Supporting Information

Self-Assembly of Oligomeric Linear Dipyrromethene Metal Complexes

Qing Miao, Ji-Young Shin, Brian O. Patrick and David Dolphin*

Department of Chemistry, University of British Columbia

Table of Contents

General Information	2-
Experimental Procedures	2-
Selected Crystal Data and Details of the Data Collection for 7 and 10-16	7-
¹ H NMR and ¹³ C NMR Spectra of 1-9, 12 and 15	, -24-
Comparison of ¹ H NMR Spectra between 7 and 12, 9 and 15	-30-
Optical Spectra of Compounds 7, 9-15 and 20-33	31-
Comparison of the Experimental and Calculated Optical Spectra	-32-

General Information:

All chemicals were purchased from Fisher Scientific, Aldrich Chemical Co. or Alfa Aesar and used without further purification. Thin layer chromatography (TLC) was performed with Merck Silica Gel 60 F_{254} . Column chromatography was performed using basic alumina from Fisher (60-325 mesh, Brockman activity I), silica gel from Silicycle Chemical Division (230-400 mesh) or gel permeation on Bio-Beads S-X1 beads (200-400 mesh). ¹H NMR and ¹³C NMR data were collected in CD₂Cl₂ or CDCl₃ on a Bruker Avance 300 MHz or a Bruker Avance 400 MHz spectrometer. Chemical shifts are reported relative to the residual solvent proton resonance (CD₂Cl₂ at 5.32 ppm and 54.00 ppm for ¹H NMR and ¹³C NMR, respectively; CDCl₃ at 77.23 ppm for ¹³C NMR). Mass spectra of dipyrromethenes and metal complexes were obtained by ESI Mass Spectrometry and MALDI-TOF in the presence of an added matrix DCTB. UV-Visible spectra were recorded in CH₂Cl₂ at room temperature on Cary 50 scan spectrophotometer. Crystals of **7**, **10**, **11**, **12**, **14** and **15** were obtained by *n*-hexane diffusion into a solution of CH₂Cl₂. Crystals of **13** were grown from a CHCl₃ solution with *n*-hexane diffusion. A crystal of **16** was obtained from a CHCl₃ solution with CH₃OH diffusion. The X-ray data were obtained on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-K α radiation. The structures were solved by direct methods and refined with SHELXTL crystallographic software package of Bruker-AXS. The known compound 2-methylpyrrole was prepared according to literature methods (M. Lo and G. C. Fu, *J. Am. Chem. Soc.* 2002, **124**, 4572-4573).

Experimental Procedure:



1,4-bis(1,9-dimethyl-dipyrromethane-5-yl)benzene(1)

1.96 g (14.6 mmol) terephthalaldehyde and 5.23g (64.5 mmol) 2-methylpyrrole were dissolved in 50ml CH_2Cl_2 and degassed by bubbling with argon for 10 min. 0.163 mL (2.2 mmol) Trifluoroacetic acid (TFA) was added and the solution was stirred at r.t. for 2 hours. 0.5 M aq. NaOH (50 mL) was added to quench the reaction. The mixture was extracted with CH_2Cl_2 and the organic layer was dried over anhydrous Na₂SO₄. Column chromatography (silica, CH_2Cl_2) afforded an off-white solid (1.87 g, 30%).

¹H NMR (300 MHz, CD₂Cl₂): δ = 7.73 (br. s, 4H, 4NH), 7.19 (s, 4H, Ar-H), 5.71-5.75 (m, 8H, β -dipyrromethane), 5.30 (s, 2H, H-meso), 2.19 (s, 12H, CH₃); ¹³C NMR (75 MHz, CD₂Cl₂): δ = 141.95, 131.81, 128.95, 127.72, 107.54, 106.31, 44.44, 13.28; HRESI-MS: 445.2373 [M+Na]⁺, calcd. for: C₂₈H₃₀N₄Na: 445.2368.

1,4-bis(1,9-dimethyl-dipyrrin-5-yl)benzene(2)

2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 2.21 g, 9.7 mmol) was added to the solution of **1** (1.87 g, 4.4 mmol) in CH₂Cl₂ (50 mL). After stirring overnight at r.t., a dark red solid precipitate formed. The entire reaction mixture was poured onto and filtered through a basic alumina column (CH₂Cl₂ : CH₃OH = 100:1), which afforded a dark red solid (1.44, g, 77%). ¹H NMR (300 MHz, CD₂Cl₂): 7.51 (s, 4H, Ar-H), 6.53(d, J = 2.9 Hz, 4H, β -dipyrromethene), 6.20 (d, J = 2.9 Hz, 4H, β -dipyrromethene), 2.45 (s, 12H, CH₃); ¹³C NMR (75 MHz, CD₂Cl₂): $\delta = 154.56$, 140.35, 138.25, 138.10, 130.54, 129.26, 118.10, 16.57; Anal. Calcd. for: C₂₈H₂₆N₄·H₂O: C, 77.04; H, 6.46; N, 12.83. Found: C, 76.62; H, 6.09; N, 12.50 UV/Vis (CH₂Cl₂) $\lambda_{max} nm$ ($\epsilon \times 10^{-4}$): 442 (4.83) and 321 (1.58)

1,9-dimethyl-5-(4-cyanophenyl)dipyrromethane(3)

A mixture of *p*-cyanobenzaldehyde (2.62 g, 20 mmol) and 2-methylpyrrole (3.57 g, 44 mmol) in CH_2Cl_2 (100 mL) was flushed with argon for 10 min and treated with TFA (0.223 mL, 3 mmol). The reaction mixture was stirred at r.t. for 3 hrs. And then 0.2 M aq. NaOH (100 mL) was added to quench the reaction. After extraction with ethyl acetate, the organic layer was washed with H₂O and brine, and dried over anhydrous Na₂SO₄. Column chromatography (silica, CH_2Cl_2) afforded a pale yellow solid (4.26 g, 77%).

¹H NMR (300 MHz, CD₂Cl₂): δ = 7.78 (br. s, 2H, 2NH), 7.61 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.35 (d, *J* = 8.2 Hz, 2H, Ar-H), 5.78 (t, *J* = 2.5 Hz, 2H, β -pyrrole), 5.68 (t, *J* = 3.0 Hz, 2H, β -pyrrole), 5.41 (s, 1H, H-meso), 2.21 (s, 6H, CH₃); ¹³C NMR (75 MHz, CD₂Cl₂): δ = 148.93, 132.82, 130.36, 129.65, 128.28, 119.41, 111.03, 108.07, 106.57, 44.70, 13.25; HRESI-MS: 298.1318 [M+Na]⁺, calcd. for: C₁₈H₁₇N₃Na: 298.1320.

1,9-dimethyl-5-(4-formylphenyl)dipyrromethane(4)

A solution of DIBAL-H (1 M in hexanes, 31.0 mL, 31.0 mmol) was added drop-wise to a solution of **3** (4.26 g, 15.5 mmol) in CH₂Cl₂ (150 mL). The reaction mixture was stirred at room temperature for 4 hrs and then quenched with 200 mL of saturated aq. NH₄Cl and stirred for another 2 hrs. After the aqueous layer was removed, 10% aq. NaOH (200 mL) was added to the organic layer which formed an emulsion. The aqueous phase was extracted with CH₂Cl₂. The combined organic layers were washed with brine and dried over Na₂SO₄. Column chromatography (silica, CH₂Cl₂) afforded a pale yellow solid (2.99 g, 69%). ¹H NMR (300 MHz, CD₂Cl₂): δ = 9.97 (s, 1H, CHO), 7.83 (br. s, 2H, 2NH), 7.82 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.41 (d, *J* = 8.2 Hz, 2H, Ar-H), 5.77 (br. s, 2H, β -pyrrole), 5.70 (t, *J* = 3.0 Hz, 2H, β -pyrrole), 5.43 (s, 1H, H-meso), 2.21 (s, 6H, CH₃); ¹³C NMR (75 MHz, CD₂Cl₂): δ = 192.35, 150.44, 135.76, 130.68, 130.37, 129.53, 128.16, 107.98, 106.52, 44.84, 13.26; HRESI-MS: 301.1314 [M+Na]⁺, calcd. for: C₁₈H₁₈N₂ONa: 301.1317

4,4-difluoro-3,5-dimethyl-8-(4-formylphenyl)-4-bora-3a,4a-diaza-s-indacene(5)

2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1.66 g, 7.3 mmol) was added to the solution of 4 (1.85 g, 6.65 mmol) in CH_2Cl_2 (50 mL). After stirring for 1.5 hrs at room temperature, a dark red solid precipitated from the reaction mixture. After adding triethylamine (4.63 mL, 33.3 mmol) to the reaction mixture, the precipitate dissolved. The reaction mixture was then treated with boron trifluoride etherate (4.10 mL, 33.3 mmol). After stirring for another 2 hrs, the entire reaction mixture was filtered through a basic alumina column (eluent: CH_2Cl_2). The crude product was then purified by column chromatography (silica, CH_2Cl_2), which afforded a red solid (0.98 g, 45%).

¹H NMR (300 MHz, CD₂Cl₂): δ = 10.12 (s, 1H, CHO), 8.00 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.68 (d, *J* = 8.2 Hz, 2H, Ar-H), 6.70 (d, *J* = 4.1 Hz, 2H, β -pyrrole), 6.33 (d, *J* = 4.1 Hz, 2H, β -pyrrole), 2.64 (s, 6H, CH₃); ¹³C NMR (75 MHz, CD₂Cl₂): δ = 192.04, 158.97, 141.23, 140.24, 137.85, 134.72, 131.61, 130.72, 129.80, 120.45, 15.26; HRESI-MS: 347.1151 [M+Na]⁺, calcd. for: C₁₈H₁₅BF₂N₂ONa: 347.1143

4,4-difluoro-3,5-dimethyl-8-[4-(dipyrromethane-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene(6)

5 (588 mg, 1.81 mmol) was dissolved in 6.5ml of pyrrole (91 mmol). The mixture was degassed with argon for 10 min and treated with TFA (0.021 mL, 0.27 mmol). After stirring at room temperature for 3 hrs, 0.2 M aq. NaOH solution (30 mL) was added to quench the reaction. The mixture was extracted with CH_2Cl_2 and dried (anhydrous Na_2SO_4). Column chromatography (silica, CH_2Cl_2) afforded a red solid (503 mg, 63%).

¹H NMR (300 MHz, CD₂Cl₂): δ = 8.12 (br. s, 2H, NH), 7.48 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.35 (d, *J* = 8.1 Hz, 2H, Ar-H), 6.78 (d, *J* = 4.1 Hz, 2H, β -methylpyrole), 6.69-6.75 (m, 2H, β -pyrrole), 6.31 (d, *J* = 4.1 Hz, 2H, β -methylpyrrole), 6.16 (q, *J* = 2.9 Hz, 2H, β -pyrrole), 5.92 (br. s, 1H, α -pyrrole), 5.55 (s, 1H, H-meso), 2.62 (s, 6H, CH₃); ¹³C NMR (75 MHz, CD₂Cl₂): δ = 158.03, 145.35, 143.00, 134.98, 133.17, 132.55, 131.35, 130.98, 128.73, 119.93, 118.05, 108.94, 107.85, 44.40, 15.20; HRESI-MS: 463.1891 [M+Na]⁺, calcd. for: C₂₆H₂₃BF₂N₄Na: 463.1882

4,4-difluoro-3,5-dimethyl-8-[4-(dipyrrin-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene(7)

A solution of 6 (503 mg, 1.14 mmol) in CH_2Cl_2 (60 mL) was treated with DDQ (285 mg, 1.26 mmol) for 1 hr at room temperature. The solvent was removed and the residue was column chromatographed (silica, CH_2Cl_2 : $CH_3OH = 100:2$) to afford a red solid (257 mg, 51%).

¹H NMR (300 MHz, CD₂Cl₂): δ = 7.69 (s, 2H, α -pyrrole), 7.64 (s, 4H, Ar-H), 6.86 (d, *J* = 3.7 Hz, 2H, β -methylpyrrole), 6.67 (d, *J* = 3.2 Hz, 2H, β -pyrrole), 6.46 (dd, *J* = 4.3 Hz, *J* = 1.6 Hz, 2H, β -pyrrole), 6.37 (d, *J* = 4.1 Hz, 2H, β -methylpyrrole), 2.65 (s, 6H, CH₃); ¹³C NMR (75 MHz, CD₂Cl₂): δ = 158.45, 144.54, 142.38, 141.33, 141.07, 139.57, 135.25, 134.97, 131.21,

130.96, 130.38, 129.29, 120.16, 118.41, 15.25; HRESI-MS: 439.1891 $[M+H]^+$, calcd. for: $C_{26}H_{22}BF_2N_4$: 439.1906; UV/Vis (CH₂Cl₂) λ_{max} nm ($\epsilon \times 10^-$): 514 (6.89), 486 (2.53), 444 (2.44) and 345 (2.39)

4,4-difluoro-3,5-dimethyl-8-[4-(1,9-dimethyl-dipyrromethane-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene(8)

A mixture of 5 (747 mg, 2.3 mmol) and 2-methylpyrrole (414 mg, 5.1 mmol) in 30 mL CH_2Cl_2 was degassed with argon for 10 min and treated with TFA (0.027 mL, 0.35 mmol). The reaction mixture was stirred at room temperature for 1 hr, and then quenched with 0.2 M aq. NaOH solution (40 mL). The mixture was extracted with CH_2Cl_2 and dried over Na_2SO_4 . Column chromatography (silica, CH_2Cl_2) afforded a red solid (556mg, 52%).

¹H NMR (300 MHz, CD₂Cl₂): δ = 7.82 (br. s, 2H, NH), 7.49 (d, *J* = 8.1 Hz, 2H, Ar-H), 7.37 (d, *J* = 8.1 Hz, 2H, Ar-H), 6.80 (d, *J* = 3.9 Hz, 2H, β -boron dipyrrin), 6.32 (d, *J* = 4.1 Hz, 2H, β -boron dipyrrin), 5.71-5.83 (m, 4H, β -dipyrromethane), 5.44 (s, 1H, H-meso), 2.62 (s, 6H, CH₃-boron dipyrrin), 2.23 (s, 6H, CH₃-dipyrromethane); ¹³C NMR (75 MHz, CD₂Cl₂): δ = 157.97, 145.80, 143.15, 134.99, 133.02, 131.29, 131.20, 130.98, 128.72, 128.06, 119.90, 107.88, 106.46, 44.59, 15.18, 13.30; HRESI-MS: 467.2235 [M+H]⁺, calcd. for: C₂₈H₂₆BF₂N₄: 467.2219

4,4-difluoro-3,5-dimethyl-8-[4-(1,9-dimethyl-dipyrrin-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene(9)

8 (556 mg, 1.19 mmol) was dissolved in 60 mL CH_2Cl_2 and 296 mg of DDQ (1.30 mmol) was added. The mixture was stirred at room temperature for 1 hour. Removal of solvent and column chromatography (silica, CH_2Cl_2 : $CH_3OH = 100:2$) afforded a red solid (442 mg, 80%).

¹H NMR (300 MHz, CD₂Cl₂): δ = 7.60 (s, 4H, Ar-H), 6.86 (d, *J* = 4.1 Hz, 2H, β-boron dipyrrin), 6.51 (d, *J* = 4.1 Hz, 2H, β-free dipyrrin), 6.36 (d, *J* = 4.1 Hz, 2H, β-boron dipyrrin), 6.22 (d, *J* = 4.1 Hz, 2H, β-free dipyrrin), 2.64 (s, 6H, CH₃-boron dipyrrin), 2.46 (s, 6H, CH₃-free dipyrrin); ¹³C NMR (75 MHz, CD₂Cl₂): δ = 158.32, 154.82, 142.66, 140.26, 139.92, 137.40, 134.99, 134.75, 131.21, 131.00, 130.30, 129.11, 120.06, 118.27, 16.60, 15.26; HRESI-MS: 467.2215 [M+H]⁺, calcd. for: C₂₈H₂₆BF₂N₄: 467.2219; UV/Vis (CH₂Cl₂) λ_{max} nm (ε × 10⁻⁴): 514 (6.75), 481 (3.44), 455 (2.85) and 348 (2.26).

General Procedure for Synthesis of Monomeric Metal Complexes



A solution of ligand 7 or 9 (1 equiv.) in CH_2Cl_2 was treated with a solution of $M(OAc)_2 \cdot xH_2O$ (0.7 equiv.) in methanol. The reaction mixture was stirred overnight at room temperature. Removal of the solvent and purification on a GPC column afforded the desired metal complexes (yields 30%-40%).

bis[4,4-difluoro-3,5-dimethyl-8-[4-(dipyrrin-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene]Copper(II) (10)

MALDI-TOF: 937.6, calcd. for $C_{52}H_{40}B_2CuF_4N_8$: 937.3; UV/Vis (CH₂Cl₂) λ_{max} nm ($\epsilon \times 10^{-4}$): 513 (12.82), 478 (7.98) and 350 (4.97)

bis[4,4-difluoro-3,5-dimethyl-8-[4-(1,9-dimethyl-dipyrrinato-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene]Copper(II) (11)

MALDI-TOF: 994.1, calcd. for C₅₆H₄₈B₂CuF₄N₈: 993.3; UV/Vis (CH₂Cl₂) λ_{max} nm ($\epsilon \times 10^{-4}$): 511 (12.61) and 351 (3.61)

bis[4,4-difluoro-3,5-dimethyl-8-[4-(dipyrrinato-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene]Nickel(II) (12)

¹H NMR (300 MHz, CD₂Cl₂): δ = 10.31 (br. s, 4H, α -nickel dipyrrin), 8.03 (d, *J* = 3.7 Hz, 4H, β -nickel dipyrrin), 7.57 (q, *J* = 8.2 Hz, 8H, Ar-H), 6.88 (dd, *J* = 15.5 Hz, *J* = 4.1 Hz, 4H, β -nickel dipyrrin), 6.37 (d, *J* = 3.7 Hz, 4H, β -boron dipyrrin), 2.65 (s, 12H, CH₃-boron dipyrrin); ¹³C NMR (75 MHz, CD₂Cl₂): δ = 179.57, 158.47, 153.04, 142.80, 142.33, 141.16, 140.32, 138.86, 135.46, 134.94, 131.04, 130.95, 130.20, 120.16, 15.26; MALDI-TOF: 932.4, calcd. for C₅₂H₄₀B₂F₄N₈Ni: 932.3; UV/Vis (CH₂Cl₂) λ_{max} nm ($\epsilon \times 10^{-4}$): 513 (13.80), 487 (7.37) and 350 (4.72)

bis[4,4-difluoro-3,5-dimethyl-8-[4-(1,9-dimethyl-dipyrrinato-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene]Nickel(II) (13) MALDI-TOF: 988.5, calcd. for $C_{56}H_{48}B_2F_4N_8Ni$: 988.4; UV/Vis (CH₂Cl₂) λ_{max} nm ($\epsilon \times 10^{-4}$): 511 (14.45) and 353 (4.40)

bis[4,4-difluoro-3,5-dimethyl-8-[4-(1,9-dimethyl-dipyrrinato-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene]Cobalt(II) (14) MALDI-TOF: 989.7, calcd. for $C_{56}H_{48}B_2CoF_4N_8$: 989.4; UV/Vis (CH₂Cl₂) λ_{max} nm ($\epsilon \times 10^{-4}$): 501 (12.29) and 349 (3.53)

bis[4,4-difluoro-3,5-dimethyl-8-[4-(1,9-dimethyl-dipyrrinato-5-yl)phenyl]-4-bora-3a,4a-diaza-s-indacene]Zinc(II) (15)

¹H NMR (300 MHz, CD₂Cl₂): δ = 7.64 (m, 8H, Ar-H), 6.90 (d, *J* = 4.1 Hz, 4H, β-boron dipyrrin), 6.63 (d, *J* = 4.1 Hz, 4H, β-zinc dipyrrin), 6.38 (d, *J* = 4.1 Hz, 4H, β-boron dipyrrin), 6.27 (d, *J* = 3.7 Hz, 4H, β-zinc dipyrrin), 2.66 (s, 12H, CH₃-boron dipyrrin), 2.16 (s, 12H, CH₃-zinc dipyrrin); ¹³C NMR (75 MHz, CDCl₃): δ = 160.00, 158.06, 143.32, 142.22, 141.36, 139.12, 134.72, 134.20, 133.18, 130.84, 130.60, 129.36, 119.74, 117.64, 16.75, 15.18; MALDI-TOF: 993.7, calcd. for C₅₆H₄₈B₂F₄N₈Zn: 994.3; UV/Vis (CH₂Cl₂) λ _{max} nm (ε × 10⁻⁴): 493 (13.32) and 350 (3.75)

Synthesis of cobalt oligomers 16-19



67 mg of **9** (0.144 mmol) and 30 mg of **2** (0.072 mmol) were dissolved in 40 ml CH_2Cl_2 and then a solution of $Co(OAc)_2 \cdot 4H_2O$ (39 mg, 0.156mmol) in methanol (3 mL) was added. The reaction mixture was stirred overnight at r.t. Removal of the solvent and purification on a GPC column afforded the metal complexes **14** and **16-19**.

Reference compounds **20-33** were prepared following a similar synthetic procedure to that outlined above:



4,4-difluoro-3,5-dimethyl-8-(4-cyanophenyl)-4-bora-3a,4a-diaza-s-indacene (20)

¹H NMR (300 MHz, CD₂Cl₂): δ = 7.81(d, 2H, *J* = 8.5 Hz, Ar-H), 7.64 (d, *J* = 8.5 Hz, 2H, Ar-H), 6.66 (d, *J* = 4.0 Hz, 2H, β -dipyrrin), 6.34 (d, *J* = 4.1 Hz, 2H, β -dipyrrin), 2.63(s, 6H, CH₃-dipyrrin); UV/Vis (CH₂Cl₂) λ_{max} nm ($\epsilon \times 10^{-4}$): 518 (7.14) and 328 (1.41)

4,4-difluoro-3,5-dimethyl-8-(4-methylphenyl)-4-bora-3a,4a-diaza-s-indacene (21)

¹H NMR (300 MHz, CD₂Cl₂): δ = 7.43 (d, 2H, *J* = 8.1 Hz, Ar-H), 7.32 (d, *J* = 7.8 Hz, 2H, Ar-H), 6.77 (d, *J* = 4.0 Hz, 2H, β -dipyrrin), 6.31 (d, *J* = 4.2 Hz, 2H, β -dipyrrin), 2.62 (s, 6H, CH₃-dipyrrin), 2.46 (s, 3H, CH₃-Ar); UV/Vis (CH₂Cl₂) λ_{max} nm ($\epsilon \times 10^{-4}$): 511 (7.63) and 352 (1.43)

Bis[5-(4-cyanophenyl)dipyrrinato]Copper(II) (22)

MALDI-TOF: 551.4, calcd. for $C_{32}H_{20}CuN_6$: 551.1; UV/Vis (CH₂Cl₂) λ_{max} nm ($\epsilon \times 10^{-4}$): 503 (3.38), 471 (6.65) and 376 (1.28)

Bis[1,9-dimethyl-5-(4-cyanophenyl)dipyrrinato]Copper(II) (23)

MALDI-TOF: 607.3, calcd. for $C_{36}H_{28}CuN_6$: 607.2; UV/Vis (CH₂Cl₂) λ_{max} nm ($\epsilon \times 10^{-4}$): 510 (5.25), 457 (3.21) and 301 (1.49)

Bis[5-(4-cyanophenyl)dipyrrinato]Nickel(II) (24)

¹H NMR (300 MHz, CD₂Cl₂): δ = 11.79 (s, 4H, α -dipyrrin), 8.79 (s, 4H, β -dipyrrin), 7.71 (d, 4H, *J* = 8.0 Hz, Ar-H), 7.46 (d, *J* = 7.9 Hz, 4H, Ar-H), 6.78 (s, 4H, β -dipyrrin).

MALDI-TOF: 546.4, calcd. for $C_{32}H_{20}N_6Ni$: 546.1; UV/Vis (CH₂Cl₂) λ_{max} nm ($\epsilon \times 10^{-4}$): 480 (3.86) and 316 (1.93)

Bis[1,9-dimethyl-5-(4-cyanophenyl)dipyrrinato]Nickel(II) (25)

MALDI-TOF: 602.3, calcd. for $C_{36}H_{28}N_6Ni$: 502.2; UV/Vis (CH₂Cl₂) λ_{max} nm ($\epsilon \times 10^{-4}$): 515 (4.94), 452 (2.35) and 319 (1.73)

Bis[1,9-dimethyl-5-(4-cyanophenyl)dipyrrinato]Cobalt(II) (26)

MALDI-TOF: 603.3, calcd. for $C_{36}H_{28}CoN_6$: 603.2; UV/Vis (CH₂Cl₂) λ_{max} nm ($\epsilon \times 10^{-4}$): 501 (11.24) and 314 (1.67)

Bis[1,9-dimethyl-5-(4-cyanophenyl)dipyrrinato]Zinc(II) (27)

¹H NMR (300 MHz, CD₂Cl₂): δ = 7.77 (d, 4H, *J* = 8.3 Hz, Ar-H), 7.62 (d, *J* = 8.3 Hz, 4H, Ar-H), 6.46 (d, *J* = 4.0 Hz, 4H, β-dipyrrin), 6.24 (d, *J* = 4.0 Hz, 4H, β-dipyrrin), 2.12 (s, 12H, CH₃-dipyrrin); MALDI-TOF: 608.3, calcd. for C₃₆H₂₈N₆Zn: 608.2; UV/Vis (CH₂Cl₂) λ_{max} nm (ε × 10⁻⁴): 495 (12.12) and 309 (1.56)

Bis[5-(4-methylphenyl)dipyrrinato]Copper(II) (28)

MALDI-TOF: 529.1, calcd. for $C_{32}H_{26}CuN_4$: 529.2; UV/Vis (CH₂Cl₂) λ_{max} nm ($\epsilon \times 10^{-4}$): 499 (3.28), 466 (6.32) and 341 (2.11)

Bis[1,9-dimethyl-5-(4-methylphenyl)dipyrrinato]Copper(II) (29)

MALDI-TOF: 585.2, calcd. for $C_{36}H_{34}CuN_4$: 585.2; UV/Vis (CH₂Cl₂) λ_{max} nm ($\epsilon \times 10^{-4}$): 504 (7.08), 454 (4.13) and 328 (1.70)

Bis[5-(4-methylphenyl)dipyrrinato]Nickel(II) (30)

¹H NMR (400 MHz, CD₂Cl₂): 9.70 (br. s, 4H, *a*-dipyrrin), δ = 7.67 (br. s, 4H, β -dipyrrin), 7.32 (d, *J* = 8.0 Hz, 4H, Ar-H), 7.25 (d, *J* = 7.9 Hz, 4H, Ar-H), 6.80 (d, *J* = 3.7 Hz, 4H, β -dipyrrin), 2.44 (s, 6H, CH₃); MALDI-TOF: 523.9, calcd. for C₃₂H₂₆N₄Ni: 524.2; UV/Vis (CH₂Cl₂) λ_{max} nm ($\epsilon \times 10^{-4}$): 466 (3.71) and 337 (2.03)

Bis[1,9-dimethyl-5-(4-methylphenyl)dipyrrinato]Nickel(II) (31)

MALDI-TOF: 580.2, calcd. for $C_{36}H_{34}N_4Ni$: 580.2; UV/Vis (CH₂Cl₂) λ_{max} nm ($\epsilon \times 10^{-4}$): 513 (6.05), 447 (2.42) and 330 (2.10)

Bis[1,9-dimethyl-5-(4-methylphenyl)dipyrrinato]Cobalt(II) (32)

MALDI-TOF: 581.1, calcd. for $C_{36}H_{34}CoN_4$: 581.2; UV/Vis (CH₂Cl₂) λ_{max} nm ($\epsilon \times 10^{-4}$): 498 (14.02) and 330 (2.08)

Bis[1,9-dimethyl-5-(4-methylphenyl)dipyrrinato]Zinc(II) (33)

¹H NMR (300 MHz, CD₂Cl₂): δ = 7.39 (d, 4H, *J* = 8.0 Hz, Ar-H), 7.26 (d, *J* = 7.8 Hz, 4H, Ar-H), 6.57 (d, *J* = 3.9 Hz, 4H, β-dipyrrin), 6.20 (d, *J* = 4.0 Hz, 4H, β-dipyrrin), 2.47 (s, 6H, CH₃-Ar), 2.11 (s, 12H, CH₃-dipyrrin); MALDI-TOF: 586.2, calcd. for C₃₆H₃₄N₄Zn: 586.2; UV/Vis (CH₂Cl₂) λ_{max} nm (ε × 10⁻⁴): 491 (13.89) and 328 (1.86)

Selected crystal data and details of the data collection for 7 and 10-16

I. Selected crystal data and details of the data collection for 7



Selected Bond Distances and Angles of X-ray Structure of **7** Selected Bond Distances (Å): B(1)-F(1), 1.3796(15); B(1)-N(1), 1.5390(17); N(2)-H(2), 0.90(4). Selected Bond Angles (deg): C(2)-N(1)-C(5), 108.10(11); C(15)-N(2)-C(12), 107.47(19).

Experimental

Data Collection

An irregular red crystal of $C_{26}H_{21}BN_4F_2$ having approximate dimensions of 0.08 x 0.20 x 0.35 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-K α radiation.

The data were collected at a temperature of $25.0 \pm 0.1^{\circ}$ C to a maximum 20 value of 56.5°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 10.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Data Reduction

Of the 11946 reflections that were collected, 2611 were unique ($R_{int} = 0.037$); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT¹ software package. The linear absorption coefficient, μ , for Mo-K α radiation is 0.90 cm⁻¹. Data were corrected for absorption effects using the multi-scan technique (SADABS²), with minimum and maximum transmission coefficients of 0.883 and 0.993, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods³. The material crystallizes on a two-fold axis of rotation. Additionally, it crystallizes with the central phenyl ring disordered in two orientations (a roughly 3:1 ratio between the major and minor fragments). All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms except H2 (found in a difference map and refined isotropically) were placed in calculated positions and not refined. H2 is disordered about both free amine sites. The final cycle of full-matrix least-squares refinement⁴ on F² was based on 2611 reflections and 175 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma ||Fo| - |Fc|| / \Sigma |Fo| = 0.084$$

wR2 =
$$[\Sigma (w (Fo^2 - Fc^2)^2) / \Sigma w (Fo^2)^2]^{1/2} = 0.122$$

The standard deviation of an observation of unit weight⁵ was 1.00. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.13 and $-0.19 \text{ e}^{-}/\text{Å}^{3}$, respectively.

A. Crystal Data

Empirical Formula Formula Weight Crystal Color, Habit Crystal Dimensions Crystal System Lattice Type Lattice Parameters

Space Group Z value D_{calc} F₀₀₀ μ(ΜοΚα)

Diffractometer Radiation

Data Images Detector Position 2θ_{max} No. of Reflections Measured

Corrections

 $C_{26}H_{21}BN_4F_2 \\$ 438.28 red, irregular 0.08 X 0.20 X 0.35 mm monoclinic C-centered a = 6.2217(8) Å b = 30.104(4) Å c = 11.954(2) Å $\alpha = 90.0^{\circ}$ $\beta = 96.072(9)^{\circ}$ $\gamma = 90.0^{0}$ $V = 2226.4(6) Å^3$ C 2/c(#15) 4 1.308 g/cm^3 912.00 0.90 cm⁻¹

B. Intensity Measurements

Bruker X8 APEX II MoK α (λ = 0.71073 Å) graphite monochromated 1058 exposures @ 10.0 seconds 36.00 mm 56.5^o Total: 11946 Unique: 2611(R_{int} = 0.037) Absorption (T_{min} = 0.883, T_{max}= 0.993) Lorentz-polarization

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F ²
Function Minimized	$\Sigma \mathrm{w} (\mathrm{Fo}^2 - \mathrm{Fc}^2)^2$
Least Squares Weights	$w=1/(\sigma^2(Fo^2)+(0.0596P)^2+0.1923P)$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>0.00 σ (I))	2611
No. Variables	175
Reflection/Parameter Ratio	14.92
Residuals (refined on F^2 , all data): R1; wR2	0.084; 0.122
Goodness of Fit Indicator	1.00
No. Observations (I>2.00 σ (I))	1568
Residuals (refined on F): R1; wR2	0.044; 0.103
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.13 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.19 e ⁻ /Å ³

II. Selected crystal data and details of the data collection for 10



Selected Bond Distances and Angles of X-ray Structure of 10

Selected Bond Distances (Å): N(1)-B(1), 1.558(7); N(2)-B(1), 1.505(7); N(3)-Cu(1), 1.930(3); N(4)-Cu(1), 1.928(4); F(1)-B(1), 1.382(6); F(2)-B(1), 1.406(6).

Selected Bond Angles (deg): C(2)-N(1)-C(5), 108.5(5); C(10)-N(2)-C(7), 107.4(4); C(18)-N(3)-C(21), 105.2(4); C(26)-N(4)-C(23), 105.2(4); N(3)-Cu(1)-N(3)', 142.8(2); N(3)-Cu(1)-N(4), 91.85(18); N(3)'-Cu(1)-N(4), 97.34(17); N(3)-Cu(1)-N(4)', 97.34(17); N(3)'-Cu(1)-N(4)', 91.85(18); N(4)-Cu(1)-N(4)', 150.9(2); F(1)-B(1)-F(2), 108.8(4); N(2)-B(1)-N(1), 107.0(4).

Experimental

Data Collection

A red needle crystal of $C_{52}H_{40}B_2N_8F_4Cu.2CH_2Cl_2$ having approximate dimensions of 0.03 x 0.10 x 0.50 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-K α radiation.

The data were collected at a temperature of $-100.0 \pm 0.1^{\circ}$ C to a maximum 20 value of 45.0°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 60.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Data Reduction

Of the 14088 reflections that were collected, 3365 were unique ($R_{int} = 0.122$); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT¹ software package. The linear absorption coefficient, μ , for Mo-K α radiation is 6.89 cm⁻¹. Data were corrected for absorption effects using the multi-scan technique (SADABS²), with minimum and maximum transmission coefficients of 0.219 and 0.980, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods³. The material crystallizes with the Cu atom residing on a two-fold axis of rotation. Additionally, one molecule of CH_2Cl_2 is found in the asymmetric unit. This solvent molecule was disordered in multiple orientations and could not be modeled reasonably. As a result, no solvent atoms were modeled and the PLATON/SQUEEZE¹¹ program was used to correct the measured intensities to remove any residual electron density from the solvent. All remaining non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were placed in calculated positions and were not refined. The final cycle of full-matrix least-squares refinement⁴ on F² was based on 3365 reflections and 305 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma ||Fo| - |Fc|| / \Sigma |Fo| = 0.138$$

wR2 =
$$[\Sigma (w (Fo^2 - Fc^2)^2) / \Sigma w (Fo^2)^2]^{1/2} = 0.136$$

The standard deviation of an observation of unit weight⁵ was 0.85. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.46 and $-0.91 \text{ e}^-/\text{Å}^3$, respectively.

A. Crystal Data

Space Group Z value D_{calc} F₀₀₀ μ(ΜοΚα)

Empirical Formula

Crystal Color, Habit

Crystal Dimensions

Lattice Parameters

Formula Weight

Crystal System

Lattice Type

Diffractometer Radiation

Data Images Detector Position 2θ_{max} No. of Reflections Measured

Corrections

 $C_{54}H_{44}B_2N_8F_4CuCl_2$ 1107.93 red, needle 0.03 X 0.10 X 0.50 mm orthorhombic primitive a = 22.128(5) Å b = 8.569(2) Å c = 27.299(6) Å $\alpha = 90.0^{\circ}$ $\beta = 90.0^{\circ}$ $\gamma = 90.0^{\circ}$ $V = 5176(2) \text{ Å}^3$ P bcn (#60) 1.422 g/cm^3 2268.00 6.89 cm⁻¹

B. Intensity Measurements

Bruker X8 APEX II MoK α ($\lambda = 0.71073$ Å) graphite monochromated 323 exposures @ 60.0 seconds 36.00 mm 45.0^o Total: 14088 Unique: 3365 (R_{int} = 0.122) Absorption (T_{min} = 0.219, T_{max}= 0.980) Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution
Refinement
Function Minimized
Least Squares Weights
Anomalous Dispersion
No. Observations (I>0.00 σ (I))
No. Variables
Reflection/Parameter Ratio
Residuals (refined on F ² , all data): R1; wR2
Goodness of Fit Indicator
No. Observations (I>2.00 σ (I))
Residuals (refined on F): R1; wR2
Max Shift/Error in Final Cycle
Maximum peak in Final Diff. Map
Minimum peak in Final Diff. Map

Direct Methods (SIR97) Full-matrix least-squares on F^2 $\Sigma w (Fo^2 - Fc^2)^2$ w=1/($\sigma^2(Fo^2)$ +(0.0318P) ²+ 0.000P) All non-hydrogen atoms 3365 305 11.03 0.138; 0.136 0.85 1736 0.054; 0.117 0.00 0.46 e⁻/Å³ -0.91 e⁻/Å³

III. Selected crystal data and details of the data collection for 11



Selected Bond Distances and Angles of X-ray Structure of 11

Selected Bond Distances (Å): B(1)-F(1), 1.396(9); B(1)-N(2), 1.545(9); B(1)-N(1), 1.558(10); B(2)-F(4), 1.396(9); B(2)-F(3), 1.406(9); B(2)-N(5), 1.549(11); B(2)-N(6), 1.572(10); N(3)-Cu(1), 1.949(5); N(4)-Cu(1), 1.985(5); N(7)-Cu(1), 1.962(5); N(8)-Cu(1), 1.968(5). Selected Bond Angles (deg): F(2)-B(1)-F(1), 109.9(6); N(2)-B(1)-N(1), 106.8(5); F(4)-B(2)-F(3), 109.5(6); N(5)-B(2)-N(6), 106.6(6); C(10)-N(1)-C(7), 106.2(6); C(2)-N(2)-C(5), 106.9(5); C(19)-N(3)-C(22), 105.7(5); C(27)-N(4)-C(24), 106.8(5); C(30)-N(5)-C(33), 106.7(6); C(38)-N(6)-C(35), 107.9(6); C(47)-N(7)-C(50), 107.3(5); C(55)-N(8)-C(52), 105.8(5); N(3)-Cu(1)-N(7), 132.6(2); N(3)-Cu(1)-N(8), 105.1(2); N(7)-Cu(1)-N(8), 94.0(2); N(3)-Cu(1)-N(4), 94.8(2); N(7)-Cu(1)-N(4), 103.9(2); N(8)-Cu(1)-N(4), 131.9(2)

Experimental

Data Collection

A black tablet crystal of $C_{56}H_{48}B_2N_8F_4Cu.2CH_2Cl_2$ having approximate dimensions of 0.10 x 0.10 x 0.25 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-K α radiation.

The data were collected at a temperature of $-100.0 \pm 0.1^{\circ}$ C to a maximum 20 value of 45.1°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 60.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Data Reduction

Of the 32007 reflections that were collected, 7184 were unique ($R_{int} = 0.130$); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT¹ software package. The linear absorption coefficient, μ , for Mo-K α radiation is 6.34 cm⁻¹. Data were corrected for absorption effects using the multi-scan technique (SADABS²), with minimum and maximum transmission coefficients of 0.293 and 0.939, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods³. The molecule crystallizes with two molecules of methylene chloride in the asymmetric unit. All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were placed in calculated positions and not refined. The final cycle of full-matrix least-squares refinement⁴ on F^2 was based on 7184 reflections and 702 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

R1 =
$$\Sigma$$
 ||Fo| - |Fc|| / Σ |Fo| = 0.135
wR2 = [Σ (w (Fo² - Fc²)²)/ Σ w(Fo²)²]^{1/2} = 0.209

The standard deviation of an observation of unit weight⁵ was 1.03. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.10 and $-0.88 \text{ e}^{-}/\text{Å}^{3}$, respectively.

A. Crystal Data

Empirical Formula
Formula Weight
Crystal Color, Habit
Crystal Dimensions
Crystal System
Lattice Type
Lattice Parameters

Space Group Z value D_{calc} F₀₀₀ μ(ΜοΚα)

Diffractometer Radiation

Data Images Detector Position 2θ_{max} No. of Reflections Measured

Corrections

 $C_{58}H_{52}B_2N_8F_4CuCl_4$ 1164.04 yellow, plate 0.10 X 0.10 X 0.25 mm monoclinic primitive a = 18.142(2) Å b = 20.146(3) Å c = 15.483(3) Å $\alpha = 90.0^{\circ}$ $\beta = 90.191(7)^{\circ}$ $\gamma = 90.0^{0}$ $V = 5659(2) Å^3$ $P 2_1/c$ (#14) 4 1.366 g/cm^3 2396.00 6.34 cm⁻¹

B. Intensity Measurements

Bruker X8 APEX II MoK α (λ = 0.71073 Å) graphite monochromated 693 exposures @ 60.0 seconds 36.00 mm 45.1° Total: 32007 Unique: 7184 (R_{int} = 0.130) Absorption (T_{min} = 0.293, T_{max}= 0.939) Lorentz-polarization

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F ²
Function Minimized	$\Sigma \mathrm{w} (\mathrm{Fo}^2 - \mathrm{Fc}^2)^2$
Least Squares Weights	$w=1/(\sigma^2(Fo^2)+(0.0978P)^2+2.2871P)$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>0.00 σ (I))	7184
No. Variables	720
Reflection/Parameter Ratio	9.98
Residuals (refined on F ² , all data): R1; wR2	0.135; 0.209
Goodness of Fit Indicator	1.03
No. Observations (I>2.00 σ (I))	4123
Residuals (refined on F): R1; wR2	0.070; 0.174
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	1.10 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.88 e ⁻ /Å ³

IV. Selected crystal data and details of the data collection for 12



Selected Bond Distances and Angles of X-ray Structure of 12

Selected Bond Distances (Å): B(1)-F(2), 1.381(7); B(1)-F(1), 1.393(7); B(1)-N(1), 1.540(8); B(1)-N(2), 1.551(8); N(3)-Ni(1), 1.888(4); N(4)-Ni(1), 1.895(4); Ni(1)-N(3)', 1.888(4); Ni(1)-N(4)', 1.895(4). Selected Bond Angles (deg): F(2)-B(1)-F(1), 109.9(5); N(1)-B(1)-N(2), 106.6(5); C(2)-N(1)-C(5), 108.0(5); C(10)-N(2)-C(7), 108.1(5); C(18)-N(3)-C(21), 106.0(4); C(26)-N(4)-C(23), 106.6(4); N(3)'-Ni(1)-N(3), 150.6(3); N(3)'-Ni(1)-N(4), 94.0(2); N(3)-Ni(1)-N(4), 92.7(2); N(3)'-Ni(1)-N(4)', 94.0(2); N(4)-Ni(1)-N(4)', 153.5(2).

Experimental

Data Collection

A red plate crystal of $C_{52}H_{40}B_2N_8F_4Ni.2CH_2Cl_2$ having approximate dimensions of 0.03 x 0.20 x 0.50 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-K α radiation.

The data were collected at a temperature of $-100.0 \pm 0.1^{\circ}$ C to a maximum 20 value of 44.9°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 120.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Data Reduction

Of the 15765 reflections that were collected, 3328 were unique ($R_{int} = 0.083$); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT¹ software package. The linear absorption coefficient, μ , for Mo-K α radiation is 6.41 cm⁻¹. Data were corrected for absorption effects using the multi-scan technique (SADABS²), with minimum and maximum transmission coefficients of 0.427 and 0.981, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods³. The material crystallizes with one half-molecule residing on two-fold axis of rotation about the b-axis. Additionally, one molecule of CH_2Cl_2 is found in the asymmetric unit. This solvent molecule is disordered and was modeled in three orientations. All non-hydrogen atoms were refined anisotropically except the three carboin fragments from the disordered solvent molecule, which were refined isotropically. Mild restraints were employed to maintain reasonable geometried in the disordered solvent, and the respective populations of each fragments were refined such that the sum of the populations was 1. The final cycle of full-matrix least-squares refinement⁴ on F² was based on 3328 reflections and 372 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

R1 =
$$\Sigma$$
 ||Fo| - |Fc|| / Σ |Fo| = 0.130
wR2 = [Σ (w (Fo² - Fc²)²)/ Σ w(Fo²)²]^{1/2} = 0.121

The standard deviation of an observation of unit weight⁵ was 0.99. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.50 and $-0.59 \text{ e}^-/\text{Å}^3$, respectively.

A. Crystal Data

Empirical Formula
Formula Weight
Crystal Color, Habit
Crystal Dimensions
Crystal System
Lattice Type
Lattice Parameters

Space Group Z value D_{calc} F₀₀₀ μ(ΜοΚα)

Diffractometer Radiation

Data Images Detector Position 2θ_{max} No. of Reflections Measured

Corrections

C54H44B2N8F4NiCl4 1103.10 red, plate 0.03 X 0.20 X 0.50 mm primitive orthorhombic a = 22.249(2) Å b = 8.5705(7) Å c = 27.197(2) Å $\alpha = 90.0^{\circ}$ $\beta = 90.0^{\circ}$ $\gamma = 90.0^{\circ}$ $V = 5186.1(7) Å^3$ *P* bcn (#60) 4 1.413 g/cm^3 2264.00 6.41 cm⁻¹

B. Intensity Measurements

Bruker X8 APEX II MoK α (λ = 0.71073 Å) graphite monochromated 363 exposures @ 120.0 seconds 36.00 mm 44.90 Total: 15765 Unique: 3328 (R_{int} = 0.083) Absorption (T_{min} = 0.427, T_{max} = 0.981) Lorentz-polarization

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F ²
Function Minimized	$\Sigma \le (Fo^2 - Fc^2)^2$
Least Squares Weights	$w=1/(\sigma^2(Fo^2)+(0.0219P)^2+12.7278P)$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations $(I > 0.00\sigma(I))$	3328
No. Variables	372
Reflection/Parameter Ratio	8.95
Residuals (refined on F^2 , all data): R1; wR2	0.130; 0.121
Goodness of Fit Indicator	1.10
No. Observations ($I > 2.00\sigma(I)$)	2133
Residuals (refined on F): R1; wR2	0.072; 0.107
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.50 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-0.59 e ⁻ /Å ³

V. Selected crystal data and details of the data collection for 13



Selected Bond Distances and Angles of X-ray Structure of 13

N(4), 127.2(2); N(3)-Ni(1)-N(4), 91.47(17).

Data Collection

Experimental

A red tablet crystal of $C_{56}H_{48}B_2N_8F_4Ni.2CHCl_3$ having approximate dimensions of 0.08 x 0.15 x 0.35 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-K α radiation.

The data were collected at a temperature of $-100.0 \pm 0.1^{\circ}$ C to a maximum 20 value of 50.5°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 30.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Data Reduction

Of the 30194 reflections that were collected, 9772 were unique ($R_{int} = 0.045$); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT¹ software package. The linear absorption coefficient, μ , for Mo-K α radiation is 6.93 cm⁻¹. Data were corrected for absorption effects using the multi-scan technique (SADABS²), with minimum and maximum transmission coefficients of 0.727 and 0.946, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods³. The material crystallizes with two molecules of CHCl₃ in the asymmetric unit. All non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were placed in calculated positions and not refined. The final cycle of full-matrix least-squares refinement⁴ on F² was based on 9772 reflections and 720 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

R1 =
$$\Sigma$$
 ||Fo| - |Fc|| / Σ |Fo| = 0.128
wR2 = [Σ (w (Fo² - Fc²)²)/ Σ w(Fo²)²]^{1/2} = 0.230

The standard deviation of an observation of unit weight⁵ was 1.04. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.03 and $-1.07 \text{ e}^-/\text{Å}^3$, respectively.

A. Crystal Data

Empirical Formula Formula Weight Crystal Color, Habit Crystal Dimensions Crystal System Lattice Type Lattice Parameters

Space Group Z value D_{calc} F₀₀₀ μ(ΜοΚα)

Diffractometer Radiation

Data Images Detector Position 2θ_{max} No. of Reflections Measured

Corrections

 $C_{58}H_{50}B_2N_4F_4NiCl_6$ 1228.09 red, tablet 0.08 X 0.15 X 0.35 mm triclinic primitive a = 10.840(1) Å b = 14.501(2) Å c = 19.830(2) Å $\alpha = 109.761(6)^{\circ}$ $\beta = 104.839(6)^{\circ}$ $\gamma = 93.027(6)^{\circ}$ $V = 2802.2(5) Å^3$ P-1 (#2) 2 1.455 g/cm^3 1260.00 6.93 cm⁻¹

B. Intensity Measurements

Bruker X8 APEX II MoK α (λ = 0.71073 Å) graphite monochromated 1515 exposures @ 30.0 seconds 36.00 mm 50.5^o Total: 30194 Unique: 9772 (R_{int} = 0.045) Absorption (T_{min} = 0.727, T_{max}= 0.946) Lorentz-polarization

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F ²
Function Minimized	$\Sigma \text{ w} (\text{Fo}^2 - \text{Fc}^2)^2$
Least Squares Weights	$w=1/(\sigma^2(Fo^2)+(0.1325P)^2+0.4578P)$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>0.00 σ (I))	9772
No. Variables	720
Reflection/Parameter Ratio	13.57
Residuals (refined on F ² , all data): R1; wR2	0.128; 0.230
Goodness of Fit Indicator	1.04
No. Observations (I>2.00 σ (I))	4940
Residuals (refined on F): R1; wR2	0.075; 0.204
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	1.03 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-1.07 e ⁻ /Å ³

VI. Selected crystal data and details of the data collection for 14



Selected Bond Distances and Angles of X-ray Structure of 14

Selected Bond Distances (Å): B(1)-F(2), 1.378(7); B(1)-F(1), 1.389(6); B(1)-N(2), 1.540(7); B(1)-N(1), 1.547(7); B(2)-F(3), 1.370(7); B(2)-F(4), 1.388(7); B(2)-N(5), 1.544(8); B(2)-N(6), 1.555(8); N(3)-Co(1), 1.962(4); N(4)-Co(1), 1.974(4); N(7)-Co(1), 1.962(4); N(8)-Co(1), 1.979(4). Selected Bond Angles (deg): F(2)-B(1)-F(1), 109.5(4); N(2)-B(1)-N(1), 106.5(4); F(3)-B(2)-F(4), 109.9(4); N(5)-B(2)-N(6), 106.6(4); C(2)-N(1)-C(5), 108.2(4); C(10)-N(2)-C(7), 107.4(4); C(19)-N(3)-C(22), 106.9(4); C(27)-N(4)-C(24), 106.9(4); C(30)-N(5)-C(33), 107.6(4); C(38)-N(6)-C(35), 108.2(5); C(47)-N(7)-C(50), 106.3(4); C(55)-N(8)-C(52), 107.0(4); N(3)-Co(1)-N(7), 115.98(16); N(3)-Co(1)-N(4), 93.08(16); N(7)-Co(1)-N(4), 115.34(17); N(3)-Co(1)-N(8), 118.17(17); N(7)-Co(1)-N(8), 92.93(16); N(4)-Co(1)-N(8), 123.36(17).

Experimental

Data Collection

An irregular red crystal of $C_{56}H_{48}B_2N_8F_4Co.2CH_2Cl_2$ having approximate dimensions of 0.05 x 0.25 x 0.30 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-K α radiation.

The data were collected at a temperature of $-100.0 \pm 0.1^{\circ}$ C to a maximum 20 value of 45.2°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 13.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Data Reduction

The material crystallizes as a three-component twin with the two minor components related to the major component by roughly a 180° rotation about the (1 0 0) real axis. Data were integrated for all twin components, including both overlapped and non-overlapped reflections. In total 78919 reflections were integrated (20336 from component one only, 25436 from component two only, 23050 from component three only, and 10084 overlapped). Data were collected and integrated using the Bruker SAINT¹ software packages. The linear absorption coefficient, μ , for Mo-K α radiation is 5.74 cm⁻¹. Data were corrected for absorption effects using the multi-scan technique (TWINABS²), with minimum and maximum transmission coefficients of 0.746 and 0.972, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods³ using non-overlapped data from the major twin component. Subsequent refinements were carried out using an HKLF 5 format data set containing complete data from the major twin component including overlapped reflections from the minor twin components. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined. The batch scale refinement showed a roughly 3:1:1 ratio between the major and minor twin components. The final cycle of full-matrix least-squares refinement⁴ on F² was based on 10121 reflections from both twin components and 704 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma ||Fo| - |Fc|| / \Sigma |Fo| = 0.112$$

wR2 =
$$[\Sigma (w (Fo^2 - Fc^2)^2) / \Sigma w (Fo^2)^2]^{1/2} = 0.169$$

The standard deviation of an observation of unit weight⁵ was 0.99. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.23 and $-1.03 \text{ e}^{-}/\text{Å}^{3}$, respectively.

A. Crystal Data

Empirical Formula Formula Weight Crystal Color, Habit Crystal Dimensions Crystal System Lattice Type Lattice Parameters

Space Group Z value D_{calc} F₀₀₀ μ(ΜοΚα)

Diffractometer Radiation

Data Images Detector Position $2\theta_{max}$ No. of Reflections Measured

Corrections

 $C_{58}H_{52}B_2N_8F_4Cl_4Co$ 1159.43 red, irregular 0.05 X 0.25 X 0.30 mm triclinic primitive a = 10.669(1) Å b = 14.432(2) Å c = 19.145(2) Å $\alpha = 70.375(4)^{\circ}$ $\beta = 78.215(4)^{\circ}$ $\gamma = 86.892(4)$ ° $V = 2717.8(5) Å^3$ P -1 (#2) 2 1.418 g/cm^3 1194.00 5.74 cm⁻¹

B. Intensity Measurements

Bruker X8 APEX II MoK α (λ = 0.71073 Å) graphite monochromated 1348 exposures @ 13.0 seconds 36.00 mm 45.2^o Total: 58453 Unique: 10121 (R_{int} = 0.062) Absorption (T_{min} = 0.746, T_{max} = 0.972) Lorentz-polarization

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F ²
Function Minimized	$\Sigma \mathrm{w} (\mathrm{Fo}^2 - \mathrm{Fc}^2)^2$
Least Squares Weights	$w=1/(\sigma^2(Fo^2)+(0.1073P)^2+0.0000P)$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>0.00 σ (I))	10121
No. Variables	704
Reflection/Parameter Ratio	14.38
Residuals (refined on F ² , all data): R1; wR2	0.121; 0.169
Goodness of Fit Indicator	0.99
No. Observations (I>2.00 σ (I))	6424
Residuals (refined on F): R1; wR2	0.061; 0.144
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	1.23 ⁻ /Å ³
Minimum peak in Final Diff. Map	-1.03 ⁻ /Å ³

VII. Selected crystal data and details of the data collection for 15



Selected Bond Distances and Angles of X-ray Structure of **15** Selected Bond Distances (Å): B(1)-F(2), 1.384(5); B(1)-F(1), 1.385(5); B(1)-N(1), 1.545(5); B(1)-N(2), 1.559(5); B(2)-F(4), 1.383(5); B(2)-F(3), 1.389(5); B(2)-N(5), 1.533(6); B(2)-N(6), 1.555(6); N(3)-Zn(1), 1.975(3); N(4)-Zn(1), 1.970(3); N(7)-Zn(1), 1.972(3); N(8)-Zn(1), 1.982(3). Selected Bond Angles (deg): F(2)-B(1)-F(1), 109.8(3); N(1)-B(1)-N(2), 107.0(3); F(4)-B(2)-F(3), 109.6(3); N(5)-B(2)-N(6), 107.4(3); C(2)-N(1)-C(5), 107.4(3); C(10)-N(2)-C(7), 107.9(3); C(19)-N(3)-C(22), 107.8(3); C(27)-N(4)-C(24), 107.1(3); C(30)-N(5)-C(33), 107.0(3); C(38)-N(6)-C(35), 107.4(3); C(47)-N(7)-C(50), 106.7(3); C(55)-N(8)-C(52), 106.6(3); N(4)-Zn(1)-N(7), 117.81(13); N(4)-Zn(1)-N(3), 94.02(12); N(7)-Zn(1)-N(3), 122.94(13); N(4)-Zn(1)-N(8), 115.26(13); N(7)-Zn(1)-N(8), 93.78(12); N(3)-Zn(1)-N(8), 114.78(12).

Experimental

Data Collection

A red needle crystal of $C_{56}H_{48}B_2N_8F_4Zn.2CH_2Cl_2$ having approximate dimensions of 0.05 x 0.12 x 0.35 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-K α radiation.

The data were collected at a temperature of $-100.0 \pm 0.1^{\circ}$ C to a maximum 20 value of 50.4°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 20.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Data Reduction

The material crystallizes as a two-component twin with the two components related by a 180^o rotation about the (1 0 0) reciprocal axis. Data were integrated for both twin components, including both overlapped and non-overlapped reflections. In total 46377 reflections were integrated (20360 from component one only, 20257 from component two only, 5760 overlapped). Data were collected and integrated using the Bruker SAINT¹ software packages. The linear absorption coefficient, μ , for Mo-K α radiation is 7.06 cm⁻¹. Data were corrected for absorption effects using the multi-scan technique (TWINABS²), with minimum and maximum transmission coefficients of 0.705 and 0.965, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods³ using non-overlapped data from the major twin component. The material crystallizes with two molecules of methylene chloride in the lattice. Subsequent refinements were carried out using an HKLF 5 format data set containing complete data from both twin components. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in calculated positions but not refined. The batch scale refinement showed a roughly 52:48 ratio between the major and minor twin components. The final cycle of full-matrix least-squares refinement⁴ on F² was based on 18068 reflections from both twin components and 703 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma ||Fo| - |Fc|| / \Sigma |Fo| = 0.132$$

wR2 = [\Sigma (w (Fo² - Fc²)²)/ \Sigma w (Fo²)²]^{1/2} = 0.175

The standard deviation of an observation of unit weight⁵ was 0.96. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 1.49 and $-1.17 \text{ e}^{-}/\text{Å}^{3}$, respectively.

A. Crystal Data

Empirical Formula Formula Weight Crystal Color, Habit Crystal Dimensions Crystal System Lattice Type Lattice Parameters

Space Group Z value D_{calc} F₀₀₀ μ(ΜοΚα)

Diffractometer Radiation

Data Images Detector Position 2θ_{max} No. of Reflections Measured

Corrections

 $C_{58}H_{52}B_2N_8F_4ZnCl_4$ 1165.87 red, needle 0.05 X 0.12 X 0.35 mm triclinic primitive a = 10.7063(11) Å b = 14.4785(12) Å c = 19.1263(18) Å $\alpha = 70.425(4)^{\circ}$ $\beta = 78.184(4)^{\circ}$ $\gamma = 86.994(4)^{0}$ $V = 6037(3) Å^3$ P -1 (#2) 2 1.416 g/cm^3 1200.00 7.06 cm⁻¹

B. Intensity Measurements

Bruker X8 APEX MoK α (λ = 0.71073 Å) graphite monochromated 1009 exposures @ 20.0 seconds 36.00 mm 50.4^o Total: 21133 Unique: 18068 (R_{int} = 0.046) Absorption (T_{min} = 0.705, T_{max} = 0.965) Lorentz-polarization

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F ²
Function Minimized	$\Sigma \le (Fo^2 - Fc^2)^2$
Least Squares Weights	$w=1/(\sigma^2(Fo^2)+(0.0872P)^2+0.0000P)$
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>0.00 σ (I))	18068
No. Variables	703
Reflection/Parameter Ratio	25.70
Residuals (refined on F ² , all data): R1; wR2	0.132; 0.175
Goodness of Fit Indicator	0.96
No. Observations (I>2.00 σ (I))	10208
Residuals (refined on F): R1; wR2	0.066; 0.148
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	1.49 e ⁻ /Å ³
Minimum peak in Final Diff. Map	-1.17e ⁻ /Å ³

VIII. Selected crystal data and details of the data collection for 16



Selected Bond Distances and Angles of X-ray Structure of **16** Selected Bond Distances (Å): B(1)-F(2), 1.375(6); B(1)-F(1), 1.383(6); B(1)-N(1), 1.543(6); B(1)-N(2), 1.554(6); N(3)-Co(1), 1.965(3); N(4)-Co(1), 1.979(3); N(5)-Co(1), 1.974(3); N(6)-Co(1), 1.975(3). Selected Bond Angles (deg): F(2)-B(1)-F(1), 110.1(4); F(2)-B(1)-N(1), 110.0(4); F(1)-B(1)-N(1), 110.4(4); F(2)-B(1)-N(2), 109.9(4); F(1)-B(1)-N(2), 110.4(4); N(1)-B(1)-N(2), 105.9(3); C(2)-N(1)-C(5), 107.3(4); C(2)-N(1)-B(1), 127.3(4); C(5)-N(1)-B(1), 125.4(3); C(10)-N(2)-C(7), 107.7(4); C(10)-N(2)-B(1), 126.4(4); C(7)-N(2)-B(1), 125.8(3); C(19)-N(3)-C(22), 107.6(3); C(19)-N(3)-Co(1), 129.9(3); C(22)-N(3)-Co(1), 122.4(3); C(27)-N(4)-C(24), 107.0(3); C(27)-N(4)-Co(1), 128.6(3); C(24)-N(4)-Co(1), 122.0(3); C(30)-N(5)-C(33), 107.2(3); C(30)-N(5)-Co(1), 128.0(3); C(33)-N(5)-Co(1), 124.7(3); C(38)-N(6)-C(35), 108.0(3); C(38)-N(6)-Co(1), 127.2(3); C(35)-N(6)-Co(1), 124.7(3); N(3)-Co(1)-N(4), 116.50(14); N(6)-Co(1)-N(4), 120.42(15).

Experimental

Data Collection

A red needle crystal of $C_{84}H_{72}B_2F_4N_{12}Co_2.2CHCl_3$ having approximate dimensions of 0.05 x 0.10 x 0.40 mm was mounted on a glass fiber. All measurements were made on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-K α radiation.

The data were collected at a temperature of $-100.0 \pm 0.1^{\circ}$ C to a maximum 2 θ value of 50.2°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 50.0 second exposures. The crystal-to-detector distance was 36.00 mm.

Data Reduction

Of the 30263 reflections that were collected, 7078 were unique ($R_{int} = 0.054$); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT¹ software package. The linear absorption coefficient, μ , for Mo-K α radiation is 6.76 cm⁻¹. Data were corrected for absorption effects using the multi-scan technique (SADABS²), with minimum and maximum transmission coefficients of 0.785 and 0.967, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods³. The material crystallizes with one half-molecule in the asymmetric unit, residing on an inversion center. Additionally, the two outer phenyl rings are slightly disordered in two orientations. Finally, one molecule of CHCl₃ crystallizes in the asymmetric unit. All non-hydrogen atoms except the disordered minor fragments were refined anisotropically. All hydrogen atoms were placed in calculated positions but were not refined. The final cycle of full-matrix least-squares refinement⁴ on F² was based on 7078 reflections and 518 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

R1 =
$$\Sigma$$
 ||Fo| - |Fc|| / Σ |Fo| = 0.097
wR2 = [Σ (w (Fo² - Fc²)²)/ Σ w(Fo²)²]^{1/2} = 0.173

The standard deviation of an observation of unit weight⁵ was 1.03. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.87 and $-0.81 \text{ e}^{-}/\text{Å}^{3}$, respectively.

A. Crystal Data

Empirical Formula Formula Weight Crystal Color, Habit Crystal Dimensions Crystal System Lattice Type Lattice Parameters

Space Group Z value D_{calc} F₀₀₀ μ(ΜοΚα)

Diffractometer Radiation

Data Images Detector Position 2θ_{max} No. of Reflections Measured

Corrections

 $C_{86}H_{74}B_2F_4N_{12}Cl_6Co_2$ 1703.75 red, needle 0.05 X 0.10 X 0.40 mm primitive monoclinic a = 13.4104(15) Å b = 26.078(2) Å c = 12.7437(14) Å $\alpha = 90.0^{\circ}$ $\beta = 115.666(5)^{0}$ $\gamma = 90.0^{\circ}$ $V = 4017.0(7) Å^3$ $P 2_1/c$ (#14) 2 1.409 g/cm³ 1752.00 6.76 cm⁻¹

B. Intensity Measurements

Bruker X8 APEX II MoK α (λ = 0.71073 Å) graphite monochromated 967 exposures @ 50.0 seconds 36.00 mm 50.2^o Total: 30263 Unique: 7078 (R_{int} = 0.054) Absorption (T_{min} = 0.785, T_{max}= 0.967) Lorentz-polarization

Direct Methods (SIR97)
Full-matrix least-squares on F ²
$\Sigma \text{ w} (\text{Fo}^2 - \text{Fc}^2)^2$
$w=1/(\sigma^2(Fo^2)+(0.837P)^2+6.8338P)$
All non-hydrogen atoms
7078
518
13.66
0.097; 0.173
1.03
4797
0.059; 0.150
0.00
0.87 e ⁻ /Å ³
-0.81 e ⁻ /Å ³

References

(1) SAINT. Version 7.03A. Bruker AXS Inc., Madison, Wisconsin, USA. (1997-2003).

(2) <u>SADABS</u>. Bruker Nonius area detector scaling and absorption correction - V2.10, Bruker AXS Inc., Madison, Wisconsin, USA (2003).

(3) <u>SIR97</u> - Altomare A., Burla M.C., Camalli M., Cascarano G.L., Giacovazzo C., Guagliardi A., Moliterni A.G.G., Polidori G., Spagna R. (1999) J. Appl. Cryst. 32, 115-119.

(4) Least Squares function minimized: $\Sigma w (F_0^2 - F_c^2)^2$

(5) Standard deviation of an observation of unit weight:

$$\begin{split} & [\Sigma w (F_0{}^2 - F_c{}^2)^2 / (N_0 - N_V)]^{1/2} \\ & \text{where:} \quad N_0 = \text{number of observations} \\ & N_V = \text{number of variables} \end{split}$$

(6) Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

(7) Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

(8) Creagh, D. C. & McAuley, W.J.; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

(9) Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

(10) SHELXTL Version 5.1. Bruker AXS Inc., Madision, Wisconsin, USA. (1997).

(11) SQUEEZE - Sluis, P. v.d.; Spek, A. L. Acta Crystallogr., Sect A 1990, 46, 194-201.













¹H NMR (CD₂Cl₂) and ¹³C NMR (CDCl₃) Spectra of Compound 15

Comparison of ¹H NMR Spectra between 7 and 12, 9 and 15







¹H NMR Spectra of Ligand 9 (c) and Zinc Complex 15 (d)

Optical spectra of ligands (7 and 9) and their metal complexes (10-15) in CH₂Cl₂



Optical Spectra Data of the Reference Series

.

Comp.	$\lambda max(nm) / log\epsilon$	Comp.	$\lambda max(nm) / log\epsilon$
20	517.9 / 4.85	21	510.6 / 4.89
22	471.1 / 4.82	28	466.0 / 4.80
23	510.0 / 4.72	29	504.0 / 4.85
24	480.0 / 4.59	30	466.0 / 4.57
25	515.0 / 4.70	31	513.0 / 4.79
26	500.5 / 5.05	32	497.5 / 5.15
27	494.5 / 5.08	33	491.0 / 5.14

Optical Spectra of Reference Cu^{II} Complexes (22, 23, 28 and 29) and Ni^{II} Complexes (24, 25, 30 and 31)



Comparison of the Experimental and Calculated Optical Spectra

The spectra of compounds 10-17, 21 and 28-33 were recorded in CH_2Cl_2 at room temperature. The calculated spectrum of compound 10 (10-calcd.) was obtained as shown below. The calculated spectra of compound 11-17 were obtained by the same method.

I. Comparison of optical spectra for 10 and 10-calcd.



II. Comparison of Optical Spectra for 11 and 11-calcd.



III. Comparison of Optical Spectra for 12 and 12-calcd.



IV. Comparison of Optical Spectra for 13 and 13-calcd.



V. Comparison of Optical Spectra for 14 and 14-calcd.



VI. Comparison of Optical Spectra for 15 and 15-calcd.



Supplementary Material (ESI) for Chemical Communications This journal is (c) The Royal Society of Chemistry 2009



VII. Comparison of Optical Spectra for 16 and 16-calcd.

VIII. Comparison of Optical Spectra for 17 and 17-calcd.

