

Ag(III)⋯Ag(III) Argentophilic Interaction in a Cofacial Corrole Dyad

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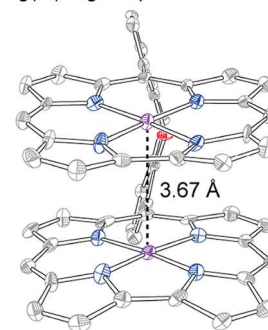
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ABSTRACT: Metallophilic interactions between closed-shell metal centers are exemplified by d^{10} ions, with Au(I) auriphilic interactions as the archetype. Such an interaction extends to d^8 species, and examples involving Au(III) are prevalent. Conversely, Ag(III) argentophilic interactions are uncommon. Here, we identify argentophilic interactions in silver corroles, which are authentic Ag(III) species. The crystal structure of a monomeric silver corrole is a dimer in the solid state, and the macrocycle exhibits an atypical domed conformation. In order to evaluate whether this represents an authentic metallophilic interaction or a crystal-packing artifact, the analogous cofacial or “pacman” corrole was prepared. The conformation of the monomer was recapitulated in the silver pacman corrole, exhibiting a short 3.67 Å distance between metal centers and a significant compression of the xanthene backbone. Theoretical calculations support the presence of a rare Ag(III)⋯Ag(III) argentophilic interaction in the pacman complex.

Ag(III) Argentophilic Interaction



INTRODUCTION

Bonding between metal centers can be categorized into three regimes: metallic, covalent, and metallophilic.¹ Of these, the less common metallophilic (dispersion) interaction forms between closed-shell metal ions and does not involve the pairing of electrons, as observed in the formation of a distinct metal–metal bond. Energy stabilization through metallophilic interactions can be rationalized with the molecular orbital diagram shown in Figure 1, adapted from Doerrer.² A filled d orbital, either $d_{x^2-y^2}$ for d^{10} ions or d_z^2 for d^8 ions, overlaps with an identical orbital on an adjacent metal center, giving rise to filled bonding (FF) and antibonding (FF*) combinations. Unfilled p orbitals can similarly produce empty bonding (EE) and antibonding (EE*) combinations. If the unfilled orbitals

are sufficiently low in energy and have the same symmetry as the filled orbitals, then the filled and unfilled orbitals can mix. This mixing lowers the energy of the FF and FF* orbitals, resulting in a net stabilization of the metallophilic pair relative to the individual metal centers.

The energy of metallophilic interactions is on the order of hydrogen bonds,³ which can have a significant influence on the ground-state geometry of a molecule or dyad. As a result, metallophilicity is often identified by X-ray crystallography, where the distance between metal centers is shorter than the sum of the van der Waals radii. Metallophilicity between Au centers, also known as auriphilic interactions,^{4,5} is most readily observed for Au(I) complexes, where the Au⋯Au contacts are less than 3.32 Å.⁶ Recent reports of Au(I)⋯Au(I) auriphilic interactions exhibit distances of 2.9579 and 2.9529 Å.⁷ While metallophilic interactions are most common between d^{10} centers, this phenomenon also prevails for d^8 [e.g., Au(III) and Pt(II)] and s^2 [e.g., Pb(II) and Bi(III)] configurations.^{1,2,8,9} An early example of a d^8 ⋯ d^8 metallophilic interaction is the binuclear μ -diphosphitoplatinum(II) complex [Pt₂(P₂O₅H₂)₄]⁴⁻, also known as Pt(pop).^{10,11} The initial crystal structure revealed a 2.925 Å distance between Pt centers,¹² and the Pt⋯Pt interaction was characterized by resonance Raman spectroscopy.¹³ The first examples of d^8 ⋯ d^8

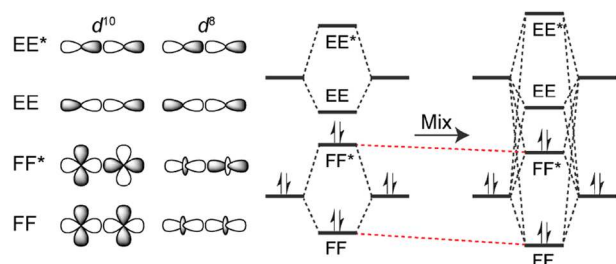
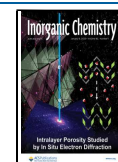


Figure 1. Illustration of the bonding and antibonding orbital interactions between filled d orbitals (FF and FF*) and empty p orbitals (EE and EE*) with the corresponding molecular orbital diagram. If the empty orbitals are low enough in energy and have the proper symmetry, they mix with the filled orbitals, lowering the energy of the FF and FF* orbitals to result in an overall stabilization of the metallophilic interaction relative to two noninteracting metal centers.

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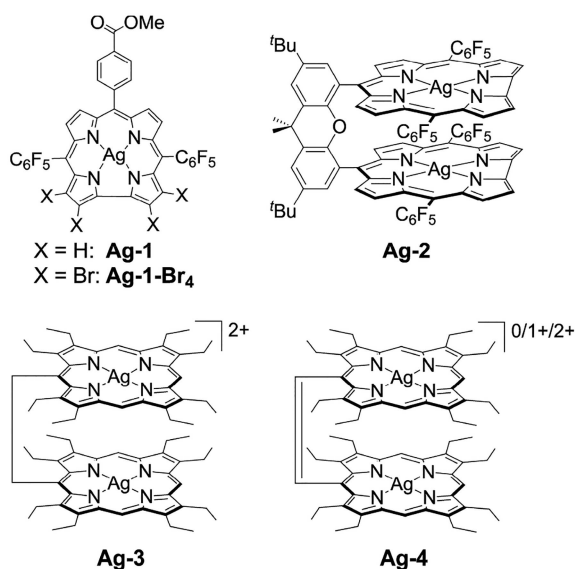
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Au(III) aurophilic interactions were observed in $[\text{Me}_4\text{N}][\text{Au}(\text{N}_3)_4]$ ¹⁴ and $[\text{Au}(\text{bpy})\text{Cl}_2][\text{AuBr}_4]$,¹⁵ which exhibit Au...Au distances of 3.507 and 3.518 Å, respectively, values that are larger than the sum of the van der Waals radii of two Au atoms (3.32 Å).⁶ These experimental observations are consistent with early computational results, which predicted that the M...M distance in metallophilic interactions increases with increasing oxidation state.¹⁶

While argentophilic interactions are pervasive for Ag(I) centers,¹⁷ they have only recently been identified for Ag(III) species. The rarity of Ag(III) complexes has hampered the observation of such interactions.^{18,19} Double oxidation of a Ag(II) porphyrin dimer with a flexible ethane linker ($-\text{CH}_2-\text{CH}_2-$) furnishes the Ag(III) dimer (Chart 1), which exhibits a

Chart 1. Corroles Examined in This Study and Other Reported Examples of Ag(III)···Ag(III) Argentophilic Interactions (Ag-3 and Ag-4)



short Ag...Ag distance of 3.659 Å in the solid state for the $[\text{SbF}_6]^-$ salt or 3.463 Å for the $[\text{PF}_6]^-$ salt. At 77 K, this complex exhibits an emission feature at 546 nm, suggestive of a metallophilic interaction. This is further supported by theoretical calculations and represents the first example of a Ag(III)···Ag(III) argentophilic interaction.²⁰ A similar study was conducted using ethene-bridged Ag(II) porphyrin dimers (Chart 1). Stepwise oxidation resulted in shorter Ag...Ag distances: 3.61 Å for Ag(II)/Ag(II), 3.53 Å for mixed-valent Ag(II)/Ag(III), and 3.45 Å for Ag(III)/Ag(III). A Bader analysis revealed that the strength of the Ag...Ag interaction increases with the oxidation state.²¹ Because β -unsubstituted silver corroles are authentic Ag(III) species,^{22–27} rather than Ag(II) complexes with a noninnocent ligand [i.e., a Ag(II) corrole radical cation], as in the case of copper corroles,^{28–31} silver corroles offer an ideal platform to observe Ag(III)···Ag(III) argentophilic interactions.

Here, we explore the electronic structure of silver corrole complexes (Chart 1) using a variety of characterization techniques and draw comparisons to $[\text{TBA}][\text{Ag}(\text{CF}_3)_4]$ as an authentic Ag(III) complex. Consistent with previous results, silver corroles are best formulated as Ag(III) complexes. A monomeric silver corrole (Ag-1) exhibits a cofacial arrangement of two corrole units in the solid state. A unique domed

conformation of the ligand enables close contact between Ag centers (3.75 Å). To determine if this dimeric structure is a consequence of an authentic metal–metal interaction or simply a crystal packing effect, the analogous cofacial corrole dyad or “pacman” derivative was prepared.³² The silver pacman Ag-2 exhibits the same structural features as the monomer with a shorter Ag...Ag distance of 3.67 Å. Theoretical calculations, including Bader and natural bond order (NBO) analyses, confirm the presence of a weak, closed-shell dispersion interaction between Ag centers, providing a rare example of a Ag(III)···Ag(III) argentophilic interaction.

EXPERIMENTAL SECTION

Materials. The following materials were used as received: hexane, dichloromethane (CH_2Cl_2), chloroform (CHCl_3), pyridine, tetrahydrofuran (THF), *N,N*-dimethylformamide (DMF), trifluoroacetic acid (TFA), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), *n*-butyllithium 2.5 M solution in hexanes (*n*BuLi), 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene, gold foil, spray-dried potassium fluoride (KF), silver(I) fluoride (AgF), silver(II) fluoride (AgF_2), tetrabutylammonium bromide (TBABr), trimethyl(trifluoromethyl)silane (TMSCF_3), and silica gel (60 Å pore size, 230–400 mesh or 40–63 μm particle size), from Sigma-Aldrich; silver(I) acetate $[\text{Ag}(\text{OAc})]$ from Strem; sodium sulfate (Na_2SO_4) from Mallinckrodt; gold(III) acetate $[\text{Au}(\text{OAc})_3]$ from Alfa Aesar; chloroform-*d* (CDCl_3) and toluene-*d*₈ from Cambridge Isotope Laboratories. Argon gas (Airgas) was passed over a Drierite column prior to use. Tetrabutylammonium hexafluorophosphate ($[\text{TBA}][\text{PF}_6]$) from Sigma-Aldrich was recrystallized from ethanol and subsequently dried under vacuum prior to use. The acetonitrile (MeCN) used for electrochemical experiments was purchased from Sigma-Aldrich, dispensed from a solvent drying system (Pure Process Technologies), and stored over 3 Å molecular sieves. Pentafluorophenyldipyrromethane, 10-(4-methoxycarbonylphenyl)-5,15-bis-(pentafluorophenyl)corrole (1) and 2,3,17,18-tetrabromo-10-(4-methoxycarbonylphenyl)-5,15-bis(pentafluorophenyl)corrole (1-Br₄) were prepared according to literature methods.³³

10-(4-Methoxycarbonylphenyl)-5,15-bis-(pentafluorophenyl)corrolotosilver(III) (Ag-1). In a round-bottom flask, 97 mg of the free-base corrole 1 (0.13 mmol) was dissolved in 13 mL of pyridine, and 132 mg of Ag(OAc) (0.791 mmol) was added. The resultant green solution was heated to 80 °C, 258 mg of Ag(OAc) (1.54 mmol) was added, and the reaction was allowed to continue for 2 h to afford a red solution. Solvent was removed by rotary evaporation. The crude reaction mixture was purified on a silica gel column packed with hexanes. The product eluted as a red band using a 1:1 mixture of hexanes and CH_2Cl_2 . Solvent was removed by rotary evaporation to afford 72 mg (63% yield) of the title product as a red solid. ¹H NMR (500 MHz, CDCl_3 , 23 °C): δ 4.12 (s, 3H), 8.31 (d, $J = 8.1$ Hz, 2H), 8.48 (d, $J = 8.1$ Hz, 2H), 8.78 (d, $J = 4.5$ Hz, 2H), 8.87 (d, $J = 4.9$ Hz, 2H), 8.92 (d, $J = 4.7$ Hz, 2H), 9.36 (d, $J = 4.4$ Hz, 2H). ¹⁹F NMR (470 MHz, CDCl_3 , 25 °C): δ -162.99 (m, 4F), -153.87 (t, $J = 20.9$ Hz, 2F), -138.57 (dd, $J^1 = 24.9$ Hz, $J^2 = 7.8$ Hz, 4F). Anal. Calcd for M^+ , where $\text{M} = \text{C}_{39}\text{H}_{15}\text{AgF}_{10}\text{N}_4\text{O}_2$: 868.01. Found by LD-MS: 868.09. UV–vis [toluene; λ , nm (ϵ , $\times 10^3$ $\text{M}^{-1} \text{cm}^{-1}$): 406 (38), 427 (116), 499 (3.7), 536 (7.6), 574 (31).

2,3,17,18-Tetrabromo-10-(4-methoxycarbonylphenyl)-5,15-bis(pentafluorophenyl)corrolotosilver(III) (Ag-1-Br₄). In a 20 mL scintillation vial, 58 mg of the free-base corrole 1-Br₄ (54 μmol) was dissolved in 5 mL of pyridine, and 208 mg of Ag(OAc) (1.2 mmol) was added. The resultant mixture was heated at 80 °C, an additional 230 mg of Ag(OAc) (1.4 mmol) was added, and the reaction was allowed to continue for 1 h to afford a red solution. The crude reaction mixture was filtered over a plug of silica gel, eluting with CH_2Cl_2 . After solvent removal, the residue was purified on a silica gel column using a 1:1 mixture of hexanes and CH_2Cl_2 . Solvent was removed by rotary evaporation to afford 31 mg (49% yield) of the

title product as a red solid. ^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 4.11 (s, 3H), 8.24 (d, J = 8.1 Hz, 2H), 8.48 (d, J = 8.1 Hz, 2H), 8.71 (d, J = 4.9 Hz, 2H), 8.74 (d, J = 4.9 Hz, 2H). ^{19}F NMR (470 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ -163.29 (m, 4F), -152.83 (t, J = 20.9 Hz, 2F), -138.88 (m, 4F). Anal. Calcd for M^+ , where $\text{M} = \text{C}_{39}\text{H}_{11}\text{AgBr}_4\text{F}_{10}\text{N}_4\text{O}_2$: 1183.65. Found by LD-MS: 1183.63. UV-vis [toluene; λ , nm (ϵ , $\times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$): 407 (55), 428 (131), 504 (4.5), 538 (12), 580 (72).

4,5-Diformyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene (4). In a 250 mL oven-dried Schlenk flask, 100 mL of dry THF was dispensed from a solvent drying station under argon. Then 2.01 g of 4,5-dibromo-2,7-di-*tert*-butyl-9,9-dimethylxanthene (4.2 mmol) was added under a flow of argon. The resultant solution was cooled to -78°C in a dry ice/acetone bath, then 7 mL of *n*BuLi (17.5 mmol) was added, and the resultant mixture was stirred at -78°C for 1 h. Then 8 mL of DMF (7.6 g, 103 mmol) was added. The reaction mixture was slowly warmed to room temperature and stirred for an additional 1 h. Water was added (~ 100 mL), and the product was extracted with CH_2Cl_2 ($\times 3$). The combined organics were washed with water ($\times 2$) and brine, dried over Na_2SO_4 , and brought to dryness. The residue was purified on a silica gel column using CHCl_3 as the eluent. Solvent was removed to afford 1.54 g (97% yield) of the title product as a white solid. ^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 1.37 (s, 18H), 1.70 (s, 6H), 7.71 (d, J = 2.5 Hz, 2H), 7.82 (d, J = 2.5 Hz, 2H), 10.68 (s, 2H). Anal. Calcd for $(\text{M} + \text{H})^+$, where $\text{M} = \text{C}_{25}\text{H}_{32}\text{O}_2$: 379.22. Found by LD-MS: 379.11. UV-vis (CH_2Cl_2 ; λ , nm): 256, 333.

Synthesis of the Pacman Corrole. In a 500 mL oven-dried Schlenk flask, 300 mL of dry CH_2Cl_2 was dispensed from a solvent drying station under argon. Then 509 mg of **4** (1.3 mmol) and 2.92 g of pentafluorophenylpyrromethane (9.4 mmol) were added under a flow of argon, followed by 150 μL (2 mmol) of TFA. The resultant solution was stirred at room temperature for 4 h protected from light. The reaction mixture was poured into a 2 L round-bottom flask containing 1.5 L of CH_2Cl_2 , and 1.85 g of DDQ (8.1 mmol) was added. The solution immediately turned dark, and the solution was stirred for 15 min. The reaction mixture was concentrated to near dryness and then poured onto a silica gel column; all of the fluorescent material was eluted with CH_2Cl_2 . After removal of the solvent, the residue was purified on a silica gel column using CH_2Cl_2 as the sole eluent. Two fluorescent products were observed. The first fraction was identified as the pacman corrole **2**, which eluted as a dark violet solution; the product was isolated as a dark purple solid in 26% yield (553 mg). The second fraction was identified as the monomeric corrole **5**, which also eluted as a violet solution; the product was obtained as a dark purple solid in 23% yield (304 mg).

4,5-Bis[5,15-bis(pentafluorophenyl)corrol-10-yl]-2,7-di-*tert*-butyl-9,9-dimethylxanthene (2). ^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 1.37 (s, 18H), 2.21 (s, 6H), 7.33 (d, J = 2.4 Hz, 2H), 7.88 (d, J = 2.4 Hz, 2H), 7.90 (d, J = 4.2 Hz, 4H), 8.00 (d, J = 4.7 Hz, 4H), 8.06 (bs, 4H), 8.47 (d, J = 4.2 Hz, 4H). ^{19}F NMR (470 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ -164.20 (m, 4F), -162.03 (m, 4F), -153.75 (t, J = 20.6 Hz, 4F), -138.26 (m, 4F), -136.45 (bs, 4F). Anal. Calcd for M^+ , where $\text{M} = \text{C}_{85}\text{H}_{52}\text{F}_{20}\text{N}_8\text{O}$: 1578.38. Found by LD-MS: 1578.38. UV-vis (CH_2Cl_2 ; λ , nm): 262, 293, 401, 522, 567, 624.

4-[5,15-Bis(pentafluorophenyl)corrol-10-yl]-5-formyl-2,7-di-*tert*-butyl-9,9-dimethylxanthene (5). ^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 1.26 (s, 9H), 1.53 (s, 9H), 1.93 (s, 6H), 7.38 (d, J = 2.4 Hz, 1H), 7.74 (d, J = 2.4 Hz, 1H), 7.86 (s, 1H), 7.88 (d, J = 2.4 Hz, 1H), 7.99 (d, J = 2.4 Hz, 1H), 8.56 (bs, 2H), 8.65 (m, 4H), 9.13 (d, J = 4.2 Hz, 2H). ^{19}F NMR (470 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ -163.45 (bs, 2F), -163.00 (bs, 2F), -154.40 (bs, 2F), -139.35 (bm, 2F), -138.45 (bm, 2F). Anal. Calcd for $(\text{M} + \text{H})^+$, where $\text{M} = \text{C}_{55}\text{H}_{42}\text{F}_{10}\text{N}_4\text{O}_2$: 979.30. Found by LD-MS: 979.34. UV-vis (CH_2Cl_2 ; λ , nm): 263, 412, 426, 521, 563, 613, 640.

4,5-Bis[5,15-bis(pentafluorophenyl)corrol-10-ylsilver]-2,7-di-*tert*-butyl-9,9-dimethylxanthene (Ag-2). In a 20 mL scintillation vial, 65 mg of free-base corrole **2** (41 μmol) was dissolved in 5 mL of pyridine, and 236 mg of $\text{Ag}(\text{OAc})$ (1.41 mmol) was added. The resultant mixture was stirred at 80 $^\circ\text{C}$ for 1.5 h. The crude

reaction mixture was filtered over a plug of silica using CH_2Cl_2 as the eluent. After solvent removal, the residue was purified on a silica gel column with CH_2Cl_2 and the product eluted as a red solution, giving 67 mg (91% yield) of the title compound as a red solid. ^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 1.40 (s, 18H), 2.23 (s, 6H), 7.39 (d, J = 2.4 Hz, 2H), 7.89 (d, J = 2.4 Hz, 2H), 8.16 (bd, J = 4.2 Hz, 4H), 8.18 (d, J = 4.7 Hz, 4H), 8.20 (bd, J = 4.8 Hz, 4H), 8.73 (d, J = 4.3 Hz, 4H). ^{19}F NMR (470 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ -165.45 (m, 4F), -163.41 (m, 4F), -155.03 (t, J = 20.8 Hz, 4F), -138.76 (dd, J = 24.2 Hz, J = 6.4 Hz, 4F), -136.57 (d, J = 23.9 Hz, 4F). Anal. Calcd for M^+ , where $\text{M} = \text{C}_{85}\text{H}_{46}\text{Ag}_2\text{F}_{20}\text{N}_8\text{O}$: 1788.14. Found by LD-MS: 1788.79. UV-vis (toluene; λ , nm): 411, 423, 502, 539, 576.

Gold Metalation of the Pacman Corrole 2. In a 10 mL microwave tube, 84 mg of **2** (53 μmol) was dissolved in 5 mL of pyridine, and 315 mg of $\text{Au}(\text{OAc})_3$ (0.84 mmol) was added. The resultant mixture was stirred at room temperature overnight. The crude reaction mixture was filtered over a plug of silica using CH_2Cl_2 as the eluent to give 9 mg of material as a red solid. Chromatography of the residue on silica gel using a 1:1 mixture of hexane and CH_2Cl_2 resolves two bands: an initial red band of the gold pacman complex (**Au-2**), followed by a green band of octaphyrin **6**.

4,5-Bis[5,15-bis(pentafluorophenyl)corrol-10-ylgold]-2,7-di-*tert*-butyl-9,9-dimethylxanthene (Au-2). ^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 1.38 (s, 18H), 2.21 (s, 6H), 7.37 (d, J = 2.4 Hz, 2H), 7.87 (d, J = 2.4 Hz, 2H), 8.19 (d, J = 4.8 Hz, 4H), 8.21 (bd, J = 4.7 Hz, 4H), 8.25 (bd, J = 4.2 Hz, 4H), 8.74 (d, J = 4.5 Hz, 4H). ^{19}F NMR (470 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ -164.17 (m, 4F), -162.04 (m, 4F), -153.67 (t, J = 20.5 Hz, 4F), -137.34 (m, 4F), -134.99 (m, 4F). Anal. Calcd for M^+ , where $\text{M} = \text{C}_{85}\text{H}_{46}\text{Au}_2\text{F}_{20}\text{N}_8\text{O}$: 1966.27. Found by LD-MS: 1966.62. UV-vis (toluene; λ , nm): 324, 406, 416, 534, 570.

[34]Octaphyrin(1.1.1.0.1.1.1.0) (6). ^1H NMR (500 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ 1.39 (s, 18H), 1.43 (s, 6H), 6.09 (bs, 2H), 6.38 (bs, 2H), 6.45 (bd, J $\sim$ 2.8 Hz, 2H), 6.48 (bs, 2H), 6.59 (bs, 2H), 6.91 (bs, 2H), 7.31 (bs, 2H), 7.42 (bs, 2H), 7.69 (bs, 2H), 7.78 (bs, 2H), 12.98 (bs, 4H). ^{19}F NMR (470 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ -165.04 (bm, 2F), -163.28 (bm, 2F), -161.35 (bm, 2F), -160.99 (bm, 2F), -153.08 (bm, 2F), -152.93 (bm, 2F), -137.84 (bm, 2F), -137.20 (bm, 2F), -131.99 (bm, 2F), -131.63 (bm, 2F). Anal. Calcd for $(\text{M} + \text{H})^+$, where $\text{M} = \text{C}_{85}\text{H}_{48}\text{F}_{20}\text{N}_8\text{O}$: 1577.37. Found by LD-MS: 1577.48. UV-vis (CH_2Cl_2 ; λ , nm): 263, 313, 416, 506, 714, 772, 926, 1052.

Tetrabutylammonium Tetrakis(trifluoromethyl)argentate ([TBA][Ag(CF₃)₄]). In a 20 mL scintillation vial, 97 mg of AgF (0.76 mmol), 424 mg of spray-dried KF (7.3 mmol), 0.5 mL of DMF, and 1.6 mL of TMSCF_3 (1.57 g, 8.5 mmol) were stirred at room temperature for 30 min. An additional 0.6 mL of TMSCF_3 (0.59 g, 3.2 mmol) was added, and the slurry was stirred for an additional 4 h. After this time, 5 mL of water was added to the reaction mixture, followed by 259 mg of TBABr (0.80 mmol). An additional 10 mL of water was added to produce a sufficiently large aqueous layer, and the reaction mixture was extracted with CH_2Cl_2 (five times). The combined organics were dried over Na_2SO_4 and subsequently brought to dryness. The residue was dissolved in a minimal amount of CH_2Cl_2 , and the reaction mixture was filtered over a plug of silica gel, eluting with CH_2Cl_2 . The filtrate was brought to dryness, the residue was dissolved in 20 mL of diethyl ether, and 100 mL of hexanes was added to precipitate the product. The solid was collected on a frit and dried under vacuum overnight to afford 75 mg (16% yield) of the title product as a white solid. ^1H NMR (500 MHz, CDCl_3 , 23 $^\circ\text{C}$): δ 1.03 (t, J = 7.4 Hz, 12H), 1.43 (sextet, J = 7.5 Hz, 8H), 1.60 (m, 8H), 3.08 (m, 8H). ^{19}F NMR (470 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ -31.25 [dd, $^2J(^{107}\text{Ag})$ = 35.6 Hz, $^2J(^{109}\text{Ag})$ = 40.7 Hz, 12F]. Anal. Calcd for M^- , where $\text{M} = \text{C}_4\text{AgF}_{12}$: 382.8859. Found by ESI-MS: 382.8868. UV-vis (CH_2Cl_2 ; λ , nm): 245.

Physical Measurements. NMR spectra were recorded on a Varian Inova-500 NMR spectrometer at the Harvard University Department of Chemistry and Chemical Biology Laukien-Purcell Instrumentation Center. ^1H NMR spectra were internally referenced to the residual solvent signal (δ = 7.26 for CHCl_3 in CDCl_3),³⁴ while ^{19}F NMR spectra were externally referenced to α,α,α -trifluorotoluene (δ = -63.72). $^1\text{H}/^{109}\text{Ag}$ heteronuclear multiple quantum coherence

(HMQC) NMR spectra were recorded on a Bruker 400 MHz Ascend Avance NEO spectrometer at the Montana State University (MSU) Department of Chemistry and Biochemistry NMR Center. The ^{109}Ag chemical shift was externally referenced to a saturated solution of AgNO_3 ($\delta = -59.0$).³⁵ Mass spectrometry (MS) spectra were recorded on a Bruker Autoflex MALDI-TOF mass spectrometer in positive-ion mode or an Agilent 6538 Q-TOF mass spectrometer in negative-ion mode at the Proteomics, Metabolomics, and Mass Spectrometry Facility at MSU. Absorption spectra were acquired using a Cary 5000 spectrometer (Agilent) or a Shimadzu UV-3101PC spectrometer. Emission spectra were recorded on a Photon Technology International QM4 fluorometer equipped with a 150 W Xe arc lamp and a Hamamatsu R2658 photomultiplier tube. Electrochemical measurements were made in a glovebox under a nitrogen atmosphere using a CH Instruments 760D Electrochemical Workstation with CHI version 10.03 software. Samples were prepared at concentrations of ~ 1 mM of the compound with 0.1 M $[\text{TBA}][\text{PF}_6]$ as the supporting electrolyte in MeCN. Cyclic voltammograms (CVs) were recorded at a scan rate of 100 mV s^{-1} using a glassy carbon button working electrode, a Ag wire reference electrode (isolated by a ceramic frit), and a Pt wire counter electrode. The CVs were internally referenced to ferrocene.

X-ray photoelectron spectroscopy (XPS) data were recorded using a Thermo Scientific K-Alpha XPS system. All samples were irradiated using a monochromated Al $K\alpha$ X-ray source (1486.6 eV energy and 0.85 eV line width) with a $400 \mu\text{m}$ spot size.³⁶ Surface charging was compensated for by a low-energy (0–14 eV) electron flood gun. The system was precalibrated with Au, Ag, and Cu standards built into the sample stage using an automated routine. Solutions of the sample were dropcast onto gold foil. Survey spectra were collected from 0 to 1350 eV with a step size of 1.0 eV. High-resolution spectra for the Ag 3d and C 1s regions were measured with a step size of 0.1 eV. Samples were calibrated to the C 1s peak at 284.8 eV.³⁷

Computational Details. Density functional theory (DFT) calculations were performed with the hybrid functional Becke-3 parameter exchange functional^{38–40} and the Lee–Yang–Parr nonlocal correlation functional (B3LYP),⁴¹ as implemented in the *Gaussian 09*, revision D.01, software package.⁴² To account for dispersion interactions, the $\omega\text{B97X-D}$ functional was utilized,⁴³ as implemented in the *Gaussian 16*, revision A.03, software package.⁴⁴ For light atoms (H, C, N, O, and F), a polarized split-valence triple- ζ basis set that includes p functions on H atoms and d functions on other atoms [i.e., the 6-311G(d,p) or 6-311G** basis set] was used.^{45,46} A Wood–Boring⁴⁷ quasi-relativistic effective core potential was used for Ag and Br (i.e., MWB28). All calculations were performed with a polarizable continuum (PCM) solvation model in toluene using a polarizable conductor calculation model (CPCM).^{48,49} All optimized geometries were confirmed as local minima structures by calculating the Hessian matrix and ensuring that no imaginary eigenvalues were present. Calculated structures were rendered using the program *Avogadro*.⁵⁰ Bader analyses^{51,52} were performed using the program *AIMAll*.⁵³ Wiberg bond orders⁵⁴ were determined by NBO analysis^{55,56} using *NBO*, version 3,⁵⁷ as implemented in *Gaussian 09*, revision D.01,⁴² for calculations using the B3LYP functional or *Gaussian 16*, revision A.03,⁴⁴ for calculations using the $\omega\text{B97X-D}$ functional.

X-ray Crystallographic Details. Diffraction-quality crystals of **Ag-1** were obtained by the slow vapor diffusion of hexane into a toluene solution of the compound to afford red needles. Diffraction-quality crystals of **Ag-2** and **6** were obtained from a toluene solution of the compound at -30°C in a nitrogen atmosphere glovebox, affording crystals of **Ag-2** as red plates and crystals of **6** as violet plates. X-ray diffraction data for **Ag-2** were collected on a Bruker three-circle platform goniometer equipped with an Apex II CCD and an Oxford cryostream cooling device at 100 K. Radiation was generated from a graphite fine-focus sealed-tube Mo $K\alpha$ source (0.71073 Å). X-ray diffraction data for **Ag-1** and **6** were collected on a vertically mounted Bruker D8 three-circle platform goniometer equipped with an Apex II CCD and an Oxford Diffraction Helijet cooling device (15 K) with synchrotron radiation (0.41328 Å) supplied by ChemMatCARS, located at the Advanced Photon Source

(APS), Argonne National Laboratory (ANL). For all samples, crystals were mounted on a glass fiber using Paratone-N oil. Data were collected as a series of φ and ω scans, integrated using *SAINT*,⁵⁸ and scaled with a multiscan absorption correction using *SADABS*.⁵⁸ The structure was solved by intrinsic phasing methods using *SHELXS-97* and refined against F^2 on all data by full-matrix least squares with *SHELXL-97*.⁵⁹ All non-H atoms were refined anisotropically. H atoms were placed at idealized positions and refined using a riding model.

RESULTS

Synthesis and Characterization of Monomeric Silver Corroles. The silver complex **Ag-1** and the 2,3,17,18-tetrabromo derivative **Ag-1-Br₄** were prepared by treating the free-base corrole³³ with $\text{Ag}(\text{OAc})$ in pyridine, following literature procedures.²² The ^1H and ^{19}F NMR spectra of both compounds exhibit sharp, well-resolved signals, which indicate that the compounds are diamagnetic. Interestingly, coupling of the β -pyrrole protons to the $^{107/109}\text{Ag}$ center is observed in the ^1H NMR spectrum (Figure S1). The ~ 0.7 Hz four-bond coupling constants are consistent with reported values (0.4–1.8 Hz).⁶⁰ This coupling can be leveraged to determine ^{109}Ag chemical shifts via two-dimensional heteronuclear NMR experiments. The inherent insensitivity of direct ^{109}Ag detection can be overcome by exciting a coupled proton and transferring the magnetization to the ^{109}Ag nucleus, significantly enhancing the signal.⁶⁰ A $^1\text{H}/^{109}\text{Ag}$ HMQC NMR experiment was performed to determine the ^{109}Ag chemical shifts of **Ag-1** and **Ag-1-Br₄**: 2518.7 and 2607.3 ppm, respectively (Figure S2). Saturated AgNO_3 was utilized as an external standard ($\delta = -59.0$).³⁵ Variable-temperature (VT) ^1H NMR spectra exhibit nominal shifts over the 25 – 100°C range, indicating the absence of low-lying triplet states (Figure S3).

The absorption spectra of **Ag-1** and **Ag-1-Br₄** exhibit a Soret band at ~ 427 nm and Q bands in the 500 – 600 nm range (Figure S4). A vibrational progression is observed for the Q bands, with Q(0,0) at ~ 575 nm, Q(1,0) at ~ 537 nm, and Q(2,0) at ~ 500 nm. These transitions are separated by $1305 \pm 71 \text{ cm}^{-1}$, which is comparable to the energetic spacing reported for free-base ($1277 \pm 63 \text{ cm}^{-1}$)³³ and gold ($1306 \pm 36 \text{ cm}^{-1}$)⁶¹ corroles. As observed for the gold analogues,⁶¹ bromination results in a nominal red shift of the absorption spectrum. Weak emission was observed for **Ag-1** at room temperature, exhibiting a broad feature centered at 665 nm (Figure S5).

The CV of **Ag-1** was recorded in MeCN; analogous data for **Ag-1-Br₄** could not be obtained because the compound is insufficiently soluble in MeCN. An irreversible reduction is observed at -1.9 V versus ferrocenium/ferrocene (Fc^+/Fc ; Figure S6a) and attributed to demetalation of the compound, as evidenced by the sharp peak around 0 V on the return scan, which is consistent with $\text{Ag}(0)$ oxidation. When a smaller potential window (Figure 2) is scanned to avoid this irreversible process, a reversible reduction is observed at -1.04 V, which is shifted to significantly more negative potentials relative to the Cu complex (-0.23 V).³⁰ A reversible oxidation is observed at $+0.56$ V, and a quasi-reversible oxidation occurs at $+1.06$ V (Figure S6b); similar phenomena are observed for the copper corrole at $+0.55$ and $+1.27$ V, respectively.³⁰ Additional waves are observed on the return scan due to the incomplete reversibility of the second oxidation. Given the similarity of **Ag-1** to the copper analogue, both oxidation features are assigned as corrole-based processes,

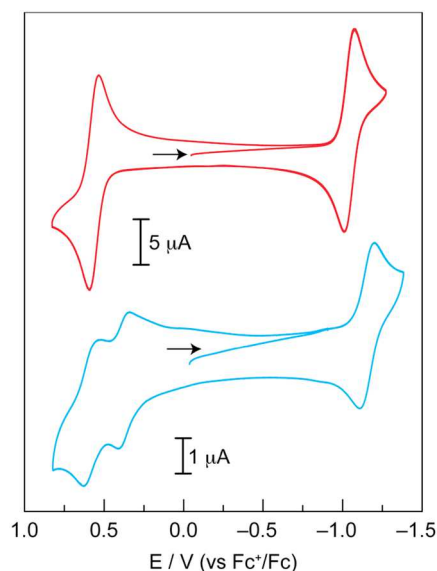


Figure 2. CVs of **Ag-1** (red line) and **Ag-2** (light-blue line) in MeCN with 0.1 M [TBA][PF₆] recorded at 100 mV s^{−1} under a nitrogen atmosphere. Note that the current scales are different for the two CVs.

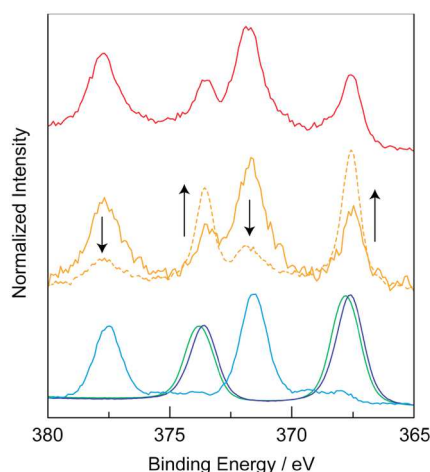


Figure 3. Ag 3d region of the XPS spectra of **Ag-1** (red line), **Ag-1-Br₄** (yellow line), and reference compounds of varying oxidation state: AgF (green line), AgF₂ (dark-blue line), [TBA][Ag(CF₃)₄] (light-blue line). Under prolonged X-ray exposure, **Ag-1-Br₄** is readily reduced (dotted lines).

consistent with previous electrochemical studies.^{22,25} Because the reduction significantly differs from the copper analogue, this processes is assigned to be metal-centered [i.e., Ag(III)/Ag(II) couple].

XPS was utilized to determine the oxidation state of the Ag center in **Ag-1** and **Ag-1-Br₄** (Figure 3). First, a series of reference compounds of varying oxidation state were examined (Figure 3, lower traces): AgF, AgF₂, and [TBA][Ag(CF₃)₄]. Both Ag(I) and Ag(II) have similar binding energies, with Ag(II) having a slightly lower binding energy; the Ag 3d_{5/2} peaks are observed at 367.8 and 367.6 eV for AgF and AgF₂, respectively. As observed for [TBA][Cu(CF₃)₄],³⁰ the peaks for the silver analogue are shifted to significantly higher binding energy, exhibiting a Ag 3d_{5/2} peak at 371.6 eV. Both corroles display two sets of peaks due to the presence of the photoreduced product. This is readily seen for **Ag-1-Br₄**, where

the initial spectrum with fewer scans (solid line) evolves to a new spectrum where the intensity of the lower-energy peaks for each transition increases (dashed line). Both corroles display nearly identical spectra, with the 3d_{5/2} and 3d_{3/2} peaks observed at 371.8 and 377.7 eV, respectively. These values are nearly identical with those reported for the silver complex of triphenylcorrole (371.70 and 377.66 eV)²² and have binding energies comparable to that of [TBA][Ag(CF₃)₄].

Diffraction-quality crystals of **Ag-1** were grown from toluene to produce fine red needles. The solid-state structure is depicted in Figure 4, and the crystallographic data are

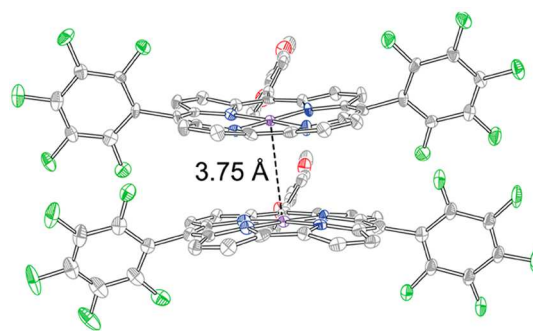


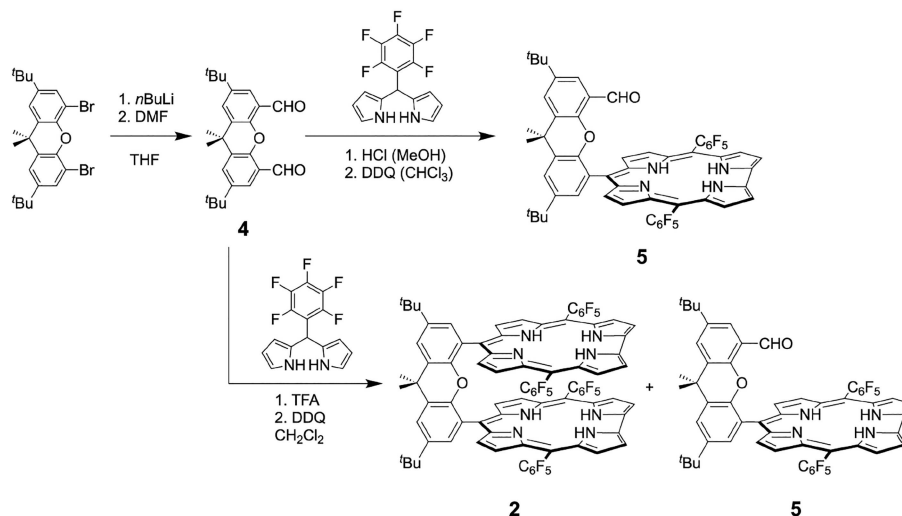
Figure 4. Solid-state structure of **Ag-1**. Thermal ellipsoids are drawn at the 50% probability level. H atoms and solvent molecules have been removed for clarity.

summarized in Table S1. Thermal ellipsoids are drawn at the 50% probability level; solvents of crystallization and H atoms have been removed for clarity. There are two silver corroles in the asymmetric unit, each with complementary conformations; the two macrocycles are domed such that the metal centers are proximal, giving a Ag⋯Ag distance of 3.75 Å. Additionally, π -stacking interactions of the pentafluorophenyl substituents likely contribute to the dimeric structure. The Ag–N bond distances range from 1.940 to 1.959 Å with an average distance of 1.949 Å. The N–Ag–N bond angles range from 79.94° to 95.71°. The five atoms of each AgN₄ unit are nearly coplanar, with a maximum displacement of 0.025 Å from the mean N₄ plane, and the two N₄ planes exhibit an 11.98° interplanar angle. The bowl shape of the macrocycle gives rise to average displacements of 0.115 ± 0.074 and 0.099 ± 0.068 Å from the mean 23-atom plane of the corrole. The domed conformation of the macrocycle is rare for metallocorroles that lack an axial ligand and/or exhibit square-planar geometry, with the metal residing largely in the corrole plane.^{62,63} Table S2 provides a comparison of the structural metrics for previously reported silver corrole complexes. The corrole conformation in **Ag-1** is unique among structurally characterized silver corrole complexes, which all exhibit a saddled conformation.

Synthesis and Characterization of Pacman Corroles.

To determine if this dimeric structure is a consequence of an authentic metal⋯metal interaction or simply a crystal packing effect, the analogous cofacial corrole dyad or “pacman” derivative was prepared. While cofacial porphyrin–corrole and corrole–corrole dyads have been previously reported, the corrole in the majority of these constructs has four β -phenyl substituents.^{64–66} Consequently, these very electron-rich macrocycles are not particularly stable in solution. The few examples of *meso*-substituted corrole–porphyrin^{67,68} and corrole–corrole^{69,70} dyads bear electron-donating mesityl substituents. It has been shown that corroles with penta-

Scheme 1. Synthetic Routes to the Monomeric Corrole 5 and Pacman Corrole 2



fluorophenyl substituents are extremely stable⁷¹ because these electron-withdrawing groups offset the inherent electron-richness of the corrole core.⁷² In an attempt to furnish a more stable pacman corrole, the synthesis of **2** (Scheme 1) was targeted.

The diformylxanthene backbone **4** was prepared from the commercially available dibromide. The HCl-catalyzed condensation of compound **4** and 5-pentafluorophenyl-dipyromethane was performed following the procedure of Koszarna and Gryko.⁷³ In this case, only the monomeric corrole derivative **5** was isolated, preserving one of the formyl groups of the xanthene backbone. The target pacman **2** was obtained through a TFA-catalyzed condensation, following a modified literature procedure.⁷⁰ In this case, both the monomer **5** and the target pacman **2** were isolated. Metalation was accomplished using Ag(OAc) in pyridine to furnish the silver complex **Ag-2** in high yield. The ¹⁰⁹Ag chemical shift for **Ag-2** is 2514.7 ppm, as determined using a ¹H/¹⁰⁹Ag HMQC NMR experiment (Figure S7).

The solid-state structure of **Ag-2** (Figure 5 and Table S1) is similar to that of **Ag-1**. The Ag–N bond distances range from 1.909 to 1.970 Å with an average distance of 1.942 Å. The N–Ag–N bond angles range from 80.96° to 95.80°. Other structural metrics are compiled in Table S2, drawing comparisons to **Ag-1** and other previously reported silver corrole complexes. The two corrole units are complementarily bowed to yield a short 3.670 Å distance between the two Ag centers; this is nearly identical with the 3.659 Å distance observed for the [SbF₆][−] salt of **Ag-3**.²⁰ To achieve this configuration, the xanthene backbone significantly compresses to give a 146° angle between the 4-C, O, and 5-C of the xanthene spacer, which is significantly contracted from the expected linear arrangement (~180°) of these atoms.⁷⁴ Indeed, the backbone of **Ag-2** is more compressed than xanthene-bridged cofacial metalloporphyrins,⁷⁵ which exhibit a 163–175° angle for the nickel(II), copper(II), and zinc(II) complexes. This demonstrates the flexibility of the xanthene backbone in cofacial corrole dyads and suggests that there is a significant driving force for the Ag...Ag interaction.

The CV of **Ag-2** (Figure 2) exhibits a reversible reduction and two reversible oxidations. The reduction event for the pacman derivative is similar to **Ag-1** but is shifted by ~100 mV

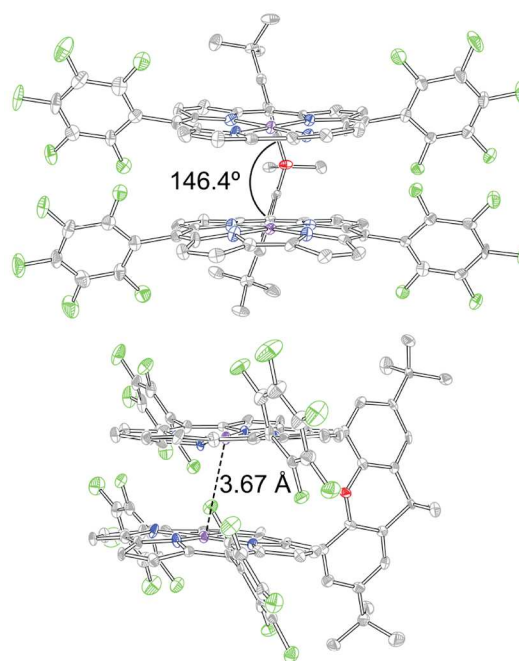


Figure 5. Solid-state structure of **Ag-2**. Thermal ellipsoids are drawn at the 50% probability level. H atoms and solvent molecules have been removed for clarity.

to more negative potentials (−1.15 V vs Fc⁺/Fc). **Ag-2** exhibits two oxidation waves that are separated by ~200 mV; the first oxidation event occurs at +0.38 V and is 180 mV more negative than **Ag-1**. This splitting of the oxidation wave is indicative of a strong interaction between the corrole subunits, which has been observed for pacman porphyrins with a xanthene spacer,^{76,77} as well as a cofacial antimony(V) bis(μ-oxo)corrole dimer.⁷⁸ While the oxidation of **Ag-2** occurs in one-electron steps, the reduction is a two-electron process. The height of the reduction wave is ~2.3 μA (Figure 2), which is nearly twice that of the oxidation waves (1.2 μA), corroborating this assignment. When a larger potential window is scanned (Figure S8), stepwise reduction of the corroles is not observed. This result is consistent with previous observations of cofacial porphyrins, where ring oxidation

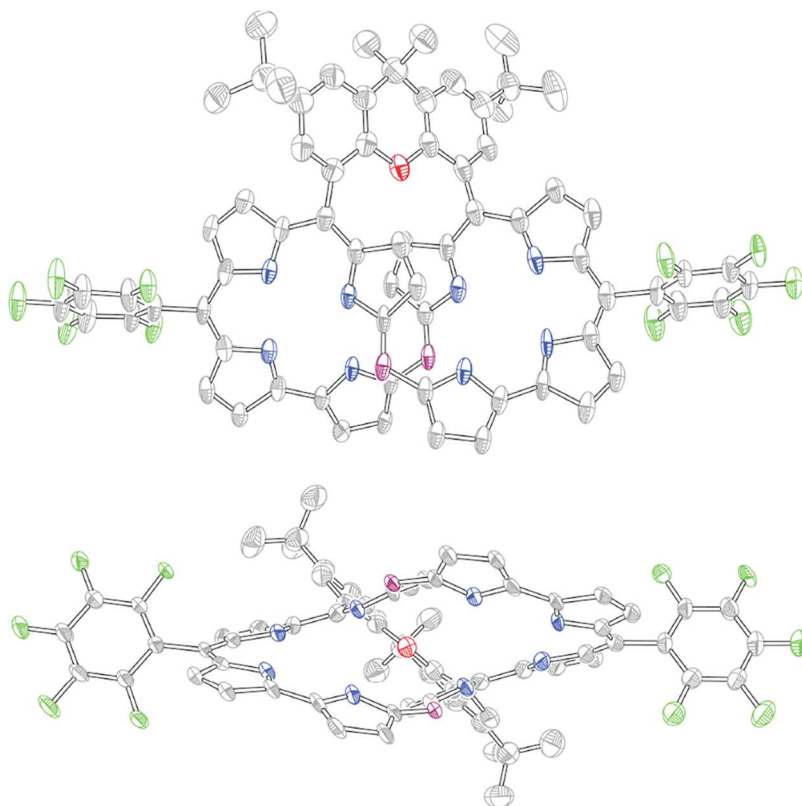
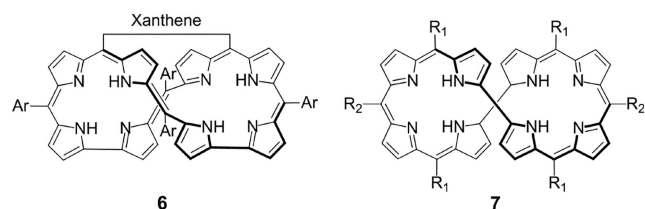


Figure 6. Solid-state structure of **6**. Thermal ellipsoids are drawn at the 50% probability level. H atoms and solvent molecules have been removed for clarity. Additionally, pentafluorophenyl substituents have been removed from the *meso*-C atoms highlighted in magenta.

occurs in two one-electron steps and ring reduction occurs in a single two-electron process when the macrocycles are sufficiently proximate. On the basis of the spectroscopic and electrochemical analyses of various cofacial porphyrin architectures, Collman proposed that the dyad acts as a single redox-active entity with mixed-valence behavior.⁷⁹ The first oxidation yields a π -based radical cation delocalized over both macrocycles. Upon the second oxidation, the two delocalized electrons become paired, giving rise to a nonclassical π -bonding interaction. Collman also concluded that successive reductions increase π -ring repulsion in the dimers, which is significant enough to minimize the interaction between the porphyrin rings, thus resulting in a single two-electron wave.

Next, **Au-2** was prepared to determine if these structural phenomena were also observed for the gold complex and to compare the Au...Au distance to known examples of Au(III)...Au(III) aurophilic interactions. Typical gold metalation procedures^{61,80} yielded the target complex, as well as the monometalated derivative, which coelutes with **Au-2**. Crystals suitable for X-ray diffraction were grown, but, surprisingly, the structure of octaphyrin **6** was obtained (Figure 6 and Table S1) rather than **Au-2**. The mother liquor from the crystallization was analyzed by thin-layer chromatography and revealed the presence of two compounds. The first, red fraction was identified as **Au-2**, while the second, green-brown fraction was identified as octaphyrin **6**. The ¹H NMR spectrum exhibits a broad singlet at $\delta = 12.98$ for the *N*-pyrrole protons, demonstrating that the compound is not aromatic. This is corroborated by the β -pyrrole protons, which appear in the $\delta = 6$ –8 region, shifted upfield relative to those of the aromatic corrole ($\delta = 8.5$ –9.5). The solid-state structure of **6** exhibits a figure-eight motif, giving a twisted Hückel configuration rather

Chart 2. Isomers of [34]Octaphyrin(1.1.1.0.1.1.1.0)



than Möbius topology.^{81–83} Given these data, as well as the similarity to the literature reports,^{84,85} **6** is assigned as [34]octaphyrin(1.1.1.0.1.1.1.0). Compound **6** is a novel isomer of this octaphyrin (Chart 2); derivatives reported by Vogel et al.⁸⁴ and Geier and Grindrod⁸⁵ cross over the bipyrrrole linkage (**7**) rather than at the *meso* positions, as in **6**. While the origin of this molecule is unclear, it is likely that the xanthene backbone templates the synthesis, enabling **6** to adopt this unique geometry. The absorption spectrum of **6** (Figure S9) exhibits a sharp feature at 715 nm and weaker transitions in the near-IR (900–1200 nm), similar to other derivatives of [34]octaphyrin(1.1.1.0.1.1.1.0).^{85,86}

DFT Calculations. Ghosh and co-workers have posited that the corrole ligand is on the edge of being noninnocent for silver complexes, depending on the peripheral substitution of the ligand.²³ They found that the corrole ligand was noninnocent in the case of β -octabromosilver corroles [i.e., a silver(II) corrole radical cation, analogous to copper corroles], while it was innocent in the case of β -unsubstituted corroles [i.e., an authentic Ag(III) complex]. These conclusions were supported by absorption spectroscopy and DFT calculations.⁸⁷ For the noninnocent complexes, calculations showed that the

Ag $d_{x^2-y^2}$ orbital is highly mixed with the corrole highest occupied molecular orbital (HOMO), as observed for copper corroles.²³ Subsequent Ag L-edge XANES experiments confirmed these assignments.²⁴

Ghosh's computational results suggest that the electronic structure of silver corroles may be tuned by modulating the energy of the corrole orbitals. Computationally, we surveyed other substitution patterns that could potentially exhibit noninnocence: **Ag-1-Br₄**, **Ag-1-Br₈**, and **Ag-1-F₈**. For each compound, three spin scenarios were calculated: a spin-restricted singlet [i.e., authentic Ag(III) complex], a spin-unrestricted, broken-symmetry singlet [i.e., antiferromagnetically coupled silver(II) corrole radical cation], and a spin-unrestricted triplet [i.e., ferromagnetically coupled silver(II) corrole radical cation]. These calculations were performed using the B3LYP functional with the 6-311G(d,p) basis set for all light atoms, a Wood–Boring quasi-relativistic effective core potential (i.e., MWB28) for Ag and Br, and a toluene CPCM solvation model. Cartesian coordinates for the optimized geometries are presented in Tables S3–S10. The results of these calculations are summarized in Figure 7, which depicts

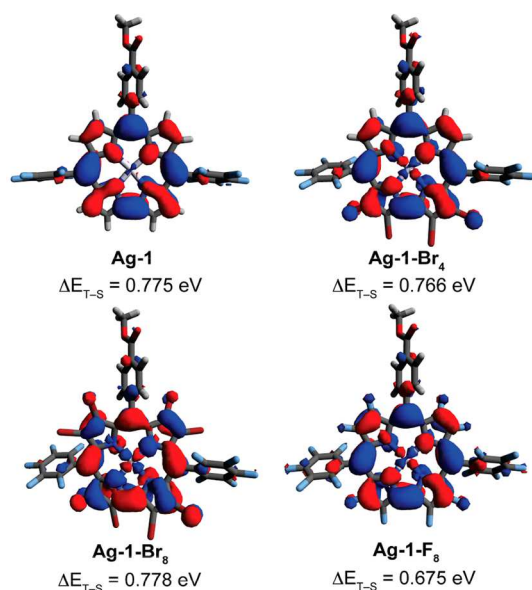


Figure 7. Summary of DFT calculations for derivatives of **Ag-1**, showing the HOMO for the spin-restricted calculations and ΔE_{T-S} . For β -substituted corroles, the Ag $d_{x^2-y^2}$ orbital is highly mixed with the corrole HOMO.

the HOMO for each derivative and reports the triplet–singlet energy gap (ΔE_{T-S}). In all cases, the spin-unrestricted singlet calculation converges to the spin-restricted case, leaving no residual spin density. The parent silver corrole **Ag-1** does not display mixing of the Ag $d_{x^2-y^2}$ orbital and corrole HOMO, while the β -substituted derivatives (**Ag-1-Br₄**, **Ag-1-Br₈**, and **Ag-1-F₈**) do, consistent with Ghosh's results.²³ In all cases, the triplet state is calculated to be significantly higher in energy for the silver complexes (0.68–0.78 eV) relative to the copper complex (0.017 eV) using the same computational methods.³⁰ These results suggest that the triplet states are prohibitively high in energy to induce any meaningful shifts by VT NMR, consistent with experimental observations.

DFT calculations were used to corroborate the electrochemistry of **Ag-1** and assign the electronic structure of these derivatives (Figure 8). Cartesian coordinates for the optimized geometries are presented in Tables S11–S14. The ground state of **Ag-1** is best described as a Ag(III) complex with an innocent corrole ligand. The one-electron reduction and oxidation events were calculated as open-shell doublets, and the spin-density plots for these derivatives are shown in Figure 8. The reduction is metal-based, yielding a spin-density plot with one electron in the $d_{x^2-y^2}$ orbital. Conversely, the oxidation is corrole-based, with one electron in the corrole b_1 HOMO. For the doubly oxidized corrole, three spin scenarios were considered: a spin-restricted singlet, a spin-unrestricted (i.e., broken-symmetry) singlet, and a spin-unrestricted triplet. It was found that the two singlet calculations produced the same result and were 0.140 eV lower in energy than the triplet state. The HOMO for [**Ag-1**]²⁺ corresponds to the canonical corrole HOMO–1 orbital of a_2 symmetry, confirming that this redox event is ligand-based, precluding the formation of a Ag(IV) species.

To examine the interaction between Ag centers, DFT calculations were performed using both the B3LYP and ω B97X-D functionals; the latter includes dispersion corrections and accounts for long-range interactions.⁴³ The structural metrics for the computed and experimental structures are summarized in Table 1. The dimeric nature of **Ag-1** was investigated by performing a geometry optimization with two molecules stacked in a cofacial arrangement (Tables S15 and S16). It was found that the ω B97X-D functional best recapitulates the experimental structure of **Ag-1** (Table S17) with an optimized Ag...Ag distance of 3.63 Å, whereas the B3LYP functional optimizes the dimer configuration with a significantly longer 5.84 Å Ag...Ag distance. Nevertheless, the dimeric structure is lower in energy than two independent molecules of **Ag-1**: 0.265 eV (6.11 kcal mol^{−1}) with B3LYP

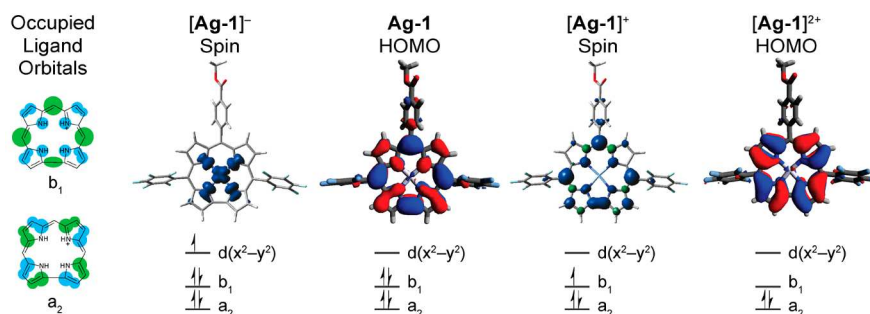


Figure 8. Summary of the results of DFT calculations for the oxidized and reduced derivatives of **Ag-1**. A qualitative molecular orbital diagram is provided to illustrate orbital occupancy. For reference, the canonical occupied corrole orbitals are included.

Table 1. Summary of the Structural and Computational Parameters Analyzing the Ag...Ag Interaction

		functional	Ag...Ag (Å)	Ct...Ct (Å) ^a	IA (deg) ^b	SA (deg) ^c	LS (Å) ^d	BCP	$\rho(r)$ (a.u.) ^e	$\nabla^2[\rho(r)]$ (a.u.) ^f	DI ^g	WBI ^h
Ag-1	X-ray	B3LYP	3.75	3.78	7.24	23.8	1.52	no			0.0178	0.0242
Ag-1	X-ray	ω B97X-D	3.75	3.78	7.24	23.8	1.52	no			0.0171	0.0230
Ag-1	DFT	B3LYP	5.84	5.83	4.74	14.3	1.44	(3, -1)	0.0001	0.0003	0.0005	0.0014
Ag-1	DFT	ω B97X-D	3.63	3.67	3.77	24.3	1.51	no			0.0232	0.0178
Ag-2	X-ray	B3LYP	3.67	3.70	3.74	12.5	0.80	(3, -1)	0.0055	0.0170	0.0308	0.0317
Ag-2	X-ray	ω B97X-D	3.67	3.70	3.74	12.5	0.80	(3, -1)	0.0054	0.0168	0.0297	0.0301
Ag-2	DFT	B3LYP	5.07	5.11	9.61	12.8	1.13	(3, -1)	0.0005	0.0013	0.0022	0.0034
Ag-2	DFT	ω B97X-D	3.57	3.63	5.81	16.9	1.06	(3, -1)	0.0066	0.0212	0.0325	0.0342
Ag-3	X-ray ⁱ	B3LYP	3.66	3.71	2.94	24.4	1.53	(3, -1)	0.0058	0.0181	0.0241	0.0341
Ag-3	X-ray ^j	ω B97X-D	3.66	3.71	2.94	24.4	1.53	(3, -1)	0.0058	0.0180	0.0231	0.0324
Ag-3 ^j	X-ray ^k	B97D	3.46	3.33 ^l		16.2 ^m	0.96	yes	0.011 ⁿ			0.07 ⁿ
Ag-4 ^o	X-ray ^p	M06	3.61	3.39 ^l		22.8 ^m	1.42	(3, -1)	0.0045	0.0174		
[Ag-4] ^{+o}	X-ray ^q	M06	3.53	3.31 ^l		23.2 ^m	1.41	(3, -1)	0.0051	0.0204		
[Ag-4] ^{2+o}	X-ray ^r	M06	3.45	3.32 ^l		17.8 ^m	1.07	(3, -1)	0.0187	0.0351		

^aCenter-to-center distance between the centroids of the N₄ unit. ^bInterplanar angle, defined as the angle between the mean 23-atom plane (or 24-atom plane in the case of **Ag-3**) of the two macrocycles. ^cSlip angle (α), defined as the average angle between the vector normal to the N₄ plane and the Ag...Ag vector. ^dLateral shift between the two Ag centers, defined as $(\sin \alpha)(\text{Ct}\cdots\text{Ct distance})$. ^eElectronic density at the BCP in atomic units. ^fLaplacian of the electronic density in atomic units. ^gElectron delocalization index between Ag centers (i.e., average number of electrons shared between the two Ag ions) from Bader analysis. ^hWiberg bond index from NBO analysis. ⁱ[SbF₆][−] salt, CCDC 1536021. ^jData reproduced from ref 20. ^k[PF₆][−] salt, CCDC 1536020. ^lCenter-to-center distance between mean 24-atom planes. ^mAngle between the vector normal to the mean 24-atom plane and the Ct...Ct vector. ⁿCalculated for the DFT-optimized geometry. ^oData reproduced from ref 21. ^pCCDC 1907233. ^qCCDC 1907234. ^rCCDC 1907235.

and 2.045 eV (47.16 kcal mol^{−1}) with ω B97X-D. This result demonstrates that there is a significant driving force for dimerization, and the ω B97X-D functional best captures this dispersion interaction. Similarly, the geometry of **Ag-2** was optimized using both the B3LYP and ω B97X-D functionals (Tables S18 and S19). Again, the ω B97X-D functional best captures the solid-state geometry of **Ag-2** (Table S20), optimizing a Ag...Ag distance of 3.57 Å, whereas B3LYP predicts a relaxed, elongated structure (5.07 Å between metal centers).

A Bader analysis⁵¹ (i.e., atoms in molecules or AIM) was performed using the *AIMAll* program⁵³ to identify interactions between the Ag centers in **Ag-1** and **Ag-2**. Complementary NBO analysis⁵⁵ was also performed, and the Wiberg bond index (WBI)⁵⁴ between the metal centers was determined. These calculations were performed for both DFT-optimized and experimental geometries using the B3LYP and ω B97X-D functionals; the results are summarized in Table 1. When the experimental solid-state structure is analyzed, the B3LYP and ω B97X-D functionals yield similar results. Analysis of the crystal structure of **Ag-1** did not identify a bond critical point (BCP) between the Ag centers. A BCP of type (3, -1) was located between the two Ag atoms only for the B3LYP-optimized geometry, with the electronic density $\rho(r) = 1.22 \times 10^{-4}$ and Laplacian of electronic density $\nabla^2[\rho(r)] = 3.42 \times 10^{-4}$. The two Ag centers exhibit a delocalization index (DI) of 4.7×10^{-4} . The DI is identical to the bond order when two atoms are connected by a bond path, which is the atomic interaction line that joins two atoms, serving as a “bridge” of electron density. This quantifiable quantum-mechanical entity denotes a bonding interaction between atoms. The presence of both a bond path and a critical point is necessary and sufficient for two atoms to be bonded.^{88,89}

Conversely, a Bader analysis identifies a (3, -1) type BCP between Ag centers in **Ag-2** for all structures. For the experimental structure, the electronic density at the BCP is $\rho(r) = 0.0055$ and the Laplacian of the electronic density is

$\nabla^2[\rho(r)] = 0.0170$. The positive value of the Laplacian indicates that this is a closed-shell interaction between the two atoms.⁹⁰ The values of these parameters are smaller than those reported for Ag(I)⋯Ag(I) argentophilic interactions (Table S21). However, this may be expected as a consequence of the longer Ag...Ag distance in **Ag-2** relative to the Ag(I) examples, given that both $\rho(r)$ and $\nabla^2[\rho(r)]$ are inversely correlated with the Ag...Ag distance (Figure S10a). The Wiberg bond order derived from NBO analysis was determined to be 0.032 for **Ag-2** and is nearly identical with the DI calculated from the Bader analysis. This value falls within the range reported for most Ag(I)⋯Ag(I) argentophilic interactions: 0.022–0.094 (Table S21). It should be noted that the Wiberg bond order does not correlate with the Ag...Ag distance (Figure S10b). Moreover, the metrics for the Ag...Ag interaction [$\rho(r)$, $\nabla^2[\rho(r)]$, and WBI] in **Ag-2** are similar to those for the [SbF₆][−] salt of **Ag-3** (Table S22), the first reported example of a Ag(III)⋯Ag(III) interaction, indicating that **Ag-2** also exhibits this phenomenon. Table 1 also includes the structural metrics and computational analysis of the [PF₆][−] salt of **Ag-3**,²⁰ as well as **Ag-4** in various oxidation states.²¹ Because different computational methods were used for these compounds, the metrics for the Bader and NBO analyses are not directly comparable. It should be noted that $\rho(r)$ and $\nabla^2[\rho(r)]$ increase with subsequent oxidations of **Ag-4**, reflecting stronger Ag...Ag interactions.

DISCUSSION

The electronic structure of silver corroles has been examined using a variety of complementary techniques including NMR, XPS, and electrochemistry in conjunction with DFT calculations. Our calculations are consistent with the results reported by Ghosh,²³ demonstrating that β substitution induces mixing of the Ag d_{x²−y²} orbital and corrole HOMO. The calculations also demonstrate that tetrabromination is sufficient to induce this mixing, suggesting that **Ag-1** is an authentic Ag(III) complex, while **Ag-1-Br₄** may be non-

innocent (i.e., silver(II) corrole radical cation). NMR studies of **Ag-1** indicate that the ^1H NMR spectrum is similar to the Au complex, rather than the Cu derivative, further supporting the Ag(III) formulation. Because the room temperature ^1H NMR spectrum of **Ag-1-Br₄** does not exhibit broadening or shifting of the signals relative to **Ag-1** (as would be expected for a noninnocent complex), this compound is also likely a Ag(III) complex. VT NMR supports this assignment because neither **Ag-1** nor **Ag-1-Br₄** demonstrate significant temperature-dependent shifts. XPS analysis of the Ag 3d region for **Ag-1** and **Ag-1-Br₄** demonstrates that the spectra are nearly identical and have binding energies similar to those of $[\text{TBA}][\text{Ag}(\text{CF}_3)_4]$, indicating that both corroles contain a Ag(III) center. To reconcile the experimentally observed Ag(III) and the calculated mixing of the Ag $d_{x^2-y^2}$ orbital and corrole HOMO in **Ag-1-Br₄**, we propose that peripheral substitution increases the covalency of the metal–ligand bond rather than modulating the electronic structure of the molecule.

For XPS studies, $[\text{TBA}][\text{Ag}(\text{CF}_3)_4]$ was utilized as a Ag(III) standard. The copper analogue has an inverted ligand field, giving rise to a Cu(I) complex rather than a Cu(III) species, as determined by X-ray spectroscopy.⁹¹ Subsequent experimental studies confirm the presence of an inverted ligand field but suggest that a Cu(III) center is present in $[\text{Cu}(\text{CF}_3)_4]^-$.⁹² In the initial proposal of the inverted ligand field in trifluoromethyl complexes of coinage metals,⁹³ Snyder hypothesized that this same phenomenon would persist for the silver and gold derivatives.⁹⁴ Although this remains to be tested further experimentally, there is compelling evidence for the presence of a Ag(III) center in the $[\text{Ag}(\text{CF}_3)_4]^-$ anion. In the initial report of this species, the complex was isolated as the silver(I) salt: $\text{Ag}[\text{Ag}(\text{CF}_3)_4]$.⁹⁵ The ^{109}Ag NMR spectrum showed two resonances: a singlet at 368.2 ppm and a septet at 2232.6 ppm. The septet exhibits a coupling constant of 40.7 Hz, which is identical with that observed in the ^{19}F NMR spectrum, indicating that this signal is due to the CF_3 -bound Ag center. Because ^{109}Ag NMR is sensitive to the oxidation state,⁶⁰ these assignments are consistent with known chemical shifts of Ag(III) ($\delta > 2000$). This chemical shift is likely not an artifact of the $-\text{CF}_3$ ligands because the $[\text{Ag}(\text{CF}_3)_2]^-$ anion exhibits a ^{109}Ag chemical shift of 565.5 ppm,⁹⁶ falling in the range reported for Ag(I) complexes.⁶⁰ The literature ^{109}Ag NMR data, in conjunction with the XPS data of Figure 3, suggest that $[\text{TBA}][\text{Ag}(\text{CF}_3)_4]$ is an authentic Ag(III) complex. Recent computational and experimental studies support this formulation.^{92,97} Although the complex does exhibit an inverted ligand field, the metal has a 3+ oxidation state.

The ^{109}Ag chemical shift further supports the Ag(III) assignment for the silver corrole complexes. By exploiting the coupling of the Ag center to the β -pyrrole protons (Figure S1), an HMQC NMR experiment was utilized for indirect ^{109}Ag detection. This overcomes the inherent difficulties of direct ^{109}Ag detection, which includes low sensitivity (10^{-4} relative to ^1H) and long relaxation times (minutes).⁶⁰ The ^{109}Ag chemical shifts for **Ag-1**, **Ag-1-Br₄**, and **Ag-2** are 2518.7, 2607.3, and 2514.7 ppm, respectively. The ~ 90 ppm downfield shift for **Ag-1-Br₄** relative to **Ag-1** likely reflects an inductive effect of the four bromo substituents. The similar chemical shifts for **Ag-1** and **Ag-2** indicate that the coordination environment of the Ag centers and the electronic structure of the complexes are nearly identical. To the best of our knowledge, this is the

first report of ^{109}Ag chemical shifts for silver porphyrinoids (i.e., tetrapyrrole and related macrocycles). It should be noted that ^{109}Ag NMR spectra have been previously reported for cryptands⁹⁸ and other nonaromatic macrocyclic ligands.⁹⁹

For canonical metallophilic interactions, the distance between metal centers is shorter than the sum of the van der Waals radii. However, the experimental Ag $\cdots$ Ag distances for **Ag-1** (3.75 Å), **Ag-2** (3.67 Å), and **Ag-3** (3.66 Å) are longer than the radii of the two Ag centers: 3.44 Å.⁶ Similarly, the Au $\cdots$ Au distances observed for Au(III) aurophilic interactions in $[\text{Me}_4\text{N}][\text{Au}(\text{N}_3)_4]$ ¹⁴ and $[\text{Au}(\text{bpy})\text{Cl}_2][\text{AuBr}_4]$,¹⁵ are 3.507 and 3.518 Å, respectively, which are both longer than the sum of the radii of two Au centers (3.32 Å).⁶ Indeed, the shortest examples of Au(III) $\cdots$ Au(III) aurophilic interactions (3.495 and 3.367 Å)^{100,101} are still longer than the sum of the radii. It has been demonstrated computationally that the M $\cdots$ M distance increases with increasing oxidation state.¹⁶ Therefore, the Ag $\cdots$ Ag distance observed in **Ag-2** is consistent with a Ag(III) $\cdots$ Ag(III) argentophilic interaction and is supported by theoretical calculations.

Complexes with metallophilic interactions often exhibit luminescence as a result of M $\cdots$ M interactions in the excited state.^{102,103} This phenomenon has been observed for a variety of species with Ag(I) $\cdots$ Ag(I) argentophilic interactions,¹⁷ and the emission features are typically quite broad (fwhm = 80–150 nm).^{104,105} Although the luminescence is enhanced at low temperatures (< 77 K), weak room-temperature emission has been observed.¹⁰⁵ In contrast to Ag(I) $\cdots$ Ag(I) argentophilic interactions, **Ag-3** exhibits an unusually sharp emission feature (fwhm = 10 nm) centered at 546 nm at 77 K.²⁰ Analogous luminescence was not reported for **Ag-4** derivatives.²¹ Weak emission was observed for **Ag-1** at room temperature, exhibiting a broad (fwhm = 60 nm) feature centered at 665 nm. This broad emission is expected for M $\cdots$ M interactions and is consistent with photoluminescence from Ag(I) $\cdots$ Ag(I) argentophilic interactions,^{17,104,105} unlike the unusually sharp emission feature reported for **Ag-3**.²⁰ Emission from **Ag-1** indicates that the Ag $\cdots$ Ag interaction persists in solution, making it the first example of an unsupported Ag(III) $\cdots$ Ag(III) argentophilic interaction.

The Ag $\cdots$ Ag interactions observed in the solid-state structures of **Ag-1** and **Ag-2** were examined computationally using Bader and NBO analyses. For both compounds, the DFT-optimized geometry using the $\omega\text{B97X-D}$ functional, which includes dispersion interactions, best represents the experimental geometry of the compounds. However, analysis of the experimental structures using the $\omega\text{B97X-D}$ and B3LYP functionals gives similar results (Table 1).

For **Ag-1**, the Bader analysis did not identify a BCP between the Ag centers for the experimental or $\omega\text{B97X-D}$ -optimized structures. This may be due to the large slip angle ($\sim 24^\circ$) between the two corrole units that diminishes the overlap between Ag centers. Interestingly, a BCP is identified for the B3LYP-optimized structure of **Ag-1**. Although the Ag $\cdots$ Ag distance is significantly extended (5.84 Å), the slip angle is smaller ($\sim 14^\circ$), resulting in a sufficient interaction to yield a BCP, albeit with very low electronic density. These results suggest that a combination of structural factors, not just the M $\cdots$ M distance, are determinant of metallophilic interactions. Even in the absence of a BCP, there is a nonzero interaction between the Ag centers, as evidenced by the DI and WBI.

Conversely, a BCP is identified between Ag centers for the calculated and experimental structures of **Ag-2**. This is due to

the decreased Ag...Ag distance and the reduced slip angle relative to **Ag-1**, resulting in increased orbital overlap of the Ag centers. The calculated electronic density $\rho(r)$ at the critical point is lower than that of previously reported Ag(I)...Ag(I) argentophilic interactions (Table S21). This is expected because $\rho(r)$ correlates with the Ag...Ag distance (Figure S10a), which is much shorter for Ag(I)...Ag(I) argentophilic interactions. The calculated WBI for the experimental structure of **Ag-2** falls within the range reported for Ag(I)...Ag(I) argentophilic interactions (Table S21). Together, these computational results indicate that **Ag-2** exhibits an authentic Ag(III)...Ag(III) argentophilic interaction.

In order to contextualize these computational results, comparisons may be drawn with the first reported example of a Ag(III)...Ag(III) argentophilic interaction: **Ag-3**.²⁰ The same computational methods as those used for **Ag-1** and **Ag-2** were used to analyze the solid-state structure of **Ag-3** (as the [SbF₆][−] salt). Although the crystal structure exhibits a substantial ~24° slip angle between porphyrin units, the decreased Ag...Ag distance results in sufficient orbital overlap to yield a BCP between metal centers. The metrics for the Ag...Ag interaction [$\rho(r)$, $\nabla^2[\rho(r)]$, and WBI] in **Ag-3** are similar to those in **Ag-2**, further supporting the existence of an argentophilic interaction in the pacman corrole complex. A shorter Ag...Ag distance was observed for the [PF₆][−] salt of **Ag-3**. The 0.2 Å difference in the metal–metal distance with different counterions suggests that crystal packing effects may modulate the metallophilic interaction in **Ag-3**. Shorter Ag...Ag contacts are achieved with a more rigid ethene linker (**Ag-4**). The Ag...Ag distance decreases upon oxidation of the complex: 3.61 Å for Ag(II)/Ag(II), 3.53 Å for mixed-valent Ag(II)/Ag(III), and 3.45 Å for Ag(III)/Ag(III). Consequently, the strength of the Ag...Ag interaction increases, as determined by a Bader analysis.²¹ It should be noted that only the doubly oxidized Ag(III)/Ag(III) derivative [**Ag-4**]²⁺ reflects a closed-shell, metallophilic interaction. Other noncovalent, supramolecular interactions (e.g., π -stacking and hydrophobic interactions) likely contribute to the calculated Ag...Ag interaction in **Ag-4** and [**Ag-4**]⁺.

The dimeric structures of **Ag-1** and **Ag-2** are enabled by various noncovalent, supramolecular interactions, including metallophilic and π -stacking interactions. Theoretical calculations confirm the presence of a closed-shell dispersion interaction between metal centers, reflective of a metallophilic interaction. While this does not necessarily reflect the dominant driving force for dimerization, it is certainly present. The argentophilic interaction is experimentally reflected by compression of the backbone in **Ag-2**. The 146° angle of the xanthene backbone is significantly smaller than the 163–175° angle previously observed for cofacial Ni(II), Cu(II), and Zn(II) porphyrins with a xanthene backbone.⁷⁵ This suggests that there are additional stabilizing interactions in **Ag-2** beyond π -stacking interactions between macrocycles that are absent in the porphyrin examples [i.e., the Ag(III)...Ag(III) argentophilic interaction]. Additionally, the semirigid xanthene backbone helps to minimize the slip angle and lateral shift between Ag centers. A comparison of the structural metrics of Table 1 reveals that the xanthene backbone affords greater overlap of the Ag centers relative to the flexible ethane or ethene linkers (**Ag-3** and **Ag-4**).

While it is difficult to disentangle the energetic contribution of these noncovalent interactions, it may be inferred from the theoretical calculations. The energy stabilization of the dimeric

structure of **Ag-1**, as calculated using the B3LYP functional, is 6.11 kcal mol^{−1}. This elongated structure with a 5.84 Å distance between Ag centers precludes the formation of significant π -stacking interactions. Despite the long Ag...Ag distance, the Bader analysis identifies a BCP between Ag centers, indicating that this structure captures the metallophilic interaction. In this limiting case, the stabilization energy of the **Ag-1** dimer is consistent with the 5–15 kcal mol^{−1} range for argentophilic interactions.¹⁷ Conversely, the energy stabilization of the dimeric structure calculated using the ω B97X-D functional is significantly larger: 47.16 kcal mol^{−1}. Because this method better accounts for intermolecular interactions, the stabilization energy reflects the sum of metallophilic, π -stacking, hydrophobic, and other noncovalent interactions.

CONCLUSION

Here, we have provided rare examples of Ag(III)...Ag(III) argentophilic interactions in silver corrole complexes. The monomeric complex **Ag-1** exhibits a dimeric structure in the solid state. Although the Bader analysis does not identify a BCP between Ag atoms, there is a nonnegligible interaction between metal centers. **Ag-1** exhibits weak emission, further supporting the presence of an argentophilic interaction in this complex. A pacman architecture (**Ag-2**) was then exploited to enforce a cofacial arrangement of two Ag(III) corroles. In the solid state, the Ag centers exhibit a close 3.67 Å contact. This metallophilic interaction results in significant compression of the xanthene backbone and an unusual domed conformation of the corrole. The Bader analysis identifies a BCP between the two metal centers in **Ag-2**, demonstrating that this is a closed-shell dispersion interaction. The argentophilic interactions reported in this study form directly from Ag(III) complexes, as opposed to the oxidation of Ag(II) species to generate the Ag(III)...Ag(III) argentophilic interaction.^{20,21} This study demonstrates that the xanthene backbone is sufficiently flexible to accommodate metallophilic interactions and may serve as a general platform to interrogate metal–metal interactions. This pacman corrole architecture can readily be extended to other, more flexible backbone spacers, such as diphenyl ether,⁶⁸ to potentially enable closer M...M interactions. Similarly, a shorter rigid backbone, such as biphenylene, may help to maximize the overlap of the corrole macrocycles (i.e., minimize the slip angle and lateral shift), similar to xanthene, while decreasing the distance between metal centers.

The potential utility of Ag(III)...Ag(III) argentophilic interactions may be inferred from the reports of other metallophilic interactions, which can impart unique physical and optical properties. For example, Ag₃[Co(CN)₆]₂ exhibits “colossal” positive and negative thermal expansion that is an order of magnitude greater than typical crystalline materials. The Ag(I) ions are arranged in a hexagonal kagomé lattice with a ~3.5 Å distance between Ag centers.¹⁰⁶ These argentophilic interactions impart flexibility in the lattice, which gives rise to this unique phenomenon.¹⁰⁷ Because many compounds with metallophilic interactions exhibit luminescence, perturbation of this emission could be leveraged for chemosensing applications. Pacman porphyrin architectures can bind guest molecules, such as 2-aminopyrimidine¹⁰⁸ or the acridinium ion,¹⁰⁹ in the cleft between macrocycles. In both cases, guest binding modulates the photophysical properties of the pacman porphyrin. Cofacial corrole dyads analogous to **Ag-2** could bind a guest molecule in the cleft to perturb the Ag(III)...Ag(III) interaction and quench any associated emission,

serving as a fluorescent turn-off sensor. The continued identification of novel platforms that support metallophilic interactions will allow molecules to be tailored for future applications.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.2c02285>.

Summary of the crystallographic data, ^1H and ^{19}F NMR spectra, other characterization data, and results of DFT calculations (PDF)

Accession Codes

CCDC 1046908, 1046909, and 2180997 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

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