



Synthesis and Molecular Structure of a Copper Octaiodocorrole

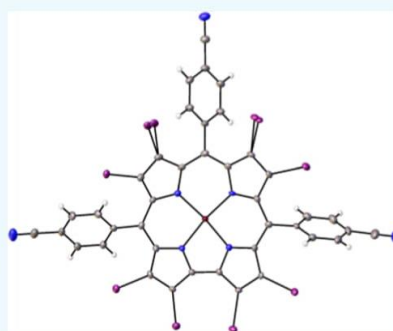
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Supporting Information

ABSTRACT: Although rather delicate on account of their propensity to undergo deiodination, β -octaiodoporphyrinoids are of considerable interest as potential precursors to novel β -octasubstituted macrocycles. Presented herein are early results of our efforts to synthesize β -octaiodocorrole derivatives. Oxidative condensation of 3,4-diiodopyrrole and aromatic aldehydes failed to yield free-base octaiodocorroles. Treatment of copper *meso*-tris(*p*-cyanophenyl)-corrole with *N*-iodosuccinimide and trifluoroacetic acid over several hours, however, yielded the desired β -octaiodinated product in \sim 22% yield. Single-crystal X-ray structure determination of the product revealed a strongly saddled corrole macrocycle with metrical parameters very close to those of analogous Cu octabromocorrole complexes. The compound was also found to exhibit an exceptionally red-shifted Soret maximum (464 nm in dichloromethane), underscoring the remarkable electronic effect of β -octaiodo substitution.



INTRODUCTION

Compared to β -octabrominated porphyrins^{1,2} and corroles,³ which serve as starting materials for a variety of other β -octasubstituted macrocycles,^{4,5} polyiodoporphyrinoids remain relatively little explored. Some progress, however, has taken place recently. Thus, we have recently reported a number of β -octaiodoporphyrin⁶ derivatives and Gross and co-workers have reported several polyiodocorrole derivatives.^{7–9} The latter group has also reported a facile copper-catalyzed transformation of gold β -iodocorroles to the corresponding β -trifluoromethyl derivatives.¹⁰ No β -octaiodocorrole derivative, however, has been reported to date.^{11–13} Reported herein is the synthesis and single-crystal X-ray structure of copper 2,3,7,8,12,13,17,18-octaiodo-5,10,15-(4'-cyanophenyl)corrole (Cu[I₈TpCNPC]), the first β -octaiodocorrole complex.

RESULTS AND DISCUSSION

Attempts at oxidative condensation of 3,4-diiodopyrrole with aromatic aldehydes via a variety of methods frequently afforded low yields of β -octaiodoporphyrins⁶ but at best only traces of corroles. Accordingly, we turned our attention to the iodination of copper tris(*para*-X-phenyl)corrole complexes, Cu[TpXPC], where X = OMe, Me, CF₃, and CN.³ Periodic acid/iodine (H₃IO₆/I₂), which we previously used to iodinate *N*-triisopropylsilylpyrrole,⁶ proved too harsh, resulting in destruction of the Cu corrole. Attempts at metal-halogen exchange on the Cu β -octabromocorroles with *n*-BuLi or Rieke magnesium,¹⁴ followed by exposure to an iodinating agent, such as *N*-iodosuccinimide (NIS), proved similarly futile. Interaction with NIS in the presence of trifluoroacetic acid (TFA) led to complete destruction of the corrole, for X = OMe and Me. In contrast, for X = CF₃ and CN, mass spectrometric analysis

indicated the formation of the desired octaiodocorrole product, Cu[I₈TpXPC] (X = CF₃ and CN). Unfortunately, for X = CF₃, isolation of the octaiodo product was frustrated by the presence of large quantities of inseparable impurities. For X = CN, on the other hand, stirring with NIS/TFA at room temperature for several hours led to modest (\sim 20%) yields of the desired product, Cu[I₈TpCNPC]. The same product was also obtained with 1,3-diiodo-5,5-dimethylhydantoin.¹⁵ Initially, the octaiodo product was contaminated with varying amounts of the I₇ and other deiodinated compounds. Varying the amount of iodinating agent (10–100 equiv) and the solvents (acetonitrile, dichloromethane, toluene, and mixtures thereof) ultimately led to a protocol affording a 22% yield of Cu[I₈TpCNPC] with no more than 2–3% of the I₇ contaminant (Scheme 1).

Full characterization of Cu[I₈TpCNPC] was hampered by the poor solubility of the compound in common solvents, presumably reflecting aggregation of the molecule. Thus, ¹H NMR spectra proved unobtainable in essentially all solvents (CDCl₃, CD₂Cl₂, 1,2-dichlorobenzene-*d*₄, acetone-*d*₆, D₂O, and pyridine-*d*₅) except tetrahydrofuran (THF)-*d*₈, in which a spectrum was obtained consisting of three doublets of equal intensity, suggesting that the ortho and meta protons of the 10-aryl group are accidentally isochronous (Figure 1). Unfortunately, the weak signals frustrated our attempts to carry out a detailed two-dimensional NMR analysis. The poor solubility of the compound also hindered our efforts to obtain X-ray quality crystals. In a stroke of luck, diffusion of heptane vapor into a 1,2-dichlorobenzene solution of a \sim 70:30 mixture of Cu[I₈TpCNPC]/Cu[I₇TpCNPC] (the product of an earlier, less

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Scheme 1

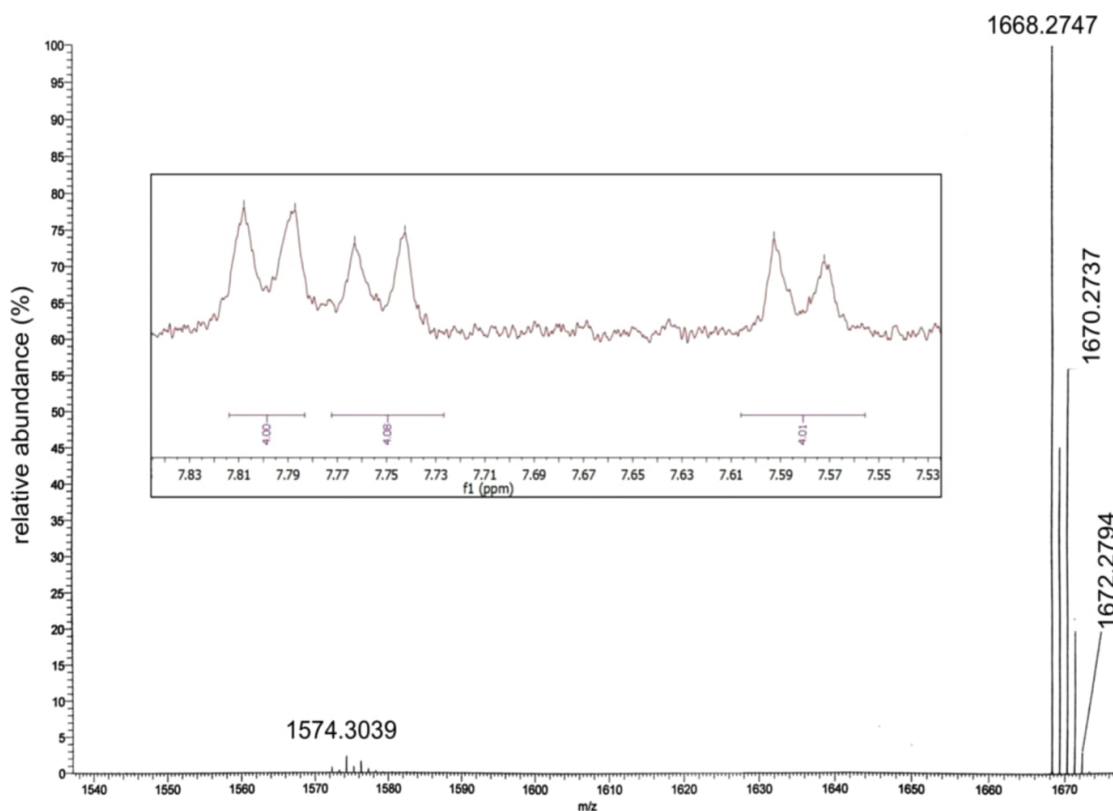
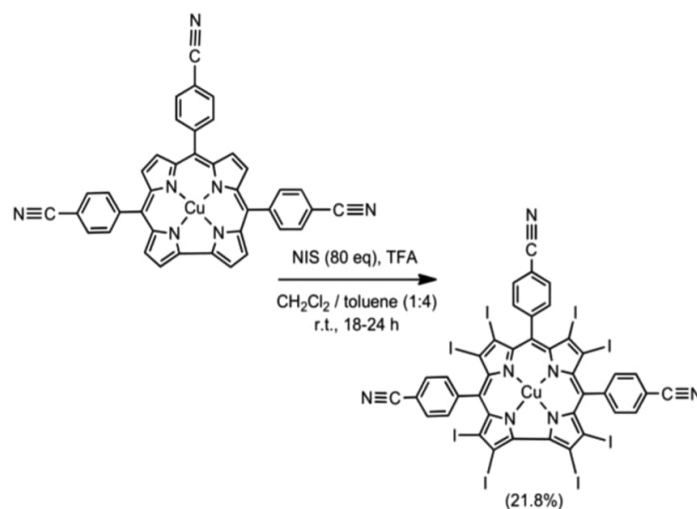


Figure 1. High-resolution electrospray ionization (ESI) mass spectrum of $\text{Cu}[\text{I}_8\text{TpCNPC}]$ in negative mode. Inset: ^1H NMR spectrum in $\text{THF-}d_8$.

optimized synthetic protocol) afforded crystals, which proved amenable to single-crystal X-ray structure determination (Figure 2 and Table 1).

As expected for a sterically hindered Cu corrole, the X-ray structure revealed a strongly but not exceptionally saddled macrocycle geometry.^{13,16} Table 2 provides a comparison of key metrical parameters of $\text{Cu}[\text{I}_8\text{TpCNPC}]$ and of other, pertinent Cu corroles.^{17–24} Thus, despite the significantly

higher van der Waals radius of I (2.15 Å) relative to Br (1.95 Å),^{25,26} the Cu–N distances and saddling dihedrals for $\text{Cu}[\text{I}_8\text{TpCNPC}]$ (see Figure 2) were found to be nearly identical to those of Cu β -octabromo-*meso*-triarylcorroles,^{19–21} suggesting that peripheral I...I interactions may not be as repulsive as implied by iodine's van der Waals radius. We may further note that the present structure is somewhat more saddled than a Cu undecaarylcorrole^{22,23} but distinctly less so

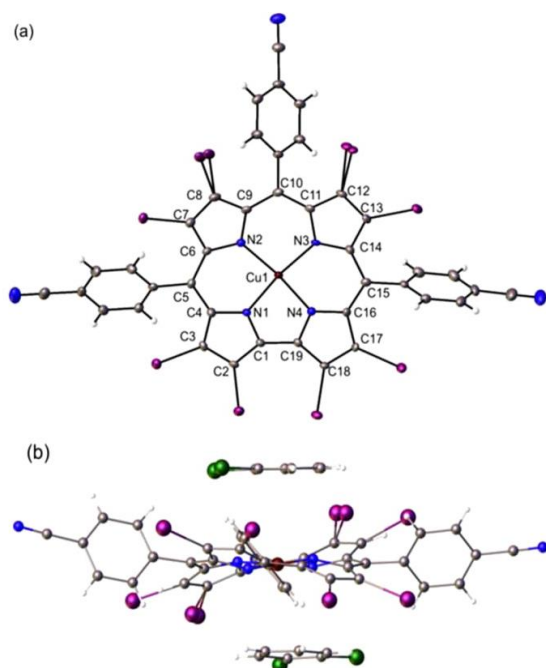


Figure 2. Thermal ellipsoid plots (50%) for $\text{Cu}[\text{I}_8\text{TpCNPC}]$: (a) top and (b) side views, the latter showing π -stacking interactions with two molecules of 1,2-dichlorobenzene. Selected distances (Å): Cu1–N1 1.925(3), Cu1–N2 1.919(3), Cu1–N3 1.925(3), and Cu1–N4 1.916(3). Saddling dihedrals ($^\circ$): C2–C1–C19–C18 45.3(8), C3–C4–C6–C7 $-65.5(12)$, C8–C9–C11–C12 57.3(11), and C13–C14–C16–C17 $-68.4(12)$.

Table 1. Crystallographic Data for $\text{Cu}[\text{I}_{7.64}\text{TpCNPC}] \cdot 4(1,2\text{-C}_6\text{H}_4\text{Cl}_2)$

chemical formula	$\text{C}_{64}\text{H}_{28.36}\text{I}_{7.64}\text{Cl}_8\text{N}_7\text{Cu}$
formula mass	2211.86
crystal system	triclinic
space group	$\bar{P}1$
λ (Å)	0.7288(1)
a (Å)	13.9951(7)
b (Å)	14.2730(8)
c (Å)	17.8450(10)
α (deg)	111.769(2)
β (deg)	91.652(2)
γ (deg)	90.047(2)
Z	2
V (Å ³)	3308.7(3)
temperature (K)	100(2)
density (g cm ⁻³)	2.220
meas. reflections	126 292
unique reflections	21 097
parameters	803
restraints	0
R_{int}	0.0399
θ range (deg)	1.493–31.899
R_1, wR_2 all data	0.0596, 0.0740
S (GooF) all data	1.157
max/min res. dens. (e Å ⁻³)	0.911/–1.270

than a Cu β -octakis(trifluoromethyl)-*meso*-triarylcorrole.²⁴ An interesting aspect of the crystal structure is that the metal-

locorrole occurs sandwiched between two 1,2-dichlorobenzene molecules, suggesting that π -stacking interactions account for the significant solubility of the complex in 1,2-dichlorobenzene.

The UV–vis spectrum of $\text{Cu}[\text{I}_8\text{TpCNPC}]$ in CH_2Cl_2 exhibits a dramatically red-shifted Soret maximum (464 nm), relative to $\text{Cu}[\text{TPC}]$ (413 nm),³ $\text{Cu}[\text{Br}_8\text{TPC}]$ (439 nm),³ and even $\text{Cu}[(\text{CF}_3)_8\text{TPC}]$ (459 nm) (Figure 3).²⁷ Given that $\text{Cu}[\text{I}_8\text{TpCNPC}]$ is in all likelihood no more saddled than $\text{Cu}[\text{Br}_8\text{TPC}]$, the strongly red-shifted Soret maximum of the former provides a nice illustration of the unique electronic effect of the β -octaiodo substitution. Interestingly, the Soret maximum of $\text{Cu}[\text{I}_8\text{TpCNPC}]$ exhibits a mild redshift in pyridine ($\lambda_{\text{max}} = 468$ nm), potentially indicating halogen bonding interactions with that solvent.

CONCLUSIONS

β -Octaiodoporphyrinoids are fragile molecules that readily undergo deiodination. Careful choice of starting materials and mild reaction conditions has allowed the synthesis and subsequently single-crystal X-ray structure determination of the first β -octaiodocorrole derivative, viz., copper 2,3,7,8,12,13,17,18-octaiodo-5,10,15-(4'-cyanophenyl)corrole ($\text{Cu}[\text{I}_8\text{TpCNPC}]$). The complex exhibits a strongly saddled corrole macrocycle with metrical parameters very similar to those of analogous Cu β -octabromocorroles and an unexpectedly red-shifted Soret maximum. Ongoing research in our laboratory focuses on developing additional, more general routes to octaiodocorrole derivatives as well as on exploiting these unique and delicate molecules as starting materials for new functionalized corroles.

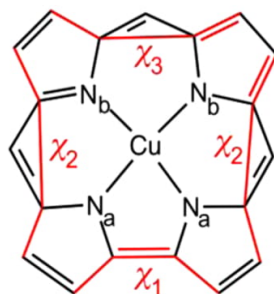
EXPERIMENTAL SECTION

Materials and Instrumentation. 4-Cyanobenzaldehyde, *N*-iodosuccinimide, and trifluoroacetic acid (HPLC-grade, $\geq 99.0\%$) were purchased from Sigma-Aldrich and used without further purification. Pyrrole (Sigma-Aldrich) was purified by passing through a pad of basic aluminum oxide 60 (activity I, 0.063–0.200 mm particle size, Merck Millipore). Copper 5,10,15-tris(4'-cyanophenyl)corrole was prepared via a one-pot protocol derived by modification of a previously reported procedure (for which the purification steps did not work well in our hands).²⁸ Silica gel 150 (35–70 μm particle size, Davisil) and neutral aluminum oxide (activity I, 0.050–0.150 mm particle size, Sigma) were used as purchased.

Ultraviolet–visible spectra were recorded on an HP 8453 spectrophotometer at room temperature in CH_2Cl_2 . ¹H NMR spectra were recorded at room temperature on a Mercury Plus Varian spectrometer (400 MHz), and high-resolution electrospray ionization (ESI) mass spectra were recorded on an LTQ Orbitrap XL spectrometer.

Synthetic Methods. *Copper 5,10,15-Tris(4-cyanophenyl)corrole.* 4-Cyanobenzaldehyde (520 mg, 4 mmol) was dissolved in pyrrole (400 mg, 6 mmol) and to the stirred mixture was added a solution (40 μL) of 10% trifluoroacetic acid in dichloromethane at room temperature. After 10 min, the solution was diluted with dichloromethane (10 mL) and a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1 g, 4.8 mmol) in 1:1 toluene/THF (4 mL) was added. After 5 min of stirring, the mixture was further diluted with dichloromethane (40 mL) and extracted twice with a saturated solution of sodium bicarbonate (50 mL each time) and twice with distilled water (50 mL each time). The organic phase was dried with

Table 2. Copper–Nitrogen Distances (Å) and Saddling Dihedrals (°) for Selected Cu Corroles



complex	Cu–N _a ^a	Cu–N _b ^a	χ ₁	χ ₂ ^a	χ ₃	ref
Cu[TPC]	1.891	1.891	27.5	53.4	48.7	17
Cu[(<i>p</i> -CF ₃ Ph) ₈ TPC]	1.902	1.897	40.9	60.1	66.0	22
Cu[Br ₈ TpMePC]	1.916	1.916	44.7	65.9	57.3	20
Cu[I ₈ TpCNPC]	1.921	1.922	45.3	67.0	57.3	this work
Cu[(CF ₃) ₈ TpCNPC]	1.921	1.925	57.2	86.4	84.5	24

^aAverage of two values for each experimental structure.

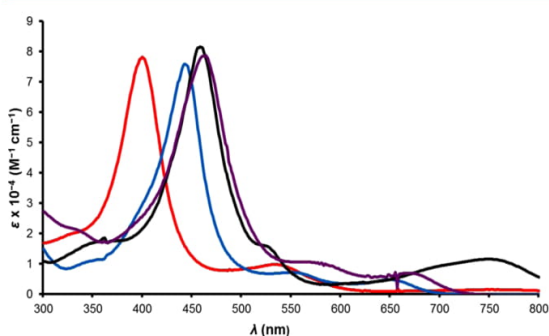


Figure 3. Comparison of the UV–vis spectra (dichloromethane) of Cu[TPC] (red), Cu[Br₈TPC] (blue), Cu[(CF₃)₈TPC] (black), and Cu[I₈TpCNPC] (purple).

anhydrous sodium sulfate and filtered. The filtrate was evaporated to dryness and the residue, whose crude weight was noted, was redissolved in pyridine (50 mL). Copper (II) acetate hydrate (1.1 equiv relative to the crude product) was added, and the solution was left to stir for 30 min. Upon removal of the solvent in vacuo, the solid residue was dissolved in a minimum volume of dichloromethane and chromatographed on silica gel column (with initially CH₂Cl₂ and then with 10% EtOAc in CH₂Cl₂ as eluent) to afford Cu[TPCNPC] as a brown solid (81.6 mg, 9.2%). All analytical data were consistent with previously reported values.²⁸

Copper 2,3,7,8,12,13,17,18-Octaiodo-5,10,15-(4'-cyanophenyl)corrole, Cu[I₈TpCNPC]. To a stirred solution of Cu[TPCNPC] (5.8 mg, 0.009 mmol) in dichloromethane (2 mL) at room temperature, was added *N*-iodosuccinimide (160 mg, 0.7 mmol) dissolved (by sonication, if necessary) in toluene (8 mL) containing a few drops of trifluoroacetic acid. The resulting solution was stirred overnight (19 h). Upon dilution with toluene (15 mL), the solution was washed twice with water (2 × 25 mL). The combined aqueous phases were extracted with toluene (25 mL), and the combined organic phases were then dried with anhydrous magnesium sulfate and filtered. The filtrate was evaporated to dryness, and the resulting residue was dissolved in dichloromethane and chromatographed on a neutral alumina column with 4:1

dichloromethane/ethyl acetate as an olive-green solid (3.3 mg, 21.8%). UV–vis (CH₂Cl₂) λ_{max} [nm, ε × 10^{−4} (M^{−1} cm^{−1}): 464 (7.85), 567 (1.06), 668 (0.69). ¹H NMR (400 MHz, THF-*d*₈, δ): 7.58 (d, 4H, ³J_{HH} = 8.2 Hz), 7.75 (d, 4H, ³J_{HH} = 8.2 Hz), 7.80 (d, 4H, ³J_{HH} = 8.3 Hz). High-resolution mass spectrometry (ESI in methanol): [M][−] = 1668.2812 (expt), 1668.2813 (calcd for CuC₄₀H₁₂N₇I₈). Crystals suitable for X-ray analysis were obtained by vapor diffusion of heptane into a concentrated 1,2-dichlorobenzene solution.

X-ray Structure Determination. X-ray data for Cu-[I₈TpCNPC] were collected on beamline 12.2.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory. The crystal, an orange lath (0.080 mm × 0.010 mm × 0.010 mm), was mounted on a MiTeGen kapton loop and placed in a 100(2) K nitrogen cold stream provided by an Oxford Cryostream 800 Plus low-temperature apparatus on the goniometer head of a Bruker D8 diffractometer equipped with a PHOTON II CPAD detector operating in shutterless mode. Diffraction data were collected using synchrotron radiation monochromated using silicon (111) to a wavelength of 0.7288(1) Å. An approximate full-sphere of data was collected using a combination of φ and ω scans with a scan speed of 0.5 s per 4° for the φ scans and 0.5 and 1 s per degree for the ω scans at 2θ = 0 and −20, respectively. Absorption corrections were applied using SADABS.²⁹ The structure was solved by intrinsic phasing (SHELXT)³⁰ and refined by full-matrix least squares on F² (SHELXL-2014)³¹ using the ShelXle GUI.³² Appropriate scattering factors were applied using the XDISP³³ program within the WinGX suite.³⁴ All nonhydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically calculated and refined as riding atoms. Electron density holes near the iodine atoms at the C7 and C13 positions indicated that these atoms do not have 100% occupancy, and the occupancies of iodine atoms at C7 and C13 (I₃ and I₆ in the cif) were allowed to freely refine. The relative occupancies of these atoms refined to approximately 85 and 80%, consistent with a ~35% contamination of the crystal by the I₇ species. A small amount of positional disorder was found for the iodine atoms bound to C8 and C12. Accordingly, the two atoms were each modeled over two sites with complementary occupancies.

■ ASSOCIATED CONTENT**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00616.

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

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