

N-Confused Tetraphenylporphyrin–Silver(III) Complex¹Hiroyuki Furuta,^{*,†,‡,§} Takuji Ogawa,[§] Yoshiya Uwatoko,^{||} and Koiti Araki[⊥]

Department of Chemistry, Faculty of Engineering, Oita University, Oita 870-1131, Japan, Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan, Institute for Fundamental Research of Organic Chemistry (IFOC), Kyushu University, Fukuoka 812-8581, Japan, Department of Physics, Faculty of Science, Saitama University, Urawa, Saitama 338-8570, Japan, and Instituto de Quimica, Universidade de Sao Paulo, Sao Paulo 26.077, 05599-970, Brazil

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The synthesis, characterization, and X-ray structure of the first example of an air-stable silver(III) complex of an N-confused tetraphenylporphyrin (5,10,15,20-tetraphenyl-2-aza-21-carbaporphyrin argentate(III) or Ag(III)NCTPP, **7**) is reported. Crystals of Ag(III)NCTPP·CH₂Cl₂ belong to the monoclinic space group *P*2₁/*c* (No. 14), with *a* = 9.038(4) Å, *b* = 15.097(3) Å, *c* = 25.578(8) Å, β = 91.32(3)°, and *Z* = 4. The lengths (Å) of the three silver–nitrogen and one silver–carbon bonds are inequivalent [Ag–N(1), 2.06(2); Ag–N(2), 2.08(2); Ag–N(3), 2.03(2); and Ag–C(17), 2.04(2)], reflecting the asymmetric structure of the NCTPP ligand. The very small distortion from a square planar geometry is shown in N–Ag–N and N–Ag–C angles (degrees): N(1)–Ag–N(2), 89.7(8); N(1)–Ag–N(3), 179(1); N(1)–Ag–C(17), 90.3(9); N(2)–Ag–N(3), 89.6(9); N(2)–Ag–C(17), 179(1); and N(3)–Ag–C(17), 90.9(1). The diamagnetic nature of Ag(III)NCTPP was confirmed by ¹H and ¹³C NMR and magnetic susceptibility measurements. Electrochemical and spectrochemical studies revealed that ring reduction and oxidation occur at –0.72, 1.21, and 1.50 V vs SHE, respectively. The potential role of NCTPP ligand for stabilization of higher oxidation states of metal ion is discussed.

Introduction

An “N-confused porphyrin” (NCTPP, e.g., **1**, **2**) is a porphyrin isomer wherein one of the four pyrrole rings is inverted.^{2,3} Recently, both theoretical^{4–6} and experimental^{2,3,7–9} studies were reported on such an exotic porphyrin which possesses three nitrogens and one carbon as chelating donor atoms. The almost square planar arrangement of those atoms and the presence of a carbanion instead of an N-pyrrole atom, endow NCTPP with interesting metal coordination properties. Latos-Grażyński and

co-workers have shown the formation of a “porphyrin-like” square planar Ni(II) complex (**3**) which has a nickel–carbon bond as well as three nickel–nitrogen bonds.³ The Ni–C bond was found to be reactive to a mild methylating agent such as methyl iodide, a process that affords a C-methylated Ni(II)-NCP (**4**).^{8b} They have also shown the nickel compounds (**3** or

* To whom correspondent should be addressed.

† Oita University.

‡ Kyoto University.

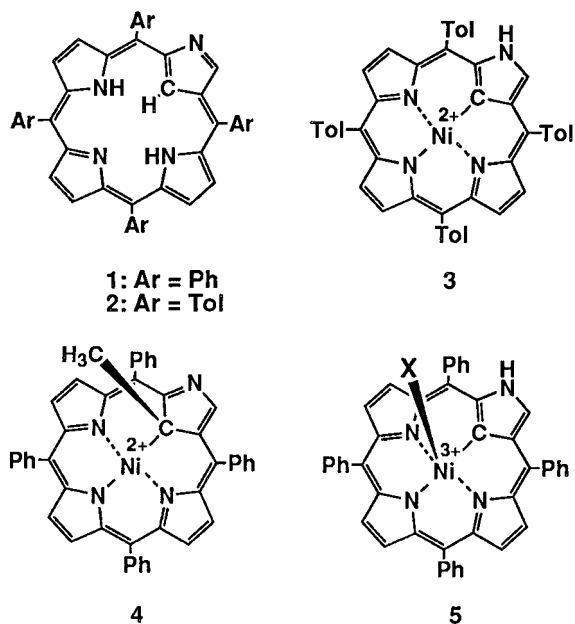
§ Kyushu University.

|| Saitama University.

⊥ Universidade de São Paulo.

Present address: Kyoto University.

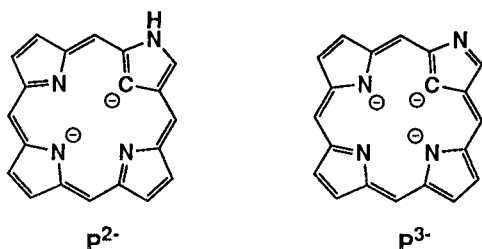
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4) can be oxidized either chemically or electrochemically to yield the unusual organometallic Ni(III) complexes Ni(III)-NCTPP·X (**5**) (X = Br[–], NO^{3–}, CN[–], OH[–], etc.).^{8c} We observed similar chemical behavior, i.e., square planar coordina-

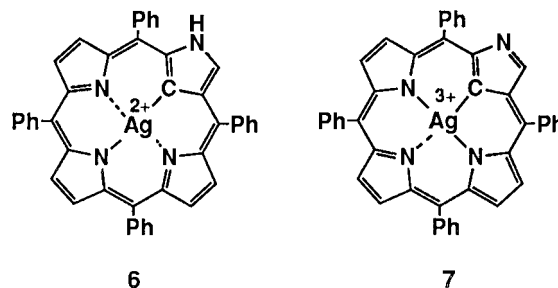
tion and reactivity toward methylating reagents, in the specific case of the Pd(II)NCTPP complex.^{7c}

Generally, porphyrins have two inner NHs and act as dianionic ligands when complexing a metal ion.¹⁰ The formation of the tetracoordinate Ni(II) complex of NCTPP (**3** and **4**) and the pentacoordinate Ni(III) complex (**5**) indicates that NCTPP also behaves as a dianionic ligand (P^{2-}). To bind a divalent metal, M(II), three hydrogens in the core (two NHs and one CH) need to be removed, such that one of them must shift to the outer peripheral nitrogen position to form a neutral complex, $M(II)P^{2-}$. However, in contradistinction to that with the porphyrins, in the case of NCTPP it is also possible to generate a trianionic ligand (P^{3-}) by simultaneously removing all three of the labile inner ring protons. Under such conditions, the coordination of a trivalent metal, M(III), would afford a neutral complex of general form, $M(III)^{3+}P^{3-}$. The possibility of changing the central charge from dianionic to trianionic makes NCTPP rather unique in the context of porphyrin chemistry. This characteristic associated with the presence of a C-donor atom may be a very interesting combination, because it could potentially stabilize atypical metal oxidation states and/or metal intermediates.



To examine such possibilities, we have explored the complexation of NCTPP with silver. This choice was motivated by the fact that silver cations generally form complexes readily and can be found in many oxidation states, more precisely, Ag(I), Ag(II), and Ag(III); further, the coordination chemistry of silver cations with porphyrins has been extensively studied.^{11–23} As such, we considered that a comparison of the relevant chemistry with that of normal metalloporphyrins could lead to a better understanding of the properties of NCTPP as a ligand.

Here we report the synthesis, characterization, and X-ray structural analysis of the first example of an air-stable NCTPP–trivalent metal complex, Ag(III)NCTPP (**7**). The potential role of NCTPP as a ligand for stabilizing higher oxidation states of metal ions is also discussed.



Experimental Section

Materials. N-Confused tetraphenylporphyrin (NCTPP, **1**) was synthesized as described before.² Silver(I) trifluoroacetate (Wako) and dichloromethane-*d*₂ (99.95%, Aldrich) were used as received. Tetrabutylammonium perchlorate (TBAP, Tokyo Kasei) and spectral grade dichloromethane (Nakarai Chemicals) were respectively used as supporting electrolyte and solvent in the electrochemical measurements. The purifications were carried out by column chromatography using silica gel (Wako-gel C-300, particle size 45–75 μm) as stationary phase. All other chemicals used were analytical grade.

Silver(III) Complex of N-Confused Tetraphenylporphyrin (Ag(III)NCTPP, **7).** A 61.5 mg (0.10 mmol) sample of NCTPP (**1**) was dissolved in 50 mL of dry CH₂Cl₂, and 44.0 mg (0.20 mmol) of silver (I) trifluoroacetate dissolved in 1 mL of MeOH was added. The reaction mixture was protected from light and stirred for 2 h at room temperature. The solvent was removed under vacuo and the crude compound was loaded on a silica column and eluted with CH₂Cl₂. The first reddish-green fraction was collected and evaporated to dryness, and the crude silver complex was recrystallized from CH₂Cl₂–hexane to give 52.7 mg (73%) of shiny black-brown crystals, Ag(III)NCTPP, **7**. ¹H NMR (CD₂Cl₂, ppm): δ 9.46 (s, 1H, outer α-CH), 8.97 (d, 1H, *J* = 4.6 Hz), 8.89 (d, 1H, *J* = 4.6 Hz), 8.73 (d, 1H, *J* = 4.6 Hz), 8.70 (d, 1H, *J* = 4.6 Hz), 8.67 (d, 1H, *J* = 4.6 Hz), 8.63 (d, 1H, *J* = 4.6 Hz), 8.18–8.13 (m, 8H, *o*-phenyl), 7.79–7.71 (m, 12H, *m*-, *p*-phenyl). ¹³C NMR (CD₂Cl₂, ppm): δ 160.85, 142.12, 141.89, 141.27, 140.51, 140.45, 139.87, 139.63, 138.97 (dd, *J*_{107,109Ag} = 75.7, 83.0 Hz), 137.54, 135.05, 134.92, 134.35, 134.33, 131.76, 130.63, 130.03, 129.96, 129.65, 129.62, 129.58, 128.65, 128.63, 128.40, 128.39, 128.31, 128.11, 128.09, 127.84, 127.65, 127.48, 127.45, 127.15, 125.25, 121.83, 121.80, 121.52, 121.50, 120.65. UV–vis (CH₂Cl₂; λ_{max}, nm (ε)): 382.0 (27 400), 447.5 (Soret, 177 000), 520.0 (16 200), 554.0 (6 750), 588.0 (4 150), 637.0 (8 820). FABMS: *m/e* = 719.1 (M + 1)⁺. Exact mass calcd for C₄₄H₂₈N₄¹⁰⁷Ag 719.1365, found 719.1283.

Instrumentation. ¹H and ¹³C NMR spectra were recorded on a JEOL alpha spectrometer operating at 500 and 125.8 MHz, respectively. The residual ¹H NMR resonances of the deuterated solvent (CHDCl₂) and ¹³C NMR resonances of CD₂Cl₂ were used as internal references. Absorption spectra were recorded on a Shimadzu UV-3000. Fast atom bombardment mass spectra (FABMS) were recorded on a JEOL JMS–HX-110 with *m*-nitrobenzyl alcohol as the matrix. Cyclic and differential pulse voltammetric measurements were performed with a PAR Model 174 and CH Instrument Model 660 using a Pt electrode. Spectroelectrochemical measurements were carried out using a homemade miniaturized three-electrode electrochemical cell mounted inside a quartz cuvette having an optical path length of 0.025 mm. The working, auxiliary, and reference electrodes were respectively a gold minigrid, a coiled platinum wire, and a Ag/Ag⁺ 0.010 M electrode.²⁴

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Table 1. Crystallographic Data for Ag(III)NCTPP·CH₂Cl₂

empirical formula	C ₄₅ H ₃₀ N ₄ AgCl ₂
fw	805.53
cryst syst	monoclinic
space group (No.)	P2 ₁ /c (#14)
unit cell dims	
<i>a</i> , Å	9.038(4)
<i>b</i> , Å	15.097(3)
<i>c</i> , Å	25.578(8)
α, deg	90
β, deg	91.32(3)
γ, deg	90
<i>V</i> , Å ³	3489(1)
<i>T</i> , °C	25
<i>Z</i>	4
cryst size, mm	0.35 × 0.13 × 0.08
<i>d</i> _{calcd} , g·cm ⁻³	1.534
radiation λ, Å	0.71069 (Mo Kα)
μ(Mo Kα), cm ⁻¹	7.64
<i>R</i> indices (<i>I</i> > 3σ(<i>I</i>)) ^a	
<i>R</i>	0.0794
<i>R</i> _w	0.1083

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

X-ray Data Collection and Refinement. Ag(III)NCTPP (7). Crystals of Ag(III)NCTPP (7) were prepared by diffusion of *n*-hexane into the dichloromethane solution of Ag(III)NCTPP. The data were collected at 25 °C on a Rigaku AFC5R diffractometer. From the total of 7124 collected reflections, 6603 were unique (*R*_{int} = 0.217). The intensities of three representative reflections, measured after every 150 reflections, declined by -9.50%. This problem was solved by introducing a linear correction factor to the data. The data were also corrected for Lorentz and polarization effects. The structure was solved by direct methods using the TEXSAN crystallographic software package of Molecular Structure Corp. The non-hydrogen atoms were refined isotropically. Crystal data are compiled in Table 1.

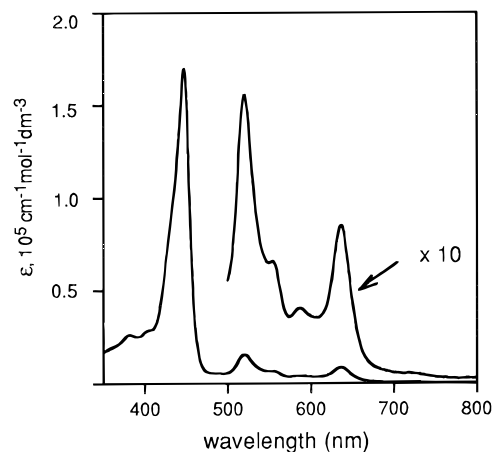
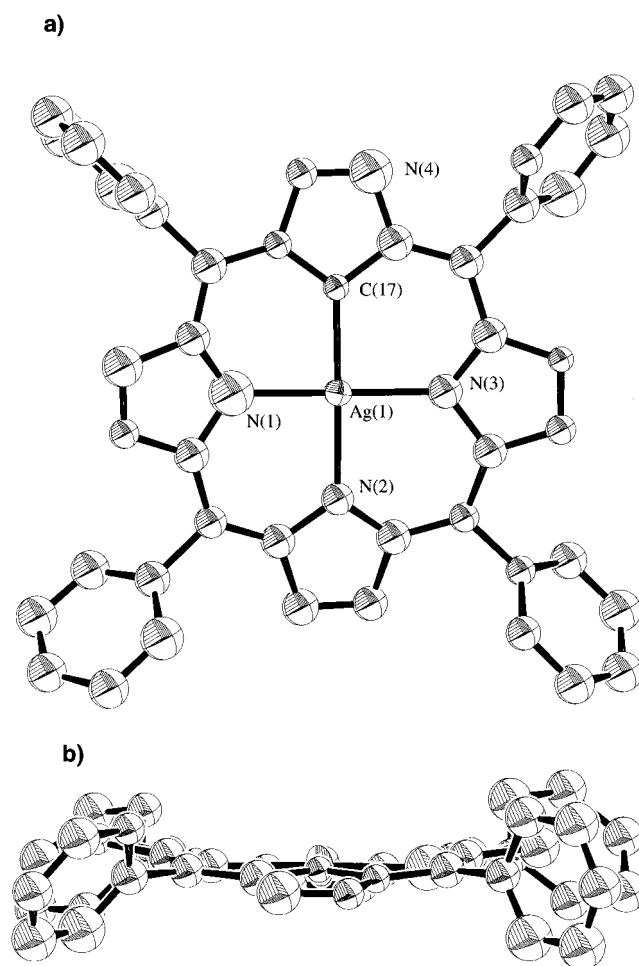
Magnetic Susceptibility Measurement. Static magnetic susceptibility measurements were undertaken from 300 to 4.2 K with a Quantum Design SQUID magnetometer. An aluminum foil box was used to hold the sample and the background was collected over the full temperature range just prior to the measurements. Data were recorded at 55 kG on sample of 32.62 mg.

Results and Discussion

The silver complex, Ag-NCTPP, was synthesized by the reaction of silver(I) trifluoroacetate with free base NCTPP (1) in CH₂Cl₂/MeOH, at room temperature. After column chromatography, the shiny black-brown crystals were obtained in 73% yield. Insertion of silver metal was confirmed by the FABMAS peak at 719.1 (1 + ¹⁰⁷Ag - 2H)⁺.

The optical spectra of AgNCTPP recorded in CH₂Cl₂ exhibited quite distinct features compared with the Ag(II) complex of tetraphenylporphyrin, Ag(II)TPP. Unlike Ag(II)-TPP which has two peaks at 539 and 569 nm (Q-bands),²² Ag-NCTPP showed four peaks at 520, 554, 588, and 637 nm in CH₂Cl₂. The Soret band appeared at 447.5 nm, i.e., about 9 nm shifted to longer wavelengths, compared with 1 (Figure 1).

Direct evidence for the nearly square planar coordination of silver atom was obtained from single-crystal X-ray analysis (Figure 2). The lengths (Å) of the three silver–nitrogen and one silver–carbon bonds are inequivalent [Ag–N(1), 2.06(2); Ag–N(2), 2.08(2); Ag–N(3), 2.03(2); and Ag–C(17), 2.04(2)], which is a reflection of the asymmetric structure of the NCTPP ligand. The very small distortion from a square planar geometry is shown in N–Ag–N and N–Ag–C angles (degrees): N(1)–Ag–N(2), 89.7(8); N(1)–Ag–N(3), 179(1); N(1)–Ag–C(17), 90.3(9); N(2)–Ag–N(3), 89.6(9); N(2)–Ag–C(17), 179(1); and N(3)–Ag–C(17), 90.9(1). Consistent

**Figure 1.** Electronic spectra of Ag(III)NCTPP (7) in CH₂Cl₂.**Figure 2.** X-ray structure of Ag(III)NCTPP (7): (a) top view and (b) side view. Solvent molecule (CH₂Cl₂) was omitted for clarity. Selected bond lengths (Å) and angles (degree) for 7: Ag–N(1), 2.06(2); Ag–N(2), 2.08(2); Ag–N(3), 2.03(2); Ag–C(5), 2.04(2); N(1)–Ag–N(2), 89.7(8); N(1)–Ag–N(3), 179(1); N(1)–Ag–C(5), 90.3(9); N(2)–Ag–N(3), 89.6(9); N(2)–Ag–C(5), 179(1); N(3)–Ag–C(5), 90(1).

with this, the deviation of Ag atom from the planes formed by the three atoms in the core (three N and one C) is within 0.01–(5) Å. The average of three Ag–N distances, 2.05(6) Å, is significantly shorter than in the Ag(II)TPP complex, 2.092 Å.²³ The bond distance of Ag(III)–C, 2.04(2) Å, is comparable with that of tetracoordinated, square planar Ag(III) complex, e.g., [Ag(III)(CF₃)_nX_{4–n}][–], 2.013 Å.²⁵

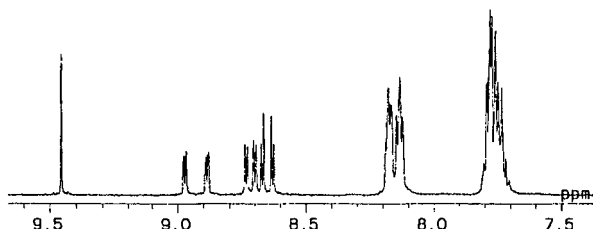


Figure 3. ^1H NMR spectrum of Ag(III)NCTPP (7) in CD_2Cl_2 .

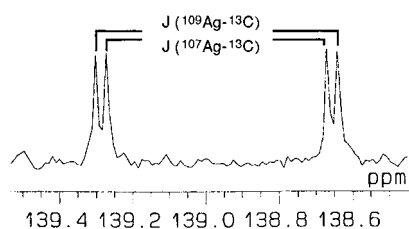


Figure 4. ^{13}C NMR spectrum of Ag(III)NCTPP (7) in CD_2Cl_2 .

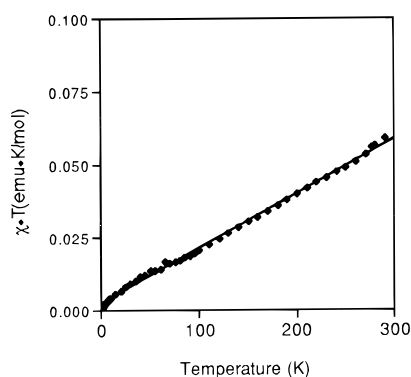


Figure 5. Temperature dependence of the paramagnetic susceptibility (χT) of Ag(III)NCTPP (7).

The ^1H NMR spectra of complex 7 in CD_2Cl_2 solution exhibits sharp signals in the normal porphyrin region, more exactly in the 7–10 ppm range (Figure 3). A sharp singlet signal at 9.46 ppm, ascribed to the outer-pointing α -hydrogen of the inverted pyrrole ring, indicates that the adjacent nitrogen is not protonated. This is in marked contrast with the corresponding Ni(II)-NCTPP (3) complex, wherein the α -hydrogen signal appeared as a doublet at 8.61 ppm due to its coupling with the outer NH proton. In addition, a broad signal around 10–11 ppm, ascribed to outer NH in the Ni(II) complex, was not observed.³ The ^{13}C NMR spectra were also recorded in the diamagnetic porphyrin region, from 120 to 160 ppm. The signal of the inner carbon, directly bonded to silver ion, was clearly observed at 138.97 ppm. The signal was split into two characteristic doublets owing to the coupling with the Ag nucleus: $J(^{107}\text{Ag}-^{13}\text{C})$, 75.7 Hz; $J(^{109}\text{Ag}-^{13}\text{C})$, 83.0 Hz²⁶ (Figure 4).

The question about the oxidation state of the silver ion, either Ag(II) or Ag(III), cannot be answered by simple analysis of the crystallographic data. However, the absence of the counteranion in the crystal structure indicates that the complex is neutral. To understand which oxidation state best describes the

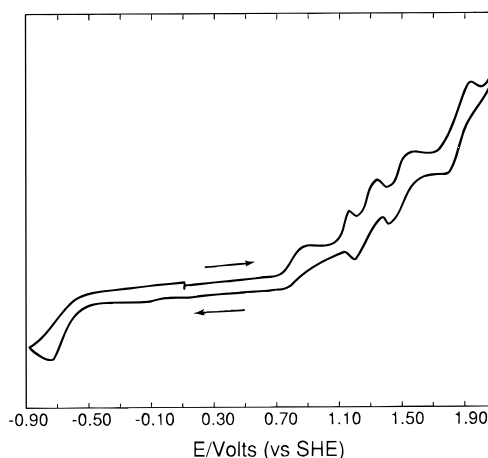


Figure 6. Cyclic voltammogram of a 2.5 mM NCTPP (1) solution in CH_2Cl_2 , 0.1 M TBAPF₆, 20 mV/s, Pt working electrode.

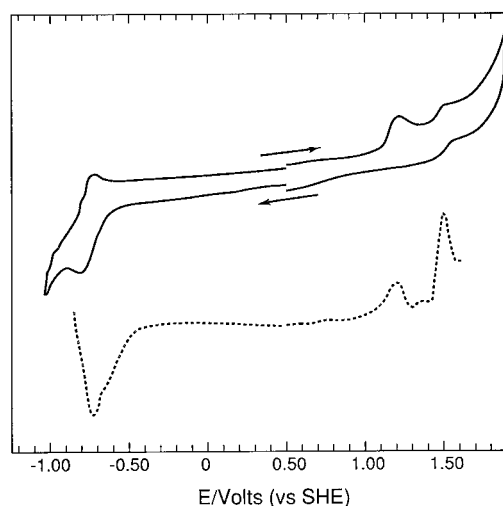


Figure 7. Cyclic voltammogram of a ~ 2.5 mM Ag(III)NCTPP (7) solution in CH_2Cl_2 , 0.1 M TBAPF₆, 100 mV/s, Pt working electrode.

metal ion in the complex, we carried out magnetic susceptibility and electrochemical studies on the sample. So, if the ligand is dianionic (P^{2-}), the oxidation state of the silver ion is +2, and the complex should be paramagnetic (d^9 configuration). On the other hand, if it is trianionic (P^{3-}), the metal ion oxidation state is +3, and the complex should be diamagnetic (d^8).

The magnetic susceptibility (χT) of AgNCTPP (7) as a function of the temperature is shown in Figure 5. Although a weak paramagnetism is observed in the low-temperature region (< 80 K), the basic magnetic profile is consistent with a diamagnetic complex, in the solid state.^{27,28} The NMR spectra confirm this result, because if the silver is coordinated to NCTPP as the paramagnetic Ag(II) ion, at least some of the signals should be broaden and/or shifted from their normal positions.²⁹

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(26) Due to the low resolution, the ratio of two coupling constants, $J(^{109}\text{Ag}-^{13}\text{C})/J(^{107}\text{Ag}-^{13}\text{C})$, was slightly smaller than the theoretical value, 1.15. See: Noltes, J. G.; Van Koten, G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U. K., 1982; Vol. 2, p 709.

(27) The observed susceptibility at room temperature was only $\chi = 1.90 \times 10^{-4}$ emu/mol, which corresponded to $0.68 \mu_B$ (Bohr magnet). The raw data were corrected for temperature-independent diamagnetism ($\chi^d = -4.81 \times 10^{-4}$ emu/mol); see, Sutter, T. P. G.; Hambright, P.; Thorpe, A. N.; Quoc, N. *Inorg. Chim. Acta* **1992**, *195*, 131–132.

(28) The temperature dependence of the susceptibility can be fit to the Curie–Weiss expression with an added constant (Q), $\chi = C/(T - \theta) + Q$, where $C = 5.0 \times 10^{-3}$ emu/mol·K, $\theta = -8.5$ K, and $Q = 1.7 \times 10^{-4}$ emu/mol. The measured Curie constant corresponds to $N = 1.3 \times 10^{-2}$ spins per Ag(III)NCTPP molecule that are tentatively assigned to impurities.

(29) Godziela, G. M.; Goff, H. M. *J. Am. Chem. Soc.* **1986**, *108*, 2237–2243.

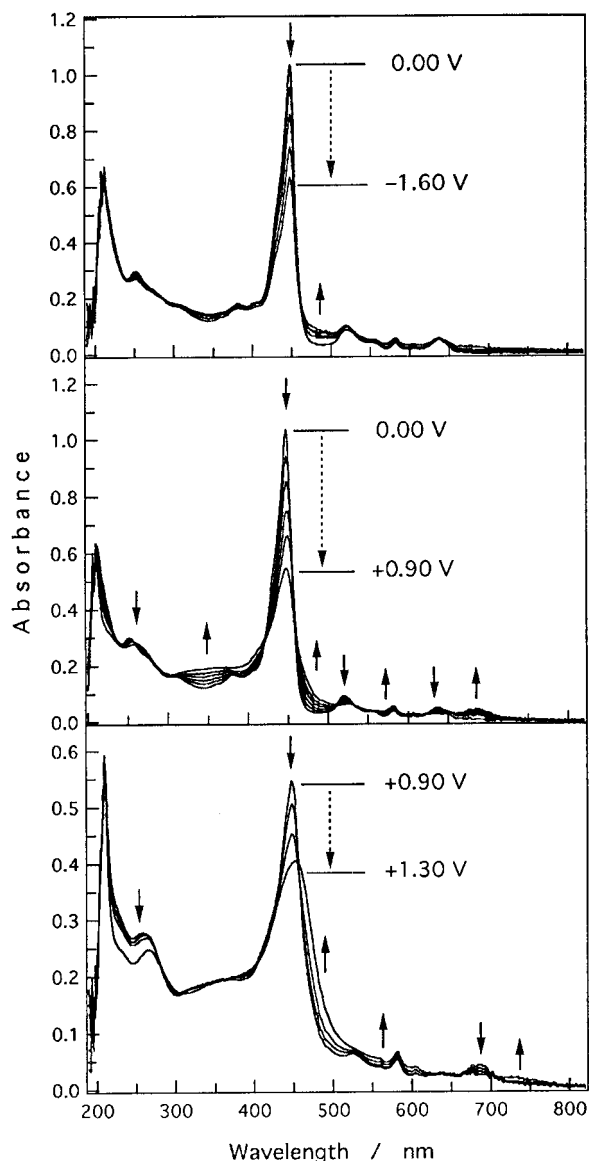


Figure 8. Spectroelectrochemistry of NCTPP (**1**) ($4 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, in CH_2Cl_2 , 0.1 M TBAPF₆). The experimental conditions are shown in the figure.

Furthermore, the substitution of a pyrrole nitrogen by a carbon as donor atom in the porphyrin macrocycle ligand strongly increases its basicity. Consequently, it should be a much stronger σ -donor than porphyrins and should stabilize much more effectively metal ions in higher oxidation states, and the complexes with the metal in low oxidation state should become increasingly less stable. It is known that when Ag(I) is coordinated by porphyrins, it is simultaneously oxidized to Ag(II).³⁰ Furthermore, Ag(II) can be easily oxidized to Ag(III), either chemically or electrochemically, due to its low potential barrier (0.54 V).^{14,16} So, because of the higher donor capability of NCTPP ligand compared to porphyrins, there is no doubt that the Ag(III) species was formed.

However, the problem relative to the P^{2-} or P^{3-} configuration of the NCTPP ligand still is not solved. In this particular case, the X-ray diffraction and ^1H NMR data were very helpful, despite the fact that there is a very small intrinsic structural difference between them. The absence of a counterion in the

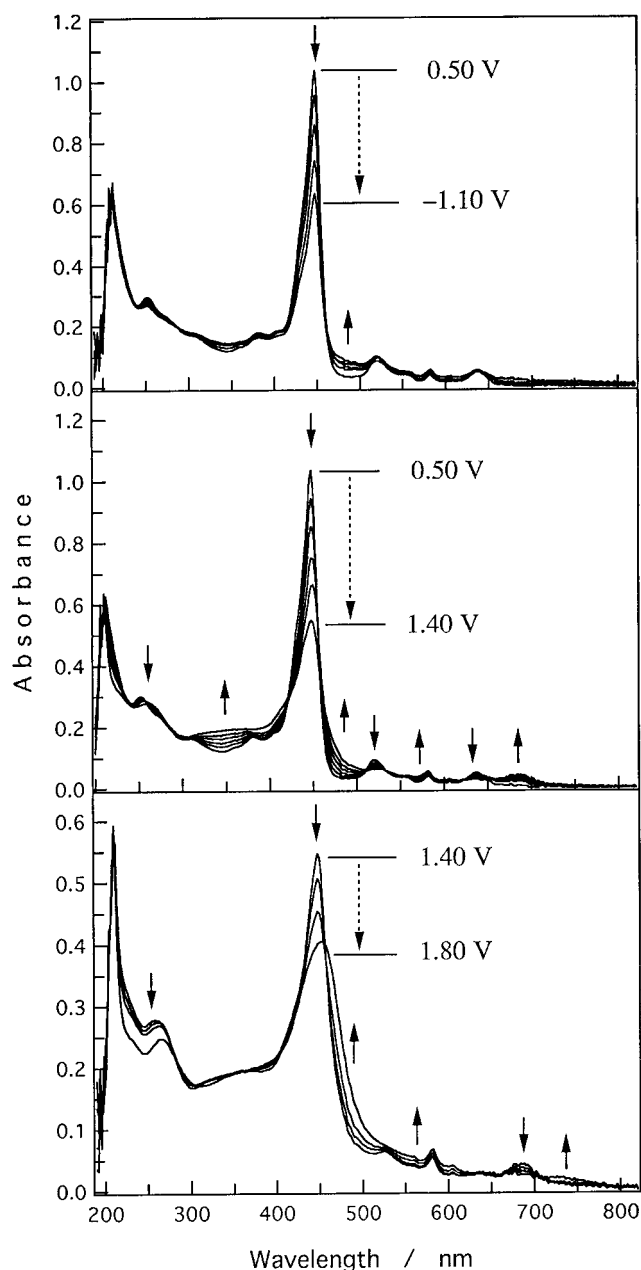


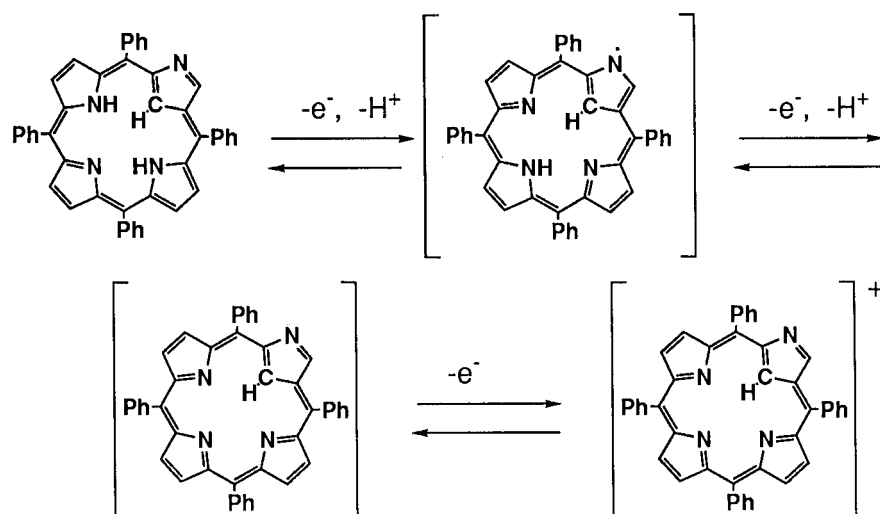
Figure 9. Spectroelectrochemistry of Ag(III)NCTPP (**7**) ($\sim 2 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, in CH_2Cl_2 , 0.1 M TBAPF₆). The experimental conditions are shown in the figure.

crystal structure of the Ag(III)NCTPP indicates that the complex is neutral and that the trianionic mode should prevail, in contrast with the Ni(II)NCTPP case. In addition, we expect that the outer pyrrole nitrogen is deprotonated in the P^{3-} configuration, and this hypothesis is confirmed by the ^1H NMR spectrum, as discussed above.

The cyclic voltammograms (CVs) for the free base ligand and the silver complex were recorded in CH_2Cl_2 , 0.1 M TBAP, at room temperature (Figures 6 and 7). In the case of the free-base NCTPP, starting at 0.1 V and scanning into the positive potentials, an irreversible anodic peak is observed at $E_{\text{pa}} = 0.87$ V. This oxidation process is followed by three well-defined reversible waves at +1.25, +1.47, and +1.85 V vs SHE. On the negative side, an irreversible cathodic wave is observed at $E_{\text{pc}} = -0.75$ V. An adsorption prepeak also can be observed in the CV of Figure 6 at 1.15 V. All peaks seem to involve monoelectronic redox processes, as can be inferred by their intensity ratios. This is in contrast with the behavior of normal

(30) Falk, J. E. *Porphyrins and Metalloporphyrins*; Elsevier: New York, 1964.

Scheme 1



porphyrins, which generally exhibit only two oxidation and reduction processes.³¹

Three redox processes were observed in the CVs of the silver complex **7**, in the -1.5 to $+1.5$ V range, at -0.72 , 1.21 , and 1.50 V vs SHE. The first and second oxidation processes of the silver complex were shifted more than 250 mV to positive potentials in comparison with the free-base NCTPP, in agreement with the coordination of the electron-withdrawing Ag(III) ion. The wave at 1.50 V was consistently less intense than the other two waves and probably is related to the amount of electrochemically active product generated in the first irreversible oxidation reaction.

A spectroelectrochemical study was carried out in order to improve our understanding about the electrochemical processes. The free-base NCTPP exhibits an absorption spectrum pattern that is similar with those of porphyrins, but all bands are red-shifted. In CH_2Cl_2 , the Soret and Q-bands appear, respectively, at 437 , 539 , 582 , 667 , and 727 nm. When the free-base NCTPP is reduced at -1.00 V, there is a decrease in the intensity of the Soret band and it shifts to 445 nm, and a shoulder appears around 472 nm (Figure 8). The Q-bands also become less intense and two new bands appear at 633 and 681 nm. When NCTPP is oxidized at 1.00 V, the Soret band lost intensity and shifted to 450 nm. Simultaneously, all the Q-bands faded and a new intense and broad band rose at 793 nm. This behavior is similar to that observed in porphyrins. In the second oxidation process at 1.40 V, the Soret band shifted to 464 nm, the band at 793 nm shifted to 812 nm, and a new band rose at 665 nm. The Soret, 665 , and 812 nm bands faded when the free base was further oxidized at 1.70 V, and broad absorptions appeared in the visible region with maxima at 450 (Soret), 500 , and 600 nm. Finally, the intensity of the Soret band envelope at 450 nm decreased and a new broad band appeared at 670 nm, when the sample was oxidized at 2.10 V. In the five redox processes, well-resolved isosbestic points were observed, suggesting that only two species are involved in each electrode reaction.

A similar spectroelectrochemical behavior was observed for the reduction and oxidations of the silver(III)-NCTPP complex, respectively, at -1.10 , 1.40 , and 1.80 V vs SHE. The spectral changes observed for the oxidations at 1.40 and 1.80 V are shown in Figure 9. The Soret band at 448 nm and the Q-bands at 520 and 638 nm became weaker, and a new band appeared

at 687 nm. When the complex was further oxidized at 1.80 V, the Soret band became even weaker and shifted to 453 nm, while the band at 687 nm faded and a new band rose around 735 nm. When this solution was mixed with the nonoxidized one, the previously formed oxidized species was regenerated. The reduction at -1.10 V caused the decrease of the Soret band. Those are evidence that the redox reactions on the silver complex are mono-electronic and localized on the NCTPP ligand.

The spectroelectrochemical data were consistent with the cyclic voltammograms for the free-base and silver(III) complex, but further studies are necessary to elucidate why the first oxidation reaction on both species is irreversible. Considering the fact that the successive voltammograms in a multiple scan experiment remained almost unchanged, we believe that a chemical reaction may be coupled with the electrochemical process.³² For example, a proton release after the electron abstraction is one of the plausible reactions (Scheme 1). This point is under examination.

The question "why the ligand valency changes from P^{2-} in Ni(II)NCTPP to P^{3-} in Ag(III)NCTPP?" is difficult to answer at present. The only structural difference between P^{2-} and P^{3-} is the absence of a hydrogen bond involving the outer nitrogen atom, in the inverted pyrrole ring. Thus, probably, the acidity of the coordinated metal ion is playing a crucial role in stabilizing the P^{3-} ligand. The strongly covalent nature of the Ag(II)-NCTPP bonds, due to the in-plane and out-of-plane π -bonding between the metal d-orbital and the ligand π -orbitals, could decrease the π -electron density, which, in turn, would make the complex more acidic and thus facilitate the dissociation of the outer NH.³³ The strong polarization of the σ -bond would also contribute to this phenomenon.

Conclusion. A new stable Ag(III)NCTPP complex (**7**) has been synthesized for the first time and characterized spectroscopically, magnetically, and electrochemically. The structure of the complex, determined by X-ray diffraction, shows the silver(III) ion bound strongly to three nitrogens and one carbon atom, in a slightly distorted pseudo-square-planar geometry. The magnetic susceptibility and NMR measurements confirmed the

(31) Davis, D. G. *The Porphyrins*, Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. V, Chapter 10.

(32) Oxidative coupling of the NCTPP ligand is another possibility; see: (a) Ogawa, T.; Nishimoto, Y.; Yoshida, N.; Ono, N.; Osuka, A. *J. Chem. Soc., Chem. Commun.* **1998**, 337–338. (b) Ogawa, T.; Nishimoto, Y.; Yoshida, Y.; Ono, N. A. Osuka, *Angew. Chem., Int. Ed.* **1999**, *38*, 176–179.

(33) Subramanian, J. *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, 1975; Chapter 13.

diamagnetic nature of the complex, excluding the possibility of the Ag(II)NCTPP complex. This led to the assignment of the structure to a Ag(III) species. Substitution of a pyrrole nitrogen atom by a carbon atom as donor in the porphyrin macrocycle, the basic effect of TPP to NCTPP exchange, greatly changed the basicity of the ligand. Consequently, NCTPP is a stronger σ -donor than TPP and should effectively stabilize metal ions in higher oxidation states, i.e., Ag(III) species. While only very small differences between the NCTPP ligand in its P^{2-} and P^{3-} forms are observed in the relevant X-ray structures, the absence of a counterion in the crystal structure of the Ag-(III)NCTPP complex strongly suggests the prevalence of the trianionic mode, in contrast to what is seen in the case of Ni-(III)NCTPP. Electrochemical and spectroelectrochemical studies also support the presence of the proposed Ag(III)NCTPP form in solution and thus serve to confirm the high stability of this species. In fact, the metal ion was not reduced, even at potentials

as low as -0.5 V. These results, and the strong donating nature of the NCTPP ligand with which they are consistent, lead us to suggest that this particular porphyrin isomer could be used to stabilize other metals in unusual oxidation states. Such studies are in progress.

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Supporting Information Available: Tables listing crystal data, atom coordinates, complete bond lengths and angles, anisotropic displacement coefficients, and calculated hydrogen parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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