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Porphyrazines as Molecular Scaffolds: Flexible Syntheses of Novel Multimetallic Complexes

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Reductive deselenation of selenodiazole-fused porphyrazines, followed by acylation of the resultant labile porphyrazinediamines, was used to prepare macrocycles bearing two Collins ligands, two oxamido residues, or two quinoline-2-carboxamido units. Peripheral coordination of copper(II) to the di-(quinoline-2-carboxamido)-porphyrazine gave a metal-linked face-to-face porphyrazine dimer array. Sequential derivatization of the two amino groups in the porphyrazinediamines was used to prepare mixed peripheral ligand systems including a dimetallic picolinamido–Schiff base porphyrazine. Such systems exhibit strong metal–metal spin coupling and are anticipated to be of value in the synthesis of novel electronic and magnetic materials.

Introduction

Polydentate ligands capable of binding multiple metal ions are of considerable interest because their derivatives are of value in the study of electron-transfer processes,[1] macrocycle-mediated spin coupling,[2−4] ultrahigh-spin molecules,[5] and biomimetic chemistry.[6] Previously, we have reported the synthesis of porphyrazines (pzs) bearing multiple thiol, amine, or alcohol peripheral substituents, along with their conversion to multimetallic coordination complexes.[7−14] Such systems exhibit electron transfer or magnetic exchange between the metal ion in the macrocyclic cavity and the metal ion or ions bound by the peripheral bidentate S_2, N_2, or O_2 ligand units.[10,12,15]

More recently, we have investigated an alternative approach to peripheral metal coordination by the fusion of salen and other polydentate ligands to the porphyrazine ring. For example, we have described the preparation of a phenanthroline-appended porphyrazine and its conversion to a variety of Ru(II) complexes including a ruthenium-linked porphyrazine trimer.[16] We have also reported the preparation of porphyrazine−Schiff base systems,[17] along with their conversion into M^1[pz]−M^2[Schiff base] complexes.[18] Following our initial reports of the spin coupling between metal ions in these novel dimetallic systems,[17,18] a detailed

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(1) *Electron Transfer and Radical Processes in Transition Metal Chemistry*; Astruc, D., Ed.; VCH Publishers: New York, 1995.
(2) Zhong, C.; Zhao, M.; Stern, C.; Barrett, A. G. M.; Hoffman, B. M. *Inorg. Chem.* **2005**, *44*, 8272.
(3) Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993.
(4) Attia, A. S.; Conklin, B. J.; Lange, C. W.; Pierpont, C. G. *Inorg. Chem.* **1996**, *35*, 1033.
(5) Goldberg, D. P.; Koulougliotis, D.; Brudvig, G. W.; Lippard, S. J. *J. Am. Chem. Soc.* **1995**, *117*, 3134.
(6) Sessler, J. I.; Sibert, J. W.; Lynch, V.; Markert, J. T.; Wooten, C. I. *Inorg. Chem.* **1993**, *32*, 621.
(7) Velázquez, C. S.; Fox, G. A.; Broderick, W. E.; Anderson, K. A.; Anderson, O. P.; Barrett, A. G. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1992**, *114*, 7416.
(8) Velázquez, C. S.; Baumann, T. F.; Olmstead, M. M.; Hope, H.; Barrett, A. G. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1993**, *115*, 9997.
(9) Baumann, T. F.; Nasir, M. S.; Sibert, J. W.; White, A. J. P.; Olmstead, M. M.; Williams, D. J.; Barrett, A. G. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **1996**, *118*, 10479.
(10) Michel, S. L.; Goldberg, D. P.; Stern, C.; Barrett, A. G. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **2001**, *123*, 4741.
(11) Goldberg, D. P.; Michel, S. L.; White, A. J. P.; Williams, D. J.; Barrett, A. G. M.; Hoffman, B. M. *Inorg. Chem.* **1998**, *37*, 2100.
(12) Goldberg, D. P.; Montalban, A. G.; White, A. J. P.; Williams, D. J.; Barrett, A. G. M.; Hoffman, B. M. *Inorg. Chem.* **1998**, *37*, 2873.
(13) Lange, S. J.; Nie, H.; Stern, C. L.; Barrett, A. G. M.; Hoffman, B. M. *Inorg. Chem.* **1998**, *37*, 6435.
(14) Cook, A. S.; Williams, D. B. G.; White, A. J. P.; Williams, D. J.; Lange, S. J.; Barrett, A. G. M.; Hoffman, B. M. *Angew. Chem., Int. Ed.* **1997**, *36*, 760.
(15) Michel, S. L.; Baum, S.; Barrett, A. G. M.; Hoffman, B. M. In *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; Wiley & Sons: New York, 2001; Vol. 50, pp 473.
(16) Montalban, A. G.; Sakellariou, E. G.; Riguet, E.; McCubbin, Q. J.; Barrett, A. G. M.; Hoffman, B. M. *Inorg. Chim. Acta* **2001**, *317*, 143.
(17) Zhao, M.; Stern, C.; Barrett, A. G. M.; Hoffman, B. M. *Angew. Chem., Int. Ed.* **2003**, *42*, 462.
(18) Zhao, M.; Zhong, C.; Stern, C.; Barrett, A. G. M.; Hoffman, B. M. *Inorg. Chem.* **2004**, *43*, 3377.

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comparison of several derivatives, [$Cu^{II}-Cu^{II}$], [$Cu^{II}-V^{IV}O$], [$ClMn^{III}-Cu^{II}$], and [$ClMn^{III}-V^{IV}O$], was carried out. This study related the ligand-mediated exchange coupling to the relative symmetries of the "magnetic orbits" and the influence of π-exchange.[19]

Herein we report the synthesis of a range of porphyrazines bearing several alterative peripheral multidentate ligands including vicinal di-(2-hydroxy-2-methylpropanamido), di-(2-methoxy-2-oxo-acetamido), di-(2-pyridine-carboxamido), and di-(2-quinolinecarboxamido) units. This study is an extension of our recent reports of metal ion coordination by di-(2-pyridine-carboxamido)-porphyrazines,[2] multidentate ligands combining porphyrazines with the Vagg system.[20]

Experimental Section

[7,8,12,13,17,18-Hexapropyl-[1,2,5]selenadiazolo[3,4-q]porphyrazinato]zinc(II) (3a). Porphyrazine **2a** (72 mg, 0.11 mmol; prepared from porphyrazine **1a**),[21] $Zn(OAc)_2$ (37 mg, 0.17 mmol), and anhydrous DMF (40 mL) were heated with stirring at 100 °C for 18 h. Rotary evaporation and chromatography ($MeOH/CH_2Cl_2$ 1:50) gave porphyrazine **3a** (66 mg, 83%) as a green solid: mp > 300 °C (pyridine), $R_f = 0.52$ ($MeOH:CH_2Cl_2$ 1:25). IR (film): 1688, 1470, 1145, 1009 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 341 (5.69), 354 (5.73), 595 (5.48), 638 (5.59) nm. ^1H NMR (400 MHz, d_5-pyridine): δ 4.07−4.13 (m, 12H), 2.47−2.56 (m, 12H), 1.37−1.42, 1.24−1.28 (m, t, $J = 7.3$ Hz, 18H). ^{13}C NMR (100 MHz, d_5-pyridine): δ 171.6, 159.5, 158.0, 157.8, 145.7, 145.2, 144.2, 144.0, 28.8, 28.7, 28.4, 26.1, 26.1, 25.9, 15.1, 14.8. MS (FAB): m/z 735 $(M + H)^+$. HRMS (FAB) Calcd for $C_{34}H_{43}N_{10}SeZn$: $(M + H)^+$ 735.2129. Found: $(M + H)^+$. 735.2104. Crystal data: $C_{34}H_{42}N_{10}SeZn \cdot C_5H_5N$; $M = 814.21$; triclinic; $P\bar{1}$; $a = 10.2170(9)$, $b = 15.4684(13)$, $c = 26.108(2)$ Å; $\alpha = 82.207(7)$, $\beta = 83.440(7)$, $\gamma = 70.071(8)°$; $V = 3833.0(6)$ $Å^3$; $Z = 4$; $D_c = 1.411$ g cm^{-3}; μ(Cu Kα) = 1.635 mm^{-1}; $T = 173(2)$ K; 37570 reflections collected; F^2 refinement; $R_1 = 0.0756$, $R_2 = 0.1673$; 22 706 observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta = 65.08°$]; 1024 parameters.

[7,8,12,13,17,18-Hexa-(4-*tert*-butylphenyl)-[1,2,5]selenadiazolo-[3,4-q]porphyrazinato]zinc(II) (3b). Porphyrazine **2b** (468 mg, 0.39 mmol; prepared from 3,4-dicyano-1,2,5-selenodiazole[22] and 3,4-di-(4-*tert*-butylphenyl)pyrroline-2,5-diimine via porphyrazine **1b**[13] following the procedure of Baum et al.),[21] $Zn(OAc)_2$ (108 mg, 0.59 mmol), and anhydrous DMF (120 mL) were heated with stirring at 100 °C for 18 h. Rotary evaporation and chromatography ($MeOH/CH_2Cl_2$ 1:50) gave porphyrazine **3b** (418 mg, 85%) as a green solid: mp > 300 °C ($CHCl_3$/EtOH/$ClCH_2CH_2Cl$/PrOH), $R_f = 0.78$ ($MeOH/CH_2Cl_2$ 1:50). IR (film): 1474, 1362, 1100, 977 cm^{-1}. UV−vis (CH_2Cl_2/MeOH 25:1): λ_{max} (log ϵ) 366 (4.77), 611 (4.54), 676 (4.77) nm. ^1H NMR (400 MHz, d_5-pyridine): δ 8.77−8.68, 7.78−7.72 (2m, 6H, overlapping solvent pyridine), 1.48, 1.47, 1.36 (3s, 27H). ^{13}C NMR (125 MHz, d_5-pyridine): δ 171.3, 159.3, 157.0, 156.8, 151.0, 147.9, 142.9, 142.2, 141.7, 133.3, 132.4, 132.2, 126.0, 125.8, 35.0, 34.9, 31.6, 31.4, 30.0. MS (FAB): m/z 1276 $(M + H)^+$. MS (MALDI): 1276.2 $(M + H)^+$. $[C_{78}H_{84}N_{10}OSeZn]0.5 \cdot [C_{79}H_{86}N_{10}OSeZn]0.5 \cdot [C_3H_8O]1.75$: $M = 1434.06$. Crstal data: triclinic; $P\bar{1}$; $a = 14.884(2)$, $b = 18.786(3)$, $c = 29.167(4)$ Å; $\alpha = 80.101(12)$, $\beta = 82.475(13)$, $\gamma = 86.301(12)°$; $V = 7957(2)$ $Å^3$; $Z = 4$; $D_c = 1.197$ g cm^{-3}; μ(Cu Kα) = 1.355 mm^{-1}; $T = 173(2)$ K; 71 401 reflections collected; F^2 refinement; $R_1 = 0.1378$, $R_2 = 0.3317$; 9494 observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta = 142.48°$]; 1887 parameters.

[7,8,12,13,17,18-Hexapropyl-2,3-di-(2-hydroxy-2-methylpropanamido)porphyrazinato]zinc(II) (8). H_2S was bubbled through porphyrazine **1a** (50 mg, 0.072 mmol) in anhydrous pyridine (50 mL) for 5 min, during which time the blue solution turned violet. $AcOCMe_2COCl$ (0.6 mL, 3.6 mmol) was added with stirring at 0 °C. After 2 h at room temperature, the solution was rotary evaporated, and the residue was dissolved in trifluoroacetic acid (4 mL). After 10 min, the mixture was poured into iced water, neutralized with saturated aqueous $NaHCO_3$, and extracted with CH_2Cl_2 (50 mL), and then the organic phase was dried and evaporated. Chromatography ($CHCl_3$) gave porphyrazine **6** (38 mg, 65%). UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 347 (4.74), 572 (4.48), 631 (4.18) nm. MS (APCI): m/z 853 $(M + H)^+$. It was used directly without further purification. Crude porphyrazine **6** (54 mg, 0.062 mmol) and $Zn(OAc)_2$ (135 mg, 0.62 mmol) in THF and MeOH (1:1, 50 mL) were heated to reflux with stirring for 3 h. Rotary evaporation and chromatography ($MeOH/CHCl_3$ 1:200) gave porphyrazine **7** (53 mg, 94%). IR (film): 3422, 1744, 1663, 1521, 1464, 1147 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} 345, 604 nm. ^1H NMR (400 MHz, d_5-pyridine): δ 10.3 (br s, 2H), 3.58−3.72 (m, 12H), 2.18 (s, 6H), 2.02−2.16 (m, 12H), 1.86 (s, 12H), 0.92−1.12 (m, 18H). MS (APCI): 915 $(M + H)^+$. Deoxygenated MeOH (40 mL) was added to crude porphyrazine **7** (53 mg, 0.058 mmol), K_2CO_3 (40 mg), and NaOMe (ca. 5 mg) (Schlenk flask), and the mixture was stirred at ambient temperature for 18 h. Rotary evaporation and chromatography (CH_2Cl_2/MeOH 50:1) gave porphyrazine **8** (39 mg, 80%): mp > 300 °C (DMSO). IR (film): 3425, 1643, 1383, 1095 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} 345, 604 nm. ^1H NMR (400 MHz, d_6-DMSO): δ 10.9 (br m, 2H), 3.76−3.86 (m, 12H), 2.24−2.34 (m, 12H), 1.66 (s, 12H), 1.18−1.28 (m, 18H). MS (APCI): m/z 831 $(M + H)^+$. $C_{44}H_{64}N_{10}O_5SZn \cdot C_2H_6O$: $M = 956.55$. Crstal data: triclinic; $P\bar{1}$; $a = 11.170(3)$, $b = 16.138(4)$, $c = 16.255(4)$ Å; $\alpha = 115.726(3)$, $\beta = 95.645(4)$, $\gamma = 100.672(4)°$; $V = 2540.7(10)$ $Å^3$; $Z = 2$; $D_c = 1.250$ g cm^{-3}; μ(Mo Kα) = 0.579 mm^{-1}; $T = 153(2)$ K; 23 380 reflections collected; F^2 refinement; $R_1 = 0.0737$, $R_2 = 0.2107$; 11 882 observed reflections [$2\theta = 57.68°$]; 599 parameters.

[7,8,12,13,17,18-Hexapropyl-2-amino-3-(2-pyridinecarboxamido)porphyrazinato]iron(III) chloride (12). Porphyrazine **11**[2] (50 mg, 0.062 mmol), $FeBr_2$ (135 mg, 0.62 mmol), and 2,6-lutidine (2 mL) in THF and PhMe (1:1, 50 mL) were heated with stirring at 100 °C for 20 h. The conversion was monitored by UV−vis spectroscopy. After rotary evaporation, the residue was dissolved in CH_2Cl_2 (40 mL), and aqueous 1 M HCl (40 mL) added. After 30 min, the separated organic layer was washed with brine, dried, rotary evaporated, and chromatographed (CH_2Cl_2/MeOH 50:1) to give porphyrazine **12** (20 mg, 40%). IR (film): 3286, 1673, 1634, 1500, 1151 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} 317, 375, 564 nm. MS(ESI): m/z Calcd for $(M - Cl)^+$ $C_{40}H_{49}FeN_{11}O$: $(M - Cl)^+$ 755.3. Found: $(M - Cl)^+$, 755.5.

[7,8,12,13,17,18-Hexapropyl-2,3-di-((methoxycarbonyl)carboxamido)porphyrazinato]zinc(II) (13). H_2S was bubbled through $Zn[pz(Pr)_6(N_2Se)]$ **3a** (116 mg, 0.16 mmol) in anhydrous pyridine (20 mL) for 150 s, during which time the blue color intensified. MeO_2CCOCl (2 × 150 μL, 1.6 mmol) was added in 2 portions

(19) Zhao, M.; Zhong, C.; Stern, C.; Barrett, A. G. M.; Hoffman, B. M. *J. Am. Chem. Soc.* **2005**, *127*, 9769.
(20) Barnes, D. J.; Chapman, R. L.; Vagg, R. S.; Watton, E. C. *J. Chem. Eng. Data* **1978**, *23*, 349.
(21) Baum, S.; Trabanco, A. A.; Montalban, A. G.; Micallef, A. S.; Zhong, C.; Meunier, H. G.; Suhling, K.; Philips, D.; White, A. J. P.; Williams, D. J.; Barrett, A. G. M.; Hoffman, B. M. *J. Org. Chem.* **2003**, *68*, 1665.
(22) Bauer, E. M.; Ercolani, C.; Galli, P.; Popkova, I. A.; Stuzhin, P. A. *J. Porphyrins Phthalocyanines* **1999**, *3*, 371.

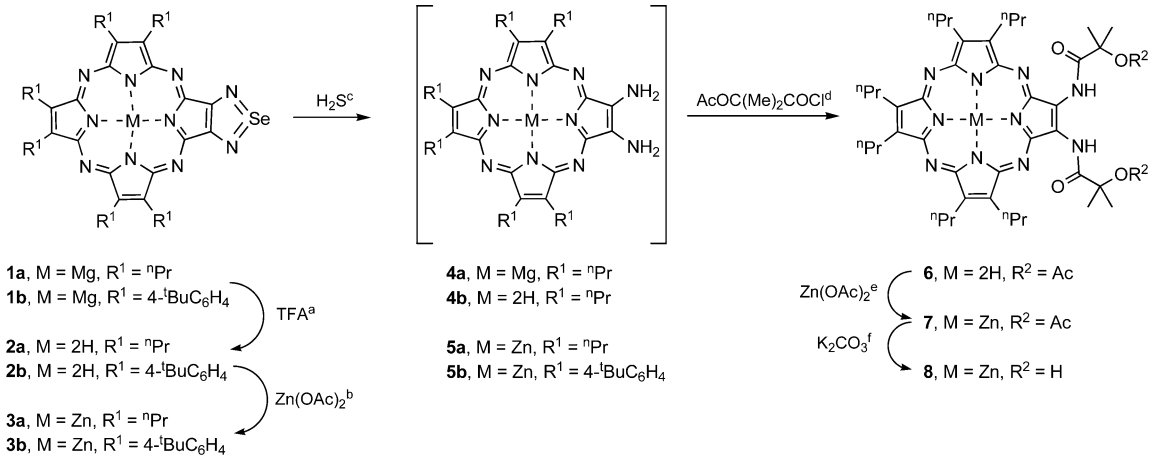
over 1 h, and the mixture was stirred at ambient temperature for 4 h. Pyridine was removed by distillation to leave a crude residue containing **5a**, which was further washed with hexanes (40 mL) and chromatographed (CH_2Cl_2/MeOH 50:1) to give porphyrazine **9**: R_f 0.47 (MeOH/CH_2Cl_2 1:50). MS(FAB$^+$): *m*/*z* 745 ($M^{+\bullet}$). HRMS (FAB$^+$) Calcd for $C_{37}H_{49}N_{10}O_3Zn$: $(M + H)^+$ 745.3281. Found: $(M + H)^+$ 745.3288. MeO_2CCOCl (2 × 150 μL, 1.6 mmol) was added, with stirring, in two portions to porphyrazine **9** in pyridine (15 mL) over 1 h. The mixture was stirred at ambient temperature overnight. MeOH (1 mL) was added, and the mixture was stirred for a further 30 min. Rotary evaporation gave a residue, which was washed with hexanes (20 mL) and chromatographed (CH_2Cl_2/MeOH 50:1, CH_2Cl_2/MeOH/Et_3N 50:1:0.1) to give porphyrazine **13** (38 mg, 29%) as blue solid: R_f = 0.28 (MeOH/CH_2Cl_2 1:50), R_f = 0.50 (EtOAc/hexanes 1:1). IR (film): 3216, 1727, 1682, 1532, 1463, 1306, 1152, 1013 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 346 (4.77), 596 (4.64), 612 (4.73), 649 (4.04) nm. ^{1}H NMR (500 MHz, d_5-pyridine): δ 9.74 (br s, 2H), 4.00−4.09 (m, 12H), 3.90 (s, 6H), 2.46−2.55 (m, 12H), 1.29−1.41, (m, 18H). ^{13}C NMR (125 MHz, d_5-pyridine): δ 162.0, 160.0, 159.8, 158.9, 154.6, 150.4, 145.0, 144.7, 144.6, 127.0, 53.5, 30.0, 28.6, 26.0, 15.1, 15.03, 14.99. MS (FAB): *m*/*z* 831 $(M + H)^+$. HRMS (FAB) Calcd for $C_{40}H_{51}N_{10}O_6Zn$: $(M + H)^+$ 831.3284. Found: $(M + H)^+$ 831.3319.

[7,8,12,13,17,18-Hexapropyl-2,3-di-(quinoline-2-carboxamido)porphyrazinato]zinc(II) (14a). H_2S was bubbled through porphyrazine **3a** (121 mg, 0.165 mmol) in anhydrous pyridine (20 mL) for 150 s, during which time the blue color intensified. 2-Quinolinecarbonyl chloride (316 mg, 1.65 mmol) suspended in PhMe (5 mL) was added, and the mixture was stirred at ambient temperature for 4 h, during which time the color changed from blue to blue-green. MeOH (1 mL) was added, and stirring was continued for 30 min. Pyridine was removed by distillation, and the residue was chromatographed (CH_2Cl_2/MeOH 10:1) to give porphyrazine **10a**: R_f 0.87 (MeOH/CH_2Cl_2 1:25). MS (FAB$^+$): *m*/*z* 814 $(M + H)^+$. HRMS (FAB$^+$) Calcd for $C_{44}H_{52}N_{11}OZn$: $(M + H)^+$ 814.3648. Found: $(M + H)^+$ 814.3627. Porphyrazine **10a** and 2-quinolinecarbonyl chloride (316 mg, 1.65 mmol) in pyridine (20 mL) were stirred for 18 h at ambient temperature. MeOH (1 mL) was added to the mixture, and stirring was continued for 30 min. Pyridine was removed by distillation to leave a crude residue, which was washed with hexanes (50 mL) and chromatographed (CH_2Cl_2/MeOH 50:1) to give porphyrazine **15a** (8 mg, 5%) as a violet solid and porphyrazine **14a** (69 mg, 43%) as a green product. Porphyrazine **14a** showed the following data: mp > 300 °C (pyridine/CH_2Cl_2/MeOH), R_f = 0.61 (MeOH/CH_2Cl_2 1:25). IR (film): 3387, 1716, 1682, 1147, 1032, 769 cm^{-1}. UV−vis (CH_2Cl_2/MeOH 25:1): λ_{max} (log ϵ) 239 (3.81), 350 (4.66), 616 (4.54) nm. ^{1}H NMR (400 MHz, d_5-pyridine): δ 13.12 (s, 2H), 8.75 (d, J = 8.4 Hz, 2H), 8.68 (d, J = 8.7 Hz, 2H, overlapping with solvent pyridine), 8.37 (d, J = 8.4 Hz, 2H), 8.00 (t, J = 8.1 Hz, 2H), 7.93 (d, J = 8.1 Hz, 2H), 7.85 (d, J = 7.8 Hz, 2H), 7.68 (t, J = 7.9 Hz, 2H), 4.18, 4.10 (t, J = 7.5 Hz, t J = 7.3 Hz, 12H), 2.69, 2.67 (2m, 12H), 1.48, 1.42−1.35, 1.26 (t, 2m, J = 7.2 Hz, 18H). ^{13}C NMR (100 MHz, d_5-pyridine): δ 162.5, 159.2, 159.1, 152.2, 151.2, 150.8, 147.0, 144.7, 144.6, 144.3, 138.3, 137.8, 131.0, 130.4, 130.0, 129.9, 129.6, 128.7, 128.5, 128.3, 126.9, 119.5, 119.4, 30.0, 29.7, 28.9, 28.7, 26.2, 26.1, 24.5, 15.4, 15.1, 15.0. MS (FAB): *m*/*z* 969 $(M + H)^+$. HRMS (FAB) Calcd for $C_{54}H_{57}N_{12}O_2Zn$: $(M + H)^+$ 969.4019. Found: $(M + H)^+$ 969.4040. Crystal data: $C_{59}H_{61}N_{13}O_2Zn\cdot 2C_5H_5N$; M = 1207.78; triclinic; $P\bar{1}$; a = 12.1703(5), b = 15.7922(7), c = 17.5468(7) Å; α = 90.108(3), β = 90.338(3), γ = 111.202(4)°; V = 3144.1(2) Å^3; Z = 2; D_c = 1.276 g cm^{-3}; μ(Cu Kα) = 0.449 mm^{-1}; T = 173(2) K; deep red blocks; 33 011 reflections collected; F^2 refinement; R_1 = 0.0823, R_2 = 0.1905; 19 487 observed reflections [$|F_o| > 4\sigma(|F_o|)$, 2θ = 65.38°]; 808 parameters. Porphyrazine **15a** showed the following data: R_f = 0.92 (MeOH/CH_2Cl_2 1:25). IR (film): 3287, 1691, 1524, 1146, 770 cm^{-1}. UV−vis (CH_2Cl_2/MeOH 25:1): λ_{max} (log ϵ) 241 (4.78), 345 (4.75), 573 (4.51), 631 (4.65) nm. ^{1}H NMR (400 MHz, d_5-pyridine/$CDCl_3$ 1:1): δ 13.01 (s, 2H), 8.88 (d, J = 8.4 Hz, 2H, overlapped with pyridine), 8.77 (d, J = 8.4 Hz, 2H), 8.57 (m, 2H), 8.17 (d, J = 7.5 Hz, 2H, overlapped with pyridine), 7.92 (d, J = 7.0 Hz, 2H), 4.37, 4.30, 4.14 (3t, J = 8 Hz, 12H), 2.78, 2.67 (2 m, 12H), 1.51−1.68, (m, 18H). MS (FAB): *m*/*z* 907 $(M + H)^+$. HRMS (FAB) Calcd for $C_{54}H_{59}N_{12}O_2$: $(M + H)^+$ 907.4884. Found: $(M + H)^+$ 907.4863.

[7,8,12,13,17,18-Hexa-(4-*tert*-butylphenyl)-2,3-di-(quinoline-2-carboxamido)porphyrazinato]zinc(II) (14b). H_2S was bubbled through porphyrazine **3b** (36 mg, 0.028 mmol) in anhydrous pyridine (8 mL) for 2 min. 2-Quinolinecarbonyl chloride (54 mg, 0.28 mmol) suspended in PhMe (2 mL) was added, and the mixture was stirred at ambient temperature for 4 h. MeOH (3 mL) was added to the solution containing crude **5b**, and the resulting mixture was stirred for 30 min. Pyridine was removed by distillation to leave a crude residue, which was washed with hexanes and chromatographed (CH_2Cl_2/MeOH 10:1) to give porphyrazine **10b**. MS (FAB): *m*/*z* 1355 ($M^{+\bullet}$). MS (MALDI): *m*/*z* 1355.5 ($M^{+\bullet}$). Porphyrazine **10b** and 2-quinolinecarbonyl chloride (54 mg, 0.28 mmol) in pyridine (8 mL) were stirred for 18 h at ambient temperature. The pyridine was removed by distillation, and the residue washed with hexanes (50 mL) and chromatographed (CH_2Cl_2/MeOH 25:1 and 50:1) to give porphyrazine **15b** (18 mg, 44%) as a violet product and porphyrazine **14b** (14 mg, 34%) as a green product. Porphyrazine **14b** showed the following data: mp > 300 °C ($CHCl_3$/EtOH/$ClCH_2CH_2Cl$/^{i}PrOH), R_f = 0.78 (MeOH/CH_2Cl_2 1:50). IR (film): 3443, 1716, 1604, 1501, 1372, 1267, 1107, 978, 839, 769 cm^{-1}. UV−vis (CH_2Cl_2/MeOH 50:1): λ_{max} (log ϵ) 374 (4.82), 641 (4.85) nm. ^{1}H NMR (400 MHz, d_5-pyridine): δ 12.73 (s, 2H), 8.85 (d, J = 8.3 Hz, 2H), 8.68 (overlapping solvent pyridine), 8.42 (d, J = 8.4 Hz, 2H), 8.02 (m, 2H), 7.78 (m, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.38 (m, 2H), 1.48, 1.47, 1.20 (3s, 54H). MS (FAB): *m*/*z* 1511 ($M^{+\bullet}$). MS (MALDI): *m*/*z* 1512.0 $(M + H)^+$. Crystal data: $[C_{101}H_{97}N_{13}O_2Zn]0.85\cdot[C_{96}H_{92}N_{12}O_2Zn]0.15\cdot[C_5H_5N]0.25\cdot[C_3H_8O]0.25$; M = 1613.22; triclinic; $P\bar{1}$; a = 14.4592(19), b = 18.004(4), c = 19.772(2) Å; α = 97.654(16), β = 100.365(10), γ = 112.803(14)°; V = 4549.1(12) Å^3; Z = 2; D_c = 1.178 g cm^{-3}; κ(Cu Kα) = 0.813 mm^{-1}; T = 173(2) K; 41 945 reflections collected; F^2 refinement; R_1 = 0.1486, R_2 = 0.3432; 8763 observed reflections [$|F_o| > 4\sigma(|F_o|)$, 2θ = 142.36°]; 1181 parameters. Porphyrazine **15b** showed the following data: R_f = 0.94 (MeOH/CH_2Cl_2 1:50). IR (film): 3286, 1684, 1516, 1487, 1267, 1108, 953 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 367 (4.88), 468 (4.44), 599 (4.64), 677 (4.90) nm. ^{1}H NMR (400 MHz, d_5-pyridine): δ 12.72 (s, 2H), 8.45, 8.03, 7.79 (3 br s, 12H, overlapping solvent pyridine), 1.49, 1.27, 0.85 (3 s, 54H). MS (FAB): *m*/*z* 1448 ($M^{+\bullet}$). MS (MALDI): *m*/*z* 1449.3 $(M + H)^+$.

***N′,N′,N″,N″*-Dicopper(II) Di-([7,8,12,13,17,18-hexapropyl-2,3-di-(quinoline-2-carboxamido)porphyrazinato])zinc (II) (18a).** 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (11 μL, 0.074 mmol) in DMF (1 mL) was added to porphyrazine **14a** (33 mg, 0.034 mmol) in DMF (5 mL). After 10 min, $CuCl_2$ (9.9 mg, 0.074 mmol) in DMF (1 mL) was added, and the mixture was stirred for 24 h at ambient temperature. Rotary evaporation and chromatography (CH_2Cl_2/MeOH 10:1) gave complex **18a** (13 mg, 37%): mp > 300 °C ($HOCH_2CH_2OH$/$ClCH_2CH_2Cl$/EtOH), R_f = 0.28

Scheme 1 [a]



[a] Reagents and conditions: (a) CF_3CO_2H, 20 °C, 20 min; (b) $Zn(OAc)_2$, DMF, 100 °C, 18 h (83−85%); (c) H_2S, pyridine, 20 °C, 2−5 min; (d) (i) $AcOC(Me)_2COCl$, pyridine, 0 °C to 20 °C, 2 h, (ii) CF_3CO_2H, 20 °C, 20 min (65%); (e) $Zn(OAc)_2$, THF, MeOH, Δ, 3 h (94%); (f) K_2CO_3, NaOMe, MeOH, 20 °C, 18 h (80%).

(MeOH/CH_2Cl_2 1:25). IR (film): 3396, 1625, 1462 cm^{-1}. UV−vis (CH_2Cl_2/MeOH 10:1): λ_{max} (log ϵ) 215 (4.56), 240 (4.66), 335 (4.63), 601 (4.38) nm. MS (FAB): *m*/*z* 2064 ($M^{+\bullet}$). HRMS (MALDI): *m*/*z* 2064.9 ($M^{+\bullet}$). Crystal data: $C_{112}H_{120}Cu_2N_{24}O_6Zn_2 \cdot 4C_2H_5OH$; $M = 2340.41$; tetragonal; $P42_1c$; $a = 17.2570(17)$, $b = 17.2570(17)$, $c = 39.409(4)$ Å; $\alpha = 90$, $\beta = 90$, $\gamma = 90°$; $V = 11736(2)$ Å^3; $Z = 4$; $D_c = 1.325$ g cm^{-3}; μ(Cu Kα) = 1.418 mm^{-1}; $T = 173(2)$ K; dark blue blocks; 113 106 reflections collected; F^2 refinement; $R_1 = 0.1671$, $w_2 = 0.4492$; 8698 observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta = 143.1°$]; 629 parameters.

***N′,N′,N″,N″*-Dicopper(II) Di-([7,8,12,13,17,18-hexa-(4-*tert*-butylphenyl)-2,3-di-(quinoline-2-carboxamido)porphyrazinato]}-zinc(II) (18b).** DBU (1.9 μL, 0.013 mmol) in DMF (1 mL) was added to porphyrazine **14b** (8.0 mg, 5.3 μmol) in DMF (5 mL). After 10 min, $CuCl_2$ (1.8 mg, 0.013 mmol) in DMF (1 mL) was added, and the mixture was stirred for 48 h at ambient temperature. Rotary evaporation and chromatography (CH_2Cl_2/MeOH 25:1 and 50:1) gave complex **18b** (2.1 mg, 25%): $R_f = 0.18$ (CH_2Cl_2/MeOH, 25:1). IR (film): 3446, 1735, 1603, 1462, 1371, 987 cm^{-1}. UV−vis (CH_2Cl_2/MeOH 25:1): λ_{max} (log ϵ) 240 (4.76), 338 (4.33), 630 (4.16) nm. MS (FAB): *m*/*z* 3140 ($M^{+\bullet}$). MS (MALDI): *m*/*z* 3140.4 ($M^{+\bullet}$).

***N,O*-Copper(II)-[7,8,12,13,17,18-hexapropyl-2-(5-*tert*-butyl-2-oxybenzylideneamino)-3-(quinoline-2-carboxamido)porphyrazinato]zinc(II) (19).** 5-*tert*-Butyl-2-hydroxybenzaldehyde (62 μL, 0.65 mmol) was added to porphyrazine **10a** (10.6 mg, 0.013 mmol) and $CuCl_2$ (17 mg, 0.13 mmol) in pyridine (5 mL). After 18 h, the pyridine was removed by distillation, and the resulting residue was chromatographed (CH_2Cl_2/MeOH 10:1) and washed with hexanes (50 mL) to give salen-porphyrazine **19** (7.6 mg, 56%) as a green-blue solid: $R_f = 0.42$ (MeOH/CH_2Cl_2 1:10). IR (film): 3384, 1655, 1463, 1156 cm^{-1}. UV−vis (CH_2Cl_2/MeOH 10:1): λ_{max} (log ϵ) 251 (4.65), 318 (4.40), 345 (4.41), 608 (4.13), 653 (4.21) nm. MS (FAB): *m*/*z* 1035 ($M^{+\bullet}$). MS (MALDI)**:** *m*/*z* 1036.7 ($M^{+\bullet}$).

***N,O*-Copper(II)-[7,8,12,13,17,18-hexapropyl-2-(5-*tert*-butyl-2-oxybenzylideneamino)-3-(2-pyridinecarboxamido)porphyrazinato]-iron(III) chloride (20).** 5-*tert*-Butyl-2-hydroxybenzaldehyde (0.05 mL, 0.3 mmol) was added to porphyrazine **12** (30 mg, 0.030 mmol) in pyridine (40 mL). After 18 h, the mixture was rotary evaporated, and the **16**-containing residue and $Cu(OTf)_2$ (110 mg, 0.3 mmol) were dissolved in EtOH and $CHCl_3$ (1:1 40 mL); the mixture was stirred overnight at ambient temperature. Rotary evaporation and chromatography (CH_2Cl_2/MeOH 25:1) gave complex **20** (30 mg, 80%): mp > 300 °C (CH_3CN/CH_2Cl_2). IR (film): 3412, 1660, 1512, 1260, 1159 cm^{-1}. UV−vis (CH_2Cl_2): λ_{max} 332, 390, 471, 576, 696 nm. MS (ESI): *m*/*z* 976.3 $(M - Cl)^+$. Crstal data: $C_{51}H_{59}ClCuFeN_{11}O_2$; $M = 1012.93$; triclinic; $P\bar{1}$; $a = 10.7996(15)$, $b = 15.203(3)$, $c = 16.414(2)$ Å; $\alpha = 91.961$, $\beta = 108.348$, $\gamma = 106.412°$; $V = 2431.1(6)$ Å^3; $Z = 2$; $D_c = 1.384$ g cm^{-3}; μ(Cu Kα) = 3.854 mm^{-1}; $T = 173(2)$ K; dark blue needles; 23 912 reflections collected; F^2 refinement; $R_1 = 0.0706$, $R_2 = 0.1840$; 4943 observed reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta = 142.2°$]; 618 parameters.

Results and Discussion

The masking of peripheral porphyrazinediamino groups via ring fusion with a selenodiazole residue, first reported by Ercolani and co-workers,[22] has proven to be a flexible method for the synthesis of a variety of extended porphyrazinic systems.[17−19,21,22] Using this strategy, the magnesium complexes **1a** and **1b** and free-base porphyrazines **2a** and **2b** were synthesized following the procedure of Baum et al. (Scheme 1).[21] The free-base macrocycles were readily remetalated[15] to yield the zinc porphyrazines **3a** and **3b** (83−85%). Slow evaporation of a methanol, dichloromethane, and pyridine solution of porphyrazine **3a** gave crystals suitable for X-ray structure determination, which confirmed the composition of the molecule. In the same way, suitably crystalline porphyrazine **3b** was obtained from a mixed-solvent system. Both crystal structures are given in the Supporting Information.

Collins and co-workers have developed a series of chelates from the metal ion complexation by two doubly deprotonated 2-hydroxy-2-methylpropanamide ligands.[23−29] The Collins

(23) Christie, J. A.; Collins, T. J.; Krafft, T. E.; Santarsiero, B. D.; Spies, G. H. *J. Chem. Soc., Chem Commun.* **1984**, 198.
(24) Anson, F. C.; Christie, J. A.; Collins, T. J.; Coots, R. J.; Furutani, T. T.; Gipson, S. L.; Keech, J. T.; Krafft, T. E.; Santarsiero, B. D.; Spies, G. H. *J. Am. Chem. Soc.* **1984**, *106*, 4460.
(25) Collins, T. J.; Coots, R. J.; Furutani, T. T.; Keech, J. T.; Peake, G. T.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1986**, *108*, 5333.
(26) Collins, T. J.; Slebodnick, C.; Uffelman, E. S. *Inorg. Chem.* **1990**, *29*, 3433.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **14a**·2py

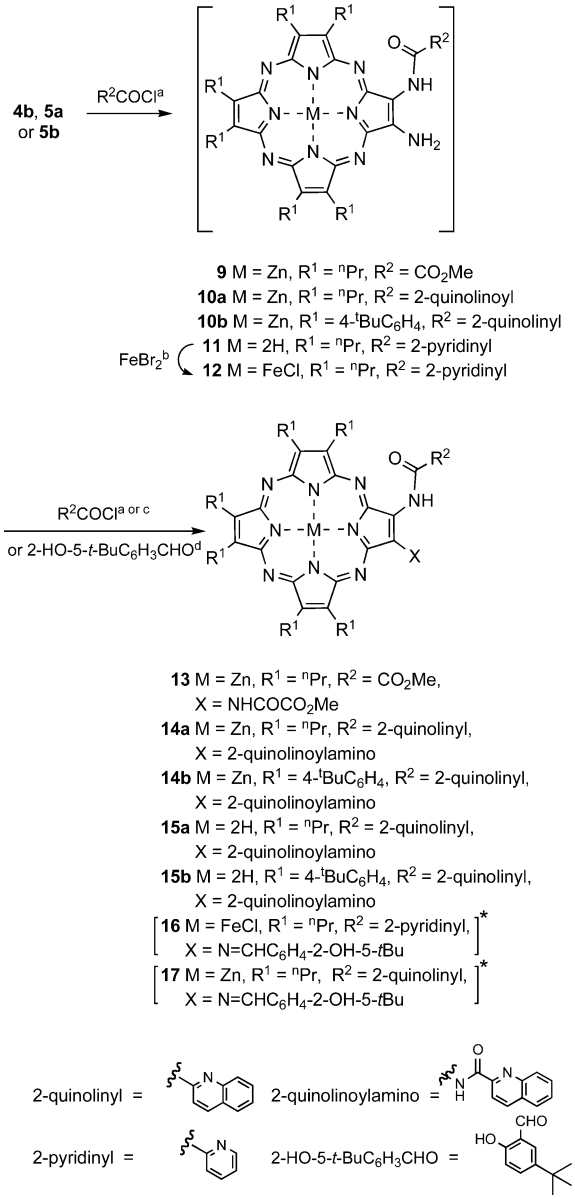
Zn−N(7)	2.0023(19)	Zn−N(2)	2.0069(18)
Zn−N(12)	1.9981(18)	Zn−N(17)	2.0099(19)
Zn−N(63)	2.137(2)		
N(2)−Zn−N(7)	86.69(7)	N(2)−Zn−N(12)	154.23(8)
N(2)−Zn−N(17)	87.31(7)	N(2)−Zn−N(63)	101.21(8)
N(7)−Zn−N(12)	87.78(8)	N(7)−Zn−N(17)	154.95(8)
N(7)−Zn−N(63)	99.71(8)	N(12)−Zn−N(17)	87.13(7)
N(12)−Zn−N(63)	104.53(8)	N(17)−Zn−N(63)	105.31(8)

chelates have two unique features that make them of considerable value in the development of novel magnetic materials. Most notable is their redox stability, which makes the ligands capable of stabilizing unusual high-valent transition metal ions such as cobalt(IV),[30,31] iron(IV),[32,33] and manganese(V)[28,34] and also allowing access to M^1-M^2 complexes with the metals at different valencies and spin states. We sought to append the Collins ligands to a porphyrazine since this may allow for the complexation of paramagnetic cations with peripherally functionalized, anionic porphyrazines, to prepare magnetically ordered charge-transfer salts, as have been reported for "simple" Collins complexes.[35]

Reaction of the free porphyrazinediamine **4a**, generated in situ from the reductive cleavage of selenodiazole **1a** using hydrogen sulfide, with excess 2-acetoxy-2-methylpropanoyl chloride and acidic workup gave porphyrazine **6** (65%). This macrocycle was immediately metalated with zinc(II) acetate to give complex **7** (94%) and saponified to provide porphyrazine **8** (80%) (Scheme 1). Slow evaporation of a DMSO solution of porphyrazine **8** yielded crystals suitable for an X-ray structure determination (Table 1). The Zn ion was coordinated to the porphyrazine core with a DMSO molecule in its apical position. Two Collins ligands are linked to the pz macrocycle through amide bonds whose C−N bond lengths (1.353(5) and 1.362(5) Å) are comparable to reported values by Collins (1.352(7) and 1.367(7) Å, respectively).[34] The carbonyl groups have a trans geometry with the N−H groups to alleviate the steric interaction. Unfortunately, attempted complexation of a variety of metal ions [Cu(II), Ni(II), Co(III)] at the peripheral β-hydroxy-amide ligands in porphyrazine **8** by deprotonation using diverse bases (NaOH, NaOMe, *t*-BuOK, $(i\text{-Pr})_2$NLi, *t*-BuLi, or Et_3N) and reaction with metal salts gave only intractable mixtures of unstable metal complexes.

(27) Collins, T. J.; Kostka, K. L.; Uffelman, E. S.; Weinberger, T. L. *Inorg. Chem.* **1991**, *30*, 4204.
(28) Workman, J. M.; Powell, R. D.; Procyk, A. D.; Collins, T. J.; Bocian, D. F. *Inorg. Chem.* **1992**, *31*, 1548.
(29) Sen Gupta, S.; Stadler, M.; Noser, C. A.; Ghosh, A.; Steinhoff, B.; Lenoir, D.; Horwitz, C. P.; Schramm, K.-W.; Collins, T. J. *Science* **2002**, *296*, 326.
(30) Anson, F. C.; Collins, T. J.; Coots, R. J.; Gipson, S. L.; Richmond, T. G. *J. Am. Chem. Soc.* **1984**, *106*, 5037.
(31) Collins, T. J.; Powell, R. D.; Slebodnick, C.; Uffelman, E. S. *J. Am. Chem. Soc.* **1991**, *113*, 8419.
(32) Collins, T. J.; Kostka, K. L.; Munck, E.; Uffelman, E. S. *J. Am. Chem. Soc.* **1990**, *112*, 5637.
(33) Kostka, K. L.; Fox, B. G.; Hendrich, M. P.; Collins, T. J.; Rickard, C. E.; Wright, L. J.; Mnck, E. *J. Am. Chem. Soc.* **1993**, *115*, 6746.
(34) Collins, T. J.; Gordon-Wylie, S. W. *J. Am. Chem. Soc.* **1989**, *111*, 4511.
(35) Eichhorn, D. M.; Telser, J.; Stern, C. L.; Hoffman, B. M. *Inorg. Chem.* **1994**, *33*, 3533.

Scheme 2 [a]



[a] Reagents and conditions: (a) MeO_2CCOCl or quinoline-2-COCl, pyridine, 20 °C, 4−18 h (5−44%); (b) $FeBr_2$, 2,6-lutidine, THF, PhMe, Δ, 20 h; 1 M HCl (40%); (c) pyridne-2-COCl.HCl, pyridine, 20 °C, 18 h; 1 M HCl; (d) or 2-HO-5-*t*-BuC_6H_3CHO, pyridine, 18 h. *Both **16** and **17** were directly converted into **20** and **19** respectively, see Scheme 4.

As a consequence, we sought to prepare porphyrazines functionalized with alternative chelating functionalities, including peripheral oxamido, 2-quinolinecarboxamido, and 2-pyridinecarboxamido groups, by amine acylation (Scheme 2). During these studies it was discovered that the two amino groups in diamines **4b**, **5a**, and **5b** underwent reaction with electrophiles at significantly different rates. In many cases, prolonged reaction of porphyrazinediamines **4b**, **5a**, or **5b** with an acylating reagent resulted in the formation of mixtures of mono- and diacylated products. Attempted diacylation using vast excesses of an acyl chloride did not drive the reaction to completion but resulted in extensive decomposition. It was found to be preferable to first isolate monoamides **9**, **10a**, and **10b** and to, subsequently, carry out the second acylation in a separate operation. Such transfor-

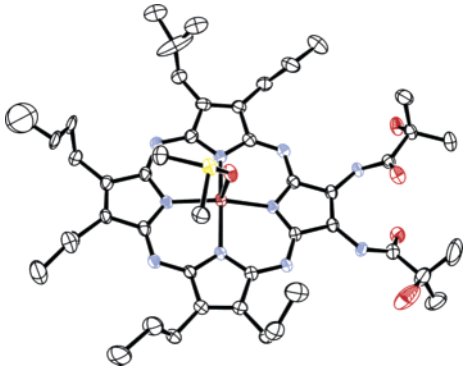


Figure 1. Molecular structure of porphyrazine **8** (50% probability ellipsoids).

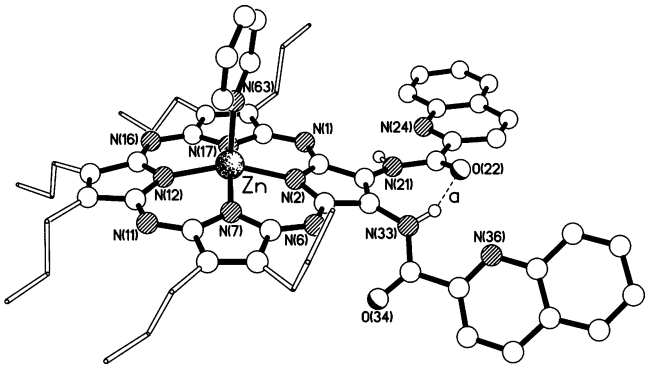
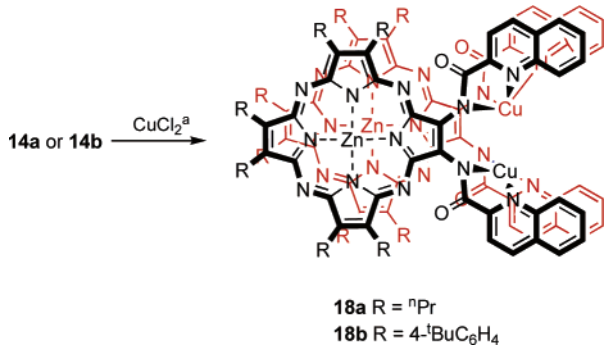


Figure 2. Molecular structure of **14a**·2py. The N−H···O hydrogen bond (a) has N···O = 2.836(3) Å, H···O = 2.13 Å, and N−H···O = 135°.

mations were less than ideal for the synthesis of symmetrical diamides **13**, **14a**, and **14b** but have proven to be immensely valuable for the synthesis of mixed-ligand systems, vide infra. Although monoamides **9**, **10a**, and **10b** were less unstable than the corresponding monoimino derivatives with 5-*tert*-butyl-2-hydroxybenzaldehyde,[17] slow aerobic decomposition was still observed, and monoamides **9**, **10a**, and **10b** were immediately used in subsequent steps. The amino-amide **11**,[2] prepared from porphyrazine **2a** via monoacylation of the derived diamine **4b** with 2-picolinyl chloride, was converted by metalation using iron(II) bromide and subsequent oxidation into the derived Fe(III) complex **12**. Although selective macrocycle metalation was possible in the presence of the amino-amide unit, the reaction proceeded with only a modest yield (40%).

During the preparation of diamides **14a** and **14b**, partial demetalation was observed, thereby giving access to free base macrocycles **15a** and **15b**. Slow evaporation of methanol/dichloromethane/pyridine solutions of diamide **14a** gave crystals suitable for X-ray structure determination. The solid-state structure of **14a** has been determined as both the nonsolvated (**14a**, see Figure S1 in the Supporting Information) and pyridine solvated (**14a**·2py, Figure 2) forms. (Note: both forms have a metal-coordinated pyridine molecule.) Since the nonsolvated version has some disorder in the porphyrazine ring (see Figure S2), the discussion will concentrate on the pyridine solvate. The five-coordinate square-based pyramidal zinc center perches almost symmetrically on top of the inner four nitrogens of the porphyrazine ring [the four Zn−N(pz) distances range between

Scheme 3 [a]



[a] Reagents and conditions: (a) $CuCl_2$, DBU, DMF 20 °C, 24-48 h (25−37%).

1.9981(18) and 2.0099(19) Å, Table 1], lying ca. 0.44 Å out of the {N(2),N(7),N(12),N(17)} plane which is coplanar to better than 0.01 Å. Not surprisingly, the Zn−N bond to the coordinated pyridine molecule [2.137(2) Å] is significantly longer than those to the porphyrazine nitrogens. The porphyrazine ring has a slightly dished conformation; the outer four nitrogens are coplanar to within ca. 0.01 Å, and although the inner and outer N_4 planes are parallel (inclined by less than 1°), they have a mean interplanar separation of ca. 0.11 Å such that the metal lies ca. 0.55 Å out of the outer {N(1),N(6),N(11),N(16)} plane (cf., ca. 0.44 Å for the inner N_4 plane). The two quinolinecarboxamido moieties have noticeably different conformations as a consequence of the intramolecular N−H···O hydrogen bond between them (Figure 2a). For the N(21)/N(24) moiety, the amide and quinoline units are inclined by ca. 10° and the amide is inclined by ca. 28° to its parent pyrrole ring, while for the N(33)/N(36) unit the corresponding twists are ca. 4 and 53°. It is noticeable that in each quinolinecarboxamido group the amide N−H is positioned proximal to the quinoline nitrogen, suggesting some N−H···N interaction; the N(21)−H···N(24) and N(33)−H···N(36) N···H separations are ca. 2.19 and 2.23 Å, respectively. The crystal structure of the related zinc-porphyrazine diamide complex, **14b**, was also determined (see Supporting Information). The di-(2-quinolinecarboxamido)-porphyrazines, **14a** and **14b**, are structurally related to the known di-(2-picolinamido)-porphyrazines,[2] but they have greater stability and solubility and, therefore, are more readily synthesized and derivatized.

Reaction of oxamido-porphyrazine **13** with copper(II) chloride and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gave a violet copper complex in moderate yield (19−52%). Unfortunately, this was unstable and not amenable to full characterization. Attempted metalation with nickel(II), zinc(II), or platinum(II) also gave unstable complexes, which were not characterized further. In contrast, reaction of the di-(2-quinolinecarboxamido)-porphyrazines, **14a** and **14b**, with copper(II) chloride and DBU gave the complexes **18a** and **18b** (Scheme 3). The crystal structure[36] of the mixed-

(36) The quality of the data set is somewhat poor, and consequently, a number of areas of the structure (such as the quinoline moieties) had to be optimized and thus the metrical parameters must be treated with some caution. The overall topology of the structure, however, is beyond question.

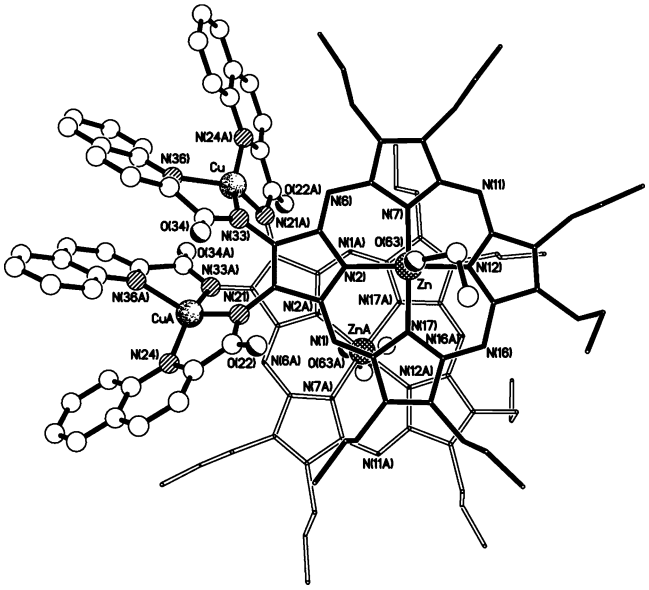


Figure 3. Molecular structure of the C_2-symmetric complex **18a**. The C_2 axis is in the plane of the paper and bisects the Zn···ZnA and Cu···CuA vectors; the Zn···ZnA and Cu···CuA separations are 4.548(3) and 4.403(3) Å respectively.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **18a**

Zn−N(2)	1.977(7)	Zn−N(7)	1.959(10)
Zn−N(12)	1.947(8)	Zn−N(17)	2.033(11)
Zn−O(63)	2.132(8)	Cu−N(33)	2.029(8)
Cu−N(36)	2.036(4)	Cu−N(21A)	2.005(14)
Cu−N(24A)	1.934(5)		
N(2)−Zn−N(7)	90.0(4)	N(2)−Zn−N(12)	165.6(5)
N(2)−Zn−N(17)	88.7(4)	N(2)−Zn−O(63)	93.6(4)
N(7)−Zn−N(12)	86.2(5)	N(7)−Zn−N(17)	161.1(5)
N(7)−Zn−O(63)	106.1(4)	N(12)−Zn−N(17)	90.3(4)
N(12)−Zn−O(63)	100.8(5)	N(17)−Zn−O(63)	92.8(6)
N(33)−Cu−N(36)	81.2(3)	N(33)−Cu−N(21A)	108.0(5)
N(33)−Cu−N(24A)	152.2(4)	N(36)−Cu−N(21A)	142.1(4)
N(36)−Cu−N(24A)	105.6(2)	N(21A)−Cu−N(24A)	83.3(4)

metal zinc−copper diamide **18a** showed the complex to be a C_2-symmetric back-to-back porphyrazine dimer linked by a pair of copper centers that each coordinate to a quinolinecarboxamido moiety from both the "upper" and "lower" porphyrazines (Figure 3). The N_8 "planes" (vide infra) of the two porphyrazine rings are offset such that their centroid···centroid separation is ca. 4.04 Å compared to a mean interplanar separation of ca. 3.32 Å; the two planes are inclined by ca. 8°. The geometry at the zinc center is the expected square-based pyramidal, although compared to **14a** and **14a**·2py the metal sits closer (ca. 0.29 Å compared to 0.47 and 0.44 Å in **14a** and **14a**·2py, respectively) to the plane of the inner four nitrogens (which are coplanar to within ca. 0.04 Å). Associated with this, three of the four Zn−N(pz) coordination distances are shorter than those seen in **14a** and **14a**·2py, although, for some reason, that to N(17) is longer (Table 2). In contrast to the dished conformations seen for **14a** and **14a**·2py, the porphyrazine ring in **18a** has a slightly twisted conformation, N(6) and N(12) lying ca. 0.15 and −0.12 Å out of and on opposite sides of the {N(1),N(2),N(7),N(11),N(16),N(17)} plane which is coplanar to within ca. 0.03 Å. The optimization of the quinoline rings[36] renders detailed analysis of the orientation of the quinolinecarboxamido moieties somewhat uncertain, but despite this, it is clear that, as in both **14a** and **14a**·2py, the amide and quinoline units are approximately coplanar (inclined by ca. 3 and 8° for the N(21)/N(24) and N(33)/N(36) units, respectively) and that the quinolinecarboxamido moieties are steeply inclined to their parent pyrrole rings. However, whereas in **14a** and **14a**·2py the inclinations of the two quinolinecarboxamido were very different (ca. 23 and 61° in **14a** and ca. 28 and 53° in **14a**·2py), in **18a** they are much more similar (ca. 50 and 42° for the N(21)/N(24) and N(33)/N(36) units, respectively). This is no doubt a consequence of the coordination to the bridging copper centers. The geometry at the copper centers is markedly distorted tetrahedral, the {Cu,N(21A),N(24A)} and {Cu,N(33),N(36)} planes being twisted so that there is an angle of ca. 51° between them (cf. 90° in ideal tetrahedron coordination) (Table 2). This structure is very similar to its closely related 2-picolinamide analogue[2] with peripheral copper centers linking the two porphyrazine rings. However, in the literature structure (which has molecular rather than crystallographic C_2 symmetry), the nickel centers linked to the porphyrazine rings lie within the plane of the inner four nitrogen atoms unlike the zinc centers here in **18a** which perch "above" them (vide supra).

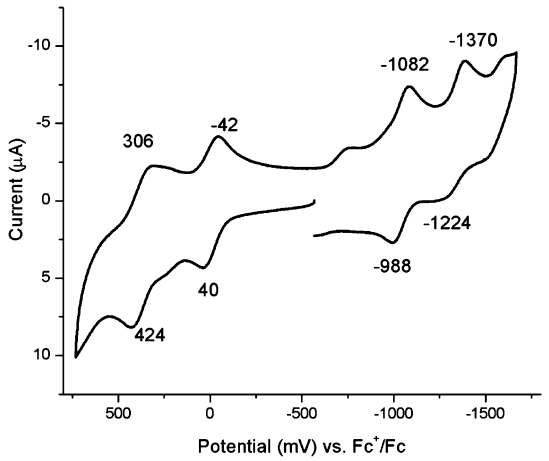
The availability of either complex, **18a** or **18b**, with peripheral propyl or 4-*tert*-butylphenyl substituents highlights the flexibility of the synthesis and allows the opportunity to fine-tune the physical properties, such as solubility, of these novel tetrametallic complexes.[15] As for the di-(2-picolinamido) analogues, we found dicopper complex **18a** to be EPR silent, an observation which leads to the conclusion that the two spins at the periphery of the dimer are strongly antiferromagnetically coupled, with a diamagnetic $S = 0$ ground state and negligible thermal population of the corresponding triplet excited state.[2]

The UV−vis spectra of dimers **18a** and **18b** exhibit intense Soret bands at $\lambda_{max} = 335$ and 338 nm and Q-bands at $\lambda_{max} = 601$ and 630 nm, respectively. Alternatively, the precursor macrocycles, **14a** and **14b,** display intense Soret bands at $\lambda_{max} = 350$ and 374 nm and Q-bands at $\lambda_{max} = 616$ and 641 nm, respectively. Therefore, by comparison, formation of the copper(II)-linked porphyrazine dimer results in a blue shift of 15 nm for the Soret band of **18a** and a blue shift of 36 nm for **18b**. As reported for our di-(picolinamido) porphyrazine dimer,[2] porphyrin sandwich complexes, and cofacial porphyrin complexes, this blue shift is a result of $\pi-\pi$ interactions between adjacent macrocycles.[37,38] The magnitude of the shift is impressive however, especially for the 4-*tert*-butylphenyl analogue **18b**, since previously, shifts of approximately 9 nm have been reported. This curious result is the subject of further study.

Significant donation of electron density from the peripheral amino groups into the macrocyclic ring system has been demonstrated previously by cyclic voltammetry.[15] Conse-

(37) Bilsel, O.; Rodriguez, J.; Milam, S. N.; Gorlin, P. A.; Girolami, G. S.; Suslick, K. S.; Holten, D. *J. Am. Chem. Soc.* **1992**, *114*, 6528.
(38) Collman, J. P.; Kendall, J. L.; Chen, J. L.; Eberspacher, T. A.; Moylan, C. R. *Inorg. Chem.* **1997**, *36*, 5603.

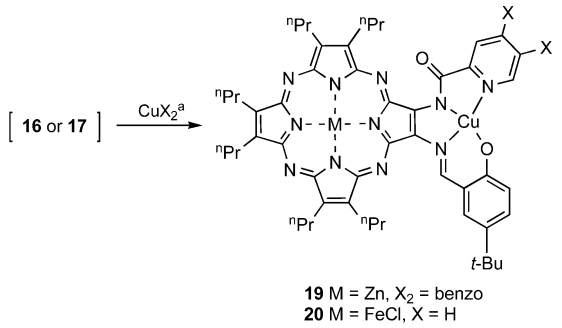
Table 3. Electrochemical Study of Dimer **18a**[a]



	pz^{2+}/pz^{+}	pz^{+}/pz	pz/pz^{1-}	pz^{1-}/pz^{2-}
18a	0.365 (118)	−0.001 (82)	−1.035 (94)	−1.297 (146)

[a] Figure shows the conversion of half-wave potentials (V vs Fc^{+}/Fc, measured in dichloromethane, with 0.1 M Bu_4NPF_6 as electrolyte, Pt disk working electrode, and at a scan rate of 110 mVs^{-1}) and E– (ΔE_p, mV).

Scheme 4 [a]



19 M = Zn, X_2 = benzo
20 M = FeCl, X = H

[a] Reagents and conditions: (a) $CuCl_2$ or $Cu(OSO_2CF_3)_2$, pyridine, 20 °C, 18 h (56%, 80%).

quently, these porphyrazines are more easily oxidized than the analogous phthalocyanines and porphyrins. However, substitution of an amino group by an electronically withdrawing acetyl or trifluoroacetyl group results in an increase in the oxidation potential of the resulting porphyrazines, which leads to a macrocycle which is more difficult to oxidize.[39] Indeed, the first and second oxidation potentials of **18a** are −0.001 and 0.365 V, indicating the dimer macrocycles are 130 mV more difficult to oxidize than 2H-[Pz((NMe$_2$)$_2$Pr$_6$)] (Table 3). In addition, dimer **18a** exhibits reduction potentials of −1.035 V and −1.297 V. The results mirror those obtained for our di-(picolinamido) porphyrazine dimer.[2]

Since the synthetic strategy employed for the majority of the derivatives involves a transient monosubstituted species, the possibility of synthesizing unsymmetrical mixed-ligand systems was explored. Toward this end, porphyrazines **10a** and **12** were allowed to react with 5-*tert*-butyl-2-hydroxybenzaldehyde, followed by copper(II) chloride or triflate and pyridine. This gave the bimetallic complexes **19** (56%) and **20** (80%) (Scheme 4). Recently, we have applied this same synthetic method for the synthesis of related complexes, **20** (M = VO, MnCl, Cu).[40] Slow diffusion of acetonitrile into

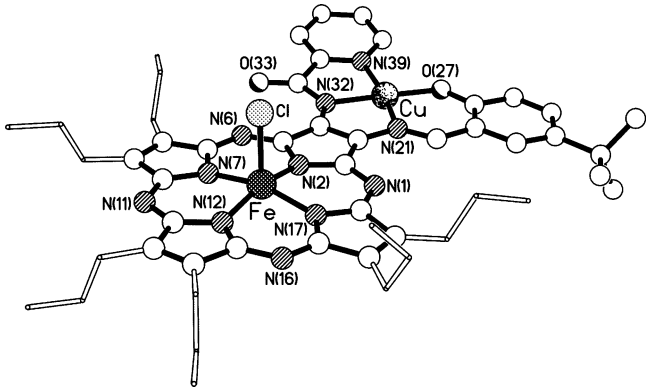


Figure 4. Molecular structure of **20**.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **20**

Fe−Cl	2.3259(15)	Fe−N(2)	1.941(4)
Fe−N(7)	1.920(4)	Fe−N(12)	1.933(4)
Fe−N(17)	1.921(4)	Cu−N(21)	1.961(4)
Cu−O(27)	1.866(4)	Cu−N(32)	1.927(4)
Cu−N(39)	1.982(5)		
Cl−Fe−N(2)	99.43(14)	Cl−Fe−N(7)	97.48(14)
Cl−Fe−N(12)	97.84(14)	Cl−Fe−N(17)	101.36(14)
N(2)−Fe−N(7)	88.96(17)	N(2)−Fe−N(12)	162.72(19)
N(2)−Fe−N(17)	88.87(17)	N(7)−Fe−N(12)	88.39(19)
N(7)−Fe−N(17)	161.14(19)	N(12)−Fe−N(17)	88.14(19)
N(21)−Cu−O(27)	94.63(17)	N(21)−Cu−N(32)	86.34(17)
N(21)−Cu−N(39)	167.71(17)	O(27)−Cu−N(32)	177.87(18)
O(27)−Cu−N(39)	96.68(18)	N(32)−Cu−N(39)	82.52(17)

a solution of complex **20** in dichloromethane gave crystals suitable for X-ray analysis. As was seen for the zinc complexes **14a**, **14a**·2py, and **18a**, the metal here in complex **20** (Figure 4) again adopts a square-based pyramidal geometry, perching ca. 0.30 Å above the porphyrazine N_8 plane; the Fe−N distances are in the range of 1.920(4)−1.941(4) Å. The coordination plane around the distorted square planar copper center is only slightly inclined to this plane (ca. 5°), even though the pyridine nitrogen N(39) lies ca. 0.21 Å out of the {Cu,N(21),O(27),N(32)} plane which is coplanar to within ca. 0.02 Å; the copper lies ca. 0.27 Å out of the N_8 plane. When the N(39) center is omitted, the {CuN_2O} plane is inclined by ca. 3° to the N_8 plane. The picolinamide moiety has a near planar conformation, the amide and pyridyl groups being inclined by only ca. 2°, but the picolinamide as a whole is slightly inclined with respect to its parent pyrrole ring (ca. 7°), thus moving N(39) out of the {CuN_2O} plane (Table 4). As is seen here in complex **20**, in the closest related literature structure (μ_2-2,3,12,13,-17,18-hexapropyl-7,8-bis((5-*tert*-butyl-2-oxybenzylidene)-imino))-chloro-copper-manganese(III),[17] the porphyrazine ring is planar (to within better than 0.01 Å) with the manganese perching on top of the inner N_4 atoms (by ca. 0.31 Å). In contrast to the out-of-plane distortion seen for the pyridyl nitrogen N(39) here in complex **20** (vide supra), in the literature structure,[17] the copper coordination sphere is symmetric (two salicylaldimine moieties cf. one salicyl-

(39) Fuchter, M. J.; Vesper, B. J.; Murphy, K. A.; Collins, H. A.; Philips, D.; Hoffman, B. M.; Barrett, A. G. M. *J. Org. Chem.* **2005**, *70*, 2793.
(40) Zhong, C.; Zhao, M.; Goslinski, T.; Stern, C.; Barrett, A. G. M.; Hoffman, B. M. *Inorg. Chem.* **2006**, submitted for publication.

aldimine and one picolinamide unit in **20**) and coplanar to within ca. 0.06 Å.

In the EPR spectrum of porphyrazine **20**, spin coupling between the Fe(III) and Cu(II) center is observable, but the exact nature of this coupling is complex. The UV−vis spectrum of **20** is also complex with absorbances at λ_{max} = 332, 390, 471, 576, and 696 nm. In addition to the B- and Q-bands observable for porphyrazines,[15] Fe(III) tetraazaporphyrin complexes of intermediate spin exhibit intense charge-transfer bands in the near-UV and near-IR regions (at approximately 400−450 and 650−725 nm).[41] It is therefore plausible that the bands at 471 and 696 nm arise from charge-transfer bands between the macrocyclic ligand or the axial ligand and the Fe(III) center.

Conclusions

Several porphyrazinediamines were converted into monoacyl, diacyl, and acyl-imine derivatives using the acid chlorides from 2-picolinic acid or 2-quinolinecarboxylic acid or using 5-*tert*-butyl-2-hydroxybenzaldehyde. The resultant polydentate ligands were converted into bimetallic complexes and tetrametallic porphyrazine dimer complexes. Extension of this work to the synthesis of alternative molecular scaffolds and the development of novel magnetic and electronic materials will be reported in due course.

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Supporting Information Available: General experimental procedures and structural data with CIF files for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(41) Stuzhin, P. A.; Hamdush, M.; Ziener, U. *Inorg. Chim. Acta* **1995**, *326*, 131.