[6]Helicene as a novel molecular tweezer for the univalent silver cation: Experimental and theoretical study

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HIGHLIGHTS

- ESI-MS method and X-ray crystallography were used for characterization of cation–π interaction.
- [6]Helicene–Ag^{+} complex was proven to be present in the gas phase.
- Monoclinic crystals of [6]helicene–silver perchlorate–monohydrate were formed in the solid state.

GRAPHICAL ABSTRACT
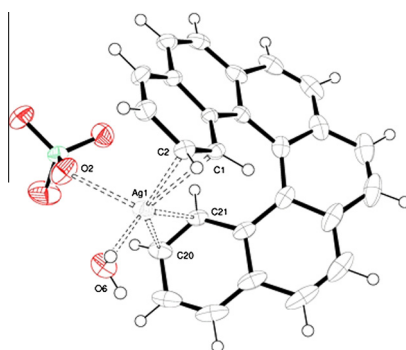
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ABSTRACT

By employing electrospray ionization mass spectrometry (ESI-MS), it was proven experimentally that the [6]helicene–Ag^{+} complex (i.e., $[Ag(C_{26}H_{16})]^+$) exists in the gas phase. Further, applying quantum mechanical DFT calculations, the most probable structure of this cationic complex $[Ag(C_{26}H_{16})]^+$ was derived. Finally, in the solid state, the complex [6]helicene–silver perchlorate–monohydrate (i.e., $C_{26}H_{16}$–$AgClO_4$–H_2O), crystallizing in the monoclinic system with the centro-symmetric $P2_1/c$ space group, was prepared and analyzed by X-ray crystallography.

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Introduction

Cation–π interaction refers to the noncovalent attraction between a cation (e.g., Li^{+}, Na^{+}, or K^{+}) and a π-system (e.g., benzene) [1]. Its strength is often comparable with the interaction between a cation and traditional ligands, including water, alcohols, and amines. As a result of the cation–π interaction, there are extraordinarily important driving forces in molecular recognition processes in many biological and artificial systems [2–5]. The cation–π interaction is a well-established phenomenon in gas phase, as well as in solid state [6–12], and is known to play an important role in the stabilization of tertiary structures of various proteins [13].

Helicenes are polycyclic aromatic compounds consisting of ortho-fused benzene rings with nonplanar topology with

C_2-symmetric axis perpendicular to the axis of helicity as a result of the steric repulsive interaction between terminal aromatic rings [14–16]. This makes them chiral even though they have no center of chirality. The highly delocalized large π-electron system of fully aromatic helicenes along with the previously mentioned inherent chirality predetermines their unique optical [17] and electronic [18] properties, as well as their use in many fields of research including supramolecular chemistry [19–24], molecular recognition [25,26], and asymmetric organo- or transition metal catalysis [27,28].

Recently, in the solid state, the complex Ag([7]helicene) [Al{OC(CF$_3$)$_3$}$_4$], crystalizing in the monoclinic system with the space group $P2_1/c$, where $a = 32.2189(8)$ Å, $b = 11.0863(2)$ Å, $c = 31.1869(7)$ Å, and $\beta = 115.412(1)°$, has been prepared by crystallization at -20 °C and analyzed by X-ray crystallography [24]. The structure determination of these racemic crystals revealed the presence of the left-handed and right-handed enantiomers (and associated counterions) in the asymmetric units. Besides, it should be noted that both anions and one coordinated dichloromethane molecule are disordered in the structure [24]. On the other hand, in the present work, electrospray ionization mass spectrometry (ESI-MS) was used as an experimental technique for characterization of the cation–π interaction between the univalent silver cation (Ag$^+$) and the electroneutral [6]helicene (C$_{26}$H$_{16}$; see Scheme 1) ligand in the gas phase. At this point it should be noted that up to now, a cation–π complex with [6]helicene has not been proven. Moreover, employing quantum mechanical DFT calculations, the most probable structure of the experimentally proven cationic complex [Ag(C$_{26}$H$_{16}$)]$^+$ was predicted. Finally, monoclinic crystals of the electroneutral complex [6]helicene–silver perchlorate–monohydrate (i.e., C$_{26}$H$_{16}$–AgClO$_4$–H$_2$O) were prepared at ambient temperature; the accurate structure of this complex in the solid state was determined by single-crystal X-ray crystallography.
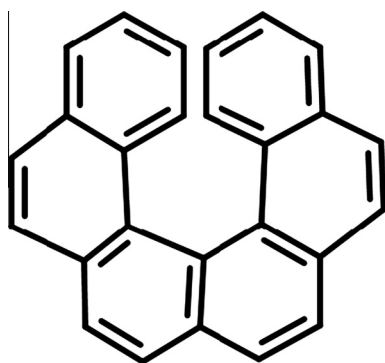
Experimental

Materials

[6]Helicene (puriss., ⩾99%) was purchased from Lach-ner, Czech Republic, while silver perchlorate (puriss., ⩾99%), AgClO$_4$, was supplied by Fluka. At this point it should be stated that silver has two stable isotopes, i.e., ^{107}Ag (natural abundance: 51.839%) and ^{109}Ag (natural abundance: 48.161%). The other chemicals used (Lachema, Brno, Czech Republic) were of reagent grade purity.

ESI-MS method

The experiments were performed with a Finnigan LCQ Advantage ion-trap mass spectrometer (ThermoFinnigan, San Jose, CA, USA) as well as with a Synapt G2 Q-ToF mass spectrometer (Waters, UK) fitted with an electrospray ionization source. Diluted solution of [6]helicene with AgClO$_4$ (both ~2.5 mg/L) in acetonitrile/chloroform (1:1) were introduced into the ESI source via a fused-silica capillary at a flow rate of 0.6 mL/h. Nitrogen was used as the nebulizer gas. The operating conditions for the ion-trap mass spectrometer were set as follows: spray voltage 4.8 kV, capillary voltage 35 V, heated capillary temperature 250 °C, sheath gas flow rate and auxiliary gas flow rate 20–30 arbitrary units. In case of the ToF mass spectrometer, we applied the following operating conditions: capillary voltage 3.5 kV, sampling and extraction cone voltage 38 and 4 V, source and desolvation temperature 100 and 350 °C, cone and desolvation gas flow rate 50 and 450 L/h. Mass spectra were recorded from m/z 50 to 1200.

X-ray crystallography

Monoclinic crystals of the electroneutral complex [6]helicene–silver perchlorate–monohydrate (i.e., C$_{26}$H$_{16}$–AgClO$_4$–H$_2$O) were prepared by slow evaporating the solvent from a solution obtained by mixing equimolecular amounts of [6]helicene and silver perchlorate in toluene at ambient temperature. Single-crystal data for [6]helicene–silver perchlorate–monohydrate were obtained using a Xcalibur PX diffractometer with monochromatized Cu(Kα) radiation ($\lambda = 1.54180$ Å) at 190 K. *CrysAlisProCCD* [29] was used for data collection, cell refinement, and data reduction. The structure was solved by charge flipping methods using the program *SUPERFLIP* [30] and refined by full-matrix least-squares on F with *CRYSTALS* [31]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were found on a difference Fourier map, those on carbon atoms were recalculated into idealized positions, and then refined with riding constraints. The crystallographic data are summarized in Table 1.

Computational methods

The theoretical calculations were carried out at the density functional level of theory using modern hybrid ωB97X-D functional of Head-Gordon et al. including empirical dispersion correction with improved behavior for non-covalently bonded systems [32] and the Ahlrichs def2-SVP basis set with effective core

Scheme 1. Structural formula of [6]helicene (C$_{26}$H$_{16}$).

Table 1
Crystallographic data and experimental details for [6]helicene–silver perchlorate–monohydrate (i.e., C$_{26}$H$_{16}$–AgClO$_4$–H$_2$O).

Empirical formula	C$_{26}$H$_{18}$AgClO$_5$
Formula weight	553.75
Temperature	190 K
Wavelength	1.54180 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 13.0193(3)$ Å
	$b = 11.7957(2)$ Å
	$c = 13.5714(3)$ Å
	$\beta = 95.5021(19)°$
Volume	2074.58(7) Å^3
Z	4
Density (calculated)	1.77 g cm^{-3}
Absorption coefficient	9.315 mm^{-1}
F(000)	1112
Crystal dimensions (mm)	0.25 × 0.68 × 0.77
Crystal color	Light brown
No. of measured/independent reflections	29,811/4282
No. of reflections with $I > 2\sigma I$	4158
No. of parameters	299
Final R, wR($I > 2\sigma(I)$)	$R_1 = 0.039$, $wR_2 = 0.050$
Goodness of fit on F^2	1.047
Extinction coefficient	46 (4)
Largest diff. peak and hole	1.91 and -1.15 e Å^{-3}