Supplementary Material (ESI) for *Dalton Transactions*

Supplementary Material for the Manuscript

Corroborative Cobalt and Zinc model compounds of α-amino-β-carboxymuconic-ε-semialdehyde decarboxylase (ACMSD)

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1. Synthesis of ligand precursor 3,5-di-*iso*-propylpyrazole-1-methanol.

3,5-Di-*iso*-propylpyrazole[1] (4.05 g, 26 mmol) was heated to 50-60 °C with 95 mL of water. Then heating was stopped and 37% aq. formaldehyde solution (37 mL) was added. The solution was heated to 80-90 °C for 6 h and stirred at room temperature overnight. The aqueous solution was extracted with dichloromethane, the organic phase was dried with $MgSO_4$ and the solvent was evaporated to yield a white solid. Yield 4.7 g (98%).

^{1}H NMR (300 MHz, $CDCl_3$): δ [ppm] 6.32 (OH), 5.87 (pz H4), 5.48, 5.46 (s, CH_2), 3.12 – 2.85 (m, ^{i}Pr-CH), 1.30, 1.28, 1.21, 1.18 (s, CH_3).

2. UV-vis spectra for 3

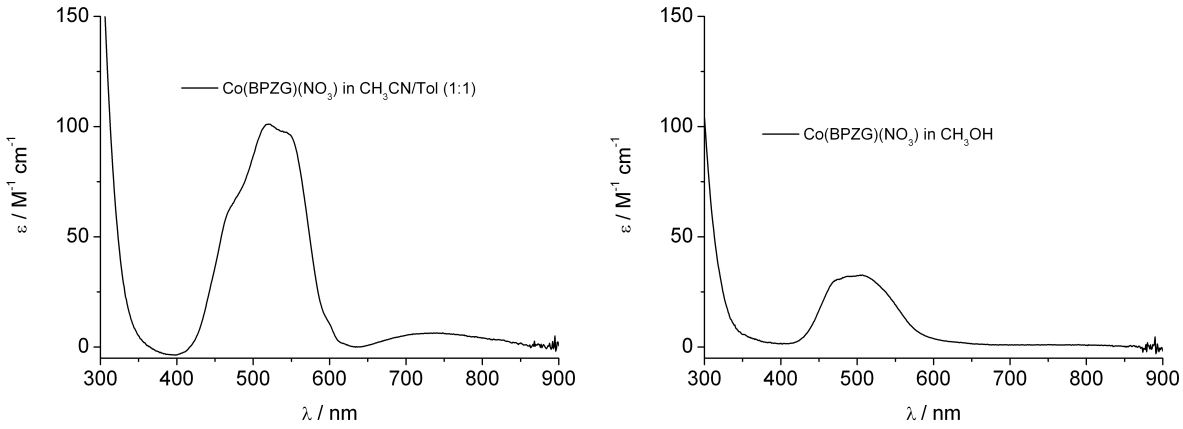

Fig. S1. UV-vis spectra of **3** in acetonitrile/toluene (1:1), left, and in methanol, right; c = 1 x 10^{-3} M.

Table S1. Main bond lengths (Å) and angles (°) for complexes **1** – **3**, **5, 6, 7**.

1		**2**		**3**[a)]		**5**[a)]		**6**		**7**	
Co(1)-Cl(1)	2.2881(8)	Co(1)-Cl(1)	2.3009(10)	Co(1)-O(1)	2.068(4)	Zn(1)-O(1)	2.124(4)	Co(1)-N(1)	2.022(2)	Co(1)-N(1)	2.032(4)
Co(1)-O(1)	1.9826(18)	Co(1)-O(1)	1.998(2)	Co(1)-O(3)	2.093(4)	Zn(1)-O(3)	2.115(4)	Co(1)-N(3)	2.343(2)	Co(1)-N(3)	2.288(4)
Co(1)-N(1)	2.302(2)	Co(1)-N(1)	2.263(3)	Co(1)-N(1)	2.229(4)	Zn(1)-N(1)	2.138(5)	Co(1)-N(4)	2.064(2)	Co(1)-N(4)	2.014(4)
Co(1)-N(3)	2.056(2)	Co(1)-N(3)	2.063(3)	Co(1)-N(3)	2.127(4)	Zn(1)-N(3)	2.343(4)	Co(1)-N(6)	2.088(2)	Co(1)-O(1)	2.026(3)
Co(1)-N(5)	2.061(2)	Co(1)-N(5)	2.057(3)	Co(1)-N(5)	2.139(4)	Zn(1)-N(5)	2.107(5)	Co(1)-O(1)	2.0510(18)	Co(1)-O(3)	1.989(3)
				Co(1)-O(2)#1	2.051(4)	Zn(1)-O(4)	2.016(4)				
O(1)-Co(1)-N(1)	77.00(7)	O(1)-Co(1)-N(1)	77.15(10)	O(1)-Co(1)-N(1)	79.61(15)	O(1)-Zn(1)-N(1)	86.64(16)	N(1)-Co(1)-N(3)	77.10(7)	N(1)-Co(1)-N(3)	78.72(14)
O(1)-Co(1)-N(3)	119.50(8)	O(1)-Co(1)-N(3)	113.96(11)	O(1)-Co(1)-N(3)	87.96(15)	O(1)-Zn(1)-N(3)	76.11(14)	N(1)-Co(1)-N(4)	111.52(8)	N(1)-Co(1)-N(4)	112.11(15)
O(1)-Co(1)-N(5)	117.22(8)	O(1)-Co(1)-N(5)	117.38(11)	O(1)-Co(1)-N(5)	92.36(15)	O(1)-Zn(1)-N(5)	92.10(16)	N(1)-Co(1)-N(6)	101.70(8)	N(1)-Co(1)-O(1)	104.40(15)
N(1)-Co(1)-N(3)	76.83(8)	N(1)-Co(1)-N(3)	76.02(10)	O(1)-Co(1)-O(3)	177.17(16)	O(1)-Zn(1)-O(3)	177.61(15)	N(1)-Co(1)-O(1)	138.76(8)	N(1)-Co(1)-O(3)	110.18(14)
N(1)-Co(1)-N(5)	77.47(8)	N(1)-Co(1)-N(5)	77.08(11)	O(1)-Co(1)-O(2)#1	86.53(14)	O(1)-Zn(1)-O(4)	83.69(14)	N(3)-Co(1)-N(4)	76.35(8)	N(3)-Co(1)-N(4)	78.78(14)
N(3)-Co(1)-N(5)	108.67(9)	N(3)-Co(1)-N(5)	113.39(11)	N(1)-Co(1)-N(3)	78.10(16)	N(1)-Zn(1)-N(3)	76.26(15)	N(3)-Co(1)-N(6)	174.80(9)	N(3)-Co(1)-O(1)	176.87(14)
Cl(1)-Co(1)-O(1)	94.70(5)	Cl(1)-Co(1)-O(1)	98.11(8)	N(1)-Co(1)-N(5)	79.27(16)	N(1)-Zn(1)-N(5)	151.42(16)	N(3)-Co(1)-O(1)	87.76(7)	N(3)-Co(1)-O(3)	86.69(14)
Cl(1)-Co(1)-N(1)	171.50(6)	Cl(1)-Co(1)-N(1)	174.70(8)	N(1)-Co(1)-O(3)	101.36(15)	N(1)-Zn(1)-O(3)	92.42(16)	N(4)-Co(1)-N(6)	99.60(9)	N(4)-Co(1)-O(1)	100.07(14)
Cl(1)-Co(1)-N(3)	106.23(7)	Cl(1)-Co(1)-N(3)	108.35(8)	N(1)-Co(1)-O(2)#1	166.10(14)	N(1)-Zn(1)-O(4)	102.42(15)	N(4)-Co(1)-O(1)	101.46(7)	N(4)-Co(1)-O(3)	131.17(15)
Cl(1)-Co(1)-N(5)	108.46(6)	Cl(1)-Co(1)-N(5)	103.39(8)	N(3)-Co(1)-N(5)	156.92(18)	N(3)-Zn(1)-N(5)	75.72(16)	N(6)-Co(1)-O(1)	96.31(8)	O(1)-Co(1)-O(3)	91.95(12)
				N(3)-Co(1)-O(3)	89.64(17)	N(3)-Zn(1)-O(3)	105.81(14)				
				N(3)-Co(1)-O(2)#1	102.66(16)	N(3)-Zn(1)-O(4)	159.80(14)				
				N(5)-Co(1)-O(3)	90.43(17)	N(5)-Zn(1)-O(3)	89.78(16)				
				N(5)-Co(1)-O(2)#1	100.39(16)	N(5)-Zn(1)-O(4)	105.82(16)				
				O(3)-Co(1)-O(2)#1	92.53(15)	O(3)-Zn(1)-O(4)	94.37(15)				

a) only one subunit is presented

Table S2: Hydrogen bonds for complexes **2**, **3, 5-7** [Å and deg].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
Complex **2**				
O(3)-H(3)...O(2)	0.84	2.04	2.772(4)	144.9
Complex **3**				
O(3)-H(3B)...O(1)#1	0.96	2.12	2.680(5)	115.8
O(3)-H(3A)...O(4)#3	0.91	1.91	2.792(6)	165.5
O(7)-H(7A)...O(5)	1.03	1.95	2.913(6)	153.5
O(7)-H(7B)...O(5)#4	0.89	2.05	2.921(6)	166.4
Symmetry transformations used to generate equivalent atoms: #1 x, -y+1/2, z+1/2; #2 x, -y+1/2, z-1/2; #3 x, y-1, z; #4 x, -y+3/2, z-1/2				
Complex **5**				
O(6)-H(6B)...O(13)	0.88	1.88	2.674(6)	147.7
O(13)-H(13C)...O(8)	0.89(2)	2.02(6)	2.767(8)	141(7)
O(13)-H(13C)...O(9)	0.89(2)	2.65(3)	3.504(10)	163(7)
O(13)-H(13D)...O(12)#1	0.90(2)	2.32(8)	2.771(7)	111(6)
O(14)-H(14B)...O(7)#3	0.90(2)	1.89(4)	2.722(9)	154(8)
O(14)-H(14A)...O(11)#3	0.93(8)	1.94(8)	2.819(12)	157(7)
O(3)-H(3A)...O(5)	0.96(7)	1.78(7)	2.688(5)	157(6)
O(3)-H(3B)...O(14)	0.86(8)	1.82(8)	2.673(6)	174(8)
O(6)-H(6A)...O(1)#1	0.84	2.01	2.700(5)	138.7
Symmetry transformations used to generate equivalent atoms: #1 x-1,y,z; #2 x+1,y,z; #3 x,-y+1/2,z-1/2				
Complex **6**				
N(2)-H(2)...N(8)#1	0.98	1.95	2.892(3)	159.9
N(5)-H(5)...O(2)#2	0.93	1.83	2.732(3)	165.1
Symmetry transformations used to generate equivalent atoms: #1 x+1/2,y-1/2,z #2 x-1/2,-y+1/2,z+1/2				
Complex **7**				
N(2)-H(2)...O(4)#1	0.93	1.87	2.762(7)	161.1
N(5)-H(5)...O(2)#2	0.94	1.80	2.738(5)	174.2
O(5)-H(5A)...O(2)	0.93	1.89	2.746(8)	150.8
O(5)-H(5B)...O(7)	0.94	1.90	2.723(12)	144.5
O(6)-H(6A)...O(5)	0.82	1.84	2.615(14)	158.3
O(6)-H(6B)...O(7)#3	0.98	1.69	2.596(13)	152.7
Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,y+1/2,z-1/2 #2 -x+1,-y+2,z+1/2 #3 -x+1,-y+1,z-1/2				

References

1) N. Kitajima, K. Fujisawa, C. Fujimoto, Y. Maro-oka, S. Hashimoto, T. Kitagawa, K. Toriumi, K. Tatsumi and A. Nakamura, *J. Am. Chem. Soc.*, 1992, **114**, 1277-1291.