When three is not a crowd: the first trinuclear complexes of N^4-substituted-3,5-dipyridyl-1,2,4-triazole ligands $[Fe^{II}_3(Rdpt)_4(NCS)_6]$

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Electronic Supporting Information (ESI)

General

The ligands, 4-methyl-3,5-di(2-pyridyl)-4*H*-1,2,4-triazole (**medpt**), 4-phenyl-3,5-bis(2-pyridyl)-triazole (**phdpt**) and 4-*iso*butyl-3,5-bis(2-pyridyl)-triazole (**ibdpt**) were prepared as described earlier.[20, 22, 39-41] $[Fe^{II}(pyridine)_4(NCS)_2]$ was prepared as described in the literature.[17] $Fe(BF_4)_2{\cdot}6H_2O$ and NaNCS were purchased from commercial sources and used as received. All complexation reactions were carried out under an inert argon or nitrogen atmosphere. All solvents were laboratory reagent grade except methanol. Methanol was dried by freshly distilling over magnesium and iodine before use.

Elemental analyses were carried out by the Campbell Microanalytical Laboratory at the University of Otago. Infrared spectra were recorded over the range 4000 – 400 cm^{-1} with a Perkin-Elmer Spectrum NBX FT-IR spectrophotometer as a potassium bromide pellet. ^{1}H and ^{13}C NMR spectra were recorded on either a Varian INOVA-500 or Varian INOVA-300 spectrometer at 25 °C. ESI mass spectra were recorded on a Bruker MicrOTOF$_Q$ spectrometer by Mr Ian Stewart.

^{57}Fe Mössbauer spectra were recorded at Otago on a WRC Mössbauer spectroscopy system by Dr Guy N. L. Jameson. Magnetic data were recorded continuously over the range 300 – 2 K with a Quantum Design Physical Property Measurement System equiped with a vibrating sample mount, using an applied field of 1 Tesla at Industrial Research Limited (IRL). Data were corrected for the diamagnetism of the sample and a background correction for the sample holder was applied. Sample masses used were 2.1 mg and 11.6 mg for **1** and **2**, respectively.

X-ray data were collected with a Bruker APEX II area detector diffractometer at the University of Otago using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The data were corrected for Lorentz and polarization effects and semi-empirical absorption corrections (SCALE) were applied. The structures were solved by direct methods (SHELXS-97) and refined against all F^2 data (SHELXL-97).[42] Hydrogen atoms, except those attached to oxygen atoms which were typically fixed and allowed to freely refine, were inserted at calculated positions and rode on the atoms to which they were attached and all non-hydrogen atoms were made anisotropic. Any deviation from this is stated in the relevant crystallographic information file.

Synthesis

$[Fe_3(phdpt)_4(NCS)_6]$

To a clear, colourless solution of **phdpt** (100 mg, 0.33 mmol) in 5 mL of methanol, under argon, was added, via syringe, a yellow solution of $[Fe(py)_4(NCS)_2]$ (80 mg, 0.165 mmol) in 3 mL methanol, resulting in a red solution that on stirring for 10-15 minutes yielded a pale yellow precipitate (55 mg, 39%). Found: C, 54.28; H, 3.09; N, 21.33; S, 11.33. Calcd. for $[Fe^{II}_3(C_{18}H_{13}N_5)_4(NCS)_6]$ (1713.35 gmol^{-1}): C, 54.68; H, 3.06; N, 21.26; S, 11.23%. IR (KBr): 3050, 2058 (C≡N), 1603, 1573, 1497, 1481, 1447, 1430, 1360, 1291, 1254, 1149, 1096, 1076, 1054, 1015, 1002, 796, 780, 723, 694, 640, 630, 612, 417 cm^{-1}.

$[Fe_3(ibdpt)_4(NCS)_6]$

To a clear, colourless solution of **ibdpt** (42 mg, 0.15 mmol) in 2 mL of methanol, under argon, was added, via syringe, a yellow solution of $[Fe(py)_4(NCS)_2]$ (36 mg, 0.075 mmol) in 1.5 mL methanol, resulting in a deep red solution that on stirring for 10-15 minutes yielded a dark red precipitate (24 mg, 39%). Found: C, 51.58; H, 4.51; N, 21.61; S, 11.84. Calcd. for $[Fe^{II}_2(C_{16}H_{17}N_5)_4(NCS)_6]$ (1633.39 gmol^{-1}): C, 51.47; H, 4.20; N, 22.30; S, 11.78%. IR (KBr): 2959, 2872, 2055 (C≡N; dilution in KBr followed by pressure to form the disk appears to have altered the spin states present), 1608, 1587, 1510, 1485, 1448, 1424, 1391, 1244, 1152, 1102, 995, 794, 744, 712, 601, 479 cm^{-1}.

Magnetic measurement diagrams

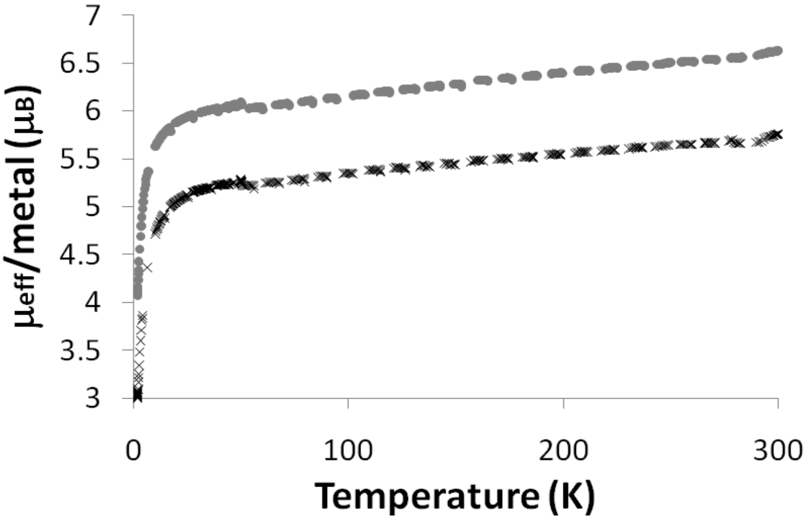

Figure S1: Magnetic moment per Fe(II) as a function of temperature for 1 (black xs) and **2** (grey circles).

Mössbauer Spectra

Experimental

^{57}Fe Mössbauer spectra were recorded by Dr. Guy N. L. Jameson at the University of Otago. Approximately 30 mg of sample was placed in a nylon sample holder (12.8 mm diameter, 1.6 mm thickness) with Kapton windows. Mössbauer spectra were measured on a Mössbauer 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 with an applied field of 47 mT perpendicular to the γ-rays. 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).

Table S1. The Mössbauer parameters for [Fe$^{II}_3$(**phdpt**)$_4$(NCS)$_6$] **1** and [Fe$^{II}_3$(**ibdpt**)$_4$(NCS)$_6$] **2** at 4.6 K.

Sample	*δ (mm s^{-1})*	*ΔE_Q (mm s^{-1})*	*Γ_L (mm s^{-1})*	*Γ_R (mm s^{-1})*	*I (%)*
1	1.16	3.04	0.30	0.30	100
2	1.00	2.86	0.23	0.25	35
	0.38	0.52	0.29	0.29	65

Crystal structure information for [$\mathrm{Fe_3}$(**phdpt**)$_4$(NCS)$_6$] (**1**)

Table S2. Crystal data and structure refinement for (**1**).

Empirical formula	$C_{78}H_{52}Fe_3N_{26}S_6$	
Formula weight	1713.37	
Temperature	91(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.3260(6) Å	α= 114.110(3)°.
	b = 14.0041(8) Å	β= 113.698(3)°.
	c = 14.1140(13) Å	γ = 96.908(2)°.
Volume	1914.7(2) Å^3	
Z	1	
Density (calculated)	1.486 Mg/m^3	
Absorption coefficient	0.789 mm^{-1}	
F(000)	876	
Crystal size	0.30 x 0.14 x 0.10 mm^3	
Theta range for data collection	1.76 to 26.46°.	
Index ranges	-15<=h<=15, -17<=k<=17, -17<=l<=17	
Reflections collected	30978	
Independent reflections	7763 [R(int) = 0.0428]	
Completeness to theta = 26.46°	98.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.6784	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7763 / 0 / 511	
Goodness-of-fit on F^2	1.070	
Final R indices [I>2sigma(I)]	R1 = 0.0364, wR2 = 0.0801	
R indices (all data)	R1 = 0.0462, wR2 = 0.0848	
Largest diff. peak and hole	0.402 and -0.325 e.Å^{-3}	

Packing Interactions in (**1**)

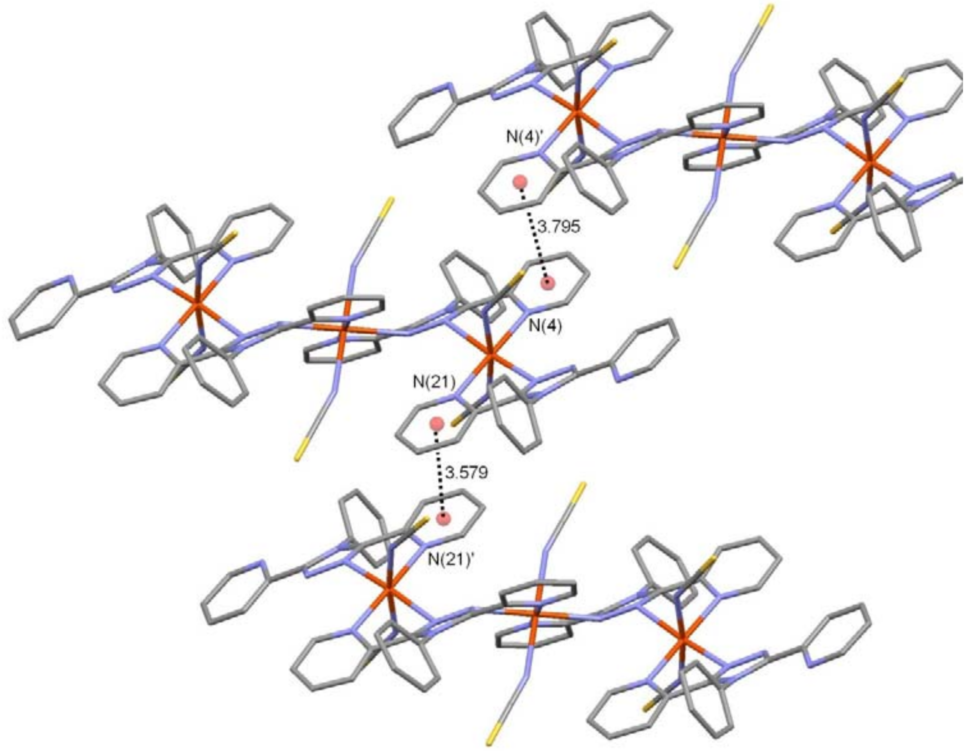

Figure S2: Perspective view of face to face π···π interactions in (1). Hydrogen atoms omitted for clarity.

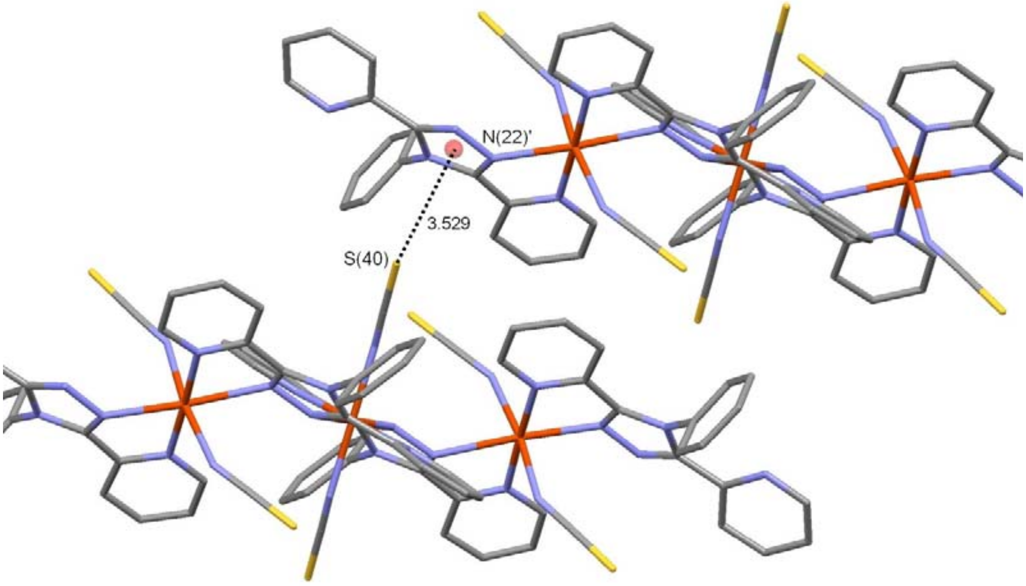

Figure S3: Perspective view of S···π interaction in (1). Hydrogen atoms omitted for clarity.