Supporting Information

One-dimensional coordination polymers of $[Co_3(dpa)_4]^{2+}$ and $[MF_6]^{2-}$ (M = Re^{IV}, Zr^{IV} and Sn^{IV})

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1. General

All reactions were carried out under a dry argon atmosphere using Schlenk techniques and glovebox methods. Solvents diethyl ether (Et₂O), acetonitrile (CH₃CN) and dichloromethane (CH₂Cl₂) were purified using an Innovative Technologies solvent purification system. Anhydrous dimethylformamide (DMF) was purchased from Alfa Aesar and used as received. 2,2'-dipyridylamine (Hdpa) was purchased from Aldrich and recrystallized from hot hexane before use. Anhydrous CoCl₂ was purchased from Aldrich and kept in an oven at 130 °C several days before use. (PPh₄)₂[ReF₆]·2H₂O ¹ and (PPh₄)₂[ZrF₆]·2H₂O were prepared as reported.² (PPh₄)₂[SnF₆] was obtained from combining commercially available (NH₄)₂[SnF₆] (Aldrich) with 2 eq of PPh₄Cl in water followed by slow evaporation.

Elemental analysis was carried out by the Service d'Analyse Elementaire of the Université of Lorraine, Nancy, France. The IR spectra of polycrystalline solids were measured on a Nicolet 6700 FT-IR using a Smart iTR accessory between 450 and 4000 cm⁻¹. Thermogravimetric Analysis curves were recorded with a Setaram MTB10–8 TGA apparatus. The sample was first left under a nitrogen flux for 3 h at room temperature, and then the temperature was increased up to 300 °C with at a rate of 1 Kmin⁻¹. Later, the temperature was slowly decreased back to room temperature. The mass of the sample was continuously measured during the whole process.



Figure S1. Room temperature infrared spectrum for 1 with peaks from DMF annotated.



Figure S2. Room temperature infrared spectrum for 2 with peaks from DMF annotated.



Figure S3. Room temperature infrared spectrum for 3 with peaks from DMF annotated.



Figure S4. TGA plot for 1. Calculated mass loss for two molecules of DMF 11.2%, found 11.2%.



Figure S5. TGA plot for 2. Calculated mass loss for two molecules of DMF 12.1%, found 10.8%.



Figure S6. TGA plot for 3. Calculated mass loss for two molecules DMF 11.8%, found 13.2%.

2. X-ray diffraction

Single Crystal. Crystals were selected under immersion oil in ambient conditions and attached to a MiTeGen microloop. The crystals were mounted in a stream of cold nitrogen at 120(2) K and centered in the X-ray beam using a video camera. Data collection was performed on a Bruker APEXII Quasar diffractometer with Mo K_{α} ($\lambda = 0.71073$ Å) radiation. The data were collected using a routine to survey reciprocal space, and were indexed by the APEX II program.³ The structures were solved using direct methods and refined by least-squares refinement on F^2 followed by difference Fourier synthesis.⁴ All hydrogen atoms were introduced at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

Powder. X-ray diffraction (XRD) patterns were collected on a PANalitycal X'pert MPD-PRO Bragg-Brentano θ - θ geometry diffractometer equipped with a goebel mirror over an angular range of $2\theta = 5-60^{\circ}$. Each acquisition lasted for 1 hour and 30 minutes. The Cu-K α radiation was generated at 45 KV and 40 mA (lambda = 0.15418 nm). The powder samples were prepared inside glass capillaries.

Simulations of the powder diffractograms were calculated with CrystalDiffract (Copyright © 2015 CrystalMaker Software Ltd.) using the single crystal .cif files.

	1	2	3	(PPh ₄) ₂ [ReF ₆]·MeCN
Empirical formula Formula weight / g.mol ⁻¹ Temperature / K Wavelength / Å Crystal system Space group Unit cell dimensions a, b and c /Å α, β and γ / °	$\begin{array}{l} C_{46}H_{46}Co_{3}F_{6}N_{14}O_{2}Re\\ 1303.96\\ 200(2)\\ 0.71073\\ Tetragonal\\ P\ 4/n\ c\ c\\ a\ =\ 13.6578(4)\\ b\ =\ 13.6578(4)\\ c\ =\ 25.5535(7) \end{array}$	$\begin{array}{l} C_{46}H_{46}Co_{3}F_{6}N_{14}O_{2}Zr\\ 1208.98\\ 200(2)\\ 0.71073\\ Tetragonal\\ P\ 4/n\ c\ c\\ a\ =\ 13.6527(4)\\ b\ =\ 13.6527(4)\\ c\ =\ 25.7947(8) \end{array}$	$\begin{array}{l} C_{46}H_{46}Co_{3}F_{6}N_{14}O_{2}Sn\\ 1236.45\\ 200(2)\\ 0.71073\\ Tetragonal\\ P 4/n c c\\ a = 13.6633(12)\\ b = 13.6633(12)\\ c = 25.701(2) \end{array}$	$\begin{array}{l} \hline C_{50}H_{43}F_6NP_2Re\\ 1020.05\\ 100(2)\\ 0.71073\\ Triclinic\\ P-1\\ a=9.9941(3)\\ b=10.9876(4)\\ c=21.1474(7)\\ \alpha=104.686(1)\\ \beta=92.005(1)\\ \gamma=106.919(1) \end{array}$
Volume / Å ³ Z, Calculated density Absorption coefficient / mm ⁻¹ F(000) Crystal size / mm θ range for data collection Limiting indices	4766.6(3) 4, 1.817 3.637 2584 $0.26 \times 0.11 \times 0.10$ $2.109 \text{ to } 26.180^{\circ}$ $-16 \le h \le 16$, $-16 \le k \le 16$, $-31 \le l \le 31$ 54328 / 2391 [<i>R</i> (int) = 0.0357]	4808.0(3) 4, 1.670 1.307 2444 0.13 × 0.07 × 0.04 2.110 to 27.342° $-17 \le h \le 17$, $-17 \le k \le 17$, $-33 \le l \le 33$ 85142 / 2729 [<i>R</i> (int) = 0.0643]	4798.1(9) 4, 1.712 1.613 2484 0.11 × 0.03 × 0.01 2.108 to 26.414° $-17 \le h \le 17$, $-17 \le k \le 17$, $-32 \le l \le 32$ 63608 / 2469 [<i>R</i> (int) = 0.0585]	2134.23(12) 2, 1.5872 2.985 1017 0.10 × 0.06 × 0.04 1.0 to 25.38° $-12 \le h \le 12$, $-13 \le k \le 13$, $-25 \le l \le 25$ 52904 / 7816 [<i>R</i> (int) = 0.0365]
Completeness to $\theta = 25.242$ Absorption correction Max. and min. transmission Refinement method	100.0 % Multi-scan 0.6938 and 0.5322 Full-matrix least-squares on F^2	Multi-scan 0.7456 and 0.6978 Full-matrix least-squares on F^2	Multi-scan 0.7454 and 0.6934 Full-matrix least-squares on F^2	99.7% Multi-scan 0.7452 and $0.6300Full-matrix least-squares on F^2$
Data / restraints / parameters Goodness-of-fit on F^2	2391 / 22 / 211 1.165	2729 / 22 / 211 1.113	2469 / 22 / 211 1.052	7816 / 0 / 541 1.0544
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1^{a} = 0.0299, wR_2^{b} = 0.0739$	$R_1^{a} = 0.0496, wR_2^{b} = 0.1128$	$R_1^{a} = 0.0387, wR_2^{b} = 0.0972$	$R_1^{a} = 0.0190, wR_2^{b} = 0.0439$
R indices (all data) Largest diff. peak and hole	$R_1^{a} = 0.0432, wR_2^{b} = 0.0819$ 0.525 and -0.452 e. Å ⁻³	$R_1^{a} = 0.0853, wR_2^{b} = 0.1331$ 0.610 and -0.799 e. Å ⁻³	$R_1^{a} = 0.0649, wR_2^{b} = 0.1163$ 0.461 and -1.055 e. Å ⁻³	$R_1^{a} = 0.0205, w R_2^{b} = 0.0461$ 1.62 and -1.04 e. Å ⁻³

Table S1 Crystal data and structure refinement for 1-3 and (PPh.).[ReF.].MeCN

 ${}^{a}R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|.$ ${}^{b}wR_{2} = [\Sigma [w(F_{o}^{2} - F_{c}^{2})^{2}] / \Sigma [w(F_{o}^{2})^{2}]]^{1/2}, w = 1/\sigma^{2}(F_{o}^{2}) + (aP)^{2} + bP, \text{ where } P = [\max(0 \text{ or } F_{o}^{2}) + 2(F_{c}^{2})]/3.$



Figure S7. Thermal ellipsoid plot of $(PPh_4)_2[ReF_6]$ ·MeCN (C: grey; F: green, Re: orange; N: light blue; P: pink). Hydrogen atoms have been omitted for clarity. Ellipsoids are drawn at 50% probability level.



Figure S8. Thermal ellipsoid plot of $[Co_3(dpa)_4(ReF_6)]$ ·2DMF, **1** (C: grey; F: green, Re: orange; N: light blue; Co: blue). Hydrogen atoms and solvents of crystallization have been omitted for clarity and only one orientation of the disordered molecule is shown. Ellipsoids are drawn at 50% probability level.



Figure S9. Thermal ellipsoid plot of $[Co_3(dpa)_4(ZrF_6)] \cdot 2DMF$, **2** (C: grey; F: green, Zr: pink; N: light blue; Co: blue). Hydrogen atoms and solvents of crystallization have been omitted for clarity and only one orientation of the disordered molecule is shown. Ellipsoids are drawn at 50% probability level.



Figure S10. Thermal ellipsoid plot of $[Co_3(dpa)_4(SnF_6)]$ ·2DMF, **3** (C: grey; F: green, Sn: light grey; N: light blue; Co: blue). Hydrogen atoms and solvents of crystallization have been omitted for clarity and only one orientation of the disordered molecule is shown. Ellipsoids are drawn at 50% probability level.



Figure S11. X-ray powder diffractogram at room temperature (blue) and simulation (red) for 1.



Figure S12. X-ray powder diffractogram at room temperature (blue) and simulation (red) for 2.



Figure S13. X-ray powder diffractogram at room temperature (blue) and simulation (red) for 3.

3. Magnetic Measurements

The magnetic measurements were carried out with the use of MPMS-XL Quantum Design SQUID magnetometer and PPMS-9 Quantum Design susceptometer. These instruments work between 1.8 and 400 K with applied dc fields ranging from -7 to 7 T (MPMS-XL) and -9 to 9 T (PPMS-9). Measurements were performed on a finely ground polycrystalline sample of **1**, **2** and **3** (21.36, 11.94 and 20.97 mg respectively) sealed in a polypropylene bag ($3 \times 0.5 \times 0.02$ cm; 29.12, 27.43 and 21.60 mg respectively). Ac susceptibility measurements were made with an oscillating field of 3 to 6 Oe with a frequency from 1 to 10000 Hz but no out-of-phase signal was detected above 1.8 K. Prior to the experiments, the field-dependent magnetization was measured at 100 K in order to detect the presence of any bulk ferromagnetic impurities. The samples appeared to be free of any significant ferromagnetic impurities. The magnetic data were corrected for the sample holder and the intrinsic diamagnetic contributions.



Figure S14. Magnetization vs. field curves for (a) 1, (b) 2 and (c) 3 below 10 K.

¹ K. S. Pedersen, M. Sigrist, M. A. Sørensen, A.-L. Barra, T. Weyhermüller, S. Piligkos, C. Thuesen, M. G. Vinum, H. Mutka, H. Weihe, R. Clérac and J. Bendix, *Angew. Chem. Int. Ed.*, 2014, **53**, 1351.

² J. Larsen, Boubekeur, P. Batail, J. Lucas, Mat. Res. Bull. 1989, 24, 845.

³ Bruker-AXS APEX2, SADABS, and SAINT Software Reference Manuals, Madison, Wisconsin, USA, 2009.

⁴ G. M. Sheldrick, *Acta Cryst.*, **2008**, *A64*, 112.