 Australia

[b]Department of Chemistry University of Otago PO Box 56, Dunedin New Zealand

E-mail: keith.murray@monash.edu

General

All reagents and solvents were purchased from Sigma–Aldrich and used as received. Infrared spectra were measured with a Bruker Equinox 55 FTIR spectrometer fitted with a 71Judson MCT detector and Specac Golden Gate diamond ATR. Mass spectrometry analyses were performed using electrospray ionization mass spectra (ESI-MS) and were recorded with a Micromass (now Waters) ZMD with Waters alliance e2695 HPLC system for automatic sample injections. MeOH was the mobile phase and had a flow rate of 100 μL min^{-1}. Microanalyses were performed by Campbell Microanalytical Laboratory, Department of Chemistry, University of Otago, Dunedin, New Zealand. Variable-temperature magnetic susceptibility data were collected with either a Quantum Design MPMS 5 superconducting quantum interference device (SQUID) magnetometer or a MPMS XL-7 SQUID magnetometer, with a scan speed of 10 K min^{-1} followed by a one minute wait after each temperature change. In cases in which steps were less than 10 K the target temperature was reached in less than 1 min; hence it takes longer to stabilise at the target temperature.

Mössbauer spectra were recorded on a spectrometer from SEE Co. (Science Engineering & Education Co., MN) equipped with a closed cycle refrigerator system from Janis Research Co. and SHI (Sumitomo Heavy Industries Ltd.). Data were collected in constant acceleration mode in transmission geometry. The zero velocity of the Mössbauer spectra refers to the centroid of the room temperature spectrum of a 25 μm metallic iron foil. Analysis of the spectra was conducted using the WMOSS program (SEE Co, formerly WEB Research Co. Edina, MN).

X-ray crystallographic measurements on **1** were collected at the Australian Synchrotron operating at approximately 16 keV (λ = 0.71073 Å). The collection temperature was maintained at specified temperatures using an open-flow N_2 cryostream. Data were collected using Blue Ice software.[1] Initial data processing was carried out using the XDS package.[2] CCDC numbers 1420398.

Table S1 Crystallographic data and structure refinement of **1**

	[Fe(3-OMe-SalEen)(thsa)]·
	100 K
Formula	$C_{20}H_{24}FeN_5O_3S$
Molecular weight / gmol-1	470.35
Crystal system	Triclinic
Space group	$P\bar{1}$
a / Å	8.3940 (17)
b / Å	9.3500 (19)
c / Å	13.675 (3)
α / °	82.26 (3)
β / °	73.44 (3)
γ / °	82.14 (3)
Cell volume / Å^3	1013.9 (4)
Z	2
Absorption coefficient / mm^{-1}	0.880
Reflections collected	27497
Independent reflections, R_{int}	5929, 0.0501
Max. and min. transmission	0.9913 and 0.9741
Restraints/parameters	1/277
Final R indices [$I>2\sigma(I)$]: R_1, wR_2	0.0401, 0.1123

Table S2 Intermolecular interaction distances, Å, [Fe(3-OMe-SalEen)(thsa)], **1,** at 100 K

Interactions	**100 K**
1D chain along *c* axis	
π-π	3.043
π-π	3.028
C17-H17··· O1	2.6365(15)
C17-H17··· O2	2.6397(17)
C19-H19··· O2	2.4515(16)
1D chain along *a* axis	
π-π	3.690
C8-H8···S1	2.8065(11)
N4-H4B···O2	2.5575(16)
N4-H4A···N5	2.1275(15)
1D chain along *b* axis	
C3-H3A···π	2.656
C12-H12A···π	2.918

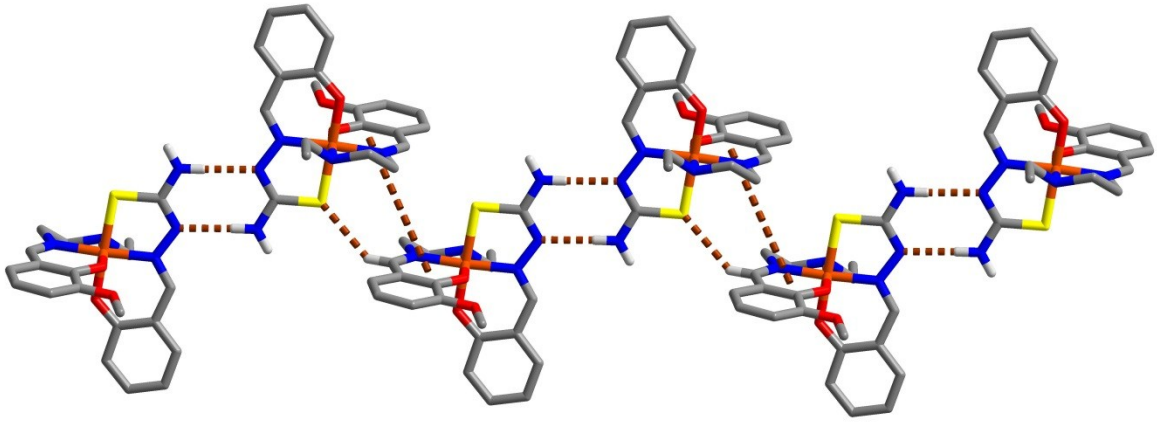

Figure S1 N-H···N and π-π interactions connecting the adjacent π-π chains in an ac plane

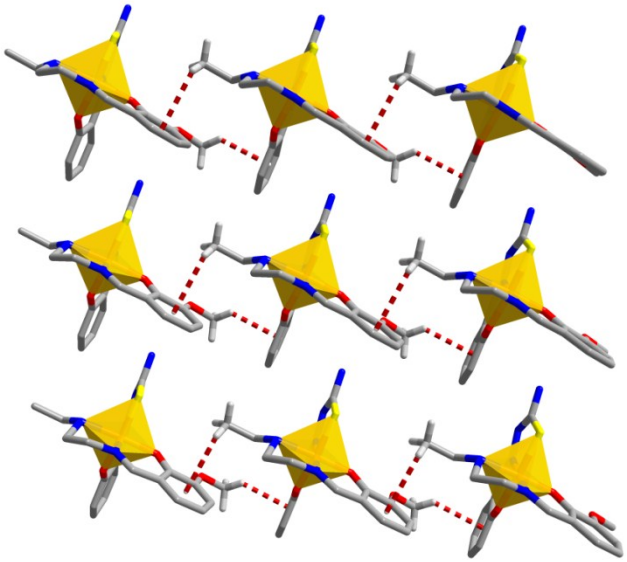

Figure S2 C-H···π interaction in [Fe(3-OMe-SalEen)(thsa)] **1** that connect the metal centres along the *b* axis into higher dimensionlity

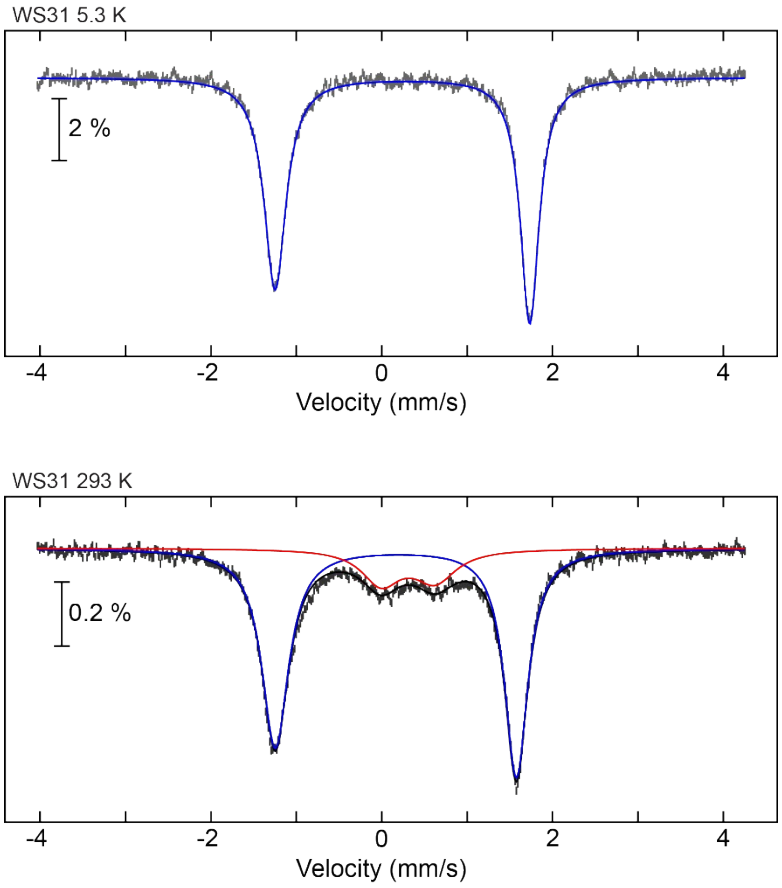

Figure S3 ^{57}Fe Mössbauer spectra for **1** at 5.3 K (top) and 293 K (bottom)

Table S3 ^{57}Fe Mössbauer spectral parameters for **1**

T (K)	Spin State	δ(mm/s)	ΔE_Q (mm/s)	Γ(mm/s)	I (%)
5.6	LS	0.24	2.98	0.31(0.27)	100
293	LS	0.16	2.82	0.38(0.31)	80
	HS	0.31	0.63	0.55(0.60)	20

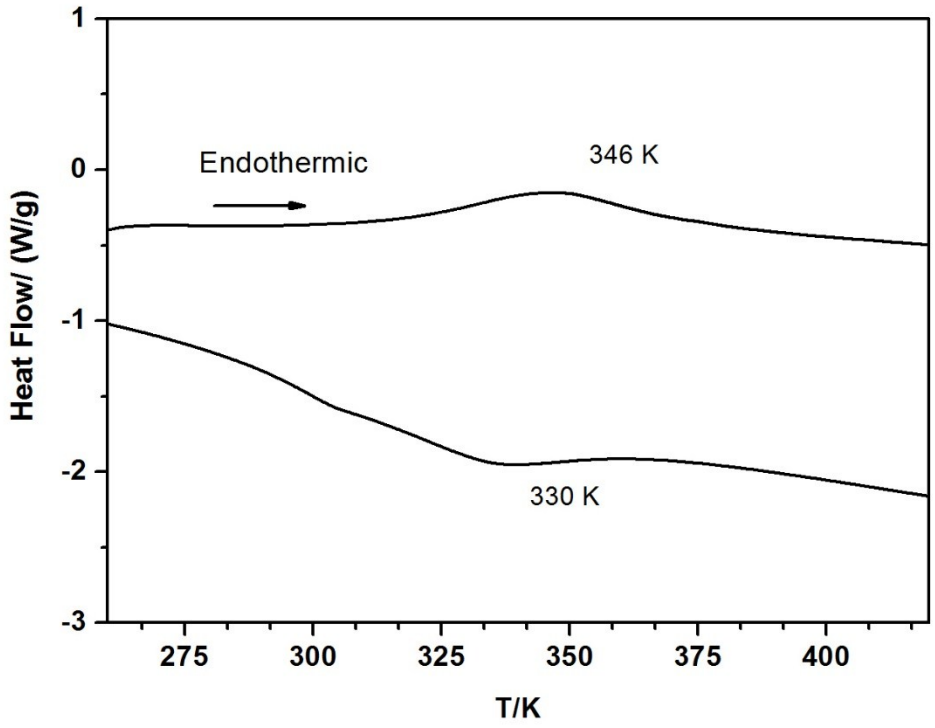

Figure S4 DSC plot for compound **1**

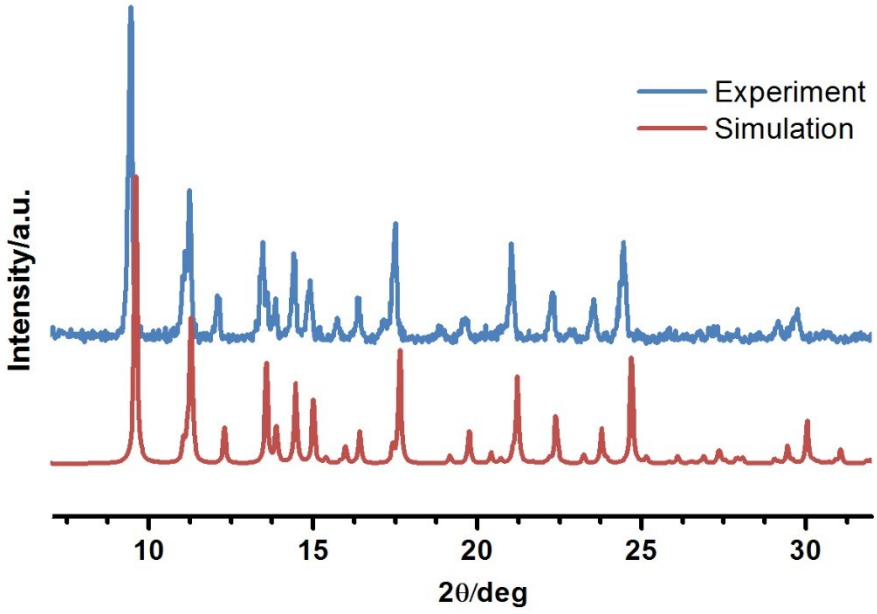

Figure S5 PXRD of bulk sample of **1** comparing to the simulated single crystral X-ray diffraction data

References

1. T. M. McPhillips, S. E. McPhillips, H.-J. Chiu, A. E. Cohen, A. M. Deacon, P. J. Ellis, E. Garman, A. Gonzalez, N. K. Sauter, R. P. Phizackerley, S. M. Soltis and P. Kuhn, *J. Synchrotron Radiat.*, 2002, **9**, 401-406.
2. W. Kabsch, *J. Appl. Crystallogr.*, 1993, **26**, 795-800.
3. Ablov AV, Goldanskii VI, Turta KI, Stukan RA, Zelentsov VV, Ivanov EV and G. NV, *Dokl Akad Nauk SSSR*, 1971, **196**, 1101.
4. Zelentsov VV, Ablov AV, Turta KI, Stukan RA, Gerbeleu NV, Ivanov EV, Bogdanov AP, Barba NA and B. VG, *Russ J Inorg Chem*, 1972, **17**, 1000.
5. Ivanov EV, Zelentsov VV, Gerbeleu NV and A. AV, *Dokl Akad Nauk SSSR*, 1970, **191**, 827.
6. N.A.Ryabova, V.I.Ponomarev, V.V.Zelentsov and L.O.Atovmyan, *Kristallografiya(Russ.)(Crystallogr.Rep.)* 1981, **26**, 101.
7. E. W. T. Yemeli, G. R. Blake, A. P. Douvalis, T. Bakas, G. O. R. Alberda van Ekenstein and P. J. van Koningsbruggen, *Chem. Eur. J.*, 2010.
8. C. Faulmann, K. Jacob, S. Dorbes, S. Lampert, I. Malfant, M.-L. Doublet, L. Valade and J. A. Real, *Inorg. Chem.*, 2007, **46**, 8548-8559.
9. S. Hayami, S. Miyazaki, M. Yamamoto, K. Hiki, N. Motokawa, A. Shuto, K. Inoue, T. Shinmyozu and Y. Maeda, *Bull. Chem. Soc. Jpn.*, 2006, **79**, 442-450.
10. A. Tissot, R. Bertoni, E. Collet, L. Toupet and M.-L. Boillot, *J. Mater. Chem.*, 2011, **21**, 18347-18353.