

Supporting Information for

From Co(III)-pyrazolate triangles to rings: A carboxyl-pyrazole parallel

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General Procedures.

All manipulations were undertaken under air. Solvents were used as purchased without any further purification. Other reagents purchased from commercial sources were used without further purification. 4-NO₂-pz was prepared according to previously published procedure.¹ Bruker-400 Fourier transform spectrometer was used for NMR spectroscopy. All spectra were recorded at room temperature unless mentioned otherwise. IR spectra of the various compounds dispersed in KBr pellets were recorded with a Nicolet 6700 FTIR spectrometer while the thermogravimetric analyses (TGA/DTA) were performed on a Thermal Advantage Q500/1000 thermal analysis instrument at a temperature range of 25-1000 °C under dinitrogen atmosphere with a heating rate of 5 °C min⁻¹.

Experimental procedure – Syntheses

[PPN]₂[Co₃(μ₃-O)(μ-4-NO₂-pz)₆(NO₂)₃]·3THF·C₆H₁₂ (1): A thf solution (25 mL) of Na₃Co(NO₂)₆ (0.15 g, 3.7 x 10⁻⁴ mol) was stirred for 10 min until partial dissolution of the starting material took place. Addition of solid 4-NO₂-pzH (0.10 g, 9.2 x 10⁻⁴ mol), excess of Et₃N (1.27 mL, 9.2 x 10⁻³ mol) and PPNCl (0.21 g, 3.7 x 10⁻⁴ mol), followed. The mixture was heated at reflux overnight. Bright yellow crystals of X-ray quality were isolated after 5 days by layering hexane over the thf filtrate (v/v 1:1). Yield

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based on Co: 0.10 g (34.1 %). $C_{102}H_{96}Co_3N_{23}O_{22}P_4$ (2296.6): calcd. C 53.34, H 4.21, N 14.03; found C 53.55, H 4.49, N 13.94; IR bands (KBr): cm^{-1} 2927, 2869, 1513, 1413, 1343, 1296, 1184, 1117, 1051, 818, 753, 723, 693, 587, 542; TGA: exp. weight loss % [Theor. Weight loss, temperature ($^{\circ}C$)]: 9.87 [9.39, 25 - 147, removal of thf molecules], 44.94 [47.00, 210 - 600 $^{\circ}C$, removal of 2 PPN counter ions], 22.25 [29.20, 600 - 1000, removal of pz ligands].

[TBA]₂[Co(μ -OH)(μ -4-NO₂-pz)(μ -3,5-Me₂-pz)]₁₀[NO₂]₂·9THF (2): A thf solution (25 mL) of Na₃Co(NO₂)₆ (0.3 g, 7×10^{-4} mol) and was stirred for 10 min until partial dissolution of the starting material took place. Addition of solid 4-NO₂-pzH (0.09 g, 7.9×10^{-4} mol), 3,5-Me₂-pzH (0.037 g, 3.8×10^{-4} mol), NaOH (0.25 g, 6.2×10^{-3} mol) and TBABr (0.45 g, 1.4×10^{-3} mol), followed. The mixture was heated at reflux overnight. Red block crystals of X-ray quality were isolated after 2 days by layering hexane over the thf filtrate (v/v 1:1) or by letting the filtrate stand at 4 $^{\circ}C$. Yield based on Co: 1.10 g (20 %). $C_{148}H_{246}Co_{10}N_{52}O_{41}$ (3999.1): calcd. C 44.45, H 6.20, N 18.21; found C 44.75, H 6.39, N 18.25. IR bands (KBr): cm^{-1} 2985, 2892, 1515, 1450, 1383, 1294, 1203, 1156, 1102, 1040, 818, 776, 734, 571; TGA: exp. weight loss % [theor. Weight loss, temperature ($^{\circ}C$)]: 15.50 [16.22, 25 - 150, removal of 9 thf molecules], 62.40 [63.9, 200 - 1000 $^{\circ}C$, removal of the 2 TBA counter ions and 20 pyrazolate ligands in two overlapping steps].

[PPN]₂[Co(μ -OH)(μ -4-NO₂-pz)(μ -3,5-Me₂-pz)]₁₂[NO₂]₂·8THF (3): A thf solution (25 mL) of Na₃Co(NO₂)₆ (0.6 g, 1.4×10^{-3} mol) and was stirred for 10 min until partial dissolution of the starting material took place. Addition of solid 4-NO₂-pzH (0.17 g, 1.5×10^{-3} mol), 3,5-Me₂-pzH (0.072 g, 7.5×10^{-4} mol), NaOH (0.25 g, 6.2×10^{-3} mol) and PPNCl (0.21 g, 3.7×10^{-4} mol), followed. The mixture was heated at reflux overnight. Red block crystals of X-ray quality were isolated after 2 months by layering hexane over the thf filtrate (v/v 1:1). Yield based on Co: 0.10 g (41 %). $C_{192}H_{230}Co_{12}N_{62}O_{44}P_4$ (4941.3): calcd. C 46.67, H 4.69, N 17.57; found C 46.92, H 4.71, N 17.76. IR bands (KBr): cm^{-1} 2935, 2875, 1509, 1434, 1399, 1327, 1291, 1165, 1112, 1014, 997, 814, 754, 722, 693, 546, 532; TGA: exp. weight loss % [theor. Weight loss, temperature ($^{\circ}C$)]: 8.62 [8.74, 25 - 136, removal of 6 thf molecules], 70.40 [72.11, 200 - 1000 $^{\circ}C$, removal of the 2 PPN counter ions and 24 pyrazolate ligands in two overlapping steps].

X-ray Crystallography

Diffraction data collected at 150 K were corrected for Lorenz and polarization effects. An analytical absorption correction based on face indexing was applied for all three structures. Because of the weak diffraction of the crystal of **2**, no meaningful data could be collected at high 2θ -angles. In **1**, three THF and one adventitious cyclohexane (a common impurity in n-hexane, used in the crystallization process) were located and refined. The large interstitial solvent content of **2** and **3** was obvious from the large solvent-accessible voids of their unit cells after the Co-pyrazolate molecules, Bu_4N^+ , PPN^+ and NO_2^- ions were located. Some crystallographically ordered solvent molecules were located from difference maps and were refined. At that point, the program SQUEEZE (part of the WinGX crystallographic package) was used to generate modified structure factors for the final refinement of **2** and **3**. The total interstitial solvent molecule contents of **2** and **3** were determined by TGA. The Ph-groups of **3** were refined as rigid hexagons. H-atoms have been included in calculated positions for the pyrazole and hydroxide ligands of structures **1** – **3** and Bu_4N^+ of **2**, but not for the interstitial solvent molecules, nor for the and PPN^+ ions. In the $C2/m$ structure of **1**, two one-half PPN^+ ions per asymmetric unit were found with their P-N-P atoms on the crystallographic mirror plane, resulting in disorder of their associated Ph-groups. Solution of the structure in $C2$ space group only removed part of the disorder without lowering the final R-value, or improving the standard deviation of bond lengths and angles. Therefore, the $C2/m$ solution was preferred.

Bond Valence Sum Calculations (BVS)

Compound	Atom	BVS_{av} value
1	Co	3.00
	$\mu_3\text{-O}$	1.8 (O²⁻)
2	Co	3.11 (Co^{III})
	$\mu\text{-O}$	1.10 (OH)
3	Co	2.98 (Co^{III})
	$\mu\text{-O}$	1.06 (OH)

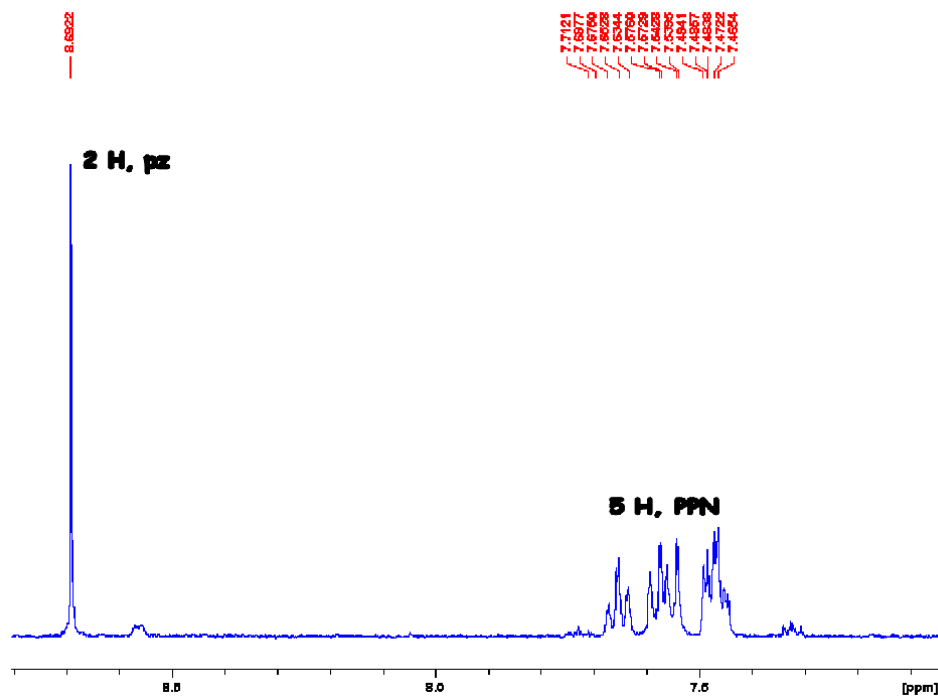


Fig. S1 ¹H-NMR of {Co₃}.

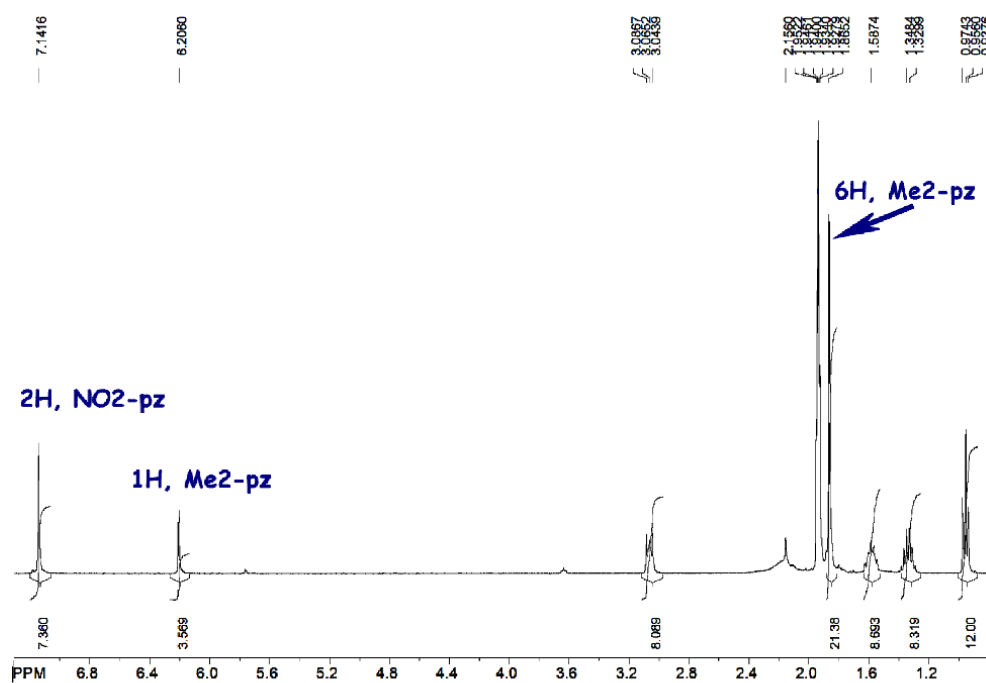


Fig. S2 ¹H-NMR of {Co₁₀}.

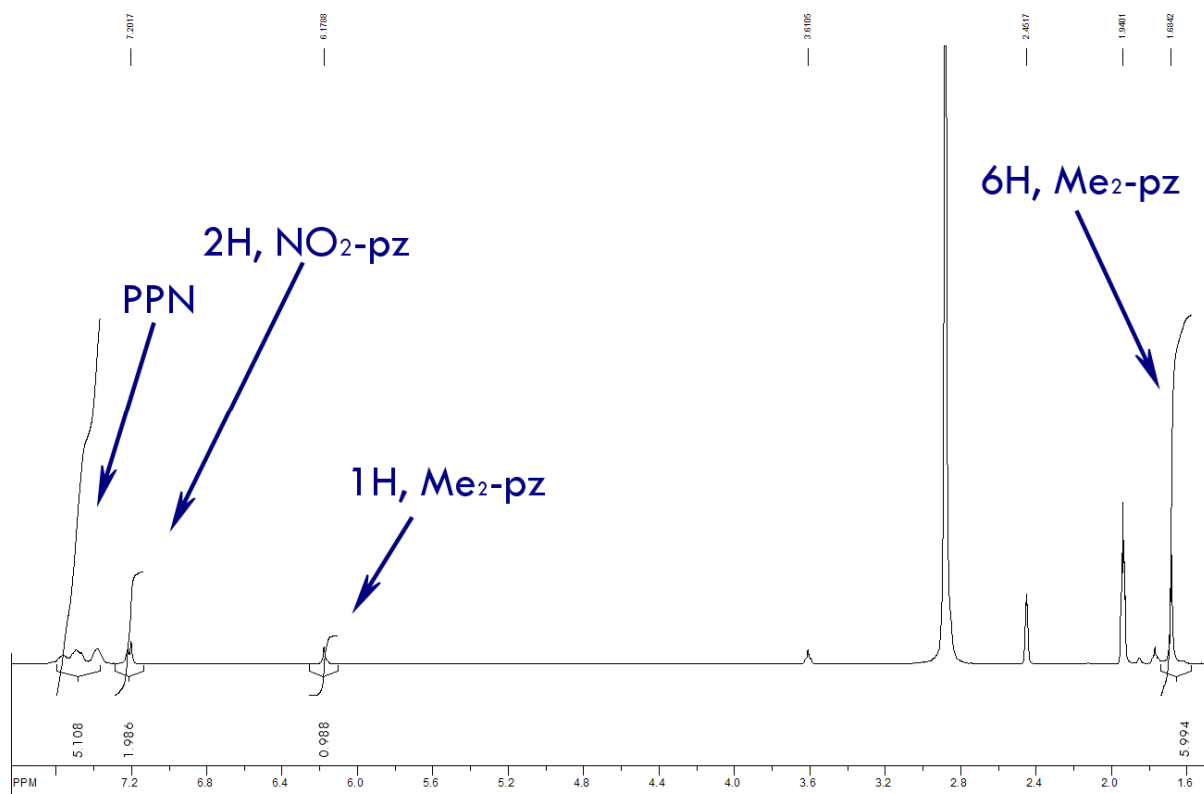


Fig. S3 ¹H-NMR of {Co₁₂}.

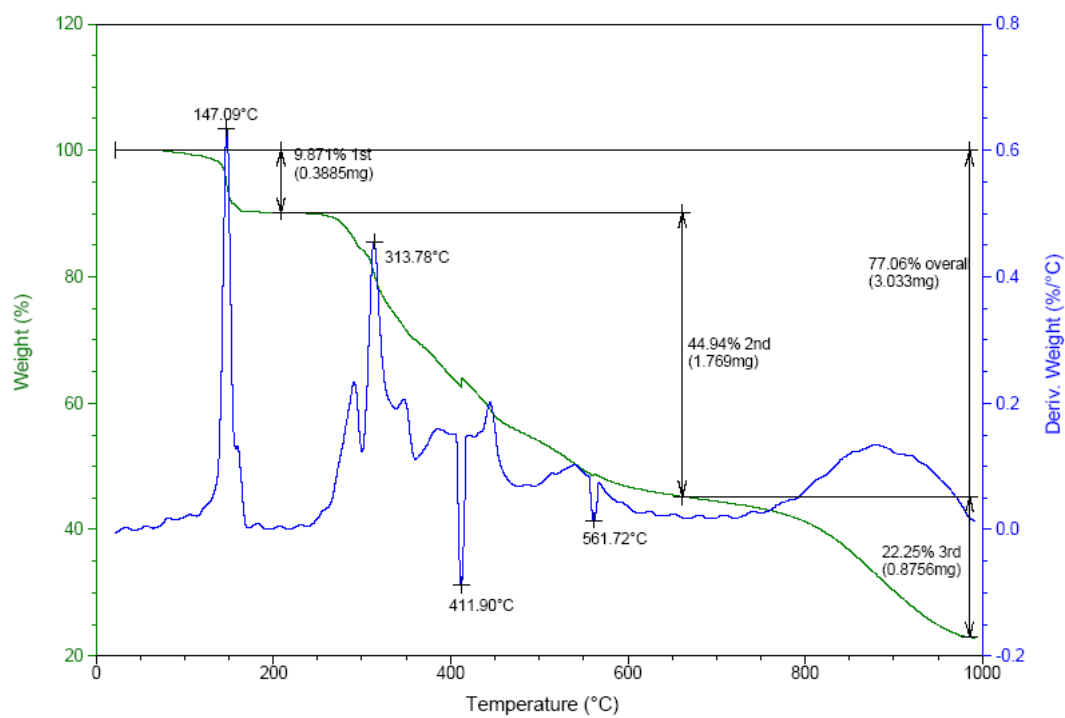


Fig. S4 TGA/DSC spectrum of $\{Co_3\}$.

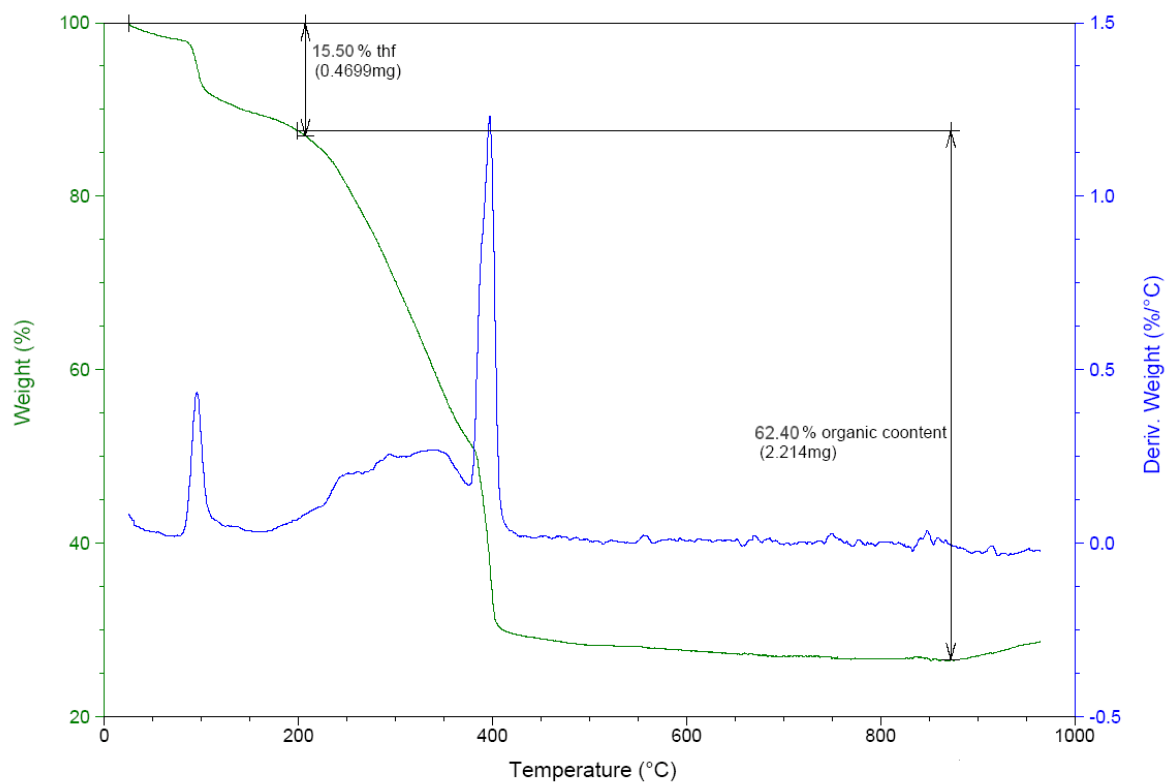


Fig. S5 TGA/DSC spectrum of $\{Co_{10}\}$.

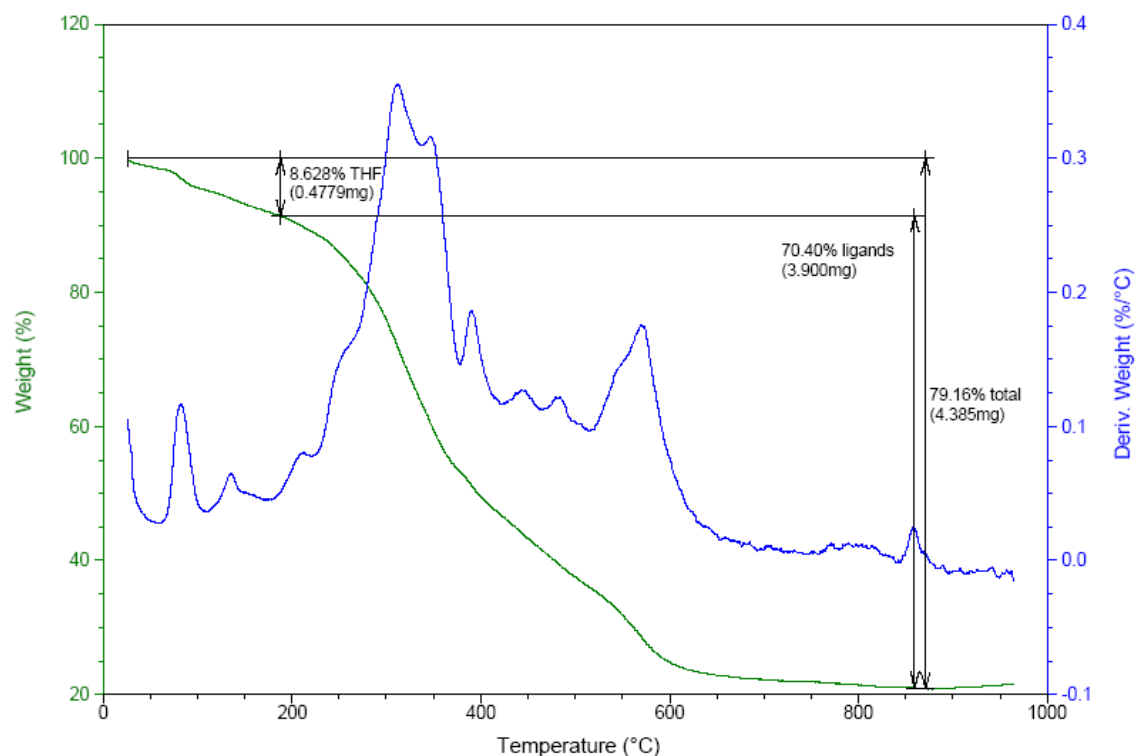
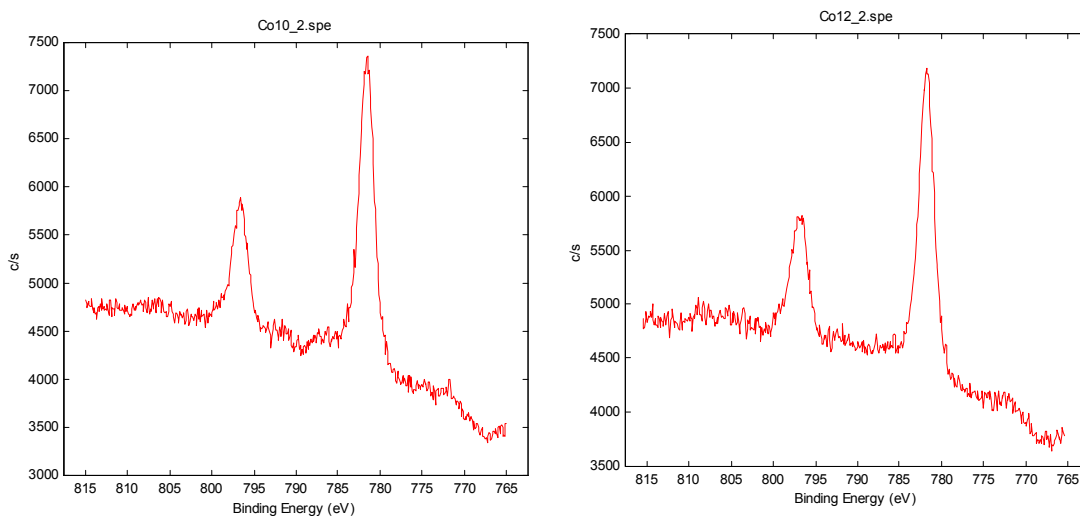


Fig. S6 TGA/DSC spectrum of $\{Co_{12}\}$.

X-ray Photoelectron Spectroscopy.

XPS measurements were carried out with a PHI 5600 ESCA system (Physical

Electronics). A single species with binding energy of 781 eV ($Co\ 2p_{3/2}$) is observed for both $\{Co_{10}\}$ and $\{Co_{12}\}$.



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References

1. M. K. Ehlert, S. J. Rettig, A. Storr, R. C. Thompson and J. Trotter, *Can. J. Chem.* 1991, 432.