Supporting Information for:

Cobalt Complexes of the Chelating Dicarboxylate Ligand "esp": A Paddlewheel-Type Dimer and a Heptanuclear Coordination Cluster

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Synthetic Procedures

General Procedures. All reagents were obtained from commercial sources and used as received, except as noted. All work was performed with oven-dried glassware under a dry, nitrogen atmosphere using standard Schlenk technique or an inert-atmosphere glovebox, except as noted. Flash chromatography was performed using SiliCycle SiliaFlash P60 silica gel (40-63 µm/230-400 mesh) in the indicated solvents. For air-free manipulations, solvents were dried and de-oxygenated in the following ways: tetrahydrofuran (THF), toluene, and hexanes were dried using a VAC Atmospheres solvent system and sparged with nitrogen prior to use. Dichloromethane was dried over CaH₂ and distilled under nitrogen immediately prior to use.

NMR spectroscopy and mass spectrometry experiments were performed in the Paul Bender Chemical Instrumentation Center in the Chemistry Department at the University of Wisconsin-Madison. NMR spectra were recorded on a Bruker Avance-500 MHz spectrometer (¹H; 125 MHz for ¹³C), and a cryoprobe was used for obtaining routine spectra at +24.0 °C. ¹H chemical shifts are reported on a ppm scale referenced to tetramethylsilane (TMS) at 0 ppm.

esp-diCN ($\alpha, \alpha, \alpha', \alpha'$ -tetramethyl-1,3-benzenedipropionitrile): Isobutyronitrile and di-isopropylamine were passed through plugs of oven-dried alumina prior to use to remove any water and N-oxide. n-Butyllithium (25 mL of a 2.5 M solution in hexanes, 2.04 equiv) was added slowly to a solution of ⁱPr₂NH (8.8 mL, 2.05 equiv) in 40 mL of THF at -78 °C. The mixture was stirred for 20 min at -78 °C. Isobutyronitrile (5.6 mL, 26.4 mmol, 2.04 equiv) was then added dropwise via syringe. The pale yellow reaction mixture was stirred at -78 °C for 40 min. A solution of α , α '-dichloro-mxylene (5.36 g) in 20 mL of THF was then transferred via cannula into the reaction flask. The resulting orange, slightly turbid mixture was allowed to stir at room temperature for 10 minutes. The reaction was guenched by addition of H₂O (60 mL) and transferred to a separatory funnel with 150 mL of ethyl acetate. The organic layer was collected, washed with 15 mL of saturated aqueous NaCl, dried over MgSO₄, and concentrated under reduced pressure. The resulting orange/yellow liquid (or solid dissolved in EtOAc) was then passed through a plug of silica, eluting with EtOAc. The colored impurities, suspected to be polymeric substances, remain on the silica while the desired compound elutes quickly (attempts at recrystallizing the product from colored solutions are successful but with lower yields or purity). The resulting colorless solution was concentrated until solid begins to precipitate. At this point, EtOAc was added until a nearly-saturated solution was obtained, hexanes were added (until the mixture was ca. 2-10% EtOAc by volume), and the slightly cloudy mixture was stored in a refrigerator overnight to yield white crystals, which were collected by filtration and air-dried.

Yield: 5.45 g, 74%. Spectral data matched those from the literature.¹

H₂esp (α,α,α',α'-tetramethyl-1,3-benzenedipropionic acid): esp-diCN (7.73 g) and KOH (9.96 g) were added to a Schlenk flask with a stirbar, and the flask was evacuated and backfilled with nitrogen. Anhydrous ethylene glycol (40 mL) was added via cannula, and the reaction flask was fitted with a condenser with a nitrogen feed. The reaction mixture was heated at 180 °C for 9 hours before cooling to room temperature. Chloroform (90 mL) and water (90 mL) were used to transfer the reaction mixture to separatory funnel. 6 M HCl (60 mL) was added, and the organic layer was collected. The aqueous layer was washed with 2 x 350 mL EtOAc, and the combined organic layer was washed with 2 x 100 mL water and 2 x 100 mL brine. After drying over MgSO₄ and removal of the volatiles under reduced pressure, the slightly yellow mixture was passed through a plug of silica, eluting with EtOAc to remove unknown byproducts that are difficult to remove otherwise. The resulting mixture was concentrated under reduced pressure until a solid began to precipitate, EtOAc was added until a nearly-saturated solution is obtained, hexanes were added (until the mixture was ca. 2-10% EtOAc by volume), and the slightly cloudy mixture was stored cold overnight to yield white crystals, which were collected by filtration.

Yield: 8.41 g, 93.9%. Spectral data matched those from the literature.¹

Compound	Co ₂ (esp) ₂ (EtOH) ₂	Co ₇ (OH) ₄ (Hesp) ₂ (esp) ₄ (MeCN) ₂ ·4MeCN			
Molecular Formula	$C_{36}H_{52}Co_2O_{10}$	$C_{108}H_{144}Co_7N_6O_{28}$			
Formula Weight (g mol ⁻¹)	762.63	2386.79			
Crystal System	Triclinic	Triclinic			
Space Group	P 1	P 1			
<i>a,</i> Å	12.0937(5)	14.4865(8)			
<i>b,</i> Å	13.2312(6)	17.3169(9)			
<i>c,</i> Å	14.6240(6)	22.954(1)			
α, °	115.783(2)	94.052(3)			
β <i>,</i> °	91.404(2)	94.507(3)			
γ, °	114.197(2)	95.506(3)			
<i>V,</i> Å ³	1862.5(1)	5696.2(5)			
Ζ	2	2			
λ, Å	1.54178	0.71073			
R_1 (I > 2 σ (I); all data) ^a	0.0378; 0.0401	0.0496; 0.0593			
wR_2 (I > 2 σ (I); all data) ^b	0.1057; 0.1082	0.1232; 0.1295			

Table S1 Crystallographic data

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ^b $wR_2 = \sqrt{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]}; w = \frac{1}{[\sigma^2(F_o^2) + (aP)^2 + bP]}; P = [max(0 \text{ or } F_o^2) + 2F_c^2]/3$

Table S2 Selected bond distances for Co₂(esp)₂(EtOH)₂

Co1–O(EtOH)	2.022(2) Å	Co2–O(EtOH)	2.051(1) Å		
Co1–O(esp)	2.008(2) – 2.106(2) Å	Co2–O(esp)	2.012(2) – 2.076(2) Å		

Atoms	Coordination Sphere	Distances (Å)
	octahedral, cis-(MeCN) ₂ (OH) ₄ :	
	μ ₃ - <i>Ο</i> Η (Ο1)	2.080(3)
	μ ₃ - <i>Ο</i> Η (O3)	2.081(3)
Co1	μ ₃ - <i>Ο</i> Η (O2)	2.090(3)
	μ₃- <i>Ο</i> Η (O4)	2.090(3)
	MeC <i>N</i> (N1)	2.109(4)
	MeC <i>N</i> (N2)	2.126(4)
	tetrahedral:	
Co2	μ ₂ -RCO(κ ¹ <i>O</i>) (O28, O16)	1.9582[1]
	μ ₃ - <i>Ο</i> Η (Ο1, Ο3)	1.96[1]
05	RCO(μ₂- <i>O</i>) (05, 017)	1.962[2]
	μ ₂ -RCO(κ ¹ <i>O</i>) (O26, O14)	1.97[1]
	pseudo-trigonal bipyramidal:	
	μ₃- <i>Ο</i> Η (O2, O4)	2.00[2]
603	μ ₂ -RCO(κ ¹ <i>O</i>) (O11, O23)	2.014[3]
Co6ª	μ ₂ -RCO(κ ¹ <i>O</i>) (O9, O21)	2.06[1]
00	κ²RC(κ¹ <i>O</i>)(μ₂-κ¹Ο) (O6, O18)	2.07[1]
	RC(κ ¹ <i>O</i>)(OH) (O7, O19)	2.24[3]
	κ²RC(κ¹Ο)(μ₂-κ¹ <i>Ο</i>) (O5, O17)	2.359[8]
	octahedral, <i>cis</i> -(OH)₂(RCO <i>O</i>)₄:	
	μ ₂ -RCO(κ ¹ <i>O</i>) (O10, O22)	2.05[1]
6.4	μ ₂ -RCO(κ ¹ <i>O</i>) (O15, O27)	2.071[2]
C04	μ ₃ - <i>Ο</i> Η (O3 <i>,</i> O1)	2.083[4]
C07°	μ ₃ - <i>Ο</i> Η (O2, O4)	2.10[1]
	μ ₂ -RCO(κ ¹ <i>O</i>) (O12, O24)	2.11[1]
	μ ₂ -RCO(κ ¹ <i>O</i>) (O13, O25)	2.15[1]

Table S3 Coordination description of the cobalt centers in $Co_7(OH)_4(Hesp)_2(esp)_4(MeCN)_2 \cdot 4 MeCN$

^a Grouped cobalt atoms are not *crystallographically* related but are related by an idealized molecular C_2 axis.

References

1 C. G. Espino, K. W. Fiori, M. Kim and J. Du Bois, J. Am. Chem. Soc., 2004, **126**, 15378-15379.