Synthesis, structure and magnetic study of a novel mixed-valent $Co^{II}_{10}Co^{III}_{4}$ shield constructed by mixed pyridine-alcoholate ligands

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Table S1 Selected bonds lengths (Å) and angles (°) for **1**.

Bond lengths (Å)			
Co(1)−O(1)	1.899(3)	Co(4)-O(12)	1.934(3)
Co(1)−O(2)	1.895(3)	Co(4)−N(6)	1.939(4)
Co(1)−O(3)	1.943(3)	Co(4)−N(7)	1.828(4)
Co(1)−O(4)	1.928(3)	Co(5)−O(1)#1	2.275(3)
Co(1)−N(1)	1.925(4)	Co(5)−O(2)#1	2.020(3)
Co(1)−N(2)	1.828(4)	Co(5)−O(9)	2.134(3)
Co(2)−O(3)	2.149(3)	Co(5)−O(10)	2.113(4)
Co(2)−O(4)	2.135(3)	Co(5)−O(12)	2.104(3)
Co(2)−O(5)	1.981(3)	Co(5)−O(13)#1	2.055(3)
Co(2)−O(6)	2.231(3)	Co(6)−O(1)	2.115(3)
Co(2)−O(11)	2.078(3)	Co(6)−O(4)	2.154(3)
Co(2)−N(3)	2.152(4)	Co(6)−O(11)	2.072(3)
Co(3)−O(5)	2.012(3)	Co(6)−O(13)	2.073(3)
Co(3)−O(6)	2.030(3)	Co(6)−O(14)	2.092(3)
Co(3)−O(7)	2.372(3)	Co(6)−O(14)#1	2.080(3)
Co(3)-O(8)	2.034(3)	Co(7)−O(6)	2.063(3)
Co(3)−N(4)	2.111(4)	Co(7)−O(7)	2.096(3)
Co(3)−N(5)	2.165(4)	Co(7)−O(11)	2.082(3)
Co(4)−O(7)	1.889(3)	Co(7)−O(12)	2.156(3)
Co(4)−O(8)	1.891(3)	Co(7)−O(13)#1	2.084(3)
Co(4)−O(9)	1.969(3)	Co(7)−O(14)	2.087(3)
Bond angles (°)			
O(1)−Co(1)−O(3)	103.83(15)	N(6)−Co(4)−O(9)	89.99(16)
O(1)−Co(1)−O(4)	86.07(13)	N(7)−Co(4)−O(7)	171.02(16)
O(1)−Co(1)−N(1)	83.42(17)	N(7)−Co(4)−O(8)	85.12(17)
O(2)−Co(1)−O(1)	86.47(14)	N(7)−Co(4)−O(9)	83.75(17)
O(2)−Co(1)−O(3)	169.14(14)	N(7)−Co(4)−O(12)	97.16(17)
O(2)−Co(1)−O(4)	93.51(14)	N(7)−Co(4)−N(6)	94.5(2)
O(2)−Co(1)−N(1)	94.80(17)	O(2)#1−Co(5)−O(1)#1	74.23(13)
O(4)−Co(1)−O(3)	83.91(13)	O(2)#1−Co(5)−O(9)	105.86(13)
N(1)−Co(1)−O(4)	166.16(17)	O(2)#1−Co(5)−O(10)	93.95(15)

N(1)−Co(1)−O(3)	89.88(16)	O(2)#1−Co(5)−O(13)#1	98.74(13)
N(2)−Co(1)−O(1)	171.17(16)	O(2)#1−Co(5)−O(12)	176.69(13)
N(2)−Co(1)−O(2)	84.88(17)	O(9)−Co(5)−O(1)#1	174.13(12)
N(2)−Co(1)−O(3)	84.91(16)	O(10)−Co(5)−O(1)#1	92.30(14)
N(2)−Co(1)−O(4)	96.23(16)	O(10)−Co(5)−O(9)	93.55(15)
N(2)−Co(1)−N(1)	95.51(19)	O(12)−Co(5)−O(1)#1	102.90(12)
O(3)−Co(2)−O(6)	174.72(11)	O(12)−Co(5)−O(9)	77.17(13)
O(3)−Co(2)−N(3)	95.39(14)	O(12)−Co(5)−O(10)	84.46(14)
O(4)−Co(2)−O(3)	74.33(12)	O(13)#1−Co(5)−O(1)#1	79.82(12)
O(4)-Co(2)−O(6)	104.74(12)	O(13)#1−Co(5)−O(9)	94.40(13)
O(4)−Co(2)−N(3)	76.56(14)	O(13)#1−Co(5)−O(10)	162.57(16)
O(5)−Co(2)−O(3)	103.82(13)	O(13)#1−Co(5)−O(12)	82.22(12)
O(5)−Co(2)−O(4)	174.63(12)	O(1)−Co(6)−O(4)	75.44(12)
O(5)−Co(2)−O(6)	77.58(12)	O(11)−Co(6)−O(1)	94.45(13)
O(5)−Co(2)−O(11)	102.89(13)	O(11)−Co(6)−O(4)	82.00(12)
O(5)−Co(2)−N(3)	98.74(15)	O(11)−Co(6)−O(13)	174.64(11)
O(11)−Co(2)−O(3)	94.41(12)	O(11)−Co(6)−O(14)	84.19(12)
O(11)−Co(2)−O(4)	82.34(12)	O(11)−Co(6)−O(14)#1	100.35(13)
O(11)−Co(2)−N(3)	153.33(14)	O(13)−Co(6)−O(1)	83.29(13)
O(11)−Co(2)−O(6)	80.31(12)	O(13)−Co(6)−O(4)	92.72(12)
N(3)−Co(2)−O(6)	89.39(13)	O(13)−Co(6)−O(14)	97.89(13)
O(5)−Co(3)−O(6)	81.75(12)	O(13)−Co(6)−O(14)#1	84.79(13)
O(5)−Co(3)−O(7)	96.64(12)	O(14)−Co(6)−O(1)	177.62(10)
O(5)−Co(3)−O(8)	165.13(15)	O(14)−Co(6)−O(4)	102.40(12)
O(5)−Co(3)−N(4)	78.47(15)	O(14)#1−Co(6)−O(1)	97.59(12)
O(5)−Co(3)−N(5)	102.28(15)	O(14)#1−Co(6)−O(4)	172.85(11)
O(6)−Co(3)−O(7)	79.91(12)	O(14)#1−Co(6)−O(14)	84.60(13)
O(6)−Co(3)−O(8)	103.81(13)	O(6)−Co(7)−O(7)	86.08(13)
O(6)−Co(3)−N(4)	158.22(15)	O(6)−Co(7)−O(11)	84.26(12)
O(6)−Co(3)−N(5)	78.60(14)	O(6)−Co(7)−O(12)	92.58(12)
O(8)−Co(3)−O(7)	71.22(12)	O(6)−Co(7)−O(13)#1	172.57(11)
O(8)−Co(3)−N(4)	93.36(15)	O(6)−Co(7)−O(14)	95.74(12)
O(8)−Co(3)−N(5)	92.39(15)	O(7)−Co(7)−O(12)	74.98(12)
O(7)−Co(4)−O(8)	86.09(14)	O(11)−Co(7)−O(7)	93.97(12)
O(7)−Co(4)−O(9)	105.11(14)	O(11)−Co(7)−O(12)	168.72(11)
O(7)−Co(4)−O(12)	85.21(14)	O(11)−Co(7)−O(13)#1	103.12(12)
O(7)−Co(4)−N(6)	84.22(17)	O(11)−Co(7)−O(14)	84.11(12)
O(8)−Co(4)−O(9)	168.57(14)	O(13)#1−Co(7)−O(7)	94.10(13)
O(8)−Co(4)−O(12)	93.56(14)	O(13)#1−Co(7)−O(12)	80.32(12)
O(8)−Co(4)−N(6)	93.48(16)	O(13)#1−Co(7)−O(14)	84.37(12)
O(12)−Co(4)−O(9)	85.26(14)	O(14)−Co(7)−O(7)	177.20(12)
O(12)−Co(4)−N(6)	166.86(16)	O(14)−Co(7)−O(12)	107.02(12)

Symmetry transformations used to generate equivalent atoms: #1 −*x*, −*y*, −*z*

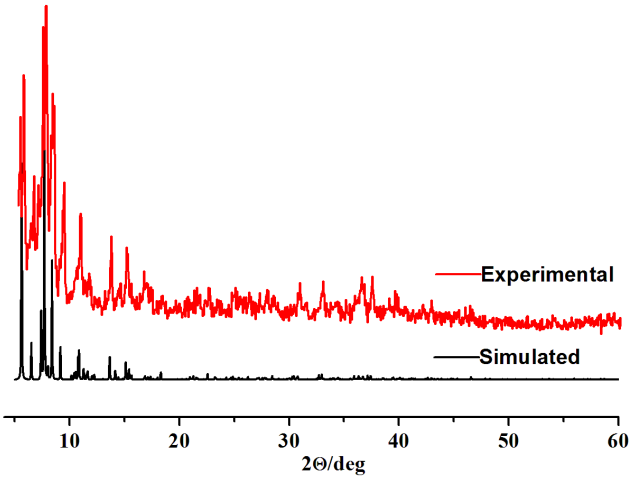

Fig. S1 Experimental and simulated powder X-ray diffraction patterns.

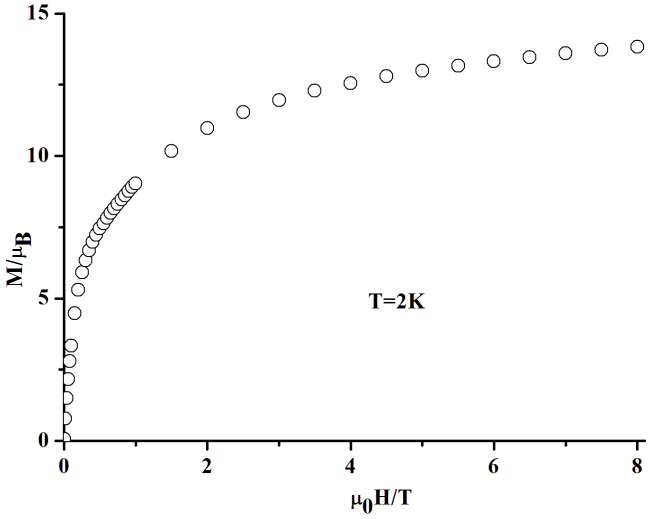

Fig. S2 Plot of $M/N\beta$ *vs.* H at 2 K.

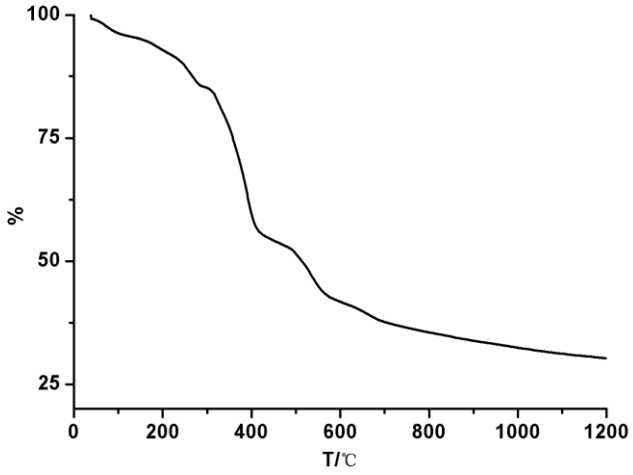

Fig. S3 TGA curve for **1**. The weight loss of 3.45% from 100 to 200°C is corresponding to 5 lattice water molecules

Synthesis for **1**.

$Co(NO_3)_2 \cdot 6H_2O$ (0.78 g, 2.00 mmol), hmpH (0.10 g, 1 mmol) and $pdmH_2$ (0.14 g, 1.00 mmol) in was dissolved in MeOH/MeCN (20/2 mL) . The mixture was stirred for a 10 min and then Et_3N (1.00 mL, 7.10 mmol) was add under vigorous stirring, which caused a rapid color change from pink to red brown. The solution was stirred for1 h, filtered, and the filtrate left undisturbed at ambient temperature. After one week, red-brown prism crystals were collected by filtration, washed with cold MeCN (2 × 5 mL), and dried under ambient temperature. Yield: 108 mg (37% based on hmpH). Elemental analysis calcd. (%) for $Co_{14}C_{90}H_{98}N_{14}O_{28}$ (loss of all lattice H_2O): C 40.81, H 3.73, N 7.40; Found (%): C 40.53, H 4.00, N 7.66.