

Isomeric Fe(II) MOFs: from a diamond-framework spin-crossover material to a 2D hard magnet

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Electronic Supporting Information

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General experimental details

All chemicals were sourced commercially and were used without additional purification. Infrared spectra were recorded on a Perkin Elmer spectrum 100. UV-vis spectra were obtained as methanol solutions in a quartz cell of path length 1 cm, using a Jasco V-660 spectrometer.

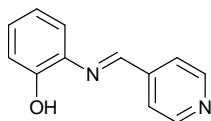
The Mössbauer spectrum was recorded in zero magnetic field at 80 K on an ES-Technology MS-105 Mössbauer spectrometer with a 100 MBq ^{57}Co source in a rhodium matrix at ambient temperature. The spectrum was referenced against a 25 μm iron foil at 298 K and spectrum parameters were obtained by fitting with Lorentzian curves. The sample was prepared under a dry nitrogen atmosphere by grinding with boron nitride powder prior to mounting in the sample holder. Elemental analyses were performed by Warwick Analytical Services.

Magnetisation measurements were made as a function of temperature (T) and applied magnetic field (H) using a Quantum Design MPMS-5 SQUID magnetometer. Samples were randomly orientated powders placed in Kel-F capsules. The capsule was centred using a pure Ni sample. The data were corrected for the measured diamagnetism of the capsule and the diamagnetic contributions of the sample using Pascal's constants.^[1]

For X-ray crystallography, single crystals were coated in inert oil prior to transfer to a cold nitrogen gas stream on an Oxford Diffraction Gemini four-circle system with Ruby CCD area detector and held at 100(2) K with the Oxford Cryosystem Cobra cryocooler. Structures were solved by direct methods (SHELXTL) with additional light atoms found by Fourier methods. All non-hydrogen atoms were added at calculated positions and refined using a riding model.

Synthetic Procedures

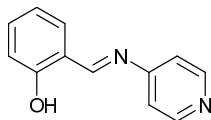
Preparation of 2-((pyridin-4-yl)methyleneamino)phenol (HL¹)



HL¹

Isonicotinaldehyde (1.07 g, 10.0 mmol), 2-aminophenol (1.09 g, 10.0 mmol) were stirred in methanol (40 mL) overnight. The volume was reduced to *ca* 20 mL under reduced pressure. The resulting solid was isolated by filtration and washed with cold hexane. (Yield 1.80 g, 91 %.) NMR data corresponded with the literature report.^[2]

Preparation of N-salicylidene-4-aminopyridine (HL²)



HL²

A 250 mL round-bottom flask fitted with a PTFE stopcock sidearm was charged with a suspension of salicylaldehyde (2.44 g, 20.0 mmol) and 4-aminopyridine (0.94 g, 10 mmol) in dry toluene (200 mL). A Soxhlet extractor and condenser equipped with excess CaH₂ thimble was fitted. The condenser outlet was fitted with a T-joint allowing the reaction to be performed under an atmosphere of dry dinitrogen. The system was heated to reflux for 3 d. Toluene was removed to *ca.* 50 mL *in vacuo* under Schlenk conditions and the solution was left overnight. The resulting yellow precipitate was isolated by filtration (yield 1.5 g, 75 %). NMR data corresponded with literature report.^[3]

Preparation of [FeL¹₂]

HL¹ (0.36 g, 1.8 mmol) was stirred with NaH (0.13 g, 5.34 mmol) in dry THF (20 mL) overnight. The resulting pink solution was filtered *via* cannula into a solution of Fe₂Cl₄·3THF (0.21 g, 0.44 mmol) in dry THF (10 mL) at room temperature. The resulting deep red solution was stirred overnight at ambient temperature and evaporated to dryness. The MeCN extracts (2 × 20 mL) were filtered and DCM (10 mL) was added to induce

crystallization. The resulting brown solid was washed dried *in vacuo*. (yield 0.12 g, 30 %).

Elemental Analysis: Found (calculated for $C_{24}H_{18}FeN_4O_2$): C 63.73 (64.02), H 4.46 (4.03), N 12.39 (12.44) %.

IR (cm^{-1}): 3050 w, 2161w, 1596 m, 1581 m, 1556 w, 1471 vs, 1444 m, 1412 m, 1282 s, 1257 vs, 1174 w, 1145 w, 1119 w, 1034 w, 1000 w, 869 m, 812 s, 799 s, 725 vs, 694 w.

UV in MeCN (λ , nm; ϵ , $M^{-1}cm^{-1}$): 221 (23991), 282 (16420), 366 (12068)

Single crystals $[FeL^1_2] \cdot 1\frac{1}{4}(H_2O) \cdot \frac{1}{2}(MeOH)$ were grown from wet methanol.

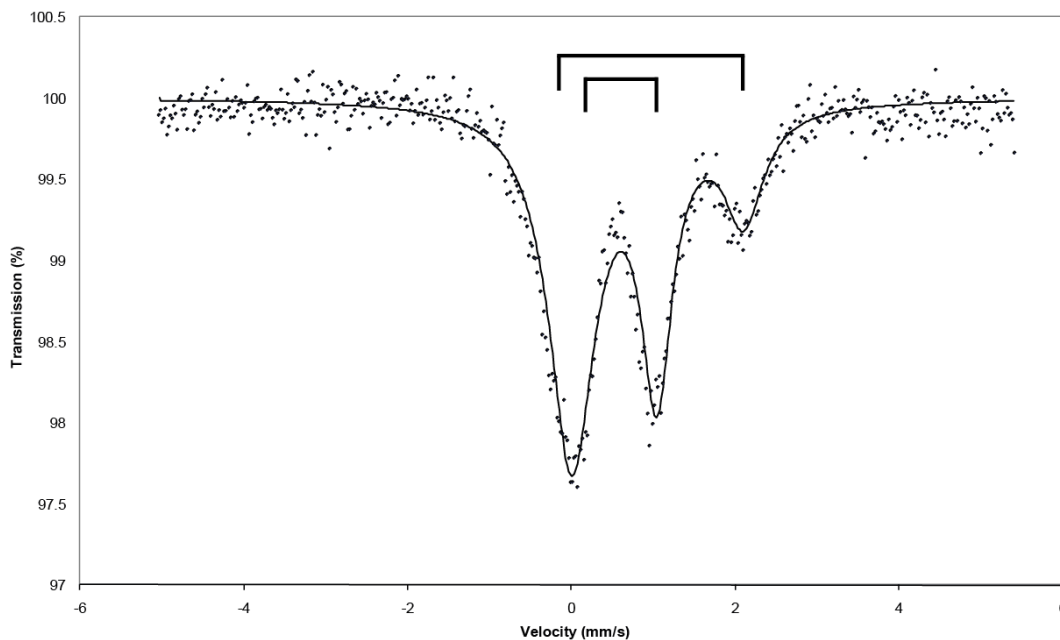
Preparation of $[FeL^2_2]_n$

A mixture of HL^2 (0.400 g, 2.0 mmol) and LiOMe (0.114 g, 3.0 mmol) in dry MeOH (20 mL) in a Schlenk tube was stirred for 30 min. To the mixture was added a solution of $FeCl_2$ (0.127 g, 1.0 mmol) in MeOH (10 mL) *via* a cannula. The resulting brown solution was stirred overnight at ambient temperature. The solid was collected by filtration and dried *in vacuo* for 4 h. (yield 0.42 g, 93 %). Single crystals were grown in an NMR tube using a small scale reaction with the starting materials having a concentration of 2.0 M.

Elemental Analysis: Found (calculated for $C_{24}H_{18}FeN_4O_2$): C 64.67 (64.02). H 4.48 (4.03), N 12.18 (12.44)%.

IR (cm^{-1}): 1580 vs, 1527 s, 1491 m, 1464 s, 1448 s, 1420 w, 1384 w, 1350 m, 1327 m, 1207 s, 1176 s, 1145 vs, 1125 w, 1089 w, 1059 w, 1027 w, 1008 m, 972 m, 922 s, 864s m, 837 s, 753 vs, 736 s, 658 w.

Mössbauer spectrum of $[\text{FeL}^1_2]_n$



Assignment	δ	ΔE_Q	Γ	%
HS Fe(II)	0.92	2.36(2)	0.32(2)	35(2)
LS Fe(II)	0.54	0.95	0.26	65(2)

Fig. S1. Mössbauer spectrum of complex 1 at 80 K showing high spin (HS) and low spin (LS) centers. δ = isomer shift, ΔE_Q = quadrupole splitting, Γ = half width at half maximum height, % shows relative amount of the two spin centers. Errors 0.01 mms^{-1} unless shown otherwise.

Layer structure of $[\text{FeL}_2]_n$

Fig. S. 2 depicts the mutual arrangement of the layers which are related by an a glide orthogonal to the c axis with the overall effect of reflecting and off-setting alternate layers in the stack. The undulations of the organic ligands are accommodated efficiently by interdigitation and no solvent is included (as confirmed by microanalysis). The Fe(1)-Fe(1) inter-plane distances are *ca* 11.2 Å and 10.9 Å.

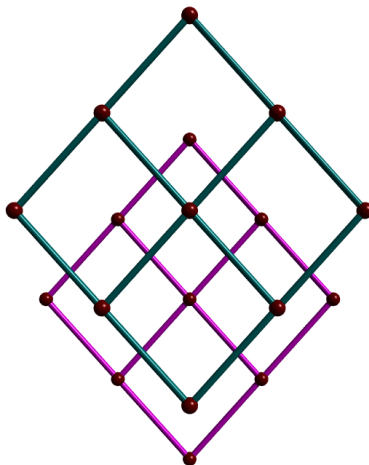
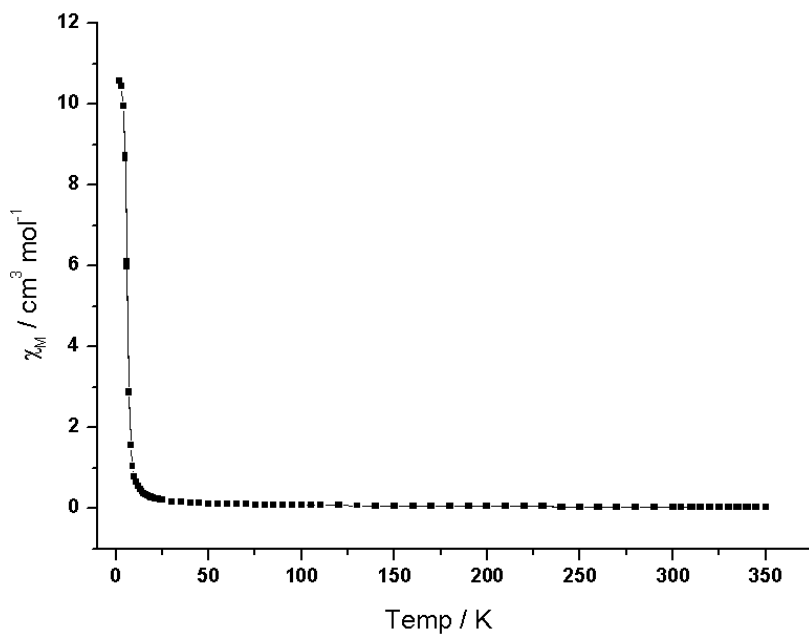


Fig. S2 Two adjacent layers in $[\text{FeL}_2]_n$ viewed along the c axis.

Magnetic data for $[\text{FeL}_2]_n$



S. 2. χ_M vs. T for $[\text{FeL}_2]_n$ measured at 1000 Oe

References

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- [2] H. Ö. Demir, İ. Kaya, M. Saçak, *Polym. Bull.* 2008, 60, 37.
- [3] F. Robert, A. D. Naik, B. Tinant, R. Robiette, Y. Garcia, *Chem. Eur. J.* 2009, 15, 4327.