

**Structural Diversity in a Series of Metal Complexes with a Dinucleating Ligand
Containing Carboxyamido Groups**

Supporting Information

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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. Potassium hydride (KH), as a 30% dispersion in mineral oil, was filtered with medium porosity glass frit and washed 5 times each with pentane and Et₂O. The solid KH was dried under vacuum and stored under an inert atmosphere. 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.

Bis[N-(6-pivalamido-2-pyridylmethyl)]amine¹ and 3,5-bis(chloromethyl)-(tetrahydropyran-2-yl)-1H-pyrazole² and were prepared according to literature methods with minor variations.

Preparative Methods

Ligand Synthesis

3,5-Bis[bis(N-6-pivalamido-2-pyridylmethyl)aminomethyl]-1H-pyrazole (H₅bppap). 3,5-Bis(chloromethyl)-(tetrahydropyran-2-yl)-1H-pyrazole (0.62 g, 2.38 mmol), bis[N-(6-pivalamido-2-pyridylmethyl)]amine (2.00 g, 5.01 mmol), sodium carbonate (5.36 g, 50.1 mmol) and acetonitrile were refluxed in air. The reaction mixture was then allowed to cool to room temperature after 24 hours. Solid material was filtered and the filtrate was concentrated under reduced pressure to a yellow residue. The residue was dissolved in ethanol (60 mL) in a 250 mL round bottom flask. Concentrated HCl (20 mL) was then added and the mixture was stirred for 21 hours with the flask capped by a rubber septum. Solvent was removed under vacuum and the orange oil left over was dissolved in water (100 mL). Saturated aqueous Na₂CO₃ solution (100 mL) was slowly added to the solution until the pH was found to be 9. The mixture was then extracted by dichloromethane (3 X 50 mL). The 3 organic portions were then combined, dried over anhydrous Na₂SO₄ and filtered. The filtrate was concentrated to dryness *in vacuo* to give a light orange oil. The product was purified by recrystallization from acetone and hexane. The white crystalline solid formed slowly overnight was then filtered and collected on a medium porosity glass frit. The product was washed by a minimum amount of cold diethyl ether and dried under reduced pressure, 1.78 g (84 %). Mp: 173 °C (decomp). ¹H-NMR (500 MHz, CDCl₃) δ 8.11 (d, *J* = 8.3, 4H, Ar_{py}-H), 8.07 (s, 4H, Ar_{py}NH(CO)), 7.65 (t, *J* = 7.90, 4H, Ar_{py}-H), 7.19 (s, 4H, Ar_{py}-H), 6.17 (s, 1H, Pz-H), 3.74 (s, 4H, Pz-CH₂N), 3.69 (s, 8H, Ar_{py}-CH₂N), 1.32 (s, 36H, C(CH₃)); ¹³C-NMR (500 MHz, CDCl₃) δ 177.30, 157.46, 151.29, 139.07, 119.10, 112.50, 104.97, 59.51, 40.00, 27.69. FTIR (KBr, cm⁻¹): ν(NH) 3432, 3351, 3257, ν(CO) 1686. HRMS (ES⁺; *m/z*): 909.5219 [M⁺]. Exact mass calcd for C₄₉H₆₆N₁₂O₄Na [M+Na], 909.5228.

Complex Synthesis

μ-{3,5-Bis[bis(N-6-pivalamido-2-pyridylmethyl)aminomethyl]-1H-pyrazolato}dii ron(II) trifluoromethanesulfonate [Fe^{II}₂H₂bppap](OTf). A solution of 3,5-bis[bis(N-6-pivalamido-2-pyridylmethyl)aminomethyl]-1H-pyrazole (H₅bppap) (171.0 mg, 0.1929 mmol) in anhydrous tetrahydrofuran (THF) (10 mL) was treated with solid KH (26.7 mg, 0.666 mmol). After gas evolution ceased, solid Fe(OTf)₂ (140.6 mg, 0.3972 mmol) was added and the solution turned light orange as Fe(OTf)₂ dissolved slowly. The solution was stirred for 12 hours and the solution changed from orange to bright yellow and cloudier gradually. The solvent was then removed *in vacuo* and the residue left was redissolved in anhydrous CH₂Cl₂. Insoluble materials were filtered. The solvent was then removed under reduced pressure to afford an orange-yellow solid, 217.3 mg (98 %). X-ray quality crystals were obtained by diffusion of pentane in a CH₂Cl₂ solution of the isolated metal salt. Anal. Calcd (found) for [Fe^{II}₂H₂bppap](OTf)·0.3CH₂Cl₂, C_{50.3}H_{65.6}F₃Cl_{0.6}Fe₂N₁₂O₇S: C, 51.73 (51.62); H, 5.25 (5.48); N, 13.97 (14.36). FTIR (KBr, cm⁻¹): ν(NH) 3306, ν(CO) 1695, 1675. μ_{eff} = 6.35.

μ -{3,5-Bis[bis(N-6-pivalamido-2-pyridylmethyl)aminomethyl]-1H-pyrazolato}dicobalt(II) tetrphenylborate [Co^{II}₂H₂bppap](BPh₄). A solution of 3,5-bis[bis(N-6-pivalamido-2-pyridylmethyl)aminomethyl]-1H-pyrazole (H₅bppap) (91.3 mg, 0.103 mmol) in anhydrous methanol (MeOH) (5 mL) was treated with solid NaOMe (18.7 mg, 0.346 mmol). After 15 minutes, solid Co(OAc)₂ (38.0 mg, 0.215 mmol) was added and the solution turned green immediately. Solid NaBPh₄ (38.0 mg, 0.111 mmol) was then added after 1 hour, followed by the immediate formation of a lime green precipitate. The solid was filtered, washed by MeOH (2 x 5 mL) and Et₂O (2 x 5 mL) and dried under vacuum, 116.7 mg (86 %). X-ray quality crystals were obtained by layering pentane on a CH₂Cl₂/MeOH mixture of the isolated metal salt. Anal. Calcd (found) for [Co^{II}₂H₂bppap](BPh₄)·MeOH·CH₂Cl₂, C₇₅H₈₉BCl₂Co₂N₁₂O₅: C, 62.68 (62.64); H, 6.24 (6.28); N, 11.69 (11.95). FTIR (KBr, cm⁻¹): ν (NH) 3276, 3227, ν (CO) 1704. UV/vis (MeCN): $\lambda_{\max}(\epsilon)$ = 439 (sh), 473 (248), 598 (70), 650 (76). μ_{eff} = 4.75. HRMS (ES+; m/z): 1001.3732 [M⁺]. Exact mass calcd for C₄₉H₆₃N₁₂Co₂O₄ [M⁺], 1001.3759.

Hydroxo- μ -{3,5-Bis[bis(N-6-pivalamido-2-pyridylmethyl)aminomethyl]-1H-pyrazolato}diiron (II) trifluoromethanesulfonate [Fe^{II}(OH)Fe^{II}H₃bppap](OTf). Yellow microcrystalline [Fe^{II}₂H₃bppap](OTf) (25.0 mg, 0.0218 mmol) was dissolved in acetone in an argon atmosphere. Water (10.0 μ L, 0.556 mmol) was injected into the solution by a microsyringe and the solution was then stirred for an hour. Analytically pure product was isolated as yellow rod-like crystals by layering pentane on top of the acetone solution. The isolated crystalline product was filtered, washed by Et₂O (10 mL) and dried under vacuum for an hour, 20.2 mg (79 %). X-ray quality crystals were obtained by layering pentane on top of an acetone solution of the metal salt. Anal. Calcd (found) for [Fe^{II}₂H₃bppap(OH)](OTf)·CH₃C(O)CH₃, C₅₂H₇₂F₃Fe₂N₁₂O₅S: C, 52.14 (52.48); H, 5.86 (5.58); N, 13.77 (13.66). FTIR (KBr, cm⁻¹): ν (NH) 3515, 3323, ν (CO) 1712, 1690, 1674. μ_{eff} = 6.25.

Hydroxo- μ -{3,5-Bis[bis(N-6-pivalamido-2-pyridylmethyl)aminomethyl]-1H-pyrazolato}dicobalt(II) tetrphenylborate [Co^{II}(OH)Co^{II}H₃bppap](BPh₄). Green isolated salt of [Co^{II}₂H₂bppap](BPh₄) (30.0 mg, 0.0227 mmol) was dissolved in acetone in an argon atmosphere. Water (10.0 μ L, 0.556 mmol) was injected into the solution by a microsyringe and the solution was then stirred for an hour. Green needle-like microcrystals were obtained by layering pentane on an acetone solution of the isolated metal salt, 19.2 mg (63 %). Anal. Calcd (found) for [Co^{II}₂H₃bppap(OH)](BPh₄), C₇₃H₈₅BCo₂N₁₂O₅: C, 65.47 (64.86); H, 6.40 (6.28); N, 12.55 (11.76). FTIR (KBr, cm⁻¹): ν (OH) 3613, ν (NH) 3385, 3329, ν (CO) 1696. UV/vis (MeCN): $\lambda_{\max}(\epsilon)$ = 453 (sh), 488 (179), 586 (89). μ_{eff} = 5.19. HRMS (ES+; m/z): 1019.3881 [M⁺]. Exact mass calcd for C₄₉H₆₅N₁₂Co₂O₅ [M⁺], 1019.3865.

Hydroxo- μ -{3,5-Bis[bis(N-6-pivalamido-2-pyridylmethyl)aminomethyl]-1H-pyrazolato}dicobalt(II) trifluoromethanesulfonate [Co^{II}(OH)Co^{II}H₃bppap](OTf). To a solution of H₅bppap (40.0 mg, 0.0451 mmol) in DMA (5 mL), solid KH (5.7 mg, 0.14 mmol) was added. After gas evolution ceased, anhydrous Co(OAc)₂ (16.9 mg, 0.0904 mmol) was added and the solution turned dark brown gradually. Solid KOTf (9.0 mg, 0.048 mmol) was added after one hour and the reaction mixture turned murkier after a few minutes. The reaction mixture was further stirred for an hour and then filtered. The brown filtrate was dried *in vacuo* to afford a brown residue which was redissolved in acetone to give a green solution. Water (10.0 μ L, 0.556 mmol) was injected by a microsyringe and the solution was stirred for an hour. The filtrate was dried *in vacuo* to afford a dark green crude product (25.0 mg, 47 %). X-ray quality crystals were obtained by repeated recrystallization from dichloromethane and pentane. FTIR (KBr, cm⁻¹): ν (OH) 3576, ν (NH) 3289, 3211, ν (CO) 1690. UV/vis (MeCN): $\lambda_{\max}(\epsilon)$ = 448 (170), 489 (188), 586 (89).

Physical Methods

^1H NMR and ^{13}C 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. Magnetic moments of the metal complexes were measured by Evan's method in DMSO.³

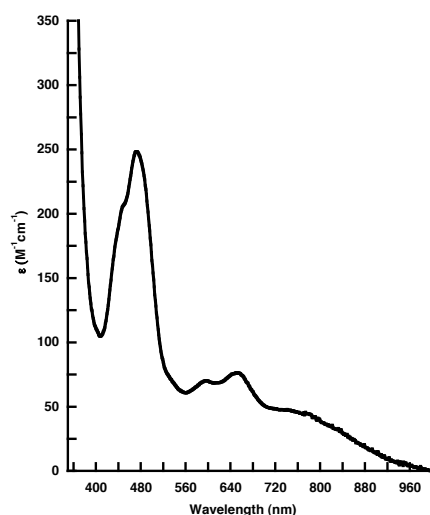


Figure S1. Visible absorbance spectra for $[\text{Co}^{\text{II}}_2\text{H}_2\text{bppap}](\text{BPh}_4)$ in MeCN

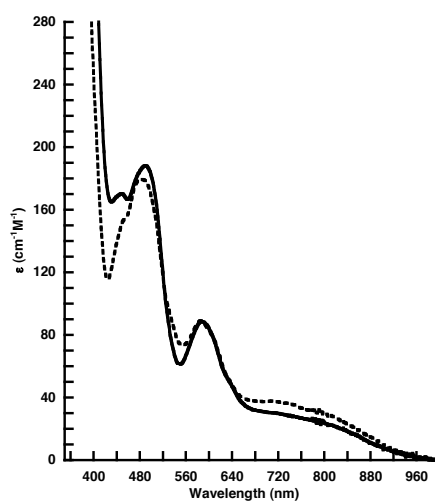


Figure S2. Visible absorbance spectra for $[\{\text{Co}^{\text{II}}(\text{OH})\}\text{Co}^{\text{II}}\text{H}_3\text{bppap}](\text{OTf})$ in MeCN (—) and $[\{\text{Co}^{\text{II}}(\text{OH})\}\text{Co}^{\text{II}}\text{H}_3\text{bppap}](\text{BPh}_4)$ in MeCN (⋯).

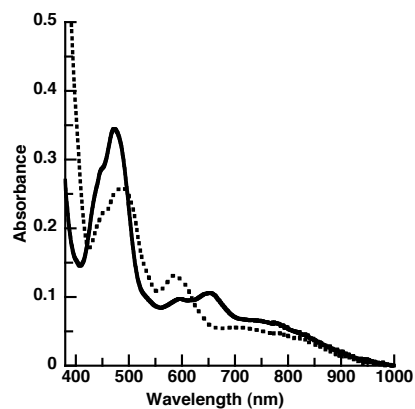


Figure S3. Visible absorbance spectra of 1.5 mM of $[\text{Co}^{\text{II}}_2\text{H}_2\text{bppap}](\text{BPh}_4)$ in MeCN (—) and after addition of 40 equiv. of H_2O (···) in a 1.00 cm quartz cuvette.

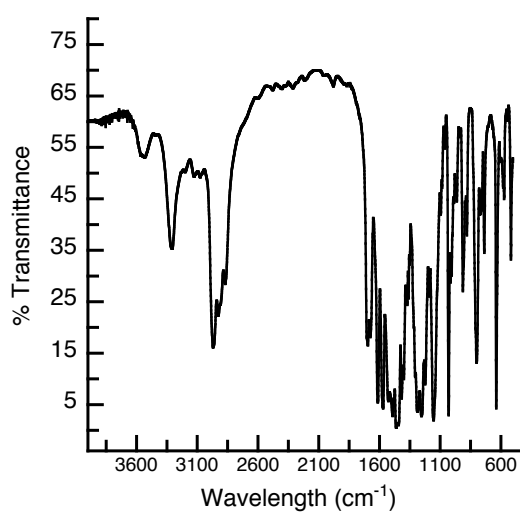


Figure S4. FT-IR spectrum of $[\text{Fe}^{\text{II}}_2\text{H}_2\text{bppap}](\text{OTf})$ in KBr.

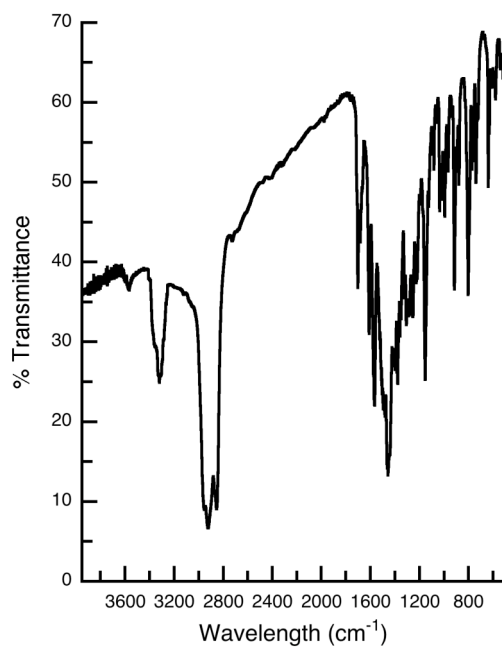


Figure S5. FT-IR spectrum of $[\text{Fe}^{\text{II}}_2\text{H}_2\text{bppap}](\text{OTf})$ in Nujol.

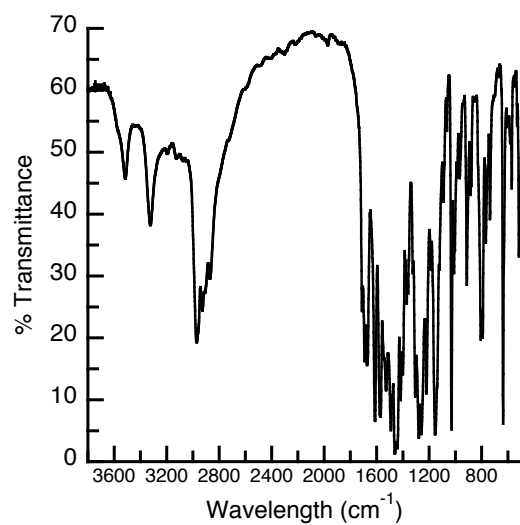


Figure S5. FT-IR spectrum of $[\{\text{Fe}^{\text{II}}(\text{OH})\}\text{Fe}^{\text{II}}\text{H}_3\text{bppap}](\text{OTf})$ in KBr.

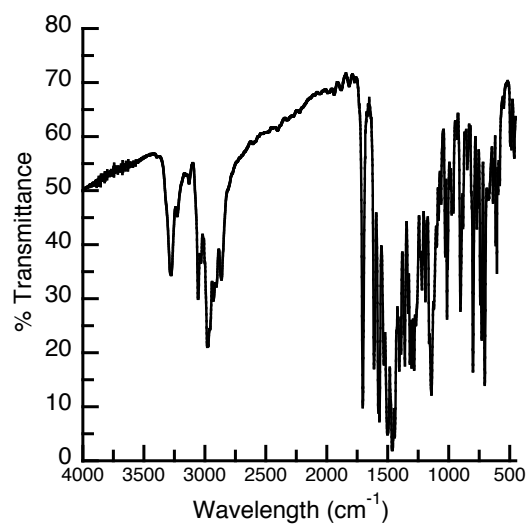


Figure S6. FT-IR spectrum of $[\text{Co}^{\text{II}}_2\text{H}_3\text{bppap}](\text{BPh}_4)$ in KBr.

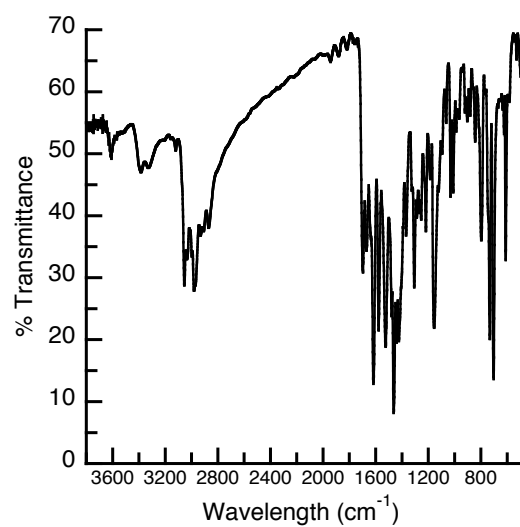


Figure S7. FT-IR spectrum of [$\{\text{Co}^{\text{II}}(\text{OH})\}\text{Co}^{\text{II}}\text{H}_3\text{bppap}\}(\text{BPh}_4)$] in KBr.

Table S1. Selected bond lengths and angles for $[\text{Fe}^{\text{II}}_2\text{H}_2\text{bppap}]^+$ and $[\{\text{Fe}^{\text{II}}(\text{OH})\}\text{Fe}^{\text{II}}\text{H}_3\text{bppap}]^+{}^a$

distance (Å) or angle (deg)	$[\text{Fe}^{\text{II}}_2\text{H}_2\text{bppap}]^+$	$[\{\text{Fe}^{\text{II}}(\text{OH})\}\text{Fe}^{\text{II}}\text{H}_3\text{bppap}]^+$
Fe1–O1	1.970(2)	-
Fe1–O5	-	1.938(2)
Fe1–N1	2.226(2)	2.243(2)
Fe1–N2	2.112(2)	2.195(3)
Fe1–N3	2.143(2)	2.200(2)
Fe1–N4	2.066(2)	2.040(2)
Fe2–O3	1.957(2)	2.005(2)
Fe2–O4	2.267(18)	2.233(2)
Fe2–N7	2.264(2)	2.279(2)
Fe2–N8	2.193(2)	2.208(2)
Fe2–N9	2.216(2)	2.196(2)
Fe2–N10	2.137(2)	2.121(2)
O1–Fe1–N4	115.12(8)	-
O1–Fe1–N2	84.55(8)	-
O1–Fe1–N3	107.67(8)	-
O1–Fe1–N1	160.98(8)	-
O5–Fe1–N4	-	109.71(9)
O5–Fe1–N2	-	101.92(10)
N4–Fe1–N2	114.49(8)	112.66(10)
O5–Fe1–N3	-	97.68(9)
N4–Fe1–N3	120.34(8)	126.98(0)
N2–Fe1–N3	108.94(8)	104.38(9)
O5–Fe1–N1	-	172.62(9)
N4–Fe1–N1	76.47(8)	77.50(9)
N2–Fe1–N1	76.72(8)	76.04(9)
N3–Fe1–N1	75.93(8)	76.18(9)
O3–Fe2–N10	125.23(8)	131.17(9)
O3–Fe2–N9	103.51(8)	100.36(9)
N10–Fe2–N9	120.99(8)	117.83(9)
O3–Fe2–O8	82.90(8)	81.86(9)
N10–Fe2–N8	108.39(8)	110.89(9)
N9–Fe2–N8	108.68(7)	108.13(8)
O3–Fe2–O4	83.27(7)	81.20(8)
N10–Fe2–O4	79.07(7)	79.08(8)
N9–Fe2–O4	75.60(7)	77.22(8)
N8–Fe2–O4	166.13(7)	162.92(8)
O3–Fe2–N7	154.12(8)	150.71(8)
N10–Fe–N7	74.33(7)	73.39(8)
N9–Fe2–N7	73.86(7)	74.26(8)
N8–Fe2–N7	74.01(7)	72.99(9)
O4–Fe–N7	119.71(7)	123.91(8)

^a There are two independent cations in the asymmetric unit for the complex. Metrical parameters for one of them are reported.

Table S2. Selected bond lengths and angles for $[\text{Co}^{\text{II}}_2\text{H}_2\text{bppap}]^+$ and $[\{\text{Co}^{\text{II}}(\text{OH})\}\text{Co}^{\text{II}}\text{H}_3\text{bppap}]^+$

distance (Å) or angle (deg)	$[\text{Co}^{\text{II}}_2\text{H}_2\text{bppap}]^+$	$[\{\text{Co}^{\text{II}}(\text{OH})\}\text{Co}^{\text{II}}\text{H}_3\text{bppap}]^+$
Co1–O1	1.9573(15)	-
Co1–O5	-	1.931(2)
Co1–N1	2.1725(19)	2.186(2)
Co1–N2	2.0283(19)	2.122(2)
Co1–N3	2.1346(18)	2.125(2)
Co1–N4	2.0577(18)	2.042(2)
Co2–O3	1.9605(15)	1.984(2)
Co2–N7	2.1686(18)	2.190(3)
Co2–N8	2.0205(19)	2.033(3)
Co2–N9	2.1147(18)	2.130(3)
Co2–N10	2.0541(18)	2.018(3)
O1–Co1–N4	109.87(7)	-
O1–Co1–N2	90.20(7)	-
O1–Co1–N3	104.37(7)	-
O1–Co1–N1	167.85(7)	-
O5–Co1–N4	-	1097.94(4)
O5–Co1–N2	-	100.86(9)
N4–Co1–N2	118.64(7)	122.52(10)
O5–Co1–N3	-	99.36(9)
N4–Co1–N3	123.43(7)	112.91(10)
N2–Co1–N3	104.54(7)	110.61(9)
O5–Co1–N1	-	175.25(9)
N4–Co1–N1	78.79(7)	77.66(9)
N2–Co1–N1	77.99(9)	76.70(9)
N3–Co1–N1	76.32(7)	77.91(9)
O3–Co2–N10	109.87(7)	114.61(9)
O3–Co2–N9	104.91(7)	102.09(11)
N10–Co2–N9	122.00(7)	111.32(10)
O3–Co2–O8	90.07(7)	89.94(12)
N10–Co2–N8	118.33(7)	121.26(11)
N9–Co2–N8	106.27(7)	114.18(10)
O3–Co2–N7	167.85(7)	165.79(9)
N10–Co2–N7	78.72(7)	78.48(10)
N9–Co2–N7	76.23(7)	76.67(10)
N8–Co2–N7	78.05(7)	77.95(12)

X-ray Crystallographical 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. 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.

$[\text{Fe}^{\text{II}}_2\text{H}_2\text{bppap}](\text{OTf})\cdot\text{CH}_2\text{Cl}_2$

A yellow crystal of approximate dimensions 0.14 x 0.22 x 0.25 mm was mounted on a glass fiber and data collection was 20 sec/frame scan time for a sphere of diffraction data. 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 H(6) and H(12) were located from a difference-Fourier map and refined (x, y, z and U_{iso}). The remaining hydrogen atoms were included using a riding model. There was one molecule of

dichloromethane solvent present. One of the chlorine atoms was disordered and included using two components with partial site-occupancy-factors (0.80/0.20) and isotropic thermal parameters. The tert-butyl unit defined by atoms C(35)-C(38) showed higher than expected thermal motion. A reasonable disorder model could not be identified.

Least-squares analysis yielded $wR2 = 0.1258$ and $Goof = 1.042$ for 722 variables refined against 12521 data (0.78Å), $R1 = 0.0463$ for those 10158 data with $I > 2.0\sigma(I)$.

[Co^{II}H₂bppap](BPh₄)•CH₂Cl₂•MeOH

A green crystal of approximate dimensions 0.10 x 0.14 x 0.35 mm was mounted on a glass fiber and data collection was 25 sec/frame scan time for a sphere of diffraction data. 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 included using a riding model. There was one molecule of methanol and one molecule of dichloromethane present per formula-unit. The dichloromethane was disordered. Atom Cl(2) was included using multiple components and partial site-occupancy-factors (0.75/0.25). The methanol was located near an inversion center. The hydrogen atoms were fixed in calculated positions resulting in short carbon-hydrogen interactions. It is possible that the carbon/oxygen positions are disordered but this could not be determined from the experiment. The current assignment resulted in the best agreement with the thermal parameters.

Least-squares analysis yielded $wR2 = 0.1338$ and $Goof = 1.023$ for 886 variables refined against 16092 data (0.77Å), $R1 = 0.0471$ for those 13339 data with $I > 2.0\sigma(I)$.

[Fe₂H₃bppap(OH)](OTf)•1.5CH₃C(O)CH₃

A yellow crystal of approximate dimensions 0.18 x 0.28 x 0.34 mm was mounted on a glass fiber and the data collection was 25 sec/frame scan time for a sphere of diffraction data. 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 included using a riding model. There were two molecules of the formula-unit present ($Z = 4$). There were also three molecules of acetone solvent (1.5 per formula-unit) present. Atom S(2) was disordered and included using multiple components and partial site-occupancy-factors (0.80/0.20).

Least-squares analysis yielded $wR2 = 0.1736$ and $Goof = 1.042$ for 1502 variables refined against 28486 data (0.75Å), $R1 = 0.0600$ for those 23176 data with $I > 2.0\sigma(I)$.

[Co₂H₃bppap(OH)](OTf)•2CH₂Cl₂

A green crystal of approximate dimensions 0.14 x 0.21 x 0.24 mm was mounted on a glass fiber and the data collection was 30 sec/frame scan time for a sphere of diffraction data. The diffraction symmetry was $2/m$ and the systematic absences were consistent with the monoclinic space group $P2_1/c$ that was later determined to be correct. Hydrogen atoms were included using a riding model. Disordered atoms were included using multiple components with partial site-occupancy-factors. It was necessary to apply DFIX⁷ restraints to the tert-butyl groups defined by atoms C(8)-C(11) and C(19)-C(22). There were two molecules of dichloromethane solvent present.

Least-squares analysis yielded $wR2 = 0.1339$ and $Goof = 1.030$ for 813 variables (12 restraints) refined against 13150 data (0.78Å), $R1 = 0.0519$ for those 9829 data with $I > 2.0\sigma(I)$.

X-ray Crystallography Collection Data

Table S3. Crystallographic data of $[\text{Fe}^{\text{II}}_2\text{H}_2\text{bppap}](\text{OTf})\cdot\text{CH}_2\text{Cl}_2$ and $[\{\text{Fe}^{\text{II}}(\text{OH})\}\text{Fe}^{\text{II}}\text{H}_3\text{bppap}](\text{OTf})\cdot 1.5\text{CH}_3\text{C}(\text{O})\text{CH}_3$.

	$[\text{Fe}^{\text{II}}_2\text{H}_3\text{bppap}](\text{OTf})\cdot\text{CH}_2\text{Cl}_2$	$[\{\text{Fe}^{\text{II}}(\text{OH})\}\text{Fe}^{\text{II}}\text{H}_3\text{bppap}](\text{OTf})\cdot 1.5(\text{C}_3\text{H}_6\text{O})$
empirical formula	$\text{C}_{51}\text{H}_{65}\text{Cl}_2\text{F}_3\text{Fe}_2\text{N}_{12}\text{O}_7\text{S}$	$\text{C}_{54.5}\text{H}_{74}\text{F}_3\text{Fe}_2\text{N}_{12}\text{O}_{9.5}\text{S}$
formula weight	1229.81	1250.02
T (K)	153(2)	93(2)
λ (Å)	0.71073	0.71073
crystal system	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	11.5239(6)	10.8889(5)
b (Å)	13.2419(7)	21.3269(9)
c (Å)	20.3198(11)	26.8112(12)
α (deg)	85.1888(7)	93.1871(6)
β (deg)	77.8930(7)	95.8320(6)
γ (deg)	71.2408(6)	104.1291(6)
V (Å ³)	2870.3(3)	5985.8(5)
Z	2	4
ρ_{calcd} (mg m ⁻³)	1.423	1.387
μ (mm ⁻¹)	0.705	0.594
F(000)	1280	2624
crystal size (mm ³)	0.25 x 0.22 x 0.14	0.34 x 0.28 x 0.18
reflections collected/unique	32646	72181
R(int)	0.0267	0.0233
data / restraints / parameters	12521 / 0 / 702	28486 / 0 / 1502
R ^a	0.0463	0.0600
R _w ^b	0.1258	0.1736
GOF ^c	1.042	1.042

^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 S4. Crystallographic data of [Co^{II}₂H₃bppap](BPh₄)•MeOH•CH₂Cl₂ and [{Co^{II}(OH)}Co^{II}H₃bppap(OH)](OTf)•2CH₂Cl₂.

	[Co ^{II} ₂ H ₃ bppap](BPh ₄)•CH ₂ Cl ₂ •MeOH	[{Co ^{II} (OH)}Co ^{II} H ₃ bppap](OTf)•2CH ₂ Cl ₂
empirical formula	C ₇₅ H ₈₉ BCl ₂ Co ₂ N ₁₂ O ₅	C ₅₂ H ₆₉ Cl ₄ Co ₂ F ₃ N ₁₂ O ₈ S
formula weight	1438.15	1338.91
T (K)	148(2)	88(2)
λ (Å)	0.71073	0.71073
crystal system	Triclinic	Monoclinic
space group	$P\bar{1}$	$P2_1/c$
a (Å)	12.5951(6)	13.1790(4)
b (Å)	14.1855(7)	30.5726(9)
c (Å)	21.3797(11)	14.9417(4)
α (deg)	98.6178(6)	90.0000
β (deg)	95.1664(6)	97.8767(4)
γ (deg)	105.5654(6)	90.0000
V (Å ³)	3604.0(3)	5963.5(3)
Z	2	4
ρ _{calcd} (mg m ⁻³)	1.325	1.491
μ (mm ⁻¹)	0.594	0.842
F(000)	1512	2776
crystal size (mm ³)	0.35 x 0.14 x 0.10	0.24 x 0.21 x 0.14
reflections collected/unique	41320	68267
R(int)	0.0222	0.0468
data / restraints / parameters	16092 / 0 / 886	13150 / 12 / 813
R ^a	0.0471	0.0519
R _w ^b	0.1338	0.1339
GOF ^c	1.023	1.030

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

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