



Improved syntheses of β -octabromo-*meso*-triarylcorrole derivatives



Jan Capar^a, Steffen Berg^a, Kolle E. Thomas^a, Christine M. Beavers^b, Kevin J. Gagnon^b, Abhik Ghosh^{a,*}

^a Department of Chemistry and Center for Theoretical and Computational Chemistry, UiT –The Arctic University of Norway, 9037 Tromsø, Norway

^b Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720-8229, USA

ARTICLE INFO

Article history:

Received 19 April 2015

Received in revised form 13 July 2015

Accepted 19 July 2015

Available online 26 July 2015

Keywords:

Reductive demetallation

Corrole

Metalloporphyrin

Octabromocorrole

Iron

ABSTRACT

In spite of significant applications as starting materials for a variety of metalloporphyrin derivatives, free-base β -octabromo-*meso*-triarylcorroles continue to be viewed as inaccessible. The reasons range from the need for tedious column-chromatographic purification to limitations of the reductive demetallation protocol for selected systems. Here we report that column chromatography may be entirely avoided for a number of β -octabromo-*meso*-tris(*p*-X-phenyl)corrole derivatives, where X = CF₃, NO₂, F, H, CH₃, and OCH₃; instead, analytically pure products may be obtained by recrystallization from chloroform/methanol. In addition, we have presented an optimized synthesis of the heretofore inaccessible, sterically hindered ligand β -octabromo-*meso*-tris(2,6-dichlorophenyl)corrole, H₃[Br₈TDCPC], via reductive demetallation of the corresponding Mn(III) complex. With our earlier report of β -octabromo-*meso*-tris(pentafluorophenyl)corrole, H₃[Br₈TPFPC], a comprehensive set of optimized synthetic protocols are thus in place for a good number of β -octabromo-*meso*-triarylcorrole ligands. Furthermore, we have illustrated the use of these ligands by synthesizing the iron complexes Fe[Br₈TDCPC]Cl and Fe[Br₈TDCPC](py)₂, of which the latter lent itself to single-crystal X-ray structure determination.

© 2015 Published by Elsevier Inc.

1. Introduction

Over a decade has elapsed since copper β -octabromo-*meso*-tris(*p*-X-phenyl)corroles, Cu[Br₈TpXPC] (X = CF₃, H, CH₃, OCH₃), were synthesized via direct bromination of β -unsubstituted copper triarylcorroles, Cu[TpXPC] [1]. Subsequently, the reductive demetallation method also afforded octabrominated free-base corroles, H₃[Br₈TpXPC] (Fig. 1) [2,3]. Since then, both copper and free-base octabromocorroles have seen important applications [4]. Thus, the copper complexes have been derivatized to copper β -octakis(trifluoromethyl)-*meso*-triarylcorroles, Cu[(CF₃)₈TpXPC], [5] and to copper undecaarylcorroles, [6] both by means of palladium coupling reactions. The octabrominated free-base corroles were used to synthesize the first gold [7,8] corroles and also unique diboron corroles, [9] the latter differing markedly with respect to both chemical structure and conformation from β -unsubstituted diboron corroles [10]. Despite these significant advances, applications of β -octabromo-*meso*-triarylcorroles have languished for a variety of reasons. In this study, we have addressed some of these problems and present protocols providing greatly improved access to several of these ligands.

Tedious column-chromatographic purification, a common bane of porphyrin chemistry, is also a problem for both Cu [Br₈TpXPC] and H₃ [Br₈TpXPC] derivatives. A key result of this study is that, for X = CF₃, NO₂, F, H, CH₃, and OCH₃, column chromatography may be largely or entirely averted, with analytically pure products obtained simply via recrystallization. Detailed protocols are given below for Cu [Br₈TPC] and H₃ [Br₈TPC] (TPC = *meso*-triphenylcorrole).

Another difficulty in this area is that the original reductive demetallation procedure fails for certain copper β -octabromocorroles. Thus, we failed to efficiently demetallate copper tris(pentafluorophenyl)corrole, Cu[TPFPC], and its β -octabromo derivative, Cu[Br₈TPFPC]. Taking a cue from another early demetallation protocol by Chang and coworkers, [11] where manganese corroles were demetallated with SnCl₂/CH₂Cl₂/HCl, we successfully demetallated Mn[Br₈TPFPC] in up to 86% yield [3]. Recently, we have also reported a high-quality single-crystal X-ray structure of the free base H₃[Br₈TPFPC] [12].

In the same vein, Dehaen and coworkers failed to cleanly demetallate copper β -octabromo-*meso*-tris(2,6-dichlorophenyl)corrole, Cu[Br₈TDCPC], with SnCl₂/HCl in 2:1 acetonitrile/dichloromethane, obtaining partially debrominated free-base corroles instead [13]. The same conditions did lead to demetallation of Cu[Cl₈TDCPC], albeit in poor yield (20%) [13]. Thus, as of today, the highly desirable, sterically hindered ligand H₃[Br₈TDCPC] has not been reported. Here we report an optimized protocol for the synthesis of this ligand via demetallation of the corresponding

* Corresponding author.

E-mail address: abhik.ghosh@uit.no (A. Ghosh).

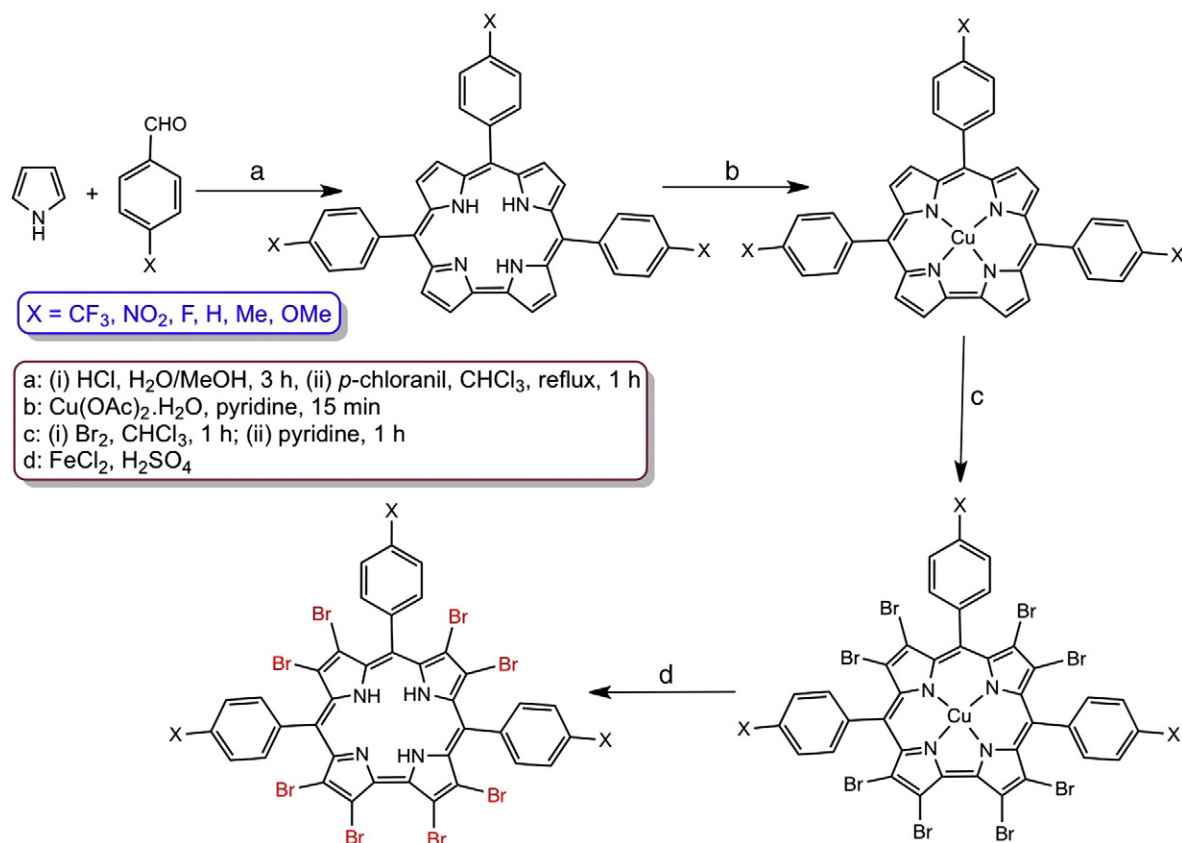


Fig. 1. Standard synthetic route to β -octabromo-*meso*-tris(*p*-X-phenyl)corrole derivatives.

manganese complex, Mn[Br₈TDCPC], which has been recently reported by Gross and coworkers (Fig. 2) [14].

Finally, to illustrate the use of H₃[Br₈TDCPC] as a ligand, we describe its conversion to two iron complexes – Fe[Br₈TDCPC]Cl and

Fe[Br₈TDCPC](py)₂ (py = pyridine; see Fig. 2). These are the first examples of iron β -octabromocorroles. The latter complex also lent itself to single-crystal X-ray structure determination, as described below.

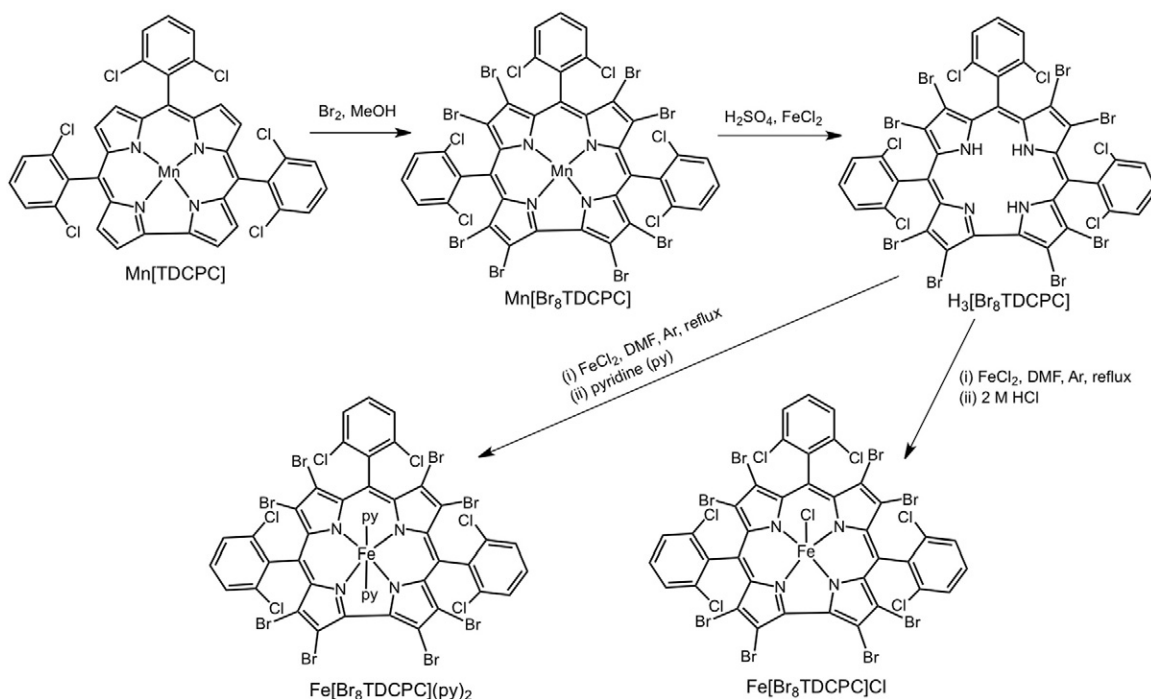


Fig. 2. Synthesis of free-base and iron Br₈TDCPC derivatives.

2. Experimental section

2.1. Materials

Unless otherwise mentioned, all reagents and solvents were obtained from Sigma-Aldrich. Silica gel (DAVISIL® LC150A 35–70 μm) was used as the stationary phase in all flash chromatographic purification. The β -unsubstituted free bases $\text{H}_3[\text{TpXPC}]$ [15] and $\text{H}_3[\text{TDCPC}]$ [15] and the corresponding copper complexes [1] were prepared as previously described. The Cu complexes $\text{Cu}[\text{TDCPC}]$ and $\text{Cu}[\text{Br}_8\text{TDCPC}]$ were synthesized according to Dehaen and coworkers [13]. The Mn complexes $\text{Mn}[\text{TDCPC}]$ [16] and $\text{Mn}[\text{Br}_8\text{TDCPC}]$ [14] were synthesized according to procedures reported by Gross and coworkers. The analytical data for all known compounds mentioned below were fully consistent with published literature values [1,15].

2.2. Instrumentation

UV–visible spectra were recorded on an HP 8453 spectrophotometer. Unless otherwise stated, all NMR spectra (400 MHz for ^1H and 376 MHz for ^{19}F) were recorded on a Mercury Plus Varian spectrometer at 298 K in $\text{THF-}d_8$. The ^1H NMR spectra were referenced to $\delta = 3.58$ ppm (residual protons in $\text{THF-}d_8$) and the ^{19}F NMR spectra were referenced to 2,2,2-trifluoroethanol- d_3 ($\delta = -77.8$). High Resolution Mass Spectra (HRMS) were recorded on an LTQ Orbitrap XL spectrometer.

2.3. Synthesis and purification of $\text{Cu}[\text{Br}_8\text{TPC}]$

The synthetic procedure employed is slightly modified relative to that reported earlier [1]. To $\text{Cu}[\text{TPC}]$ (0.105 g, 0.179 mmol) dissolved in CHCl_3 (50 mL) was added dropwise a solution of 275 μL (5.34 mmol) of liquid bromine dissolved in CHCl_3 (20 mL) over a period of 30–40 min, followed by stirring for 1 h, all at room temperature. Pyridine (474 μL) dissolved in CHCl_3 (20 mL) was then added dropwise over a period of 30–40 min, followed by stirring for an additional hour. The reaction was stopped by washing the reaction mixture twice with 20% w/v sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$, 90 mL). The organic layer was dried with anhydrous sodium sulfate, filtered, and rotary-evaporated to dryness. The entire procedure was repeated 5 times.

The crude $\text{Cu}[\text{Br}_8\text{TPC}]$ thus obtained could be purified with column chromatography on silica gel, with eluents of gradually increasing polarity, ranging from 1:1 CH_2Cl_2 /hexane through pure CH_2Cl_2 to pure CHCl_3 . Evaporation of the brown bands resulted in a 52% yield of $\text{Cu}[\text{Br}_8\text{TPC}]$. In all, the column chromatography required about 1 L of CH_2Cl_2 and 2 L of CHCl_3 .

The time-consuming and solvent-wasting nature of the column chromatography prompted us to investigate recrystallization as an alternative method of purification. In the final, successful protocol, crude $\text{Cu}[\text{Br}_8\text{TPC}]$, obtained from all 5 preparations, was combined and redissolved in a minimum volume of CHCl_3 and layered with an equal volume of methanol. The precipitated $\text{Cu}[\text{Br}_8\text{TPC}]$ was filtered after 1–2 days, washed with methanol, and dried to give a combined yield of 0.556 g of the final product (51% relative to 0.525 g $\text{Cu}[\text{TPC}]$, i.e. from all 5 batches). Although this product is suitable for further chemical transformations, a second recrystallization was carried out to yield 0.505 g of analytically pure product (46% relative to 0.525 g $\text{Cu}[\text{TPC}]$), which was characterized as previously reported [1,15].

2.4. Synthesis and purification of $\text{H}_3[\text{Br}_8\text{TPC}]$

Demetallation of $\text{Cu}[\text{Br}_8\text{TPC}]$ was carried out essentially according to the original literature procedure for reductive demetallation [2]. A 50-mL round-bottomed flask equipped with a magnetic stirrer was charged with $\text{Cu}[\text{Br}_8\text{TPC}]$ (63 mg, 0.052 mmol) and anhydrous FeCl_2 (31.1 mg, 0.245 mmol). Concentrated H_2SO_4 (2 mL) was added dropwise under

stirring. The solution was alternately stirred for 30 min and sonicated for 30 min for a total of 2 h. The reaction mixture was then quenched with distilled water, washed 3–4 times with saturated aqueous NaHCO_3 , and extracted with CHCl_3 . The organic phase was dried with anhydrous Na_2SO_4 and filtered and the filtrate was rotary-evaporated to dryness.

The original method of purification involved column chromatography with 1:1 CH_2Cl_2 /hexane as eluent [2]. This process was both tedious and required large quantities of solvent. In the new method, crude $\text{H}_3[\text{Br}_8\text{TPC}]$ was dissolved in a minimum volume of CHCl_3 and layered with an equal volume of methanol. After standing for 1–2 days, the solution was filtered to yield purified $\text{H}_3[\text{Br}_8\text{TPC}]$ in 53% yield (32 mg). A second recrystallization yielded the analytically pure free base (29 mg), which was characterized as previously reported [1,15].

2.5. Synthesis and purification of *para*-substituted $\text{Cu}[\text{Br}_8\text{TpXPC}]$ ($X = \text{CH}_3$, OCH_3 , CF_3 , NO_2 and F) [1]

Copper β -octabromo-*meso*-triarylcorroles with *para*- X -substituted *meso* aryl groups could also be effectively purified by the recrystallization method described above. The optimum CHCl_3 /methanol ratios, however, varied somewhat with X , being 1:2 for $X = \text{F}$ and 1:3 for $X = \text{CH}_3$, OCH_3 , and CF_3 . The times required for crystallization were also somewhat longer, i.e. at least 2 days, compared with $\text{Cu}[\text{Br}_8\text{TPC}]$.

For $X = \text{NO}_2$, exposure to methanol led to decomposition of the $\text{Cu}[\text{Br}_8\text{TpNO}_2\text{PC}]$. Fortunately, recrystallization could be achieved over a period of 2 days by layering a saturated CHCl_3 solution with an equal volume of hexane.

Full spectroscopic details of the $\text{Cu}[\text{Br}_8\text{TpXPC}]$ derivatives with $X = \text{F}$ and NO_2 have not been published to date and accordingly are presented below.

2.6. Characterization of $\text{Cu}[\text{Br}_8\text{TpFPC}]$

Yield 72%. UV–vis (CH_2Cl_2): λ_{max} , nm ($\epsilon \times 10^{-4}$, $\text{M}^{-1} \text{cm}^{-1}$): 445 (10.19), 649 (0.65). ^1H NMR: δ 7.58 (dd, 4H, 5,15-*o* or -*m*, 4-FPh), 7.52 (dd, 2H, 10-*o* or -*m*, Ph), 7.28–7.17 (overlapping triplets, 4H, $J = 8.8$ Hz, 5,15-*m* or -*o* and 2H, $J = 8.8$ Hz, 10-*m* or -*o* Ph). ^{19}F NMR ($\text{THF-}d_8$): $\delta = -110.81$ to -110.93 (m, 1F, 10-*p*-F, Ph); -110.99 to -111.11 (m, 2F, 5,15-*p*-F, Ph). MS (ESI⁻, major isotopomer): $[\text{M}]^- = 1271.3785$ (expt), 1271.3706 (calcd).

2.7. Characterization of $\text{Cu}[\text{Br}_8\text{TpNO}_2\text{PC}]$

Yield 98.5%. UV–vis (CH_2Cl_2): λ_{max} , nm ($\epsilon \times 10^{-4}$, $\text{M}^{-1} \text{cm}^{-1}$): 439 (7.15), 644 (0.67). ^1H NMR: δ 8.36 (d, 4H, $^3J = 8$ Hz, 5,15-*m* or -*o*, 4- NO_2Ph); 8.31 (d, 2H, $^3J = 8$ Hz, 10-*m* or -*o*, 4- NO_2Ph); 7.82 (d, 4H, $^3J = 8$ Hz, 5,15-*o* or -*m*, 4- NO_2Ph); 7.76 (d, 2H, $^3J = 8$ Hz, 10-*o* or -*m*). MS (ESI⁻, major isotopomer): $[\text{M}]^- = 1352.3518$ (expt), 1352.3542 (calcd). Elemental analysis: 32.95% C (calcd 32.84%), 1.16% H (calcd 0.89%), 6.63% N (calcd 7.24%).

2.8. Recrystallization of $\text{H}_3[\text{Br}_8\text{TpXPC}]$

Purification of the *para*-substituted free bases $\text{H}_3[\text{Br}_8\text{TpXPC}]$ by means of recrystallization was somewhat less efficient, relative to $\text{H}_3[\text{Br}_8\text{TPC}]$. A good strategy leading to analytically pure octabromocorrole free bases involved an initial column chromatography followed by crystallization from CHCl_3 /methanol (or CHCl_3 /hexane), as described above.

2.9. Synthesis of $\text{H}_3[\text{Br}_8\text{TDCPC}]$

Two different syntheses of $\text{H}_3[\text{Br}_8\text{TDCPC}]$ are described below, with the first clearly much more successful than the second.

2.10. Demetallation of Mn[Br₈TDCPC]

Into a 25-mL round-bottomed flask were placed Mn[Br₈TDCPC] (20 mg, 0.014 mmol) and 10 equiv anhydrous FeCl₂ (17.9 mg, 0.14 mmol). Concentrated H₂SO₄ (95–97%, 2.5 mL, Merck) was added. The mixture was then stirred at room temperature. The progress of the reaction was monitored by taking very small amounts of the reaction mixture into a small vial, adding distilled water, extracting with CH₂Cl₂, washing once with saturated aqueous NaHCO₃, and monitoring with UV–vis spectroscopy, followed by TLC and comparing with the starting material. After 1.5 h, the reaction was quenched by carefully pouring the mixture into distilled H₂O (300 mL), followed by extraction with CH₂Cl₂. The green organic phase was washed once with distilled water and then twice with saturated aqueous NaHCO₃. The organic phase was dried with anhydrous Na₂SO₄ and filtered and the filtrate was rotary-evaporated to dryness. The residue was chromatographed on a silica gel column with *n*-hexane/CH₂Cl₂ (5:1, followed by 1:1) as eluent to afford the pure free base. Yield: 14.45 mg (75%). UV–vis (CH₂Cl₂) λ_{max}, nm (ε × 10⁻⁴, M⁻¹ cm⁻¹): 441 (4.70), 590 (0.73), 624 (0.49), 677 (0.42). ¹H NMR (400 MHz, CDCl₃) δ, ppm: 7.56–7.66 (m, 9H, aryl). MS (HR-ESI, major isotopomer): [M]⁺ = 1364.27 (expt), 1364.26 (calcd).

2.11. Demetallation of Cu[Br₈TDCPC]

Into a 25-mL round-bottomed flask were placed Cu[Br₈TDCPC] (5.5 mg, 0.00386 mmol) and 5 equiv of anhydrous FeCl₂ (2.45 mg, 0.0193 mmol). Concentrated H₂SO₄ (95–97%, 2 mL, Merck) was added. The mixture was alternately stirred and sonicated at 50 °C. The progress of the reaction was monitored by UV–vis spectroscopy. After 4 h the reaction mixture was cooled down to r. t. and the reaction was quenched by pouring the mixture into 300 mL distilled H₂O, then extracted with CH₂Cl₂. The green organic phase was washed once with distilled water and then twice with saturated aqueous NaHCO₃. The organic phase was dried with anhydrous Na₂SO₄, filtered and rotary-evaporated to dryness. The residue obtained was chromatographed on a silica gel column first with 5:1 *n*-hexane/CH₂Cl₂ to get the recovered Cu[Br₈TDCPC], then with 2:1 *n*-hexane/CH₂Cl₂ to collect 0.7 mg of the pure free-base in 14% yield.

2.12. Synthesis of Fe[Br₈TDCPC]Cl

Iron insertion into free-base H₃[Br₈TDCPC] was carried out essentially according to the procedure reported by Gross and coworkers [17,18]. Free-base H₃[Br₈TDCPC] (0.030 g, 0.022 mmol) and anhydrous FeCl₂ (0.056 g, 0.44 mmol, 20 equiv) were dissolved in dry DMF (25 mL) under argon. The mixture was heated to reflux and the reaction mixture was monitored by thin-layer chromatography. After the solution had been refluxed for 40 min, no more starting material was detected with thin-layer chromatography and heating was discontinued. Upon cooling to room temperature, the reaction mixture was rotary evaporated to dryness. The residue was dissolved in diethyl ether and chromatographed on a short column of silica gel with diethyl ether as eluent. After the evaporation of the diethyl ether, the product was dissolved in CH₂Cl₂, washed twice with 2.0 M aqueous HCl, and then twice with water. The organic phase was dried with anhydrous Na₂SO₄, followed by rotary evaporation of the solvent. After chromatography on a short column of silica gel with CH₂Cl₂ as eluent, pure Fe[Br₈TDCPC]Cl was obtained in 92% yield (0.029 g, 0.020 mmol). UV–vis (CH₂Cl₂) λ_{max}, nm (ε × 10⁻⁴, M⁻¹ cm⁻¹): 419 (4.31), 566 (0.68). ¹H NMR (400 MHz, CDCl₃) δ 10.56 (s, 1H, 10-*para*), 9.16 (s, 4H, 5,15-*meta*), 8.32 (s, 2H, 5,15-*para*), -4.52 (s, 2H, 10-*meta*). MS (HR-ESI), major isotopomer: [M-Cl]⁺ = 1416.30 (expt), 1416.29 (calcd).

2.13. Synthesis of Fe[Br₈TDCPC](py)₂

Iron insertion was carried out exactly as described above for Fe[Br₈TDCPC]Cl. Thus, free-base H₃[Br₈TDCPC] (0.030 g, 0.022 mmol) and anhydrous FeCl₂ (0.056 g, 0.44 mmol, 20 equiv) were dissolved in dry DMF (25 mL) under argon. The reaction mixture was heated to reflux and monitored by TLC. Heating was discontinued after no more starting material could be detected by TLC, in about 40 min. After rotary evaporation of the solvent, the residue was dissolved in diethyl ether and chromatographed on a short column of silica gel with diethyl ether as eluent. The iron–corrole dietherate (characterized only by means of mass spectrometry) thus obtained was dissolved in a minimum volume of diethyl ether/*n*-heptane containing a few drops of pyridine. Crystallization over several hours led to Fe[Br₈TDCPC](py)₂ in 90% yield (0.031 g, 0.0198 mmol). X-ray quality crystals were obtained by recrystallization of Fe[Br₈TDCPC](py)₂ by diffusion of *n*-heptane into a concentrated benzene solution (over 3–4 weeks). UV–vis (CH₂Cl₂): λ_{max}, nm (ε × 10⁻⁴, M⁻¹·cm⁻¹) 425 (6.71), 573 (1.14), 780 (0.37). ¹H NMR (400 MHz, CDCl₃): δ 9.59 (s, 2H), 7.61 (s, 4H), 7.41 (s, 3H). (The axial pyridines exhibited complex dynamic behavior in the ¹H NMR and could not be readily assigned.) MS (HR-ESI, major isotopomer): [M]⁺ = 1575.26 (expt), 1575.49 (calcd).

2.14. X-ray structure determination of Fe[Br₈TDCPC](py)₂

X-ray data were collected on beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory. A 115 × 110 × 10 μm³ green plate was mounted on a MiTeGen® kapton loop and placed in a 100(2) K nitrogen cold stream provided by an Oxford Cryostream 700 Plus low temperature apparatus on the goniometer head of a Bruker D8 diffractometer equipped with an APEXII CCD detector. Diffraction data were collected for synchrotron radiation monochromated with silicon(111) to a wavelength of 0.9322(1) Å. An approximate full-sphere of data was collected with 0.3° ω scans. The structure was solved by intrinsic phasing (SHELXT) and refined by full-matrix least squares on F² (SHELXL-2014). All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically calculated and refined as riding atoms. Key crystal data are as follows. Empirical formula: C_{56.44}H_{33.05}Br₈Cl₆FeN₆; formula weight: 1703.04. Crystal system: monoclinic. Space group P2₁/n. Unit cell dimensions: *a* = 16.316(5) Å, *b* = 18.168(5) Å, *c* = 19.625(6) Å, α = 90°, β = 94.533(4)°, γ = 90°, and *V* = 5799(3) Å³. Reflections collected: 40077; independent reflections: 6091 [R(int) = 0.0858]. Final R indices [I > 2σ(I)]: R1 = 0.0597, wR2 = 0.1207. R indices (all data): R1 = 0.0969, wR2 = 0.1388. Additional details may be obtained from the crystallographic information file provided as Supporting information.

3. Discussion

Our key findings may be summarized as follows.

Even by the standards of porphyrin and corrole chemistry, where column chromatography is the standard method of purification, the column chromatography of many Br₈TpXPC derivatives is unusually tedious [2]. The compounds ‘tail’ badly and accordingly purification demands both long times and prodigious quantities of solvent. In the new protocols outlined above, we have completely averted column-chromatographic purification for all Cu[Br₈TpXPC] (X = CF₃, NO₂, F, H, CH₃, and OCH₃) derivatives. Recrystallization was found to work effectively for all such complexes, saving a lot of both time and solvent. Recrystallization was also found to be valuable for the purification of the corresponding free bases H₃[Br₈TpXPC].

We have presented optimized procedures for the synthesis of the new, sterically hindered free-base corrole, H₃[Br₈TDCPC], and for its complexation to iron. The two iron complexes reported are the first examples of iron octabromocorroles. Applications in areas such as biomimetic catalysis of atom and group transfer reactions may now be

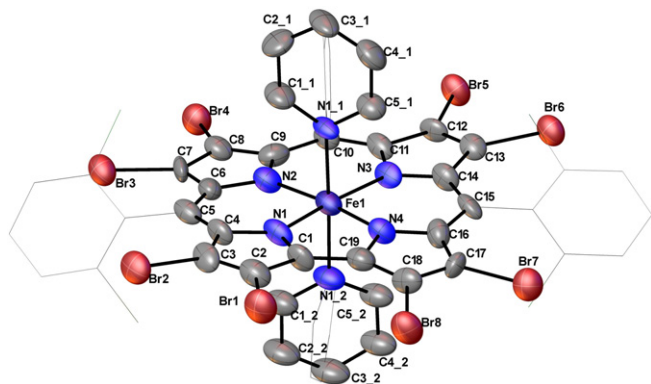


Fig. 3. Thermal ellipsoid plot for $\text{Fe}[\text{Br}_8\text{TDCPC}](\text{py})_2$. Selected distances: Fe1–N1 1.893(9) Å; Fe1–N2 1.934(10) Å; Fe1–N3 1.930(9) Å; Fe1–N4 1.884(10) Å; Fe–N_{py} 2.032(9) Å.

expected [19]. A few interesting physical properties of the new iron complexes are pointed out below.

Extensive ^1H NMR, DFT and ab initio computational studies have established that FeCl triarylcorroles are generally best described as an intermediate-spin $S = 3/2$ $\text{Fe}(\text{III})$ center antiferromagnetically coupled to a corrole $^{2-}$ radical leading to an overall $S = 1$ ground state [20–24]. Walker and coworkers, however, have emphasized that the nature of the spin coupling is sensitive to the displacement of the iron above the corrole N_4 plane. Thus, for the undecasubstituted complex octamethyltriphenylcorrolatoiron chloride, $\text{Fe}[\text{Me}_8\text{TPC}]\text{Cl}$, the spin coupling is ferromagnetic, leading to an unusual $S = 2$ ground state. At this point, the spin state of $\text{Fe}[\text{Br}_8\text{TDCPC}]\text{Cl}$ (i.e., $S = 1$ or 2) has not been determined; such a determination will be carried out and reported in due course.

Fig. 3 depicts the thermal ellipsoid plot for $\text{Fe}[\text{Br}_8\text{TDCPC}](\text{py})_2$. The Fe–N distances involving the anionic corrole nitrogens, averaging around 1.91 Å, are shorter than those involving the axial pyridines, which average around 2.02 Å. These distances are typical of low-spin $\text{Fe}(\text{III})$ complexes with all-nitrogen coordination and similar to those found for $\text{Fe}[\text{TDCPC}](\text{py})_2$. An interesting feature of the present structure is that the 2,6 C–H bonds on the axial pyridines act as hydrogen bond donors toward the chlorines of the 5,15-dichlorophenyl groups. As shown in Fig. 4, the C–H...Cl hydrogen bond distances all lie in the range 3.54–3.82 Å. Despite the low energies associated with such interactions, the presence of four such interactions per molecule apparently stabilize the observed conformation, where the two axial pyridines and the 5,15-dichlorophenyl groups are all roughly coplanar.

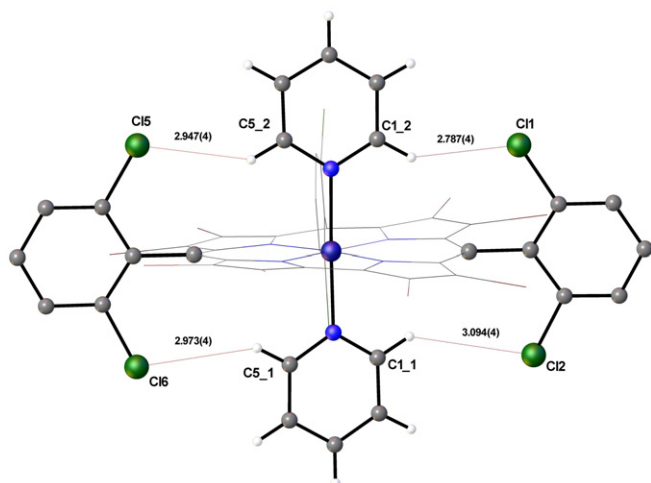


Fig. 4. C–H...Cl hydrogen bonding interactions in $\text{Fe}[\text{Br}_8\text{TDCPC}](\text{py})_2$.

4. Concluding remarks

As a result of this work, improved syntheses are now available that afford near-gram quantities of several free-base β -octabromo-*meso*-triarylcorroles, including $\text{H}_3[\text{Br}_8\text{TpXPC}]$ ($\text{X} = \text{CF}_3, \text{NO}_2, \text{F}, \text{H}, \text{CH}_3, \text{and OCH}_3$) and ~ 100 mg of the sterically hindered ligand $\text{H}_3[\text{Br}_8\text{TDCPC}]$. To this list may be added the perhalogenated ligand $\text{H}_3[\text{Br}_8\text{TPFPC}]$, which we reported in our earlier work [3]. Furthermore, we have illustrated the use of these ligands by synthesizing the first iron octabromocorroles. We look forward to seeing additional applications of these ligands in the synthesis of new reagents, catalysts, and materials with novel properties.

Acknowledgment

This project was supported by FRINATEK projects 163054 and 231086 of the Research Council of Norway and by the Advanced Light Source, Berkeley, California. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

References

- [1] I.H. Wasbotten, T. Wondimagegn, A. Ghosh, *J. Am. Chem. Soc.* 124 (2002) 8104–8116.
- [2] C. Capar, K.E. Thomas, A. Ghosh, *J. Porphyrins, Phthalocyanines* 12 (2008) 964–967.
- [3] C. Capar, L.-K. Hansen, J. Conradie, A. Ghosh, *J. Porphyrins, Phthalocyanines* 14 (2010) 509–512.
- [4] I. Aviv-Harel, Z. Gross, For a review of corrole applications, *Chem. Eur. J.* 15 (2009) 8382–8394.
- [5] K.E. Thomas, J. Conradie, L.-K. Hansen, A. Ghosh, *Eur. J. Inorg. Chem.* 12 (2011) 1865–1870.
- [6] S. Berg, K.E. Thomas, C.M. Beavers, A. Ghosh, *Inorg. Chem.* 51 (2012) 9911–9916.
- [7] A. Alemayehu, A. Ghosh, *J. Porphyrins Phthalocyanines* 15 (2011) 106–110.
- [8] E. Rabinovitch, I. Goldberg, Z. Gross, *Chem. Eur. J.* 17 (2011) 12294–12301.
- [9] A.M. Albrett, K.E. Thomas, S. Masek, A. Młodzianowska, J. Conradie, C.M. Beavers, A. Ghosh, P.J. Brothers, *Inorg. Chem.* 53 (2014) 5486–5493.
- [10] A.M. Albrett, J. Conradie, P.D.W. Boyd, G.R. Clark, A. Ghosh, P.J. Brothers, *J. Am. Chem. Soc.* 130 (2008) 2888–2889.
- [11] H.Y. Liu, L. Chen, F. Yam, H.Y. Zhan, X. Ying, X.L. Wang, H.F. Jiang, C.K. Chang, *Chin. Chem. Lett.* 19 (2008) 1000–1003.
- [12] J. Capar, J. Conradie, C.M. Beavers, A. Ghosh, *J. Phys. Chem. A* 119 (2015) 3452–3457.
- [13] T.H. Ngo, W.V. Rossom, W. Dehaen, W. Maes, *Org. Biomol. Chem.* 7 (2009) 439–443.
- [14] A. Kumar, I. Goldberg, M. Botoshansky, Y. Buchman, Z. Gross, *J. Am. Chem. Soc.* 132 (2010) 15233–15245.
- [15] B. Koszarna, D.T. Gryko, *J. Org. Chem.* 71 (2006) 3707–3717.
- [16] Z. Gross, G. Golubkov, L. Simkhovich, *Angew. Chem. Int. Ed.* 39 (2000) 4045–4047.
- [17] L. Simkhovich, A. Mahammed, I. Goldberg, Z. Gross, *Chem. Eur. J.* 7 (2001) 1041–1055.
- [18] L. Simkhovich, I. Goldberg, Z. Gross, *Inorg. Chem.* 41 (2002) 5433–5439.
- [19] J.T. Groves, *J. Inorg. Biochem.* 100 (2006) 434–447.
- [20] E. Steene, T. Wondimagegn, A. Ghosh, *J. Phys. Chem. B* 105 (2001) 11406–11413; addition/correction: *J. Phys. Chem. B* 106 (2002) 5312–5312.
- [21] O. Zakhariava, V. Schünemann, M. Gerdan, S. Licocchia, S. Cai, F.A. Walker, A.X. Trautwein, *J. Am. Chem. Soc.* 124 (2002) 6636–6648.
- [22] E. Steene, T. Wondimagegn, A. Ghosh, *J. Am. Chem. Soc.* 125 (2003) 16300–16309.
- [23] For a review, see: F.A. Walker, S. Licocchia, R. Paolesse, *J. Inorg. Biochem.* 100 (2006) 810–837.
- [24] B.O. Roos, V. Veryazov, J. Conradie, P.R. Taylor, A. Ghosh, *J. Phys. Chem.* 112 (2008) 14099–14102.