Electronic Supplementary Material (ESI) for CrystEngComm.

Co-Co and Co-Fe Cyano-bridged Pentanuclear Clusters Based on Methylpyrazinyl-Diamine Tetradentate Ligand: Spin Crossover and Metal Substitution Effects

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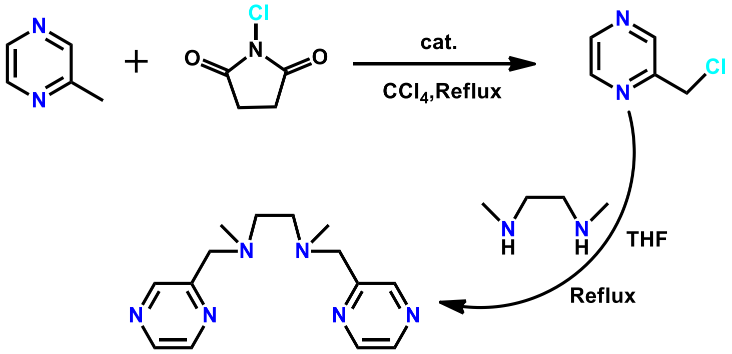
Synthesis of *N,N'*-dimethyl-*N,N'*-bis((2-pyrazinylmethyl)-1,2-ethanediamine ($^{2Me}L_{pz}$). To a solution of 4 g (42.5 mmol) of 2-methyl-pyrazine in 60 mL tetrachloromethane was added 8.10 g (60.8 mmol) of *N*-chlorosuccinimide and 0.51 g (2.12 mmol) of the catalyst benzoperoxide. The mixture was refluxed for 14 hours in dark. After the reaction was complete (monitored by TLC), the mixture was separated by filtration and the filtrate was concentrated in vacuo giving crude product 2-(chloromethyl)-pyrazine.[14] Then to a solution of 3.24 g (25.6 mmol) of 2-(chloromethyl)-pyrazine in 50 mL tetrahydrofuran was added 1.1 g (12.2 mmol) of *N,N'*-dimethyl-ethylenediamine and 5.1 g (52.0 mmol) of trimethylamine. The mixture was stirred for 24 hours at reflux and then added 30 mL aqueous solution of 3 M NaOH. After removal of the solvent in vacuum, the dark brown residue was extracted with dichloromethane (30 mL×3), then washed with saturated NaCl solution (15 mL) and purified on silica gel. Elution with ethyl acetate/methanol (ratio 10:1) followed by methanol/ammonia (ratio 10:1) solvent system afforded the $^{2Me}L_{pz}$ ligand (c.a. 50% yield). ^{1}HNMR (300 MHz, $CDCl_3$) δ: 8.69 (s, 2H), 8.52 (m, 2H), 8.47 (m, 2H), 3.75 (s, 4H), 2.68 (s, 4H), 2.31 (s, 6H).



Synthesis of $[Co^{II}(^{2Me}L_{pz})]_3[Co^{III}(CN)_6]_2$ (1). $CoCl_2{\cdot}6H_2O$ (0.024g, 0.01mmol), $^{2Me}L_{pz}$ (0.027g, 0.01mmol) and sodium cyanoborohydride (0.0124g, 0.02mmol) were mixed with an ethanol-acetonitrile mixture (15 mL, 1:4 ratio) in a Teflon-lined stainless steel autoclave (25 mL capacity). The solution was kept at 140 °C for 3 days and then cooled to room temperature at 5 ℃ h^{-1}. Finally, orange block crystals of **1** were obtained as a product. They were washed 3 times with ethanol and dried in air. Yield is 60%. Elemental analysis for dehydrated sample: calc. C 45.55, H 4.25, N 29.51; exp. C 45.31, H 4.45, N 29.08.

Synthesis of $[Fe^{II}_{2.1}Co^{II}_{0.9}(^{2Me}L_{pz})]_3[Co^{III}(CN)_6]_2$ (2). A mixture of $Fe(ClO_4)_2{\cdot}6H_2O$ (0.0216 g, 0.06 mmol), (0.0216 g, 0.06 mmol), $^{2Me}L_{pz}$ (0.027g, 0.1 mmol) and sodium cyanoborohydride (0.0124g, 0.02 mmol) was stirred in ethanol (15mL) for 30 min. The resulting solution was transferred into a 15mL Teflon-lined stainless steel reactor, which was kept at 140 ℃ for 3 days and then cooled to room temperature at 5 ℃ h^{-1}. As a result, brown block crystals of **2** are formed. They were washed with methanol (15mL) and dried in air. Yield is 60%. Elemental analysis for dehydrated sample: calc. C 45.76, H 4.27, N 29.65; exp. C 45.72, H 4.20, N 29.83.

Synthesis of $[Fe^{II}_{1.5}Co^{II}_{1.5}(^{2Me}L_{pz})]_3[Co^{III}(CN)_6]_2$ (3) and $[Fe^{II}_{0.9}Co^{II}_{2.1}(^{2Me}L_{pz})]_3[Co^{III}(CN)_6]_2$ (4). Complex **3** and **4** were synthesized similarly to **2**. The ratio between $Fe(ClO_4)_2{\cdot}6H_2O$ and $CoCl_2{\cdot}6H_2O$ was 1:1 (**3**) and 2:3 (**4**). Elemental analysis for **3** (dehydrated): calc. C 45.70， H 4.26, N 29.61; exp. C 45.92, H 4.05, N 29.32. Elemental analysis for **4** (dehydrated): calc. C 45.64, H 4.26, N 29.57; exp. C 45.38, H 4.58, N 29.72.

Physical characterization

Magnetic susceptibility measurements of the reported Fe(II) complexes were recorded with a Quantum Design MPMS SQUID magnetometer, operating with an applied field of 0.1 at temperatures from 10 to 300 K at rate of 2 K min^{-1}. PXRD patterns were recorded on a D8 ADVANCE X-ray diffractometer (Kα radiation, $\lambda = 0.154056$ nm). The ^{57}Fe Mössbauer spectra were measured in a transmission geometry employing a Mössbauer spectrometer operating in a constant acceleration mode and equipped with a ^{57}Co(Rh) source. The isomer shift values are referred to metallic α-Fe at room temperature. Elemental analyses were performed using an Elementar Vario EL elemental analyser. The IR spectra were recorded using KBr discs in the range 4000–500 cm^{-1} with a Perkin-Elmer Spectrum. Inductively coupled plasma atomic emission spectrometry analysis (ICP-AES) analyses were carried out with a SPECTRO CIROS VISION emission spectrometer. Samples were digested in HNO_3.

Single crystal X-ray diffraction

Single-crystal X-ray data were collected on a Bruker D8 Quest diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). A multi-scan absorption correction was performed. The structures were solved using direct methods and refined by full-matrix least-squares on F^2 using SHELXS and SHELXL[1] and the graphical user interface Olex2.[2] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions refined using idealized geometries (riding model) and assigned fixed isotropic displacement parameters.

Structures contain solvent accessible voids (up to 215 Å^3) that include just a minor electron density inside (were considered empty). These voids most probably originate from the crystallization water that easily leaves the crystal (see IR and TGA below). All structures were refined as racemic twins with BASF parameters indicated in Table S2. Ligand molecules were treated as disordered between two positions. The ration between Fe and Co in **2** was constrained as one finds from ICP-AES measurements. CCDC−1569642-1569644 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

1 G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.*, 2008, **64**, 112–122.

2 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

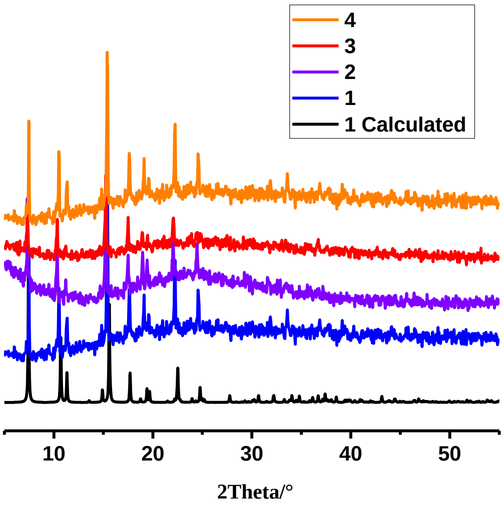


Figure S1. PXRD patterns measured on the polycrystalline samples of **1-4** and a simulated pattern from the single crystal structure of **1**.

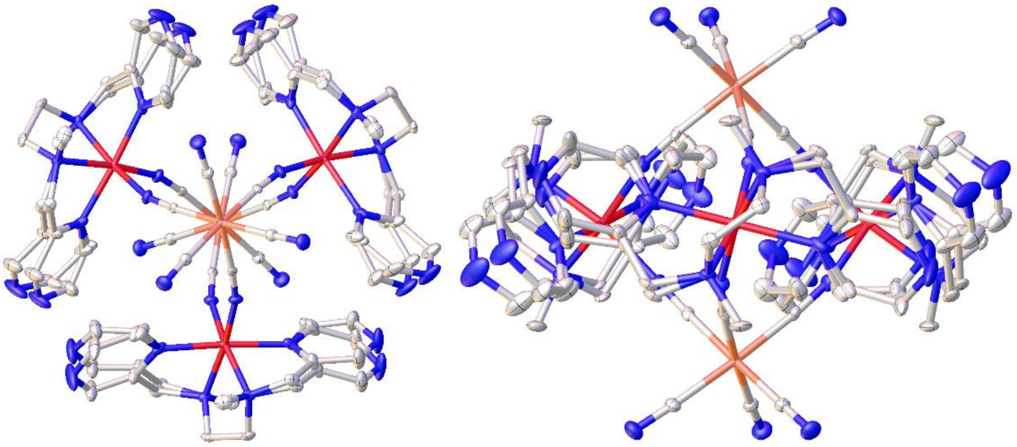


Figure S2. Crystal structure of **2** at 100 K: top view (along the axis of the bipyramid) (left) and side view (right) of the pentanuclear cluster. The tetradentate ligand was found to be disordered over two positions. Color code: red, Co^{II}/Fe^{II}; orange, Co^{III}; blue, N; gray, C. Hydrogen atoms have been omitted for clarity.

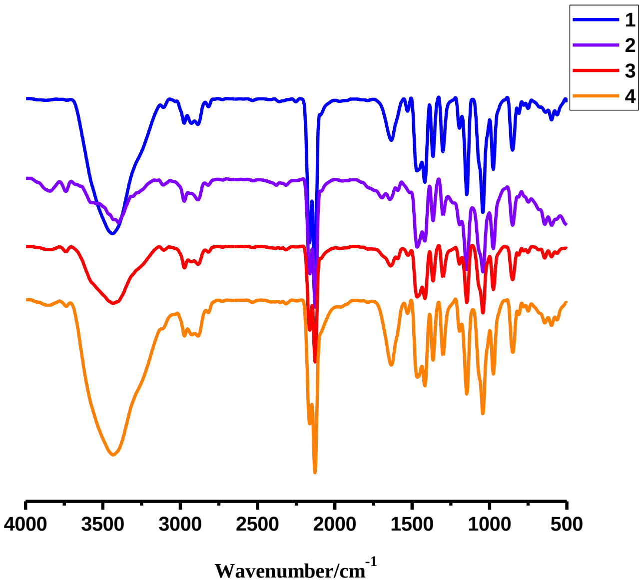


Figure S3. Solid-state infrared (IR) spectra recorded for **1-4** (as synthesized) at room temperature.

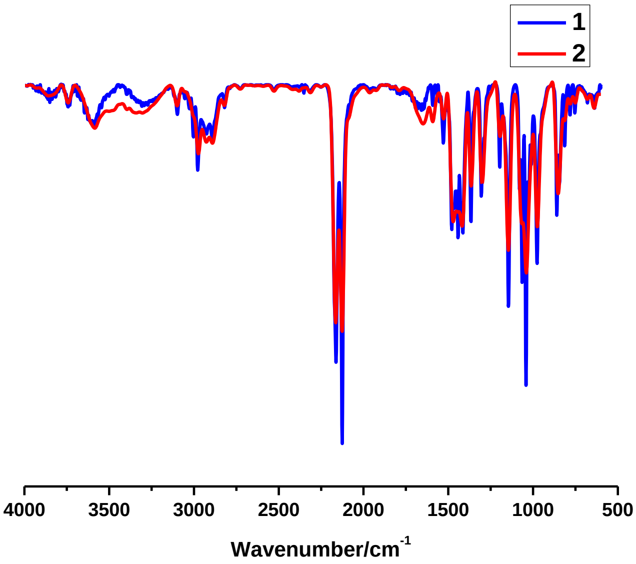


Figure S4. Solid-state infrared (IR) spectra recorded for **1** and **2** (dehydrated) at room temperature.

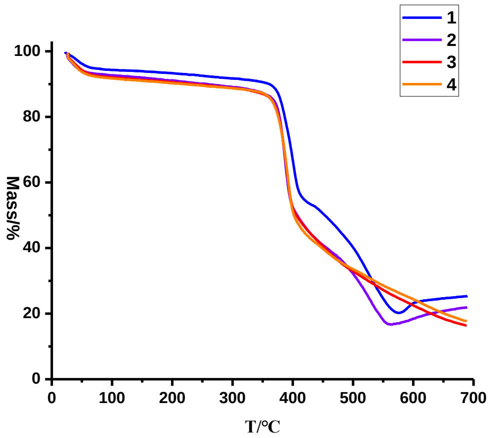


Figure S5. Thermogravimetric analysis (TGA) curves for **1-4** from 30 to 700 °C at a 10 K min^{-1} temperature rate under N_2 atmosphere.

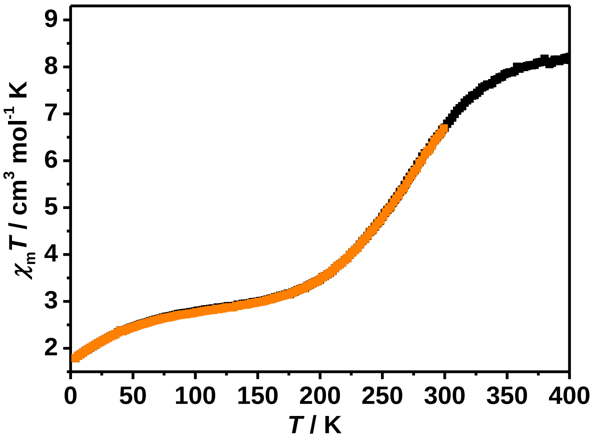


Figure S6. Thermal variation of $\chi_M T$ as a function of T for **2** at a scan rate of 2 K min^{-1}. It was scanned from 300 to 2 K first (orange) and then from 2 to 400 K (black).

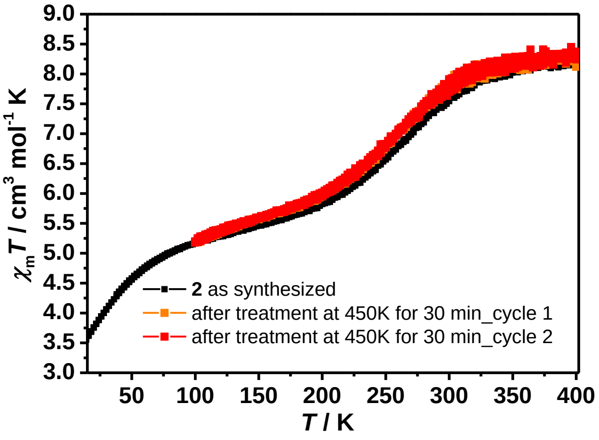


Figure S7. Thermal variation of $\chi_M T$ as a function of T for **2** (as synthesized) and after treatment at 450 K for 30 minutes.

Table S1. ^{57}Fe Mössbauer parameters of **2** at different temperatures.

T (K)	Comment	δ (mm/s)	ΔE_Q (mm/s)	w (mm/s)	Assignment	RA (%)
77	Doublet	0.456(7)	0.257(15)	0.184(12)	LS Fe^{II}	100
200	Doublet	0.83(7)	1.86(14)	0.16(11)	HS Fe^{II}	12(7)
	Doublet	0.431(11)	0.24(2)	0.16(2)	LS Fe^{II}	88(6)
303	Doublet	0.71(4)	1.67(9)	0.23(7)	HS Fe^{II}	40(10)
	Doublet	0.36(2)	0.2(1)	0.2(1)	LS Fe^{II}	60(10)

Table S2. Crystal data and refinement details for **1** and **2**.

	$[Co^{II}(^{2Me}L_{pz})]_3[Co^{III}(CN)_6]_2$ **(1)**	$[Fe^{II}_{2.1}Co_{0.9}{}^{II}(^{2Me}L_{pz})_3][Co_2{}^{III}(CN)_6]_2$ **(2)**	
***T* / K**	123	100	298
Empirical formula	$C_{54}H_{60}Co_5N_{30}$	$C_{54}H_{60}Co_{2.9}Fe_{2.1}N_{30}$	$C_{54}H_{60}Co_{2.9}Fe_{2.1}N_{30}$
Formula weight / g mol^{-1}	1423.97	1417.47	1417.47
Crystal system	trigonal	trigonal	trigonal
Space group	*R*32	*R*32	*R*32
***a* / Å**	15.6215(15)	15.5034(10)	15.6964(15)
***b* / Å**	15.6215(15)	15.5034(10)	15.6964(15)
***c* / Å**	24.797(3)	24.835(2)	24.965(3)
***V* / Å^3**	5240.4(11)	5169.6(8)	5326.7(12)
Z	3	3	3
ρ_{calc} / *g* cm^{-3}	1.354	1.366	1.326
μ / mm^{-1}	1.219	1.173	1.138
***F*(000)**	2187.0	2181.0	2181.0
Reflections collected	7245	8472	7090
Independent reflections	2133	2118.0	2177
R_{int}	0.0843	0.0602	0.0952
Goodness-of-fit on F^2	1.062	1.035	1.002
Final *R* indexes^a	$R_1 = 0.0428$	$R_1 = 0.0340$	$R_1 = 0.0441$
[I>=2σ (I)]	$wR_2 = 0.0834$	$wR_2 = 0.0708$	$wR_2 = 0.0970$
Final *R* indexes	$R_1 = 0.0701$,	$R_1 = 0.0478$,	$R_1 = 0.1017$
[all data]	$wR_2 = 0.0915$	$wR_2 = 0.0754$	$wR_2 = 0.1224$
BASF	0.50(4)	0.48(3)	0.50(3)

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