Cationic Tetrasilver Complex of Hexaphenylbenzene

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Polycyclic aromatic hydrocarbons (PAHs), due to the overall planarity of the molecules and their extended delocalized π system, have attracted considerable current attention concerning materials science.[1−3] Incorporation of metal ions into the PAH system through cation−π interactions has meanwhile had a further dramatic influence on the reactive properties of the fused polyaromatic solid surfaces[4−6] and resulted in potential applications in electrical conductors and photosensitive devices.[7,8] In an extension of our earlier work,[7,9] we now report a silver(I) complex with the propeller ligand hexaphenylbenzene (HPB). HPB, as an important organic molecule, and its derivatives have been structurally characterized.[10,11] To our surprise, however, HPB's potential for building supramolecular architecture for its unique geometry and overall dimensions has been neglected.[12] In this preliminary report, we present our results to show how the silver(I) ions are coordinated around the highly symmetrical propeller to build up a two-dimensional supramolecular architecture.

The reaction[13] of HPB with AgClO$_4$ in toluene leads to formation of the colorless complex, [Ag$_4$(HPB)(ClO$_4$)$_4$]. The compound is sparingly soluble in common organic solvents. It is reasonably stable in ambient daylight for 1 week, but shows moisture sensitivity under atmospheric conditions. The X-ray structural determination[14] reveals a two-dimensional framework constructed by Ag(I)−O linkage as well as π coordination of HPB with Ag(I). As illustrated in Figure 1, the center of the propeller coincides with the inversion center so that only half of the molecule is crystallographically unique. There exist two independent silver ions around the propeller, bridged by interactions with the same phenyl ring, C(16)−C(21). Each metal center interacts asymmetrically with two phenyl rings. While Ag(1) involves one η^1 and one η^2 bonding at Ag−C distances ranging from 2.420(9) to 2.75(1) Å, Ag(2) involves two η^2 interactions instead, at Ag−C separations ranging from 2.572(9) to 2.68 Å. The next closest contact between the silver atom and the C atoms is 2.88 Å, too long to be considered as evidence of an effective interaction. Thus, each centrosymmetrical HPB molecule interacts with four pseudotetrahedral Ag(I) ions in a hexa-η^2-di-η^1 fashion to form a cationic tetrasilver moiety, which is further linked to

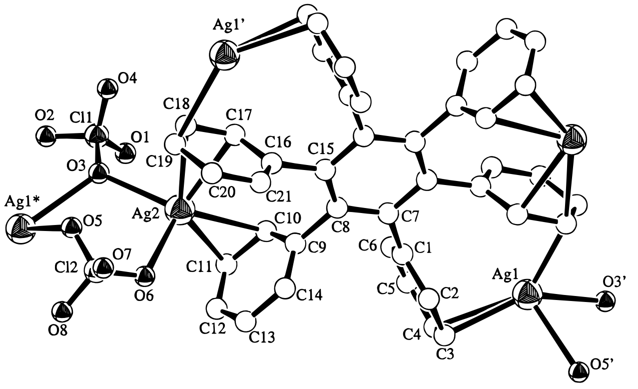

Figure 1. View of the molecular structure of [Ag$_4$(HPB)(ClO$_4$)$_4$] at the 50% probability level. Selected bond lengths (Å) and angles (deg): Ag(1)−O(3) 2.478(8), Ag(1)−O(5) 2.50(1), Ag(1)−C(3) 2.402(9), Ag(1)−C(4) 2.72(1), Ag(1)−C(19) 2.75(1), Ag(2)−O(3) 2.412(7), Ag(2)−O(6) 2.44(1), Ag(2)−C(10) 2.669(8), Ag(2)−C(11) 2.572(9), Ag(2)−C(17) 2.593(10), Ag(2)−C(18) 2.68(1); O(3)−Ag(1)−O(5) 71.2(3), C(3)−Ag(1)−O(3) 141.3(3), C(3)−Ag(1)−O(5) 94.6(3), C(3)−Ag(1)−C(19) 137.4(3), O(3)−Ag(1)−C(4) 119.7(3), O(3)−Ag(1)−C(19) 80.7(3), O(5)−Ag(1)−C(4) 108.9(3), O(5)−Ag(1)−C(19) 110.0(3), C(4)−Ag(1)−C(19) 140.3(3), O(3)−Ag(2)−O(6) 98.7(3), O(3)−Ag(2)−C(11) 112.7(3), O(3)−Ag(2)−C(10) 129.0(3), O(6)−Ag(2)−C(11) 102.3(4), O(6)−Ag(2)−C(10) 118.6(3), C(11)−Ag(2)−C(17) 115.2(3), C(11)−Ag(2)−C(18) 145.6(3), C(17)−Ag(2)−C(10) 84.2(3), C(10)−Ag(2)−C(18) 114.9(3), O(3)−Ag(2)−C(17) 108.1(3), O(3)−Ag(2)−C(18) 86.2(3), O(6)−Ag(2)−C(17) 118.8(4), and O(6)−Ag(2)−C(18) 102.9(4).

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(13) To a solution of hexaphenylbenzene (5.4 mg, 0.1 mmol) in 6 mL of toluene, which was heated gently to dissolve the hexaphenylbenzene, was added AgClO$_4$ (12.5 mg, 0.6 mmol). After about 20 min of stirring, the resultant colorless solution was introduced into a 7 mm diameter glass tube and layered with *n*-hexane as a diffusion solvent. The glass tube was sealed under Ar and wrapped with aluminum foil. After standing at room temperature for 3 weeks colorless prismatic crystals were obtained. (Anal. Calcd for C$_{21}$H$_{15}$Cl$_2$Ag$_2$O$_8$: C, 36.98; H, 2.22. Found: C, 36.40; H, 2.31.) **CAUTION:** Perchlorate salts of metal complexes with organic ligands are potentially explosive. Suitable care should be taken during the synthesis.

(14) Crystal data: C$_{21}$H$_{15}$Cl$_2$Ag$_2$O$_8$, M = 681.99, monoclinic, space group $P2_1/c$, crystal size 0.2 × 0.2 × 0.2 mm, a = 10.543(2) Å, b = 11.934(4) Å, c = 16.884(3) Å, β = 94.08(2)°, V = 2118.9(8) Å^3, Z = 4, D_c = 2.138 g/cm^3, μ(Mo Kα) = 21.44 cm^{-1}, F(000) = 1332.00, T = 293(2) K, 5116 reflections collected, 4859 unique reflections (R_{int} = 0.052), R = 0.056, R_w = 0.052.

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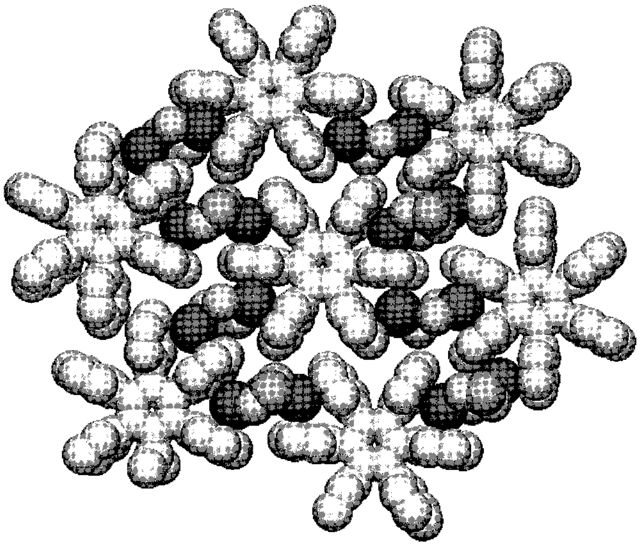

Figure 2. Two-dimensional sheet framework of $[Ag_4(HPB)(ClO_4)_4]$ (uncoordinated O and Cl omitted for clarity).

the adjacent counterpart by bridging of the two separate perchlorate ions between two metal centers, Ag(1)−O(3)−Ag(2) and Ag(1)−O(5)−Cl(1)−O(6)−Ag(2). The overall structure thus formed is a neutral two-dimensional framework, shown in Figure 2.

An essential feature of the structure presented here is the special arrangement and high degree of silver ions ordering around the peripheral rings of each hexaphenylbenzene molecule forming a novel 2-D sheet framework, which, to the best our knowledge, has not been described before. There is only one report in the literature describing HPB coordinated compound, $(\eta^6\text{-}C_6Ph_6)Co(\eta^2\text{-}C_2Ph_2)$, where the central benzene ring of C_6Ph_6 symmetrically interacts with the cobalt ion in an η^6 fashion.[12] In the present work, each peripheral benzene ring of the HPB molecule participates in η^2 and/or η^1 coordination binding to the silver ions. This is distinctive with conventional Werner type σ donation or ferrocene type η^5 coordination. Also, owing to the unique aromatic shape and the bulky hexasubstituted benzene preventing the approaching of the two adjacent hexaphenylbenzene molecules, the construction of the polymeric 2-D sheet is accomplished by utilizing the perchlorate anion bridging the cationic tetrasilver-HPB units. This is in sharp contrast to the pronounced interlinkage of metal ions and the aromatic hydrocarbons observed in our recently reported silver complexes having W-type sandwich and helical frameworks where the perchlorate anions act only as spacers to fill the unsaturated coordination environment of the metal ion.[7,9] In addition, it was found from the X-ray analysis that hexaphenylbenzene molecule in the present work retains its propeller conformation. The dihedral angles between the planar phenyl ring and the central benzene range from 76° to 88°, significantly larger than those observed in the noncoordinated HPB molecule (62−70.7°).[10] This twist is undoubtedly attributable to steric interference involving the silver(I)−π interaction of the peripheral rings. One can presume that the HPB group tends to reduce the intramolecular repulsions by displacing neighboring peripheral rings in a direction perpendicular to the central ring.

In conclusion, for a bulky hexasubstituted benzene, HPB, the coordination of silver(I) to the ligand can be realized by utilizing both cation−π interactions and anion bridging under proper synthesis conditions to construct a 2-D sheet network with a propeller architecture. Its unique structural features highlight potential application as functional materials. Further studies are directed toward the development of the structure-controlling process involving changing reaction conditions such as solvents and anions in an aim to design other novel frameworks and to explore the potential electrical properties in the system.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure determination of $[Ag_4(HPB)(ClO_4)_4]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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