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Synthesis and Crystal Structures of Binuclear Metallocyclophane with N-Heterocyclic Carbene Linkage by the $\pi-\pi$ Stacking Interaction

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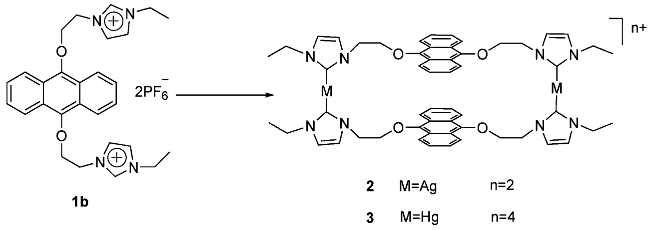
Summary: The synthesis and crystal structures of binuclear silver(I) and mercury(II) metallocyclophanes with N-heterocyclic carbene linkages by the $\pi-\pi$ stacking interaction are described.

Introduction

Since the discovery of stable imidazoline-2-ylidene by Arduengo et al. in 1991,[1] N-heterocyclic carbenes (NHCs) have received considerable attention due to their strong σ-donor ability to complex with transition metals and main group elements.[2] As ancillary ligands, N-heterocyclic carbene complexes are an attractive alternative to the widely utilized phosphine complexes in organometallic catalysis.[3]

On the other hand, much interest has been focused on metallocyclophane for many years owing to its particular molecular recognition properties and potential applications as chemsonsors and electron transfer assemblies.[4−6] Recently, a variety of N-heterocyclic carbene-linked cyclophanes and their metal complexes have been reported.[7] However, to our best knowledge, there are only a few examples[8] of binuclear metallocyclophanes bearing an N-heterocyclic carbene linkage derived from flexible ligands. Our group has prepared a series of bimetallocyclophanes by the $\pi-\pi$ stacking interaction approach from a flexible phosphine ligand in high yield.[5b] In contrast to the weak-link approach[9] in which the formation of the dinuclear complex is favored owing to the coordination of hemilabile ligands with transition metal centers in a bidentate fashion, the new method does not need two coordination positions to a metal center in the flexible ligand. Herein we report the synthesis and X-ray crystal structures of binuclear silver(I) (**2**) and mercury(II) (**3**) metallocyclophanes from a flexible bicarbene ligand by the $\pi-\pi$ stacking interaction.

Scheme 1



Results and Discussion

The imidazolium precursor 9,10-bis(*N*-ethylimidazoliumethoxy)anthracene dichloride **1a** was prepared by reaction of 9,10-bis(2-chloroethoxy)anthracene[10] with *N*-ethylimidazole in a 1:2 molar ratio and was obtained as a pale yellow powder with poor solubility in common organic solvents. The corresponding hexafluorophosphate salt **1b** was obtained by anion exchange with NH$_4$PF$_6$ in methanol. **1a** and **1b** show similar ^{1}H and ^{13}C NMR spectra, and the chemical shifts are consistent with those of other known imidazolium salts.[2b]

Reaction of imidazolium salt **1b** with Ag$_2$O in CH$_3$CN gave the bisilver cyclophane **2** (Scheme 1). Diffusion of ether into a DMSO and acetone solution of **2** afforded pale yellow crystals of **2**, which were relatively stable in the air and slightly light sensitive. In the ^{1}H NMR spectrum of **2**, the carbonium proton resonance

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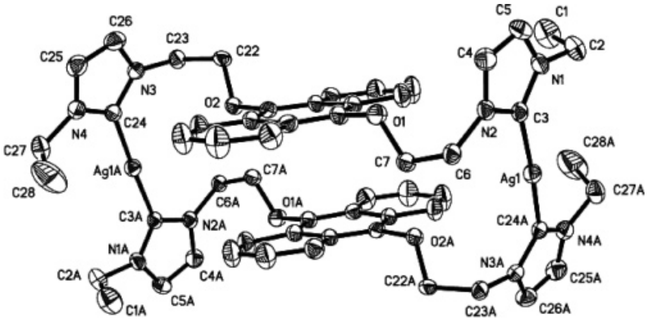

Figure 1. ORTEP view of the cationic part of **2** with 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

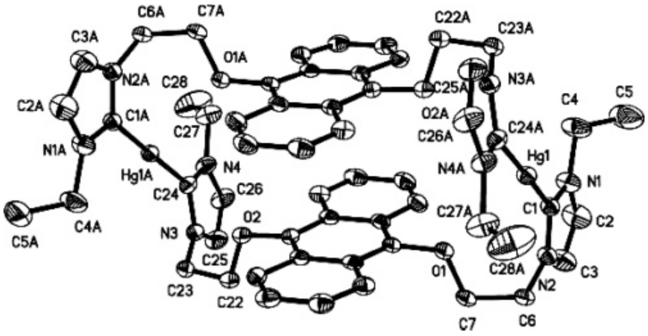

Figure 2. ORTEP view of the cationic part of **3** with 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity.

disappeared. However, the peak for the Ag-carbene carbon in the ^{13}C NMR spectrum could not been found; it could be detected only by the absence of the resonance for its carbonium carbon at 136.59 ppm.

The bimercury cyclophane **3** was obtained by reaction of imidazolium salt **1b** with $Hg(OAc)_2$ in high yield according to the literature method.[11] **3** is very stable in air and has good solubility in acetone and acetonitrile. Crystals of **3** suitable for single-crystal X-ray diffraction were obtained from slow diffusion of ether into its acetonitrile solution. The formation of the mercury-carbene complex was confirmed by the disappearance of the carbonium proton in the ^{1}H NMR spectrum and the appearance of a resonance at 175.4 ppm in the ^{13}C NMR.

The molecular structures of complex **2** and **3** in the solid state are depicted in Figure 1 and Figure 2, respectively. They have similar structures and crystallize as bimetallocyclophanes. Two anthracene rings in the molecule of complexes **2** and **3** are parallel, with a distance of 3.64 and 3.68 Å, respectively, and exhibit a significant $\pi-\pi$ stacking interaction.[12] The significant difference is that there are trans- and cis-configurations of the $-CH_2CH_2-$ linkages on the 9,10-dioxyanthracene units in **2** and **3**, respectively.

The dihedral angles of two imidazolium rings coordinated to the same metal atoms are 9.1° (**2**) and 14.2° (**3**). The separation of Ag(1)−Ag(1A) is 11.797 Å, which is longer than that of Hg(1)−Hg(1A) (10.468 Å). The geometry at the Ag or Hg atom is nearly linear, with a C−Ag−C bond angle of 176.0° (**2**) and C−Hg−C bond angle of 176.3° (**3**), and with bond distances of Ag−C(3) = 2.075(6) Å, Ag−C(24A) = 2.076(6) Å, Hg(1)−C(24A) = 2.053(7) Å, and Hg(1)−C(1) = 2.060(7) Å (Table 2).

Table 1. Crystal Data and Structure Refinement for 2 and 3

	2	3
empirical formula	$C_{56}H_{60}Ag_2F_{12}N_8O_4P_2\cdot 2DMSO\cdot Et_2O$	$C_{56}H_{60}F_{24}Hg_2N_8O_4P\cdot 7CH_3CN$
fw	1645.18	2177.53
temperature (K)	293(2)	293(2)
wavelength (Å)	0.71073	0.71073
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$	$C2/c$
unit cell dimens		
a (Å)	11.563(6)	21.634(3)
b (Å)	14.122(7)	34.632(5)
c (Å)	14.828(8)	4.4450(19)
α (deg)	62.189(8)	90
β (deg)	75.631(9	26.142(2)
γ (deg)	66.245(8)	90
volume (Å^3)	1954.8(17)	8739.8(19)
Z	1	4
calcd density (Mg/m^3)	1.397	1.655
abs coeff (mm^{-1})	0.675	3.687
F(000)	842	4296
cryst size (mm)	0.18 × 0.16 × 0.10	0.22 × 0.18 × 0.14
θ_{max}, θ_{min} (deg)	1.56, 25.01	1.18, 26.40
no. of data collected	13 008	25 327
no. of unique data	6871	8945
no. of refined params	521	609
goodness-of-fit on F^2	1.098	1.034
final R indices [$I > 2\sigma(I)$]		
R1	0.0558	0.0408
wR2	0.1555	0.1073
R indices (all data)		
R1	0.0869	0.0789
wR2	0.1836	0.1398

[a] GOF = $[\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of parameters refined. [b] R1 = $\sum(||F_o| - |F_c||)/\sum|F_o|$; wR2 = $\{w[\sum(|F_o| - |F_c|)^2]/\sum|F_o|^2\}^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 2 and 3

2		3	
	Bond Lengths		
Ag(1)−C(3)	2.075(6)	Hg(1)−C(24A)	2.053(7)
Ag(1)−C(24A)	2.076(6)	Hg(1)−C(1)	2.060(7)
N(1)−C(3)	1.344(7)	N(1)−C(1)	1.324(9)
N(1)−C(5)	1.387(8)	N(1)−C(2)	1.384(11)
N(2)−C(3)	1.360(7)	N(2)−C(1)	1.330(8)
N(2)−C(4)	1.377(7)	N(2)−C(3)	1.357(10)
	Bond Angles		
C(3)−Ag(1)−C(24A)	176.0(2)	C(24A)−Hg(1)−C(1)	176.3(3)
N(1)−C(3)−Ag(1)	128.6(4)	N(1)−C(1)−Hg(1)	127.9(5)
N(2)−C(3)−Ag(1)	126.7(4)	N(2)−C(1)−Hg(1)	124.4(5)
N(1)−C(3)−N(2)	104.6(5)	N(1)−C(1)−N(2)	107.7(6)

A perspective view of the packing diagram of cyclophane **2** is shown in Figure 3. It displays a unidirectional linear chain conformation with intermolecular Ag−Ag contacts of 3.456 Å, which is very close to the van der Waals radii for two silver atoms[13] and shorter than the known Ag−Ag interactions in the literature.[14−16]

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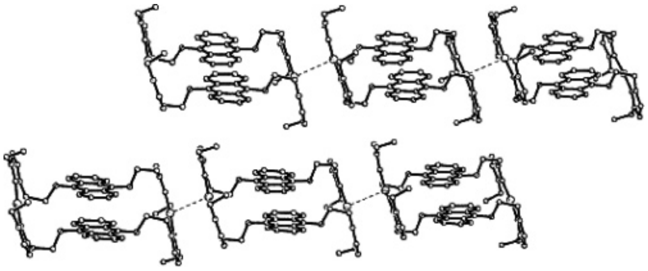

Figure 3. Packing diagram of the cationic part of **2**. Hydrogen atoms have been omitted for clarity.

Thus the argentophilic interactions led to the formation of a unidirectional linear chain conformation. For the cyclophane **3**, no intermolecular metal−metal and other interactions are observed.

Conlusion

We have synthesized N-heterocyclic carbene bisilver(I) and bimercury(II) cyclophanes **2** and **3** in high yields by the $\pi-\pi$ stacking interaction. The chemistry of complex **2** as a carbene transfer reagent[17] with transition metals and the investigation of the photophysical behaviors of **2** and **3** are being carried out, and it is expected that this type of bimetallocyclophanes could possess some novel properties in supramolecular chemistry.

Experimental Section

General Procedures. 9,10-Bis(2-chloroethoxy)anthracene and *N*-ethylimidazole were prepared as reported in the literature. All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques, and solvents were purified by standard procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer. Chemical shifts, δ, are reported in ppm relative to the internal standard TMS. *J* values are given in Hz. Elemental analyses were measured using a Yanaco MT-3 elemental analyzer.

Preparation of 1a and 1b. A mixture of 1,2-bis(2-chloroethoxy)anthracene (3.35 g, 10 mmol) and 1-ethylimidazole (2.11 g, 22 mmol) was refluxed in 1,4-dioxane (60 mL) for 3 days, giving a pale yellow precipitate. The product **1a** was filtered and washed with 1,4-dioxane and recrystallized from methanol and ethyl ether. Yield: 3.21 g, 61%. Anal. Calc for $C_{28}H_{32}Cl_2N_4O_2$: C, 63.76; H, 6.11; N, 10.62. Found: C, 63.68; H, 6.01; N, 10.55. ^{1}H NMR (300 MHz, d_6-DMSO, 25 °C): δ 9.75 (s, 2imi*H*, 2 H), 8.13 (s, 4 or 5imi*H*, 2 H), 8.06 (s, 4 or 5imi*H*, 2 H), 7.89−7.86 (m, An-*H*, 4 H, An = anthracene), 7.54−7.51 (m, An-*H*, 4 H), 4.90 (t, *J* = 4.5 Hz, OC*H*$_2$CH$_2$, 4 H), 4.48 (t, *J* = 4.3 Hz, OCH$_2$C*H*$_2$, 4 H), 4.35 (q, *J* = 7.4 Hz, C*H*$_2$CH$_3$, 4 H), 1.51 (t, *J* = 7.2 Hz, CH$_2$C*H*$_3$, 6 H) ppm. ^{13}C NMR (75 MHz, d_6-DMSO, 25 °C): δ 145.89, 136.87, 125.99, 124.13, 123.09, 122.46, 121.79, 73.21, 66.31, 49.41, 44.32, 15.42 ppm.

NH_4PF_6 (1.96 g, 12 mmol) was added to the methanol solution of **1a** (2.64 g, 5 mmol). A white precipitate formed immediately, which was collected by filtration, washed with small portions of methanol, and dried in a vacuum to give **1b** as a pale yellow powder. Yield: 3.54 g, 95%. Anal. Calc for $C_{28}H_{32}F_{12}N_4O_2P_2$: C, 45.05; H, 4.32 N, 7.51. Found: C, 45.10; H, 4.36; N, 7.42. ^{1}H NMR (300 MHz, d_6-DMSO, 25 °C): δ 9.49 (s, 2imi*H*, 2 H), 8.05 (s, 4 or 5imi*H*, 2 H), 7.99 (s, 4 or 5imi*H*, 2 H), 7.89−7.86 (m, An-*H*, 4 H), 7.55−7.51 (m, An-*H*, 4 H), 4.87 (t, *J* = 4.5 Hz, OC*H*$_2$CH$_2$,4 H), 4.47 (t, *J* = 4.3 Hz, OCH$_2$C*H*$_2$, 4 H), 4.34 (q, *J* = 7.4 Hz, C*H*$_2$CH$_3$, 4 H), 1.51 (t, *J* = 7.3 Hz, CH$_2$C*H*$_3$, 6 H) ppm. ^{13}C NMR (75 MHz, d_6-DMSO, 25 °C): δ 145.84, 136.59, 126.12, 124.16, 123.08, 122.39, 121.71, 72.99, 49.49, 44.45, 15.27 ppm.

Bisilver Cyclophane 2. To a solution of **1** (746 mg, 1.0 mmol) in CH_3CN (60 mL) was added Ag_2O (364 mg, 1.57 mmol), and the mixture was refluxed under argon for 20 h. The resulting solution was filtered and concentrated to 5 mL, and Et_2O (30 mL) was added to precipitate a pale yellow powder. Isolation by filtration yielded **2a**. Yield: 432 mg, 61%. Anal. Calc for $C_{56}H_{60}Ag_2F_{12}N_8O_4P_2$: C,47.54; H, 4.27; N, 7.92. Found: C, 47.62; H, 4.19; N, 7.85. ^{1}H NMR (300 MHz, *d*-DMSO, 25 °C): δ 7.64 (s, 4 or 5imi*H*, 2 H), 7.55 (s, 4 or 5imi*H*, 2 H), 7.26−7.23 (m, An-*H*, 4 H), 6.89−6.86 (m, An-*H*, 4 H), 4.75 (t, OC*H*$_2$CH$_2$, 4 H), 4.42 (q, *J* = 7.0 Hz C*H*$_2$CH$_3$, 8 H), 3.99 (t, OCH$_2$C*H*$_2$, 4 H), 1.63 (t, *J* = 7.2 Hz, CH$_2$C*H*$_3$, 6 H) ppm. ^{13}C NMR (75 MHz, d_6-DMSO, 25 °C): δ 145.06, 124.57, 123.30, 123.05, 121.63, 120.91, 74.48, 51.39, 46.32, 17.62 ppm.

Bimercury Cyclophane 3. To a solution of **1** (746 mg, 1.0 mmol) in CH_3CN (70 mL) was added $Hg(OAc)_2$ (350 mg, 1.1 mmol), and the mixture was refluxed under argon for 24 h. The resulting solution was evaporated to dryness, and the residue was washed with water. Recrystallization from CH_3CN and Et_2O produced a pale yellow powder. Yield: 850 mg, 90%. Anal. Calc for $C_{56}H_{60}Hg_2F_{24}N_8O_4P_4$: C, 35.58; H, 3.19; N, 5.93. Found: C, 35.62; H, 3.23; N, 5.86. ^{1}H NMR (300 MHz, *d*-DMSO, 25 °C): δ 8.05 (s, 4 or 5imi*H*, 2 H), 7.99 (s, 4 or 5imi*H*, 2 H), 7.83−7.79 (m, An-*H*, 4 H), 7.49−7.46 (m, An-*H*, 4 H), 4.95 (t, *J* = 4.2 Hz, OC*H*$_2$CH$_2$, 4 H), 4.44−4.35 (m, OCH$_2$C*H*$_2$ and C*H*$_2$CH$_3$, 8 H), 1.50 (t, *J* = 7.2 Hz, CH$_2$C*H*$_3$, 6 H) ppm. ^{13}C NMR (75 MHz, d_6-DMSO, 25 °C): δ 175.30, 173.93, 144.85, 136.51, 125.99, 124.71, 124.01, 122.91, 73.87, 50.74, 46.06, 44.45, 16.44 ppm.

X-ray Crystallography. Suitable crystals of **2** and **3** were mounted on a glass fiber in a random orientation. The structures were solved by direct methods, and all non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using the SHELXTL package. Data collection was performed at room temperature on a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 20 mA using Mo Kα radiation (0.71073 Å). An empirical absorption correction was applied using the SADABS program. All hydrogen atoms were generated geometrically (C−H bond lengths fixed at 0.96 Å), assigned appropriated isotropic thermal parameters, and included in structure factor calculations. More details on data collection and structure calculation are summarized in Table 1.

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Supporting Information Available: Data for complexes **2** and **3** in cif format. This material is available free of charge via the Internet at http://pubs.acs.org.

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