J. Am. Chem. Soc. **2000,** *122,* 803−807

Doubly N-Confused Porphyrin: A New Complexing Agent Capable of Stabilizing Higher Oxidation States

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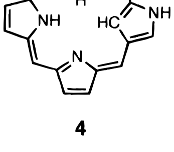
Received July 29, 1999. Revised Manuscript Received November 10, 1999

Abstract: A doubly N-confused porphyrin (N_2CP), 2-ethoxy-5,10,15,20-tetrapentafluorophenyl-3,7-diaza-21,22-dicarbaporphyrin, and its Ag(III) and Cu(III) complexes were synthesized for the first time, via an acid-catalyzed condensation of pentafluorobenzaldehyde and *meso*-pentafluorophenyl-2,3′-dipyrromethane. ^{1}H NMR and single-crystal X-ray diffraction analyses reveal the arrangement of the three hydrogens (two CH and one NH) in the core of N_2CP both in solution and in the solid state, respectively. The diamagnetic silver(III) complex has a square-planar tetracoordination and short Ag(III)−C bond distances of 1.987(8) and 2.011(8) Å. Similarly, the diamagnetic Cu(III) complex shows a square-planar coordination with Cu(III)−C bond distances of 1.939(3) and 1.934(4) Å. The trianionic nature of the N_2CP ligand and a possibility of stabilizing the higher oxidation state by "confusion" are discussed.

Introduction

Syntheses and metal coordination chemistry of porphyrin analogues have been attracting considerable interest due to the possibility of developing new porphyrin chemistry.[1] Among them, a porphyrin isomer, "N-confused porphyrin" (NCP, **1**),[2] originally synthesized by us and independently by Latos-Grażyński et al., is of interest because many "mutants" are structurally possible, and its unique properties have been revealed gradually.[3−5] One of the features of NCP chemistry, which differs from normal porphyrins, is its multivalent nature as a metal ligand. NCP was found to complex either divalent Ni(II) or trivalent silver(III) to give a square-planar complex (**2** or **3**).[3e,4a] This characteristic chameleon-like nature seems to be driven simply by deprotonation of the outward pointing NH in the "confused" pyrrole, which serves to stabilize the polarized carbon−metal bond. If such effects were observed for other N-confused porphyrins, it could provide a potent strategy for stabilizing higher oxidation states of metals,[6] especially if more than one confused pyrrole could be incorporated within any given porphyrin-like macrocycle. This idea promoted us to synthesize doubly N-confused porphyrins and to investigate their metal coordination properties. In this paper, we report the synthesis of 2-ethoxy-5,10,15,20-tetrapentafluorophenyl-3,7-diaza-21,22-dicarbaporphyrin (N_2CP, **7**) and show that it is capable of stabilizing complexes containing rather rare Ag(III) and Cu(III) centers (i.e., **8** and **9**). To the best of our knowledge, these are the first examples of a porphyrin isomer containing two confused pyrrole rings and its metal complexes.



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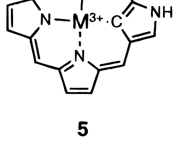

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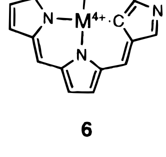

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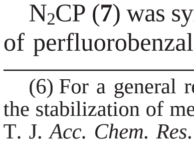

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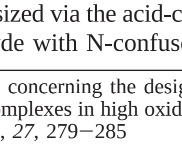

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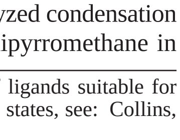

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Results and Discussion

N_2CP (**7**) was synthesized via the acid-catalyzed condensation of perfluorobenzaldehyde with N-confused dipyrromethane in

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[1] (a) Sessler, J. L.; Weghorn S. J. *Expanded, Contracted, and Isomeric Porphyrins*; Elsevier: Oxford, 1997. (b) *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds; Academic Press: San Diego, 1999; Vol. 2.

[2] At present, several names for this isomer can be spotted in the literature: carbaporphyrin, inverted porphyrin, N-confused porphyrin, mutant porphyrin, 2-aza-21-carbaporphyrin, etc. We think the general nomenclature such as 18-porphyrin (1.1.1.1.)-(C_α,N,N,N) for **1** is appropriate to identify the number and position of confused pyrrole among 14 generalized members of the N-confused (1.1.1.1.)-porphyrin series. See Figure 3 in the text.

[3] (a) Furuta, H.; Asano, T.; Ogawa, T. *J. Am. Chem. Soc.* **1994**, *116*, 767−768. (b) Ariga, K.; Kunitake, T.; Furuta, H. *J. Chem. Soc., Perkin Trans. 2*, **1996**, 667−672. (c) Ishikawa, Y.; Yoshida, I.; Akaiwa, K.; Koguchi, E.; Sasaki, T.; Furuta, H. *Chem. Lett.* **1997**, 453−454. (d) Furuta, H.; Ishizuka, T.; Osuka, A.; Ogawa, T. *J. Am. Chem. Soc.* **1999**, *121*, 2945−2946. (e) Furuta, H.; Ogawa, T.; Uwatoko, Y.; Araki, K. *Inorg. Chem.* **1999**, *38*, 2676−2682.

[4] (a) Chmielewski, P. J.; Latos-Grażyński, L.; Rachlewicz, K.; Glowink, T. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 779−781. (b) Chmielewski, P. J.; Latos-Grażyński, L. *J. Chem. Soc., Perkin Trans. 2*, **1995**, 503−509. (c) Chmielewski, P. J.; Latos-Grażyński, L.: Głowiak, T. *J. Am. Chem. Soc.* **1996**, *118*, 5690−5701. (d) Chmielewski, P. J.; Latos-Grażyński, L. *Inorg. Chem.* **1997**, *36*, 840−845. (e) Latos-Grażyński, L. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds; Academic Press: San Diego, 1999; Vol. 2, Chapter 14.

[5] (a) Hoo, P.-Y.; Shin, K.; Lee, C.-H. *Tetrahedron Lett.* **1996**, *37*, 197−200. (b) Lee, C.-H.; Kim, H.-J. *Tetrahedron Lett.* **1997**, *38*, 3935−3938. (c) Liu, B. Y.; Brückner, C.; Dolphin, D. *J. Chem. Soc., Chem. Commun.* **1996**, 2141−2142. (d) Narayanan, S. J.; Sridevi, B.; Srinivasan, A.; Chandrashekar, T. K.; Roy, R. *Tetrahedron Lett.* **1998**, *39*, 7389−7392. (e) Geier, G. R., III; Lindsey, J. L. *J. Org. Chem.* **1999**, *64*, 1596−1603.

[6] For a general review concerning the design of ligands suitable for the stabilization of metal complexes in high oxidation states, see: Collins, T. J. *Acc. Chem. Res.* **1994**, *27*, 279−285

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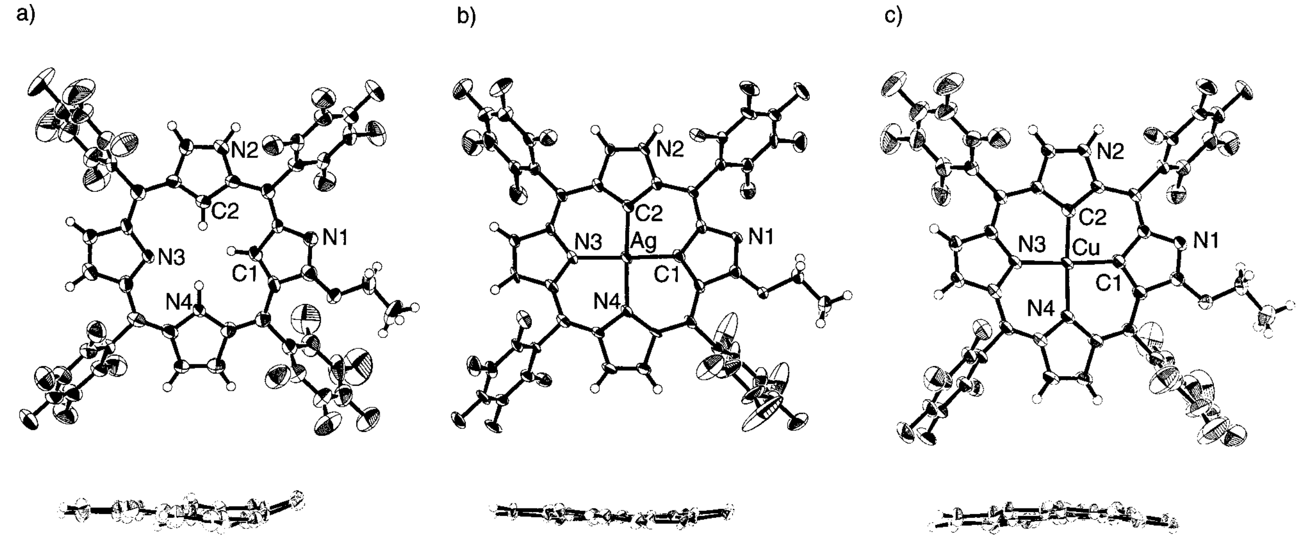
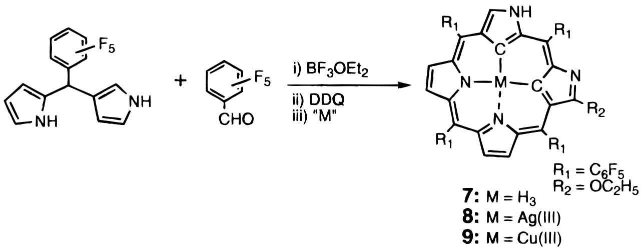


Figure 1. X-ray structures of (a) N_2CP (**7**), (b) Ag(III)−N_2CP (**8**), and (c) Cu(III)−N_2CP (**9**). Pentafluorophenyl groups and an ethoxy group were omitted for clarity in the side views. Selective bond lengths (Å) and angles (deg) are listed in Table 2.

Scheme 1



$CHCl_3$ containing a trace of EtOH (Scheme 1).[7] Following oxidation with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), a greenish product was purified by silica gel column chromatography to give **7** in ca. 2% yield.[8] The spectroscopic data obtained were consistent with the formulation of ethoxy-substituted N_2CP (**7**) as a doubly confused isomer of porphyrin.[9] In particular, two CH signals were observed in the ^1H NMR spectrum at 3.50 and 3.20 ppm in $CDCl_3$. Such findings are consistent with a weak aromatic character due to the disruption of a fully π-conjugated Kekulé structure. Not surprisingly, therefore, an upfield NH signal at 6.38 ppm is assigned to the inner pyrrolic proton; another NH signal, corresponding to the outer NH proton, was also observed in $CDCl_3$ but only at 8.95 ppm.

More direct evidence for the proposed structure of doubly confused porphyrin **7** came from a single-crystal X-ray diffraction analysis (Figure 1a).[10] The porphyrin core is slightly distorted, i.e., the confused pyrrole ring bearing the ethoxy substituent is canted 18.9° from the mean plane of the 24-atom core. In contrast, the other confused pyrrole, as well as the two "normal" pyrroles, are tilted in the opposite direction, by 16.4°, 4.4°, and 7.1°, respectively. On a very different level, the crystallographic data provided support for the fact that only one type of N_2CP isomer is formed under the reaction conditions. In this isomer, a cis-like, as opposed to trans-like, arrangement pertains for each of the confused pyrroles. The preferential production of this isomer is rationalized in terms of the different reactivity of the α- and α′-pyrrolic positions in the starting N-confused dipyrromethane.

When N_2CP (**7**) was treated with Ag(I) acetate in 10% pyridine/$CHCl_3$ at room temperature, the color of the solution was observed to change from yellow-green to blue-green, and over the course of 8 h, a shiny silver-containing product was obtained quantitatively. Observation of distinct signals in the ^1H NMR spectrum in the 10−1 ppm ranges in $CDCl_3$ led to the inference that this silver-containing product consists of diamagnetic Ag(III)N_2CP (**8**). The appearance of a signal at 10.37 ppm, ascribable to an outer NH resonance, and the absence of any signals ascribable to the three inner NH and CH protons, are considered consistent with this assignment, as were results from a single-crystal X-ray diffraction analysis (Figure 1b). This latter study revealed short Ag−C bond distances of 1.987(8) and 2.011(8) Å, which are comparable with that seen in the corresponding Ag(III)NCP (**3**) complex (i.e., 2.03 Å).[3e] The complex (**8**) is nearly square-planar, and the Ag atom is located in the plane formed by each four donor atoms in the core (two N and two C).

When Cu(II) acetate was used in place of Ag(I) acetate, a greenish complex (**9**) was obtained quantitatively. In analogy to the Ag(III)N_2CP (**8**) complex, this copper-containing product (**9**) is EPR silent. Similar to that of **8**, the ^1H NMR spectrum of **9** contains, for instance, a signal at 10.41 ppm that is ascribable to an outward-pointing NH while displaying no resonances for the three inner hydrogens. The complex (**9**) is nearly square-planar and Cu−C bond distances are 1.939(3) and 1.934(4) Å (Figure 1c), which are comparable to that seen in the $[Cu(CF_3)_4]^-$ anion (1.949−1.989 Å).[11] All of these data support that the metal oxidation state of **9** is 3+, i.e., Cu(III). Crystal data for **7**−**9** and selective bond lengths and angles for **8** and **9** are summarized in Tables 1 and 2, respectively.

Complexes **8** and **9** were also characterized by bands in their optical absorption spectra that were relatively sharpened compared to those of the starting free base ligand, **7**. In particular, these three species (**7**−**9**) display Soret transitions at 424, 442.5, and 441 nm and Q-bands at 627.5, 620, and 612.5 nm,

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[7] Small amounts (ca. 0.5%) of EtOH and bromide anion were found to be effective for this reaction. An effort with EtOH-free dry $CHCl_3$ to avoid generating products containing an ethoxy substituent led to only trace quantities of N_2CP.

[8] A corrole-type product was also isolated in 13% yield, which will be published in due course.

[9] ^1H and ^{13}C NMR spectra for **7**−**9** are given in the Supporting Information.

[10] We would like to thank Dr. Motoo Shiro (Rigaku Corporation) for help with the X-ray structural work.

[11] Naumann, D.; Roy, T.; Tebbe, K.-F.; Crump, W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1482−1483.

Table 1. Crystallographic Details for **7**−**9**

	N_2CP (**7**)	Ag−N_2CP (**8**)	Cu−N_2CP (**9**)
emp formula	$C_{46}H_{14}N_4F_{20}O$	$C_{46}H_{11}N_4F_{20}AgO$	$C_{46}H_{11}N_4F_{20}CuO$
fw	1018.61	1123.46	1079.13
color, habit	violet, prismatic	brown, prismatic	blue, prismatic
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	18.685(3)	18.734(3)	18.583(3)
b, Å	8.528(3)	8.324(1)	8.395(1)
c, Å	27.866(4)	27.674(3)	27.732(3)
α, deg	90.00	90.00	90.00
β, deg	107.1270	107.84(1)	107.69(1)
γ, deg	90.00	90.00	90.00
V, Å^3	4246(2)	4108.3(9)	4121.5(9)
Z	4	4	4
radiation (λ, Å)	Mo Kα (0.71069)		
T, °C	23.0	−150.0	−70.0
D_C, g/cm^3	1.593	1.816	1.739
μ, mm^{-1}	1.579	6.252	6.653
diffractometer	AFC7S	RAXIS−RAPID	RAXIS−RAPID
R_1[a]	0.062	0.071	0.059
wR_2[b]	0.056	0.075	0.092
GOF	1.830	1.610	1.299
indep reflns	10399	26966	37169
obsd reflns ($I > 2\sigma(I)$)	3771	5174	9431
parameters	640	649	650

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)]^{1/2}$.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for **8** and **9**

	Ag−N_2CP (**8**)	Cu−N_2CP (**9**)
M−C1	2.011(7)	1.939(3)
M−C2	1.987(9)	1.934(4)
M−N3	2.064(5)	1.969(3)
M−N4	2.047(7)	1.954(4)
C1−M−C2	86.5(3)	85.2(2)
C2−M−N3	91.6(3)	92.0(1)
N3−M−N4	90.7(2)	91.1(1)
N4−M−C1	91.3(3)	91.7(1)
C1−M−N3	177.6(3)	176.2(2)
C2−M−N4	177.7(2)	176.1(1)

respectively (Figure 2). The optical spectrum of free base **7** shows the large solvent shifts, probably due to the interaction of outward NH and solvents (see Supporting Information).

Comparison between NCP (**1**) and N_2CP (**4**), with regard to their ability to coordinate silver and copper cations, reveals the effect of the second site of pyrrolic confusion upon metal complexation. In the case of silver complexation, the presence of similar 3H arrangements in the core of both **1** and **4** suffices to have both macrocyclic materials act as trianionic ligands, thereby stabilizing the formation of Ag(III) complexes. In the case of copper, the NCP ligand serves to coordinate Cu(II), giving rise to an EPR active Cu(II)NCP complex.[12] By contrast, the doubly confused system N_2CP stabilizes a complex containing a copper(III) center. This marked different ligand-derived behavior provides an important reflection of the fact that doubly confused porphyrin **4** can readily act as a trivalent ligand, stabilizing higher oxidation states. Indeed, at least in certain circumstances, the presence of a second confusion site serves to raise the oxidation state of the coordinated metal by one level.

Furthermore, if the outward pointing NH hydrogen of **4** could be removed by oxidation, either chemically or electrochemically, the doubly confused porphyrin, such as N_2CP, might be induced to act as tetraanionic ligands and stabilize neutral M(IV) complexes (e.g., **6**). Further change in metal oxidation states from "normal" M(II) to M(III) or M(IV) by confusion is of interest, and a variety of uses for the resulting materials in the areas of, for instance, electron transfer and/or magnetic switching studies could be contemplated.

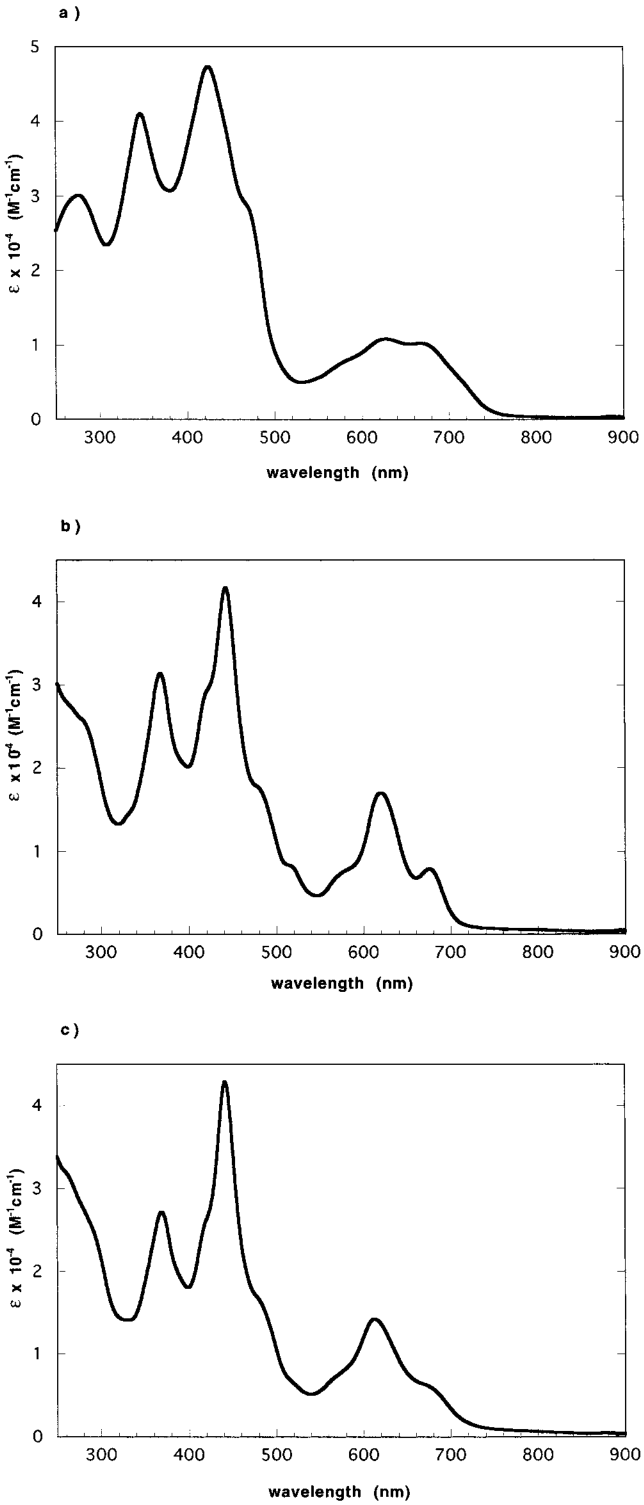

Figure 2. Optical absorption spectra of (a) N_2CP (**7**), (b) Ag(III)−N_2CP (**8**), and (c) Cu(III)−N_2CP (**9**) in $CHCl_3$.

Finally, we would like to propose a general nomenclature for the N-confused porphyrin family that involves the use of a (C,N) designation and appropriate α and β suffixes to differentiate the linkage positions. For example, N_2CP (**7**) is 18-porphyrin

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[12] A Cu(II) complex was obtained easily from a CN-substituted N-confused tetraphenylporphyrin (**1**): EPR parameter (77 K, chloronaphthalene) g = 2.03, 2.05, and 2.132, A_{Cu}=25, 25, 169 G, and A_N = 11, 11, 13 G. Private communication from Prof. Y. Ishikawa, Oita University.

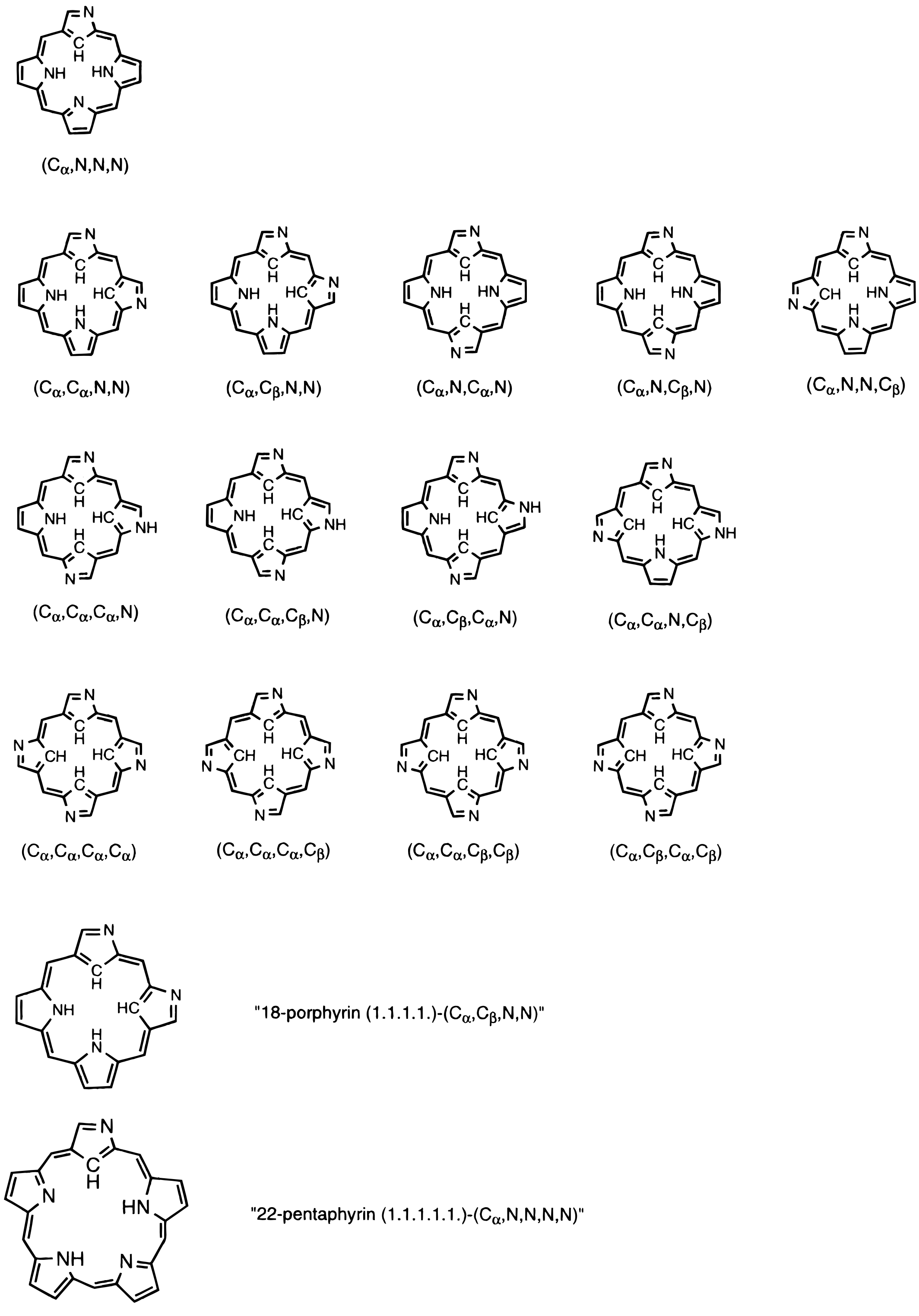

Figure 3. Proposed nomenclature for NCPs.

(1.1.1.1.)-(C_α,C_β,N,N) (Figure 3). We believe this is one of the simple methods to identify the confused position of NCP.

Conclusion

A doubly N-confused porphyrin (N_2CP) and its Ag(III) and Cu(III) complexes were synthesized for the first time. Both complexes are diamagnetic and have a square-planar coordination with two sets of metal−carbon bonds. The trianionic nature of the N_2CP ligand was demonstrated, and a possibility of stabilizing the higher oxidation state by confusion is suggested.

Experimental Section

Methods and Materials. Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Silica gel column chromatography was performed on Wakogel C-200. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 (Merck 5554). UV−visible spectra were recorded on a Shimadzu UV-2400PC spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL α-500 spectrometer (operating as 500.00 MHz for ^{1}H and 125.65 MHz for ^{13}C) using the residual solvent as the internal reference. Fast atom bombardment mass spectra (FABMS) were recorded on a JEOL-HX110 in the positive ion mode with a 3-nitrobenzyl alcohol matrix.

Preparation of *meso*-Pentafluorophenyl N-Confused Dipyrromethane. Confused dipyrromethane was obtained according to the procedure by Littler et al.[13] in 60% yield. ^{1}H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) 8.19 (s, br, 2H, NH), 6.78 (dd, 1H, α-H), 6.69 (dd, 1H, α-H), 6.50 (s, 1H, α-H), 6.15 (m, 2H, β-H), 5.98 (s, 1H, β-H), 5.82 (s, 1H, *meso*-H). FABMS: *m*/*z* (% intensity) 246.1 (100, $M^+ - C_4H_4N$), 312.1 (54, M^+).

2-Ethoxy-5,10,15,20-tetrapentafluorophenyl-3,7-diaza-21,22-dicarbaporphyrin (N_2CP, 7). To a solution of N-confused 5-(pentafluorophenyl)dipyrromethane (468 mg, 1.5 mmol) were added pentafluorobenzaldehyde (294 mg, 1.5 mmol) and Bu_4NBr (242 mg, 0.75 mmol) in 0.5% EtOH/$CHCl_3$ (750 mL) and BF_3OEt_2 (189 μL, 1.5 mmol), and the mixture was stirred for 2 h at room temperature. The reaction mixture was then passed through a silica gel column and eluted with $CHCl_3$. To a combined solution, DDQ (896 mg, 2.25 mmol) was added and stirred for 1 h at room temperature. The green-colored product was separated by silica gel column chromatography (eluent CH_2Cl_2/hexane (3:2)), followed by recrystallization from hexane/CH_2Cl_2 to give **7** as a green solid in 1−2% yield: $R_f = 0.5$ (CH_2Cl_2); mp > 300 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) 8.95 (br, 1H, outer NH), 7.36 (d, $J = 5.0$ Hz, 1H, β-H), 7.28 (d, $J = 5.5$ Hz, 1H, β-H), 7.06 (d, $J = 5.5$ Hz, 1H, β-H), 6.98 (d, $J = 5.0$ Hz, 1H, β-H), 6.94 (s, 1H, α-H), 6.40 (br, 1H, inner NH), 4.33 (q, $J = 7.0$ Hz, 2H, $CH_3\mathit{CH_2}O$), 3.52 (s, 1H, inner CH), 3.22 (s, 1H, inner CH), 1.12 (t, $J = 7.0$ Hz, 3H, $\mathit{CH_3}CH_2O$). ^{13}C NMR ($CDCl_3$, 125.65 MHz, 27 °C): δ (ppm) 172.04, 151.44, 134.48 (β-C), 131.49 (β-C), 130.21, 129.18 (β-C), 128.54 (inner C), 128.40 (β-C), 123.24, 121.94 (α-CH), 112.20, 105.01, 104.97 (inner C), 94.59, 65.41 ($CH_3\mathit{CH_2}O$), 13.87 ($\mathit{CH_3}CH_2O$) (pentafluorophenyl signals could not be assigned because of the multiple coupling of $^{13}C-^{19}F$). UV−vis ($CHCl_3$): λ_{max} [nm] ($\epsilon \times 10^{-4}$) 347.0 (4.1), 424.0 (4.7), 627.5 (1.1), 667.5 (1.0). FABMS: *m*/*z* (% intensity) 1018.1 (97, M^+), 1019.1 (100, $M^+ + 1$).

Ag(III) Complex of 2-Ethoxy-5,10,15,20-tetrapentafluorophenyl-3,7-diaza-21,22-dicarbaporphyrin (Ag(III)−N_2CP, 8). To a solution of ethoxy-substituted tetrapentafluorophenyl-N_2CP (**7**) (10.2 mg, 0.01 mmol) in 10 mL of 10% pyridine/$CHCl_3$ was added AgOAc (8.35 mg, 0.05 mmol), and the mixture was stirred at room temperature overnight. The solution was filtered with a silica gel column to remove excess silver salt and evaporated. Recrystallization from hexane/CH_2Cl_2 gave **8** as a green solid in quantitative yield: mp > 300 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) 10.37 (br, 1H, outer NH), 8.28 (d, $J = 3.0$ Hz, 1H, α-H), 8.01 (d, $J = 5.0$ Hz, 2H, β-H), 7.83 (d, $J = 5.0$ Hz, 2H, β-H), 4.55 (q, $J = 7.0$ Hz, 2H, $CH_3\mathit{CH_2}O$), 1.26 (t, $J = 7.0$ Hz, 3H, $\mathit{CH_3}CH_2O$). ^{13}C NMR ($CDCl_3$, 125.65 MHz, 27 °C): δ (ppm) 172.53, 172.49, 149.44, 148.54, 144.09, 141.99, 140.95, 132.36, 132.08, 129.87, 129.54, 126.93, 126.87, 123.83, 123.68, 119.72, 114.24, 112.27, 112.14, 112.09, 108.11, 107.58, 65.05 ($CH_3\mathit{CH_2}O$), 13.99 ($\mathit{CH_3}CH_2O$). UV−vis ($CHCl_3$): λ_{max} [nm] ($\epsilon \times 10^{-4}$) 368.0 (3.2), 442.5 (4.2), 620.0 (1.7), 676.0 (0.82). FABMS: *m*/*z* (% intensity) 1122.25 (76, M^+), 1124.26 (100, $M^+ + 2$).

Cu(III) Complex of 2-Ethoxy-5,10,15,20-tetrapentafluorophenyl-3,7-diaza-21,22-dicarbaporphyrin (Cu(III)−N_2CP, 9). To a solution of ethoxy-substituted tetrapentafluorophenyl-N_2CP (**7**) (20.4 mg, 0.020 mmol) in 20 mL of $CHCl_3$ was added $Cu(OAc)_2H_2O$ (4.2 mg, 0.021 mmol), and the mixture was stirred at room temperature overnight. The solution was filtered with a silica gel column to remove excess copper salt and evaporated. Recrystallization from hexane/CH_2Cl_2 gave **9** as a green solid in quantitative yield: mp > 300 °C. ^{1}H NMR ($CDCl_3$, 500 MHz, 27 °C): δ (ppm) 10.39 (br, 1H, outer NH), 8.31 (s, 1H, α-H), 8.08 (d, $J = 4.5$ Hz, 2H, β-H), 7.90 (d, $J = 5.5$ Hz, 1H, β-H), 7.88 (d, $J = 5.0$ Hz, 1H, β-H), 4.58 (br, 2H, $CH_3\mathit{CH_2}O$), 1.25 (t, $J = 7.0$ Hz, 3H, $\mathit{CH_3}CH_2O$). ^{13}C NMR ($CDCl_3$, 125.65 MHz, 27 °C): δ (ppm) 171.52, 150.59, 149.53, 145.99, 143.24, 132.38, 130.73, 130.02, 129.88, 128.72, 124.39, 120.91, 113.70, 110.78, 110.14, 106.55, 64.75 ($CH_3\mathit{CH_2}O$), 13.97 ($\mathit{CH_3}CH_2O$). UV−vis ($CHCl_3$): λ_{max} [nm] ($\epsilon \times 10^{-4}$) 368.0 (2.7), 441.0 (4.3), 612.5 (1.4). FABMS: *m*/*z* (% intensity) 1078.20 (100, M^+).

Single-Crystal Diffraction Analysis. Details of the crystal data are listed in Table 1. A single crystal of N_2CP (**7**) was obtained by vapor diffusion of hexane into a CH_2Cl_2 solution of **7**. The data crystal was a violet prism of approximate dimensions 0.30 mm × 0.20 mm × 0.05 mm. Data were collected at room temperature on a Rigaku AFC7S diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $22.0° < 2\theta < 24.92°$. A single crystal of Ag(III)N_2CP (**8**) was obtained by vapor diffusion of hexane into a CH_2Cl_2 solution of **8**. The data crystal was a brown prism of approximate dimensions 0.15 mm × 0.10 mm × 0.10 mm. The data were collected at a temperature of -150 ± 1 °C to a maximum 2θ value of 55.0° on a Rigaku RAXISII imaging plate with graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). A total of 147 images, corresponding to 220.5° oscillation angles, were collected. A single crystal of Cu(III)N_2CP (**9**) was obtained by vapor diffusion of hexane into CH_2Cl_2 solution of **9**. The data crystal was a blue prism of approximate dimensions 0.40 mm × 0.40 mm × 0.10 mm. The data were collected at a temperature of -70 ± 1 °C to a maximum 2θ value of 55.0° on a Rigaku RAXISII. A total of 84 images, corresponding to 220.5° oscillation angles, were collected. For all crystals, the non-hydrogen atoms were refined anisotropically. The calculations were performed using the teXsan[14] crystallographic software package of the Molecular Structure Corporation.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra for **7**−**9**, optical absorption spectra of **7**, and crystal structural data for **7**−**9**. This material is available free of charge via the Internet at http://pubs.acs.org.

JA992679G

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(14) *teXsan for Windows*, crystal structure analysis package; Molecular Structure Corporation, 1997.