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# Synthesis and structural characterization of a $[Ag_4]^{4+}$ cluster stabilized by a mixed-donor *N*-heterocyclic carbene linked cyclophane and the first reported synthesis of a *N*-heterocyclic carbene complex in water

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## Abstract

The synthesis of the tetranuclear $Ag_4^{4+}$ cluster stabilized by a *N*-heterocyclic carbene macrocycle **(3)[PF$_6$]$_4$**. Decomposition of the tetranuclear cluster **(3)[PF$_6$]$_4$** in light forms the dimeric species **(2)[PF$_6$]$_2$**. In situ synthesis of the dimeric silver *N*-hetrocyclic carbene complex (**2**)[**Br**]$_2$ in water.

*Keywords:* *N*-heterocyclic carbene; Silver carbene; Silver cluster; X-ray structures

The original reports of metal complexes of *N*-heterocyclic carbenes by Öfele and Wanzlick, [1] the continuing investigations of Lappert, [2] and the isolation of free carbenes by Arduengo [3] provided the foundation to a growing area of chemistry [4]. A recent advance is the use of silver carbene complexes as carbene transfer reagents [5]. Most of the silver complexes reported contain monodentate [4,6] carbenes as ligands, however mixed-donor multidentate [7] carbene ligands have received attention. We recently reported the silver complex [**2**][PF$_6$]$_2$ derived from the imidazolium-linked cyclophane (**1**) [7e]. In the solid state, [**2**][PF$_6$]$_2$ has a dimeric structure with the general formula [Ag$_2$(**1***)$_2$][PF$_6$]$_2$, where **1*** denotes deprotonated **1** (Fig. 1).

The interest in *N*-heterocyclic carbene complexes that possess water stability and have catalytic activity in water is an increasingly important area of research [8]. Metal complexes that contain $^{111}$Ag have potential for use in chemotherapy provided they have sufficient stability in vivo [9].

Previously, we have reported a pyridine–pyrrole carbene linked cyclophane that is exceptional in stabilizing silver clusters [7f]. We report herein the synthesis and structural characterization of the $[Ag_4]^{4+}$ cluster, [Ag$_4$(**1***)$_2$][PF$_6$]$_4$ [**3**][PF$_6$]$_4$. We also report the synthesis of a *N*-heterocyclic carbene silver complex in aqueous solution and the conversion of one silver complex to another with light.

Treatment of four equivalents of $Ag_2O$ with [**1**][PF$_6$]$_2$ in DMSO at 55 °C yields [**3**][PF$_6$]$_4$ as a white solid Eq. (1). The $^1$H- and $^{13}$C-NMR spectra of **3** give broad absorbencies for all atoms involved. However, the spectra are consistent with the structure of **3**. The most striking difference in the $^1$H-NMR spectrum is the loss of the imidazolium protons at 8.6 ppm, due to the complexation of the carbene to the bridging silver atoms. The $^{13}$C-NMR spectrum gives a carbene resonance as a broad peak from 162–165 ppm. The chemical shift and the broadness of the resonance are consistent with similar *N*-heterocyclic carbene silver complexes [7f].

The imidazolium bromide salt, [**1**][Br]$_2$, was treated with four equivalents of $Ag_2O$ in water. The reaction afforded the dinuclear silver *N*-heterocyclic complex,

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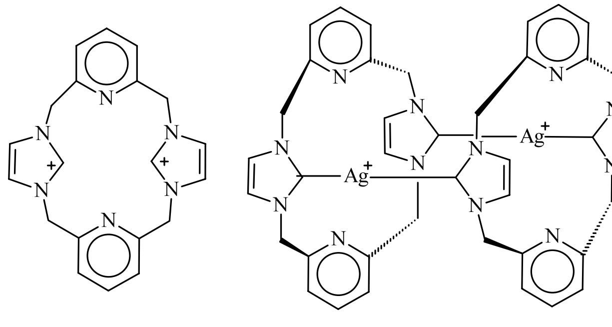


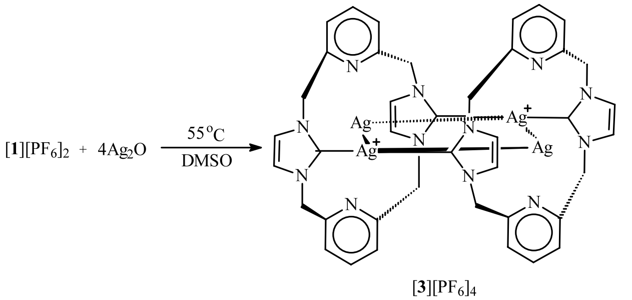
[**1**][$PF_6$]$_2$ [**2**][$PF_6$]$_2$ = [$Ag_2$(**1***)$_2$][$PF_6$]$_2$

Fig. 1. Imidazolium-linked cyclophane (**1**) and the dimeric silver complex (**2**).

[**2**][Br]$_2$. The $^1$H and $^{13}$C were virtually identical to those of the $PF_6$ counterpart [7d]. The fact that the reaction occurs in water indicates that the mechanism is concerted and kinetically controlled. Solvent is a controlling factor in determining which cation, **2** or **3**, is formed. Presumably formation of the silver cluster [**3**][$PF_6$]$_4$ is due to the solubility of the $AgPF_6$ in DMSO. This allows the additional silver atoms to insert themselves into the pockets of the [**2**][$PF_6$]$_2$. On the other hand, AgBr is insoluble in water and does not coordinate to [**2**][Br]$_2$.

Using $^1$H-NMR, water and light stability studies were performed on [**2**][Br]$_2$ and [**3**][$PF_6$]$_4$. In the absence or presence of light, the complex [**2**][Br]$_2$ showed no decomposition in $D_2O$ when monitored for 2 months. Allowing [**3**][$PF_6$]$_4$ to stand in light for 2 days induced dissociation of $AgPF_6$ affording [**2**][$PF_6$]$_2$. Studies done in the solid state as well as in solutions of acetonitrile and DMSO resulted in the formation of [**2**][$PF_6$]$_2$ from [**3**][$PF_6$]$_4$.

The light sensitivity of [**3**][$PF_6$]$_4$ prompted us to examine the UV–vis spectra of the compounds discussed here. The UV–vis spectra of [**1**][$PF_6$]$_2$, [**2**][$PF_6$]$_2$, and [**3**][$PF_6$]$_4$ in acetonitrile all show an absorption at 261 nm. Compounds [**2**][$PF_6$]$_2$, and [**3**][$PF_6$]$_4$ show an additional absorption at 232 nm. The absorption at 261 nm can be assigned to the pyridine rings in the cyclophanes. There is no one band in the UV–vis spectrum that accounts for the light sensitivity of [**3**][$PF_6$]$_4$ relative to the non-sensitivity of [**2**][$PF_6$]$_2$.



[**3**][$PF_6$]$_4$

(1)

Crystals suitable for X-ray diffraction were obtained by slow evaporation of a concentrated acetonitrile solution of [**3**][$PF_6$]$_4$. Complex [**3**][$PF_6$]$_4$ consists of an unusual centrosymmetric $[Ag_4]^{4+}$ cluster that has unique interactions involving silver cations and the carbene rings. The tetracation has three mirror planes. The $Ag_4^{4+}$ ion cluster is a planar parallelogram with Ag(1)–Ag(2) distances of 2.8512(8) Å and Ag(1)–Ag(2)–Ag(1A) and Ag(2)–Ag(1)–Ag(2A) interatomic angles of 108.14(3)° and 71.86(3)°, respectively. The Ag(1)–Ag(2) distances is comparable to that observed in elemental Ag at 2.89 Å. The non-bonding Ag(2)–Ag(2A) cross ring distance (3.3460(17) Å) is considerably longer than the bonding Ag(1)–Ag(2) (2.8512(8) Å) interactions. The theoretical investigation of the $d^{10}$–$d^{10}$ silver bonding in these and related structures is currently in progress. The bridging silver cations (Ag(1) and Ag(1A) also interact with the carbenes from the neighboring macrocycle. The C(6)–Ag(1)–C(6C) angle is linear (179.8(4)°) with the Ag–carbene bond distance of 2.133(6) Å being slightly larger than the bridging Ag–carbene distance of 2.084(9) Å in [**2**][$PF_6$]$_2$ [7d]. These values are quite consistent with a sigma bonding interaction. The non-bridging Ag(2) cations are coordinated to the pyridines with nitrogen–silver distances of 2.671(6) Å. Complex **3** also shows an interesting bonding mode with respect to the carbene rings. The carbene rings are tilted in toward the center of the molecule and exhibit short bonding contacts with the non-bridging silver cations Ag(2) of 2.350(6) Å. This may be due to π-bonding interactions. Based on previous work [7e], we have assigned this interaction as a $\eta^1$-carbene silver bond. Alternatively one could view the interaction between Ag(1), Ag(2) and C(6) as a three center-two electron bond (Fig. 2).

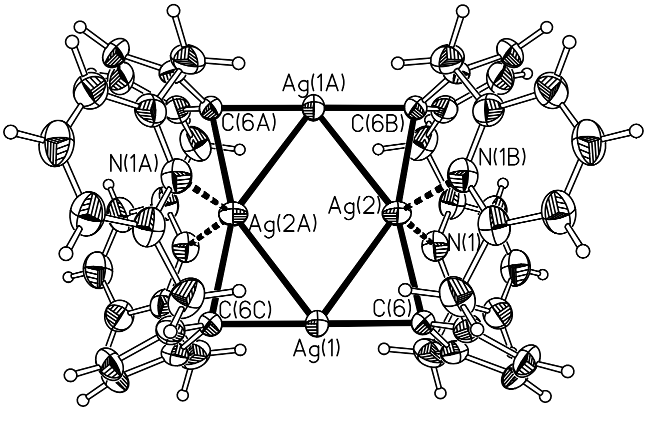


Fig. 2. Molecular structure of the tetracationic portion of [$Ag_4$(**1***)$_2$][$PF_6$]$_4$ **3** with thermal ellipsoids drawn at a 50% probability. Selected bond lengths (Å), and angles (°): Ag(1)–Ag(2) = 2.8512(8), Ag(2)–C(6) = 2.350(6), Ag(1)–C(6) = 2.133(6), Ag(2)–N(1) = 2.671(6), C(6)–Ag(1)–C(6C) = 179.8(4).

In conclusion, we have demonstrated that silver carbene complexes can be synthesized in water. In addition, the synthetic studies have shown that the nature of the product is dependent on the solvent with a dinuclear silver complex being produced in water and a tetranuclear silver complex resulting from DMSO. The tetranuclear silver complex undergoes dissociation of two $AgPF_6$ moieties with light to give the dinuclear silver complex. We are currently examining the complexation chemistry of the dinuclear silver complex with other metals and using theoretical calculations to examine the extent of $d^{10}$–$d^{10}$ bonding in the tetra silver complex.

## 1. Experimental

### 1.1. Synthesis of $[Ag_4(\mathbf{1}^*)_2][PF_6]_4$ (**3**)

[**1**][$\mathbf{PF_6}$] (0.634 g, 1.0 mmol) and $Ag_2O$ (0.928 g, 4.0 mmol) in DMSO (35 ml) were stirred for 18 h at 55 °C with exclusion of light. The solution was then filtered through Celite to obtain an orange solution. The collected material was then evaporated to obtain a brown powder. Slow evaporation of a concentrated acetonitrile solution gave **3** as colorless crystals. Yield: 0.370 g, 0.22 mmol, 44%. M.p.: $>220$ °C. Anal. Calc. for $Ag_4C_{40}H_{38}N_{12}P_4F_{24}O$: C, 28.03; H, 2.23; N, 9.81%. Found: C, 28.77; H, 2.51; N, 9.48%.

### 1.2. Synthesis of $[Ag_2(\mathbf{1}^*)_2][Br]_2$ ([**2**]$[Br]_2$)

[**1**][**Br**]$_2$ (1.61 g, 3.15 mmol), $Ag_2O$ (3.12 g, 13.48 mmol) and 50 ml of water were added to a 100 ml round bottom. The suspension was stirred for 18 h at 55 °C and then allowed to cool to room temperature. The suspension was then filtered through Celite and the filtrate was evaporated to obtain an off-white solid. Yield: 2.78 g, 2.62 mmol, 83%. M.p.: $>220$ °C. $^1$H-NMR 300 MHz ($CD_3OD$): $\delta$ 5.18 (d, 4H, $CH_2$, $J = 15.3$ Hz), 5.34 (d, 4H, $CH_2$, $J = 15.8$), 6.90 (s, 4H, N–CH–C), 7.29(d, 4H, *m*-pyridine, $J = 7.5$ Hz) 7.51 (t, 2H, *p*-pyridine, $J = 7.5$ Hz). Anal. Calc. for $Ag_2C_{40}H_{40}N_{12}Br_2O_2$: C, 43.96; H, 3.69; N, 15.39%. Found: C, 43.69; H, 3.93; N, 15.65%.

## 2. Supplementary material

Crystal data for [**3**]$[PF_6]_4$ $C_{20}H_{18}N_6Ag_2P_2F_{12}$: MW = 848.07, tetragonal, space group $P4(2)/mnm$, $a = b = 15.045(2)$ Å, $c = 15.182(3)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 3436.6(10)$ Å$^3$, $Z = 8$, $D_{calc} = 1.639$ Mg m$^{-3}$, $\mu = 1.317$ mm$^{-1}$, $T = 200$ K, Data was collected on a Nonius Kappa CCD using phi and omega scans, Refinement for data with $I > 2\sigma(I)$ (2155 reflections, $R_{int} = 0.0371$) gave $R_1(F) = 0.0471$ and $wR_2(F^2) = 0.1433$ for all data. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 181856 for compound **3**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: youngs@uakron.edu or www: http://www.ccdc.cam.ac.uk).

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