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Homoleptic Silver(I) Acetylene Complexes**

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The uptake of simple gases by metal ions is of great current interest because of possible applications in gas storage and in gas activation reactions. Owing to the easier access, homoleptic metal complexes of simple gases were predominantly studied by mass spectrometry (MS). For example, $[M(L)_n]^+$ (M = Cu, Ag: L = C_2H_4, $n = 1, 2$; [1] L = CO, $n = 1$–4;[2] L = H_2, $n = 1$–6[3]) were investigated with this method and, in some cases, thermodynamic data for the complexation could be extracted. Such experimental complexation energies may help to design gas storage systems.[4] However, MS data of the coinage metal cation/acetylene (HC≡CH) system are not available.

In condensed phases, gas-phase cations of the type $[M(L)_n]^+$ have to be partnered with suitable very weakly coordinating anions (WCAs).[5,6] Large WCAs display dimensions in the range of a few nanometers and considerably separate anions and cations, which effectively diminishes coulombic interactions[7] and resembles the situation in the gas phase, that is, they produce pseudo-gas-phase conditions in condensed phases.[5,7] In agreement with this assessment, WCA salts of unusual gas-phase complexes such as $[Au(Xe)_4]^{2+}$[8,9] or $[M(CO)_n]^+$ ($n = 1$–4, M = Cu,[10] Ag[11–13]) were prepared.

WCAs of the type $[Al(OR^F)_4]^-$ (OR^F = fluoroalkoxide)[14–17] also allow the stabilization and full characterization of salts of gas-phase cations that were previously known only from MS experiments.[7,18–21] Herein, we used the pseudo-gas-phase conditions induced by the $[Al(OR^F)_4]^-$ anions to stabilize salts of the $[Ag(\eta^2\text{-}C_2H_2)_n]^+$ ($n = 1, 3, 4$) cations. The parent compounds of all homoleptic $[M(C_2H_2)_x]^n$ complexes (M = any metal; n, x = any number) are to date unknown in condensed phases.[22–26] The exceptional stability of the $[Ag(C_2H_2)]$ model complex allowed us to analyze the fine structure of the charge-density distribution inside the valence shell of the silver atom by high-resolution X-ray diffraction at 10 K. This topological analysis provides the first experimental insight into the microscopic nature of acetylene fixation at a metal center.

When a solution of $Ag[Al\{OC(CF_3)_3\}_4]$ (Ag[A]) in CH_2Cl_2 is treated with acetylene, cooling of the concentrated, clear, colorless solution to −25 °C results in the precipitation of quantitative yields of product as large colorless blocks. If three equivalents acetylene are used, $[Ag(\eta^2\text{-}C_2H_2)_3][A]$ (**1**) is formed, and $[Ag(\eta^2\text{-}C_2H_2)_4][A]$ (**2**) is formed in an atmosphere of acetylene [Eq. (1)]. Solids **1** and **2** are stable in a closed, nitrogen-filled container up to approximately −10 °C and −20 °C, respectively, and visibly lose C_2H_2 at higher temperatures. Therefore, all further sample manipulations (Raman spectroscopy, crystal mounting) had to be performed well below the indicated decomposition temperatures (−50 to −100 °C).

$$Ag[A] + n\,C_2H_2 \xrightarrow[-20\,°C]{CH_2Cl_2} [Ag(C_2H_2)_n][A] \qquad (1)$$

The solid-state structure[27] of **1** consists of well-separated cations and anions (Figure 1). The Ag^+ ion is coordinated by three C_2H_2 molecules with approximate C_2 symmetry ($d(Ag{-}C)_{av}$ = 2.356 (2×), 2.385 (2×), 2.508 Å (2×)). According to quantum-chemical calculations, this initially unexpected structure is isoenergetic[28] to the optimized structure of the higher-symmetry D_3 global minimum.[29] The final preference for the reduced symmetry of the observed C_2 structure may be caused by seven weak H···F contacts in the range from 2.139 to 2.848 Å (av 2.487 Å, sum of van der Waals radii 2.90 Å, see the Supporting Information). Compound **2** also forms an ionic lattice[30] in which Ag and Al reside on the crystallographic $\bar{4}$ positions. Ag^+ is tetrahedrally coordinated by four HC≡CH

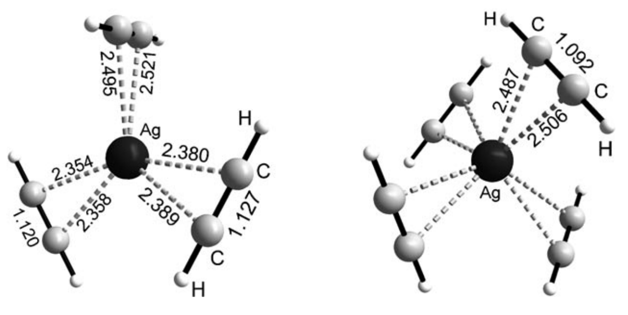

Figure 1. Ball-and-stick representations of the cations in the crystal structures of $[Ag(\eta^2\text{-}C_2H_2)_3][A]$ (**1**, left) and $[Ag(\eta^2\text{-}C_2H_2)_4][A]$ (**2**, right). Bond lengths in Å.

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molecules ($d(\mathrm{Ag{-}C})_{\mathrm{av}} = 2.497$ Å) and the overall cation structure has $\bar{4}$ point-group symmetry (Figure 1).

The present structures may be seen in analogy to the recently published $[\mathrm{Ag}(\eta^2\text{-}\mathrm{C_2H_4})_3]^+$ salt.[21] This cation could be stabilized in condensed phases although it could not previously be stabilized in the gas phase (only $n = 1,2$).[1] However, no homoleptic cationic silver acetylene complexes have been reported to date, in agreement with the generally lower binding energies of acetylene.[31] Currently, the only approximation of these species is a $[\mathrm{Ag(C_2H_2)}]^+$ moiety tightly coordinated to a fluorinated trispyrazolyl borate anion.[32] In contrast, numerous complexes with substituted or chelating alkynes exist.[23,24,26]

The experimental $C\equiv C$ bonds of the crystal structures of **1** (av 1.123 Å) and **2** (1.092(7) Å) are shorter than that of free acetylene in the gas phase (1.2033(2) Å).[33] By contrast, red shifts of the corresponding Raman bands at 1925 cm^{-1} ($n = 3$) and 1940 cm^{-1} ($n = 4$) versus 1974 cm^{-1} for free acetylene[34] suggest a $C\equiv C$ bond elongation. However, we will demonstrate below that this apparent contradiction has systematic reasons. Especially in the case of multiple covalent bonding, standard X-ray experiments tend to result in too short bond lengths arising from incomplete deconvolution of thermal smearing and chemical bond formation effects. Hence, the $C\equiv C$ bond lengths derived from these experiments are not suitable for an extended discussion of the nature of the metal-to-ligand bonding. All attempts to account for the short distances by theoretical models are immature. A full account of all aspects of this problem and their resolution will be given in an upcoming full paper. To further study this problem, and because of the thermal instability of **1** and **2** at ambient temperature, $[\mathrm{A}]^-$ was replaced by the slightly more coordinating anion $[\mathrm{Al(OC(CH_3)(CF_3)_2)_4}]^-$ ($[\mathrm{A'}]^-$), which led to formation of the molecular compound $[\mathrm{Ag}(\eta^2\text{-}\mathrm{C_2H_2})][\mathrm{A'}]$ (**3**). Crystals of **3** are of outstanding quality and are stable at room temperature in vacuo at 10^{-3} mbar (Figure 2).

The high crystal quality allowed us to record high-resolution X-ray diffraction data ($\sin\theta/\lambda_{\max} < 1.05$ Å^{-1}) at 10 K.[35] Subsequent structural refinement employing a highly flexible multipolar model[36] yielded a detailed description of the static charge-density distribution $\rho(\mathbf{r})$ as well as precise geometrical parameters (Figure 2). The resulting $C\equiv C$ bond length of 1.209(1) Å is 0.063 Å larger than in the standard X-ray model [1.146(4) Å, Promolecule, $2\theta_{\max} = 50°$, $T = 90$ K] and is in good agreement with the theoretical model (1.213 Å)[37] at the B3LYP/def-ECP(Ag)/def2-TZVPP level of approximation[38–43] and with the red-shifted experimental Raman $C\equiv C$ stretching frequency of **1** at 1914 cm^{-1} (free acetylene: 1974 cm^{-1}). Furthermore, direct comparison with the (less accurate) $C\equiv C$ bond length of 1.193(6) Å determined by neutron diffraction on solid acetylene at 15 K[44] confirms the $C\equiv C$ bond elongation in **3** arising from coordination to a metal.

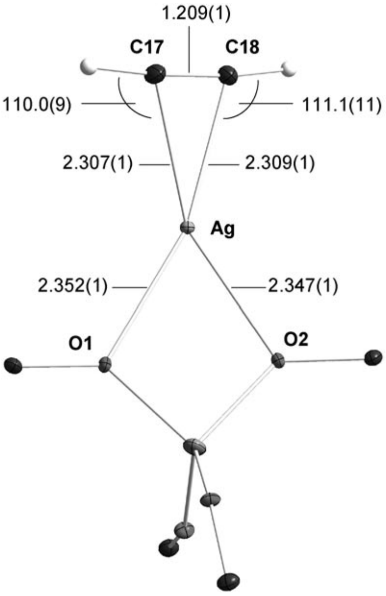

Figure 2. Crystal structure model of $[\mathrm{Ag}(\eta^2\text{-}\mathrm{C_2H_2})][\mathrm{A'}]$ (**3**) with thermal ellipsoids set at the 50% probability level at 10 K. $\mathrm{CF_3}$ and $\mathrm{CH_3}$ groups have been omitted for clarity; selected bond lengths [Å] and angles [°] are shown.

Figure 3 shows the experimental contour map of the negative Laplacian of the charge density in the $\mathrm{AgC_2}$ plane of **3** along with the superimposed bond paths. The experimental bond paths in **3** display a typical T-shaped pattern, which at first glance suggests purely electrostatic bonding between a closed-shell $\mathrm{Ag^I}$ cation and the acetylene ligand. Hence, the two Ag–C bond critical points (BCPs) and the AgCC ring critical point (RCP) have merged into a single (3,−1) bond critical point denoted TCP in Figure 3 ($\rho(\mathbf{r})_{\mathrm{TCP}} = 0.47$ e Å^{-3}).

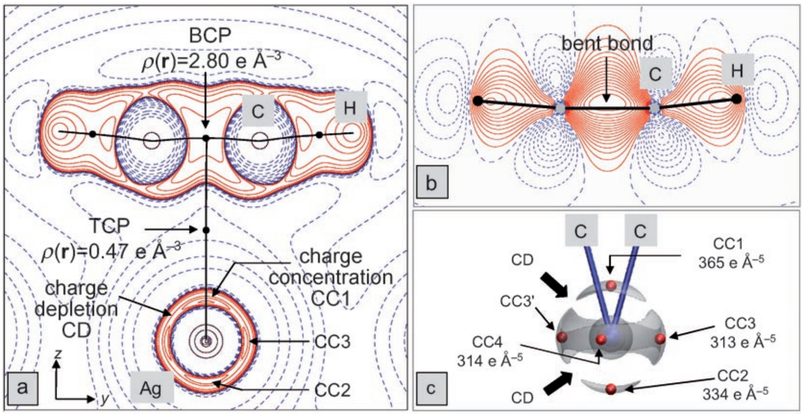

Figure 3. a) Contour map of the negative Laplacian of the experimental electron density ($L(\mathbf{r}) = -\nabla^2\rho(\mathbf{r})$) of **3** in the $\mathrm{AgC_2}$ plane. Contour levels are drawn at 0, $\pm 2.0\times10^n$, $\pm 4.0\times10^n$, $\pm 8.0\times10^n$ eÅ^{-5}, where $n = 0, \pm 3, \pm 2, \pm 1$; extra levels are at 270 and 350 eÅ^{-5}; positive and negative values are marked by solid and dashed lines, respectively. BCPs are marked by closed circles, while the T-shaped bond path is shown by a thick solid line. b) Static model deformation density of the acetylene unit (same orientation as in (a)) showing the significant bending of the $C\equiv C$ bond away from the metal center. c) Isosurface map revealing the significantly polarized valence density of the silver center by regions in which the charge is locally concentrated (six charge concentrations CC marked by small spheres) or depleted (charge depletions CD).

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However, the topology of $L(\mathbf{r})$ shows a clear polarization of the silver center. Along the $Ag\cdots C$ directrix we observe pronounced regions in which the valence density is locally depleted (denoted CD in Figure 3 a,c). Such a polarization scenario is in clear conflict with earlier theoretical studies that assumed an electrostatic bonding scenario for silver acetylene complexes.[45] In the case of the related Ni (d^{10}) tetracoordinated olefin complexes of C_{2v} symmetry, a similar polarization pattern could be identified. In that study, the local charge depletions in the valence density of the Ni atom could be related to the strength of the dominant ligand$\leftarrow$metal π back donation causing charge transfer from the metal d_{yz} orbital of b_2 symmetry into the antibonding π^* orbital of the olefin ligand.[46] Such ligand$\leftarrow$Ag π back donation is less pronounced in **3** than in Ni (d^{10}) olefin complexes but is still significant. Back donation owing to covalent Ag–C bonding is also signaled by the C–C bond path of the AgC_2 unit, which displays an exocyclic curvature. This bond-path deformation, which is even more evident in the static model deformation density maps (Figure 3 b), is obviously a result of the involvement of the $C(2p_z)$ orbitals in the $Ag(d_{yz})\rightarrow\pi(C-C)^*$ back donation. The strengthening of the charge concentration CC1 relative to CC2 might be interpreted as the charge-density analogue of the σ-donation component in the framework of the Dewar–Chatt–Duncanson (DCD) model.[47,48] Accordingly, the C≡C bond in **3** is elongated and weakened relative to that in free acetylene. This effect is also indicated by comparison of the experimental C≡C bond topology of **3** with that of the non-coordinating C≡C bond in 2,2′-ethynylenedibenzoic acid **4**[49] ($\rho(\mathbf{r}) = 2.80$ and $3.19\,e\,\text{Å}^{-3}$, $\nabla^2\rho(\mathbf{r}) = -29.6$ and $-34.8\,e\,\text{Å}^{-5}$, and $\varepsilon = 0.05$ and 0.01, respectively). The pronounced C≡C bond-path ellipticity and the reduced charge density at the bond critical point of the C≡C unit of **3** relative to **4** clearly suggest the presence of covalent bonding between the acetylene moiety and the silver center in **3**.

To complement the experimental data and stimulate experimental MS investigations, complexation enthalpies have been calculated using different theoretical methods as detailed in Table 1. For $n = 1$ and 2, MP2 calculations with a TZVPP basis set of triple-ζ quality show only minor deviations (less than 6 kJ mol^{-1}) from the enthalpies derived from the more accurate MP4(SDQ) and CCSD(T) calculations and should hence be adequate to model larger systems not accessible at acceptable computational costs with more highly correlated methods (Table 1).

Table 1: Calculated complexation energies [kJ mol^{-1}] of Ag^+ with C_2H_2 ligands ($n = 1$–4).

	$[Ag(C_2H_2)_{n-1}]^+ + C_2H_2 \rightarrow [Ag(C_2H_2)_n]^+$			
n	MP2/TZVPP[a]	MP2/QZVPP[a]	MP4(SDQ)[b]	CCSD(T)[b]
1	−139.7	−149.9	−132.6	−132.7
2	−151.5	−162.2	−148.3	−146.5
3	−69.5	−68.8	–	–
4	−39.8	−35.3	–	–

[a] The 28-valence-electron scalar relativistic def-ECP has been used for the Ag core electrons. [b] aug-cc-pVTZ basis sets have been used for C and H and the Stuttgart RSC 1997 ECP (28 electrons) with a triple-ζ-quality valence basis set for Ag.

The calculated complexation enthalpies for acetylene are smaller than for ethene[1] but larger than for CO.[2] Similar to those ligands, the complexations of the first and second acetylene molecules have comparable energies, whereas the addition of the third and fourth equivalents is distinctly less exergonic. This observation is in good agreement with the synthesized $[Ag(C_2H_2)_n]^+$ ($n = 3$, 4) salts, which are only stable at low temperatures and reversibly lose acetylene at higher temperatures.

Using the WCA $[Al\{OC(CF_3)_3\}_4]^-$, even very weakly bound Lewis acid–base complexes such as $[Ag(\eta^2\text{-}C_2H_2)_n]^+$ can be formed to complement gas-phase investigations with structural information and other physical properties that can only be obtained in condensed phases. The structure of the C_2-symmetric $[Ag(C_2H_2)_3]^+$ cation in **1** clearly would not have been investigated only on the basis of quantum chemical or mass spectrometric analyses, for example.[50] This discrepancy again highlights the importance of analyzing the properties of such labile species by experimental techniques such as X-ray crystallography. However, synthesis and characterization of **1**–**3** brought us to the cutting edge of possibilities. Only with combination of all currently available techniques such as measurement at 10 K, electron density refinements and analyses, scalar relativistic calculations, and low-temperature Raman spectroscopy could precise information about the nature of the chemical bonding in $\{Ag(C_2H_2)\}$ moieties be obtained. The approach presented herein should be understood as a paradigm to stabilize other gas-phase species that are very weakly bound and ambiguous with respect to their structures and properties. Furthermore, the condensed-phase stability of a $[Ag(C_2H_2)_4]^+$ salt suggests that novel acetylene storage systems comprising coinage metal salts of weakly coordinating anions are viable and should be investigated.

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