

Supplementary Information for

**Preparation and structures of dinuclear complexes containing
M^{II}–OH centers**

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General Methods

All reagents were purchased from commercial sources and used as received, unless otherwise noted. Solvents were sparged with argon and dried over columns containing Q-5 and molecular sieves. Acetone was purified before use.¹

3,5-Bis[bis(*N*-6-pivalamido-2-pyridylmethyl)aminomethyl]-1*H*-pyrazole (H_5bppap)² and $Mn(OTf)_2 \cdot 2MeCN$ ³ was synthesized as according to literature method. The syntheses of metal complexes were conducted in a Vacuum Atmosphere, Co. drybox under an argon atmosphere. Elemental analyses were performed on a Perkin-Elmer 2400 CHNS analyzer.

Preparative Methods

Ligand Synthesis

3,5-Bis[bis(*N*-6-neopentylamino-2-pyridylmethyl)aminomethyl]-1*H*-pyrazole ($H_5bnppap$). H_5bppap (711 mg, 0.802 mmol) was dissolved in THF (25 mL) and added dropwise to a suspension of $LiAlH_4$ (305 mg, 8.03 mmol) in anhydrous THF (100 mL) under a nitrogen atmosphere at -78 °C. The reaction was then at -78 °C for one hour before warming up to room temperature. After 18 hours, water (10 mL) and 1.0 M NaOH (10 mL) solution was added to quench any excess $LiAlH_4$. The reaction mixture was then filtered to remove the precipitated metal salts. The filtrate was extracted by dichloromethane (3 x 50 mL). The organic layer was collected and dried over anhydrous Na_2SO_4 . Solvent was then removed *in vacuo* to afford the off-white product (633 mg, 95 %) which was sufficiently pure to use without further purification. The product was dried under vacuum for 48 hours prior to use. Mp: 53 °C. ¹H-NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.78, 4H, Ar_{py-H}), 6.77 (s, 4H, Ar_{py-H}), 6.26 (t, *J* = 7.06), 4H, Ar_{py-H}), 4.61 (s, 4H, Ar_{py-NH}), 3.77 (s, 4H, $Pz-CH_2$), 3.63 (s, 8H, Ar_{py-CH_2}), 3.03 (s, 8H, $Ar_{py-NHCH_2}$). ¹³C-NMR (400 MHz, $CDCl_3$) δ 158.99, 137.94, 135.72, 125.45, 111.66, 104.26, 103.67, 59.51, 54.10, 32.00, 30.25, 27.49. FTIR (KBr, cm^{-1}): ν(NH) 3421, 3300, 3296. HRMS (ES+; *m/z*): 831.6238 [M^+]. Exact mass calcd for $C_{49}H_{75}N_{12}$ [$M+H$], 831.6232.

Complexes Synthesis

μ-{3,5-Bis[bis(*N*-6-neopentylamino-2-pyridylmethyl)aminomethyl]-1*H*-pyrazolato}-dihydroxocobalt(II) tetraphenylborate [$Co^{II}_2H_4bnppap(OH)_2$] (BPh_4). To a solution of $H_5bnppap$ (55.0 mg, 0.0622 mmol) in MeOH (5 mL) solid NaH (5.5 mg, 0.23 mmol) was added. Solid $Co(NO_3)_2 \cdot 6H_2O$ (55.0 mg, 0.18 mmol) was added and the reaction was stirred for 30 minute. Ultra pure water (2.5 mL, 0.14 mmol) was injected into the reaction mixture using a micro glass syringe and the reaction was stirred for one hour. Solid $NaBPh_4$ (23.8 mg, 0.0695 mmol) was then added, followed by the immediate formation of a lime-green precipitate. The product was filtered, washed by MeOH and Et_2O and dried under reduced pressure for one hour. Bulk recrystallization was carried out by layering pentane on the THF filtrate to afford analytically pure crystalline product (40.0 mg, 47 %). X-ray quality crystals were grown by layering pentane on a THF solution of the isolated salt. Anal. Calcd (found) for [$Co^{II}_2H_4bnppap$](BPh_4)· C_4H_8O , $C_{77}H_{103}BCO_2N_{12}O_3$ Calcd (found): C, 66.94 (67.34); H, 7.61 (7.56); N, 11.86 (12.24). FTIR (KBr, cm^{-1}): ν(NH) 3235. UV/vis (acetone): λ_{max}(ε) = 470 (420), 660 (98), 749 (70). μ_{eff} = 5.23.

μ-{3,5-Bis[bis(*N*-6-neopentylamino-2-pyridylmethyl)aminomethyl]-1*H*-pyrazolato}-dihydroxodimanganese(II) tetraphenylborate [$Mn^{II}_2H_4bnppap(OH)_2$](BPh_4). To a solution of $H_5bnppap$ (122.1 mg, 0.147 mmol) in MeOH (5 mL) solid NaH (10.3 mg, 0.429 mmol) was added. $Mn(OTf)_2 \cdot 2MeCN$ (130. mg, 0.299 mmol) was added and the solution turned slightly murky. The reaction was stirred for 30 minutes and filtered. Ultra pure water (5.5 mL, 0.31 mmol) was injected into the reaction mixture using a micro glass syringe

and the reaction was stirred for one hour. Solid NaBPh₄ (80.0 mg, 0.234 mmol) was then added, followed by the immediate formation of an off-white precipitate. The product was filtered, washed by MeOH and Et₂O and dried under reduced pressure for one hour. The isolated metal salt was then redissolved in THF and filtered through a short cotton plug. Bulk recrystallization was carried out by layering pentane on the THF filtrate to afford analytically pure crystalline product (90.0 mg, 50 %). X-ray quality crystals were grown by layering pentane on an acetone solution of the isolated metal salt. [Mn^{II}₂H₂bnppap](BPh₄)·C₄H₈O, C₇₇H₁₀₃BMn₂N₁₂O₃ Calcd (found): C, 67.73 (67.42); H, 7.60 (7.44); N, 12.31 (12.48). FTIR (KBr, cm⁻¹): ν(OH) 3643, n(NH) 3242. μ_{eff} = 8.01.

Physical Methods

¹H NMR and ¹³C NMR spectra were recorded on a Bruker DRX400 MHz spectrometer. Chemical shifts are reported in ppm relative to residual solvent. Fourier transform infrared spectra were collected on a Varian 800 Scimitar Series FTIR spectrometer. Melting point was recorded with a Laboratory Devices MET-TEMP apparatus and is uncorrected. Electronic absorbance spectra were recorded with a Cary 50 spectrophotometer using a 1.00 cm quartz cuvette.

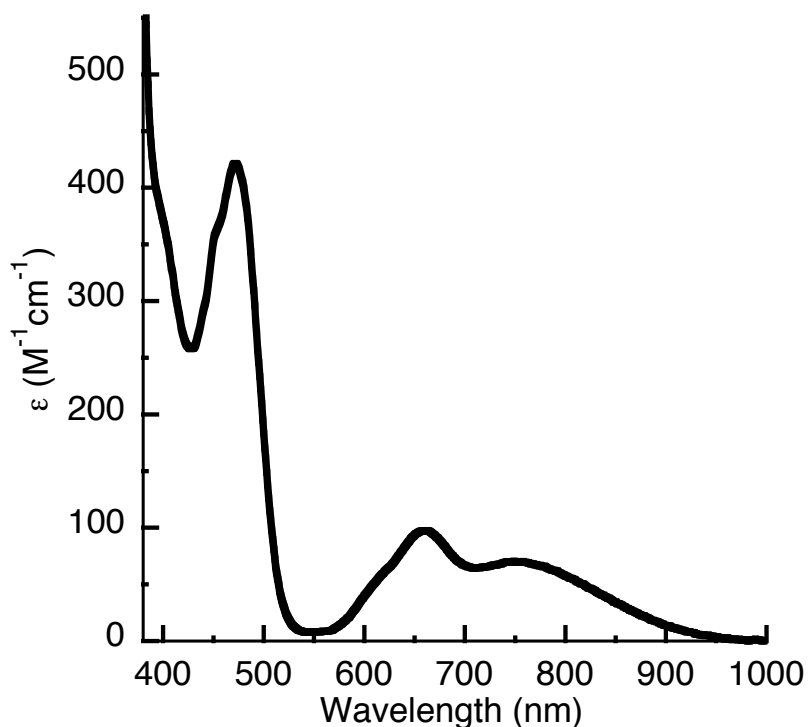


Figure S1. Visible absorbance spectrum of [Co^{II}₂H₄bnppap(OH)₂](BPh₄) in acetone.

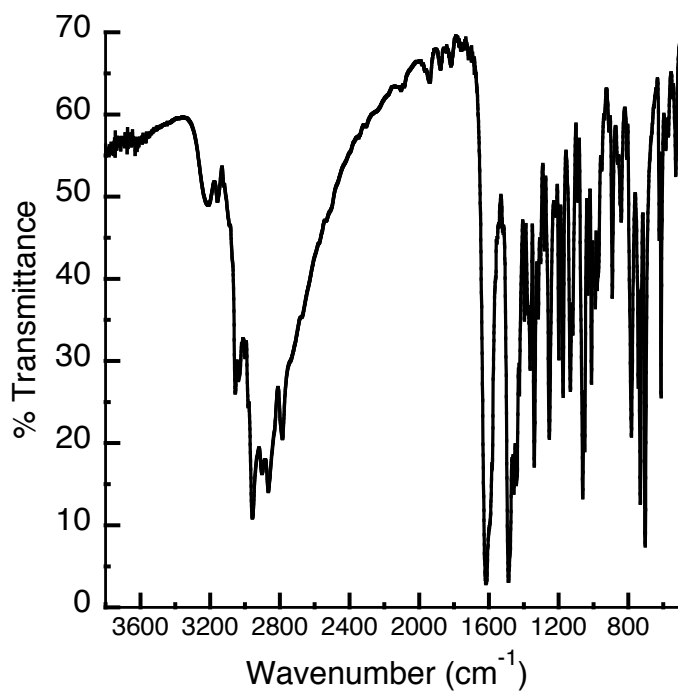


Figure S2. FT-IR spectrum of $[\text{Co}^{\text{II}}_2\text{H}_4\text{bnppap}(\text{OH})_2](\text{BPh}_4)$ in KBr.

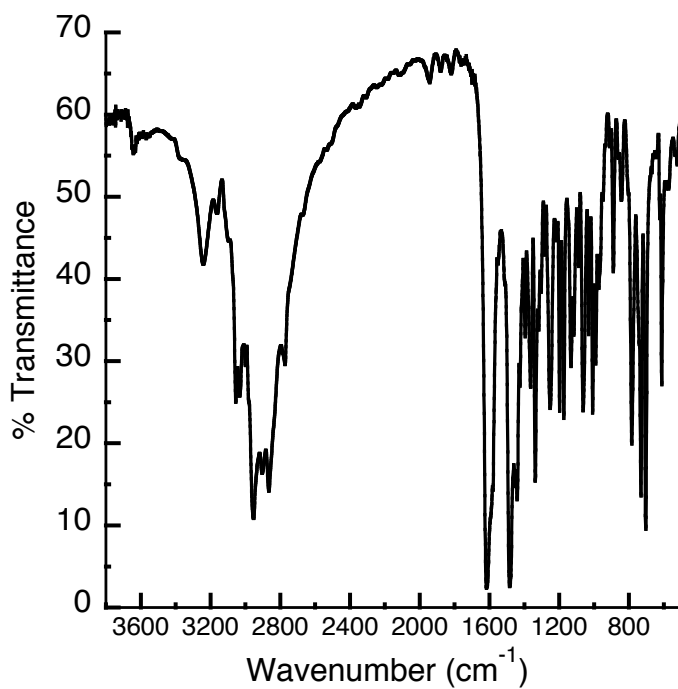


Figure S3. FT-IR spectrum of $[\text{Mn}^{\text{II}}_2\text{H}_4\text{bnppap}(\text{OH})_2](\text{BPh}_4)$ in KBr.

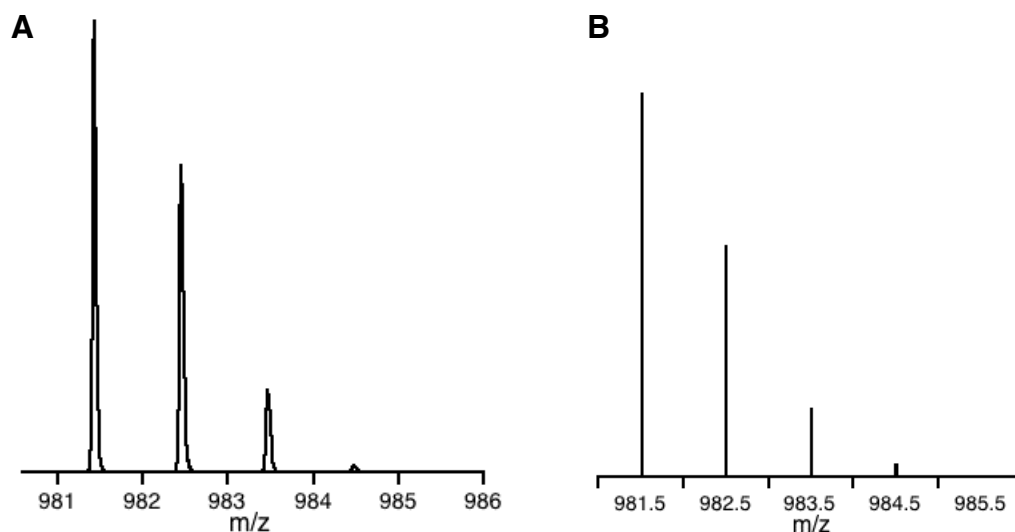


Figure S3. ESI-MS of $[\text{Co}^{\text{II}}_2\text{H}_4\text{bnppap}({}^{16}\text{OH})_2]^+$ (A) and calculated spectrum (B).

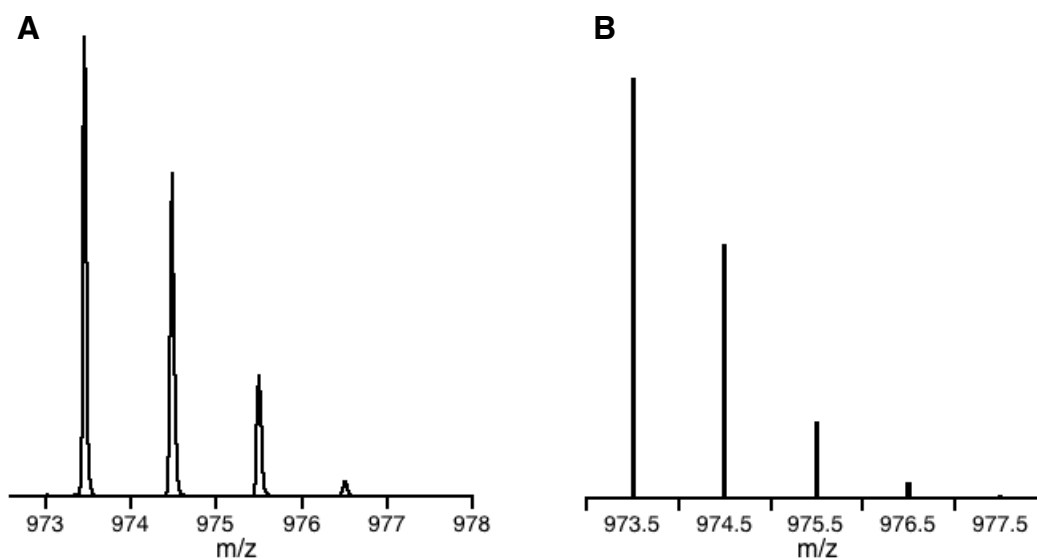


Figure S4. ESI-MS of $[\text{Mn}^{\text{II}}_2\text{H}_4\text{bnppap}({}^{16}\text{OH})_2]^+$ (A) and calculated spectrum (B).

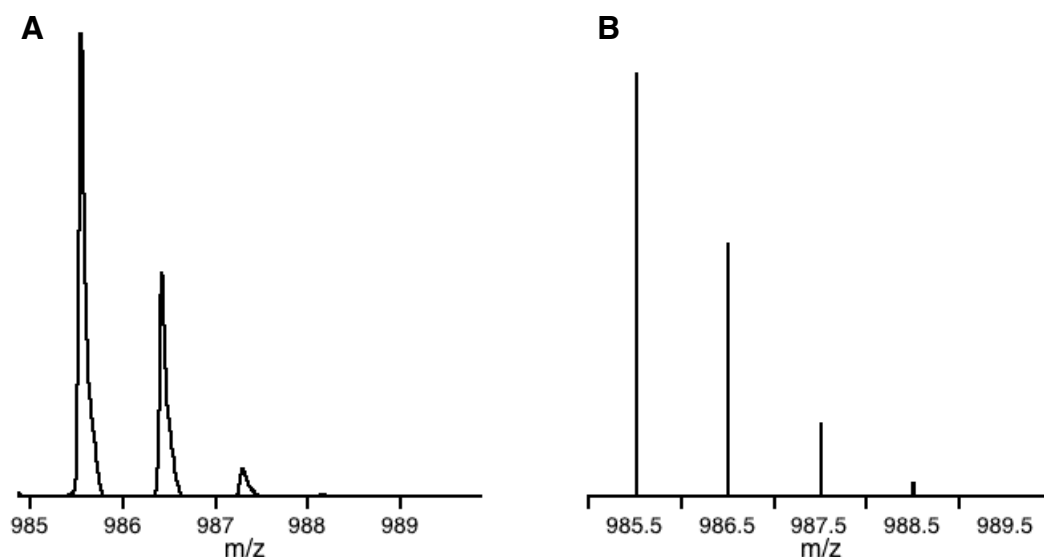


Figure S5. ESI-MS of $[\text{Co}^{\text{II}}_2\text{H}_4\text{bnppap}(^{18}\text{OH})_2]^+$ (A) and calculated spectrum (B).

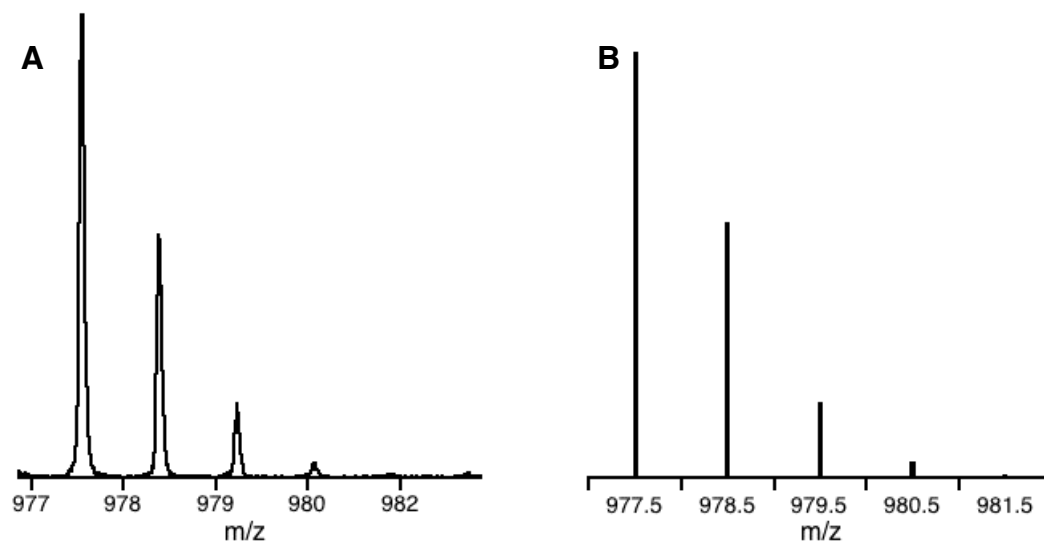


Figure S6. ESI-MS of $[\text{Mn}^{\text{II}}_2\text{H}_4\text{bnppap}(^{18}\text{OH})_2]^+$ (A) and calculated spectrum (B).

Crystallography Methods

General Crystallographic Procedures. A Bruker SMART APEX II diffractometer was used to collect all the data. The APEX2⁴ program package was used to determine the unit-cell parameters and for data collections (45 sec/frame scan time for a hemisphere of diffraction data). The raw frame data was processed using SAINT⁵ and SADABS⁶ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁷ program. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁸ for neutral atoms were used throughout the analysis.



A green crystal of approximate dimensions 0.09 x 0.20 x 0.24 mm was mounted on a

glass fiber and transferred to a Bruker SMART APEX II diffractometer. There were no systematic absences nor any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. Hydrogen atoms were either located from a difference-Fourier map and refined (x,y,z and U_{iso}) or were included using a riding model. There was one-half molecule of pentane and one-half molecule of tetrahydrofuran present per formula-unit. These solvents were included using partial site-occupancy-factors (0.5/0.5). At convergence, $wR2 = 0.1230$ and $Goof = 1.014$ for 881 variables refined against 15634 data (0.80\AA), $R1 = 0.0466$ for those 10834 data with $I > 2.0\sigma(I)$.

$[Mn^{II}_2H_4bnppap(OH)_2](BPh_4)\cdot 2(C_5H_{12})\cdot C_3H_6O$

A colorless crystal of approximate dimensions $0.23 \times 0.40 \times 0.51$ mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The diffraction symmetry was mmm and the systematic absences were consistent with the orthorhombic space groups $Pbcm$ and $Pca2_1$. It was later determined that space group $Pca2_1$ was correct. Hydrogen atoms were included using a riding model. There was solvent present which appears to be one molecule of acetone and two molecules of pentane. The pentane molecules were poorly resolved and it was necessary to restrain interatomic distances, angles and thermal parameters. The tert-butyl group defined by atoms C(8)-C(11) was also poorly resolved, however, a reasonable disorder model could not be identified. It was necessary to refine several atoms isotropically. Least-squares analysis yielded $wR2 = 0.2426$ and $Goof = 1.042$ for 837 variables (15 restraints) refined against 17304 data (0.80\AA), $R1 = 0.0786$ for those 13820 data with $I > 2.0\sigma(I)$. The absolute structure was assigned by refinement of the Flack parameter.⁹

X-ray Crystallography Collection Data

Table S1. Crystallographic data of $[\text{Mn}^{\text{II}}\text{H}_4\text{bnppap}(\text{OH})_2](\text{BPh}_4)\cdot 2(\text{C}_5\text{H}_{12})\cdot \text{C}_3\text{H}_6\text{O}$ and $[\text{Co}^{\text{II}}\text{H}_4\text{bnppap}(\text{OH})_2](\text{BPh}_4)\cdot 0.5\text{C}_5\text{H}_{12}\cdot 0.5\text{C}_4\text{H}_8\text{O}$

	$[\text{Mn}^{\text{II}}\text{H}_4\text{bnppap}(\text{OH})_2]^+$	$[\text{Co}^{\text{II}}\text{H}_4\text{bnppap}(\text{OH})_2]^+$
empirical formula	$\text{C}_{73}\text{H}_{95}\text{BMn}_2\text{N}_{12}\text{O}_2\cdot 2(\text{C}_5\text{H}_{12})\cdot \text{C}_3\text{H}_6\text{O}$	$\text{C}_{73}\text{H}_{95}\text{BCo}_2\text{N}_{12}\text{O}_2\cdot 0.5\text{C}_5\text{H}_{12}\cdot 0.5\text{C}_4\text{H}_8\text{O}$
formula weight	1495.67	1373.41
T (K)	143(2)	163(2)
λ (Å)	0.71073	0.71073
crystal system	Orthorhombic	Triclinic
space group	$Pca2_1$	$P\bar{1}$
a (Å)	23.8786(15)	13.4546(9)
b (Å)	20.3401(12)	15.3395(10)
c (Å)	17.4648(11)	19.6642(13)
a (deg)	90	99.2803(9)
b (deg)	90	96.3614(9)
g (deg)	90	104.0454(9)
V (Å ³)	8482.5(9)	3837.6(4)
Z	4	2
δ_{max} (mg m ⁻³)	1.171	1.189
μ (mm ⁻¹)	0.351	0.485
F(000)	3216	1466
crystal size (mm ³)	0.51 x 0.40 x 0.23	0.24 x 0.20 x 0.09
reflections	67332	41752
collected/unique		
R(int)	0.0327	0.0415
data / restraints / parameters	17304 / 12 / 837	15634 / 0 / 881
R ^a	0.0786	0.0466
R _w ^b	0.2426	0.1230
GOF ^c	1.042	1.014

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$. ^c Goodness of fit on F^2 .

Table S2. Selected bond lengths and angles for $[\text{Mn}^{\text{II}}\text{H}_4\text{bnppap}(\text{OH})_2](\text{BPh}_4)$ and $[\text{Co}^{\text{II}}\text{H}_4\text{bnppap}(\text{OH})_2](\text{BPh}_4)$

distance (Å) or angle (deg)	$[\text{Mn}^{\text{II}}\text{H}_4\text{bnppap}(\text{OH})_2]^+$	$[\text{Co}^{\text{II}}\text{H}_4\text{bnppap}(\text{OH})_2]^+$
M1-O1	2.003(3)	1.938(2)
M1-N4	2.128(4)	2.034(2)
M1-N3	2.204(4)	2.102(2)
M1-N2	2.234(4)	2.107(2)
M1-N1	2.330(4)	2.192(2)
M2-O2	2.006(4)	1.944(2)
M2-N10	2.137(4)	2.046(2)
N2-N9	2.230(5)	2.119(2)
N2-N8	2.207(5)	2.104(2)
N2-N7	2.285(4)	2.195(2)
O1-M1-N4	111.20(15)	106.28(8)
O1-M1-N3	101.67(15)	101.94(8)
N4-M1-N3	112.52(17)	114.64
O1-M1-N2	100.60(13)	100.48(2)
N4-M1-N2	114.75(15)	116.10(8)
N3-M1-N2	114.56(18)	114.73(8)
O1-N1-N1	174.00(16)	176.51(8)
N4-M1-N1	74.57(17)	76.99(8)
N3-M1-N1	76.94(17)	77.50(8)
N2-M1-N1	74.98(15)	76.78(8)
O2-M2-N10	113.07(16)	106.61(8)
O2-M2-N8	102.03(17)	102.23(8)
N10-M2-N8	114.23(15)	115.00(8)
O2-M2-N9	99.19(16)	100.11(8)
N10-M2-N9	115.2(2)	117.25(8)
N8-M2-N9	111.3(2)	112.95(8)
O2-M2-N7	172.13(16)	176.81
N10-M2-N7	74.46(16)	76.25(8)
N8-M2-N7	75.94(17)	77.51(8)
N9-M2-N7	74.84(16)	77.17(8)

References

1. W. L. F. Armarego, D. D. Perrin, Purification of Laboratory Chemicals, 3rd ed.; Pergamon Press: N.Y., 1988, pp 68.
2. G. K.-Y. Ng, J. W. Ziller, A. S. Borovik, *Inorg. Chem.* 2011, **50**, 7922-7924.
3. P. S. Bryan, J. C. Dabrowiak, *Inorg. Chem.* 1975, **14**, 296-299.
4. APEX2 Version 2.2-0 Bruker AXS, Inc.; Madison, WI 2007.
5. SAINT Version 7.46a, Bruker AXS, Inc.; Madison, WI 2007.
6. G. M. Sheldrick, SADABS, Version 2008/1, Bruker AXS, Inc.; Madison, WI 2008.
7. G. M. Sheldrick, SHELXTL, Version 2008/4, Bruker AXS, Inc.; Madison, WI 2008.
8. International Tables for X-Ray Crystallography 1992, Vol. C., Dordrecht: Kluwer Academic Publishers.
9. H. D. Flack, *Acta. Cryst.*, A39, 876-881, 1983.