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Highly Stable $[C_{60}AuC_{60}]^{+/-}$ Dumbbells

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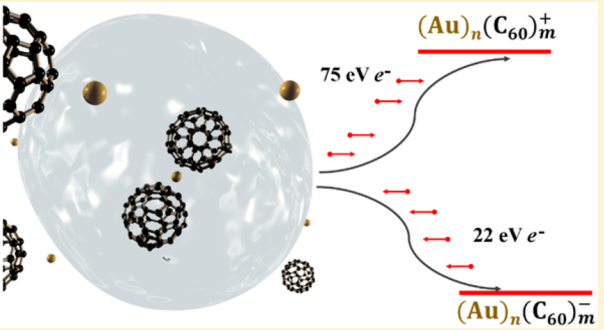
Supporting Information

ABSTRACT: Ionic complexes between gold and C_{60} have been observed for the first time. Cations and anions of the type $[Au(C_{60})_2]^{+/-}$ are shown to have particular stability. Calculations suggest that these ions adopt a C_{60}−Au−C_{60} sandwich-like (dumbbell) structure, which is reminiscent of $[XAuX]^{+/-}$ ions previously observed for much smaller ligands. The $[Au(C_{60})_2]^{+/-}$ ions can be regarded as Au(I) complexes, regardless of whether the net charge is positive or negative, but in both cases, the charge transfer between the Au and C_{60} is incomplete, most likely because of a covalent contribution to the Au−C_{60} binding. The C_{60}−Au−C_{60} dumbbell structure represents a new architecture in fullerene chemistry that might be replicable in synthetic nanostructures.



The interaction of gold with molecules provides a vivid illustration of the impact of relativity on chemistry.[1] The high nuclear charge in a gold atom induces far stronger relativistic effects than that in the lighter coinage metals, copper and silver. One consequence is that the energy of the 6s orbital is lowered by relativity, whereas that of the 5d orbital is raised. This brings these orbitals closer together energetically and leads to enhanced sd hybridization, which in turn enhances the ability of gold atoms to undergo covalent bonding.[2] This gives gold some unique and important chemical properties. Among these are the role of its compounds, particularly Au(I) complexes, in homogeneous catalysis[3,4] and as building blocks in supramolecular chemistry.[5]

In the +1 oxidation state, Au atoms normally show a coordination number of two in both cations and anions and the resulting $[AuX_2]^{+/-}$ complexes adopt linear $[X-Au-X]^{+/-}$ structures, where X is a ligand. A particularly interesting cation is $[XeAuXe]^+$, which is remarkably stable given that it consists of a combination of a noble metal and a noble gas.[6,7] The individual Au−Xe binding energies in this ion are close to 1 eV and are thought to arise from a combination of ionic bonding and a significant covalent effect.[7] The best known example of an anionic $[X-Au-X]^-$ complex is $[Au(CN)_2]^-$, which is the most stable Au(I) complex currently known.[8,9] Here too, a combination of ionic and covalent contributions is thought to be responsible for the strong binding.

The interaction of gold with fullerenes, and particularly C_{60}, has been the topic of a number of studies. The main interest has been the electronic properties derived from the metal−fullerene contact and their implication for the development of new nanoscale devices.[10−14] Chemical interactions between single gold atoms and C_{60} molecules have received far less attention and have been restricted to an infrared spectroscopic investigation of the AuC_{60} complex[15] along with a few theoretical studies.[16,17] However, nothing is known about ionic complexes involving Au and C_{60} and whether this combination shows any notable chemical features.

Here we report the first experimental observation of cationic and anionic complexes containing Au and C_{60}. The complexes were made by combining Au atoms and C_{60} molecules inside liquid helium nanodroplets. The doped droplets were then exposed to electrons, which yielded ions in the gas phase that can be detected by mass spectrometry. Low-energy electrons (22 eV) were used to create anions, and higher-energy electrons (75 eV) generated cations.

Figure 1 shows the mass spectrum observed for anions. We can identify series of ions of the type $[Au_n(C_{60})_m]^-$, where n and m are small integers. However, instead of a smooth distribution of ion sizes, these series are punctuated by anions with abnormally high abundances, so-called magic number ions.[18] For the $[Au_nC_{60}]^-$ series, the peak from the $[Au_2C_{60}]^-$ ion is particularly intense; this ion has roughly twice the abundance of $[AuC_{60}]^-$, while the $[Au_3C_{60}]^-$ ion is almost entirely absent. This suggests that $[Au_2C_{60}]^-$ has a particularly high stability, which makes it resistant to dissociation and therefore enhances its abundance. Even more extreme behavior is seen for the $m = 2$ series of $[Au_n(C_{60})_m]^-$, where $[Au(C_{60})_2]^-$

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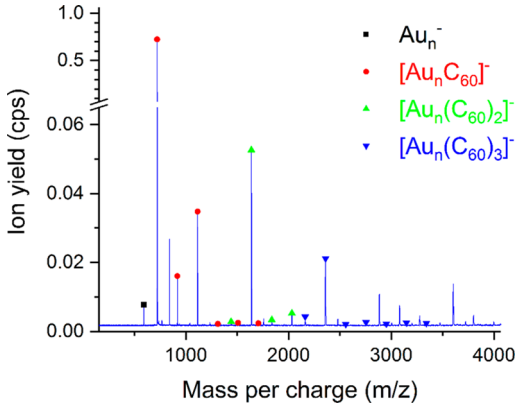

Figure 1. Mass spectrum of $[Au_n(C_{60})_m]^-$ anions. Note that only one bare Au_n^- ion, Au_3^-, is visible in this image. Note also that for the series of peaks identified as coming from $[Au_nC_{60}]^-$, $[Au_n(C_{60})_2]^-$, and $[Au_n(C_{60})_3]^-$, each series begins at $n = 1$.

almost completely dominates. There is a similar dominance for $[Au(C_{60})_3]^-$ in the $m = 3$ series.

We can also identify anomalous intensity behavior for the cations, as can be seen in Figure 2. In the $[Au_nC_{60}]^+$ series, the

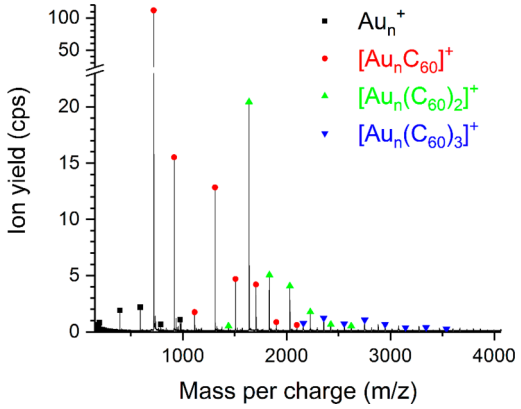

Figure 2. Mass spectrum of $[Au_n(C_{60})_m]^+$ cations. For the series of peaks identified as coming from $[Au_nC_{60}]^+$, $[Au_n(C_{60})_2]^+$, and $[Au_n(C_{60})_3]^+$, note that each series begins at $n = 1$.

$[Au_2C_{60}]^+$ ions have an abnormally low abundance and, therefore, show antimagic behavior. Similar to the anions, although not quite so extreme, the $[Au(C_{60})_2]^+$ ion is dominant in the $[Au(C_{60})_m]^+$ series. We can therefore conclude that $[Au(C_{60})_2]^{+/-}$ ions are particularly stable ions regardless of charge state.

To try and explain these findings, we have performed density functional theory (DFT) calculations, as detailed in the Supporting Information. These calculations have been used to predict dissociation energies of the ions, which are shown in Table 1. Where there is more than one possible dissociation channel, only the dissociation energy for the lowest-energy channel is shown. The calculations have been restricted to complexes with a maximum of two C_{60} molecules in order to keep the calculations affordable. We find good agreement between the theoretical predictions and our experimental findings. For example, the energy needed to remove one C_{60} molecule from $[Au(C_{60})_2]^-$ is considerably higher than that for $[Au_2(C_{60})_2]^-$, which is consistent with the magic character of the former when compared with the latter. Likewise, the

Table 1. Calculated Dissociation Energies of $[Au_n(C_{60})_m]^{+/-}$ Ions

complex	dissociation products[a]	dissociation energy/eV
$[AuC_{60}]^+$	$Au + C_{60}^+$	1.38
$[Au_2C_{60}]^+$	$Au_2 + C_{60}^+$	0.79
$[Au_3C_{60}]^+$	$Au_3^+ + C_{60}$	1.72
$[Au(C_{60})_2]^+$	$AuC_{60} + C_{60}^+$	1.47[b]
$[Au_2(C_{60})_2]^+$	$Au_2C_{60} + C_{60}^+$	1.05[b]
$[AuC_{60}]^-$	$Au + C_{60}^-$	0.83
$[Au_2C_{60}]^-$	$Au_2 + C_{60}^-$	0.98
$[Au_3C_{60}]^-$	$Au_3^- + C_{60}$	0.49
$[Au(C_{60})_2]^-$	$AuC_{60} + C_{60}^-$	0.83
$[Au_2(C_{60})_2]^-$	$Au_2C_{60} + C_{60}^-$	0.51[b]

[a]Other dissociation products are possible (see the Supporting Information), but those listed in this column are the calculated lowest-energy dissociation channels. [b]Optimized structures with a few low-lying imaginary frequencies. In these cases, zero-point corrections were not taken into account.

enhanced abundance of $[Au_2C_{60}]^-$ relative to $[AuC_{60}]^-$ is explicable in terms of the calculated dissociation energies. In the case of cations, the $[Au_2C_{60}]^+$ ion has a far lower dissociation energy than either $[AuC_{60}]^+$ or $[Au_3C_{60}]^+$, explaining the weak $[Au_2C_{60}]^+$ peak in the mass spectrum. Given this good agreement between theory and experiment, we feel that the current calculations capture the essence of the Au–C_{60} interactions.

The mass spectra clearly demonstrate new ion chemistry resulting from the interaction between Au and C_{60}. One is particularly drawn to the strongly magic character associated with the $[Au(C_{60})_2]^{+/-}$ ions, and it is tempting to draw parallels with other well-known $[AuX_2]^{+/-}$ ions.[6−9,19] The DFT calculations predict that the two C_{60} molecules are located on opposite sides of the Au atom in a dumbbell-like arrangement, as illustrated pictorially in Figure 3. The Mulliken charges on

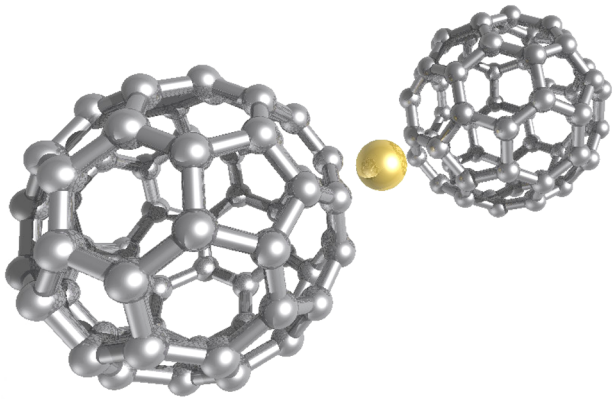

Figure 3. Calculated lowest-energy structure of $[Au(C_{60})_2]^+$.

the Au atom are +0.59 and +0.38 for the cation and anion, respectively, i.e., in both cases the metal center is positively charged. The ionization energy of C_{60} is considerably lower than that of Au, and therefore, one might expect the majority of the positive charge in the cation to reside on the C_{60} molecules. The fact that this is quite different from the Mulliken prediction suggests a significant covalent component to the bonding, as posited previously for other $[AuX_2]^+$ ions.[6,7]

Likewise, the higher electron affinity of C_{60} (2.68 eV)[21] when compared with that of a gold atom (2.31 eV)[22] should draw

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much of the excess negative charge in $[Au(C_{60})_2]^-$ toward the C_{60} molecules. However, the Mulliken analysis suggests that this anion is some way from being described as $C_{60}^{-0.5}AuC_{60}^{-0.5}$: further charge transfer from the Au occurs, creating an electron-deficient Au atom. The calculated charge on the Au atom is similar to that calculated for anions such as $[Au(CN)_2]^-$ and $[AuCl_2]^-$, where substantial contributions from both ionic and covalent bonding have been found.[8,9] It is likely that the binding in $[Au(C_{60})_2]^-$ is of a similar mixed composition.

To explore this further, we show in Figure 4a a calculated charge density difference map obtained at the optimized structure for $[Au(C_{60})_2]^+$. This image indicates that there is a small amount of charge accumulation in the form of two small blue lobes between the closest C and Au atoms. Figure 4b shows a contour plot of the electron localization function (ELF)[23] near to the Au atom. The ELF between adjacent carbon atoms has a value close to 1.0, showing (as expected) that these are strongly covalent bonds. An arc (indicated by white arrows) with ELF ≈ 0.75 lies between the Au atom and the closest C atom in each C_{60} molecule, which indicates some covalent bonding. Very similar conclusions can be drawn for the anion. We note that the calculated distance between the Au atom and the nearest carbon atom in the $[Au(C_{60})_2]^-$ anion is 2.216 Å, which is significantly longer than the Au−C distances reported for $[Au(CN)_2]^-$ (1.99 Å)[8] and $[AuC_2]^-$ ((1.95 Å).[24]

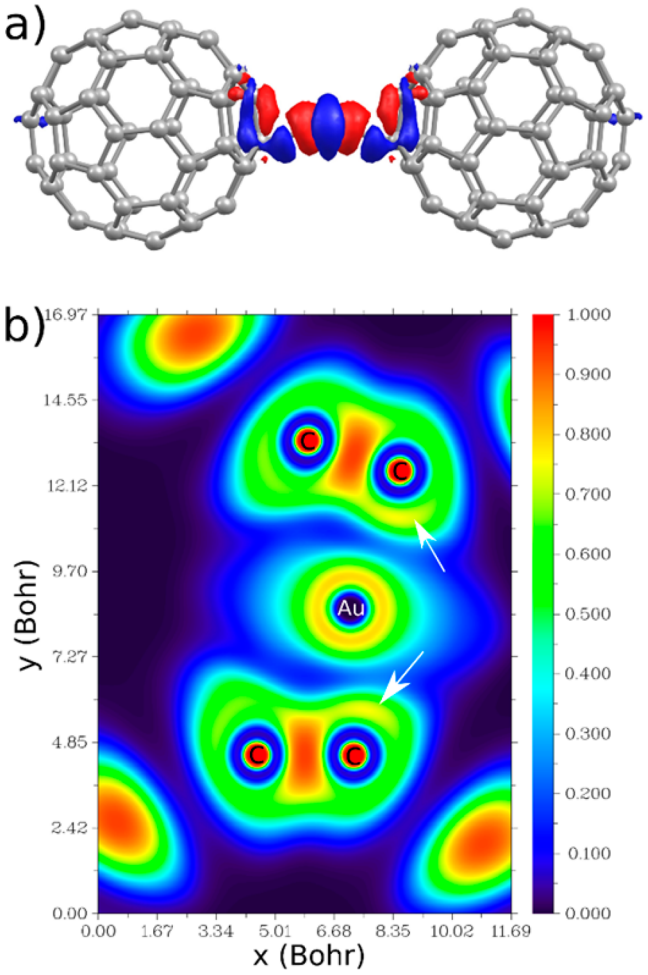

Figure 4. (a) Calculated charge density difference map for $[Au(C_{60})_2]^+$ fixed at its equilibrium geometry. This image shows the isosurface (isovalue 0.002608 e/a_0^3) of the charge density difference $\rho([Au(C_{60})_2]^+) - \rho((C_{60})_2^+) - \rho(Au)$. Blue regions indicate charge accumulation, and red regions indicate charge depletion. (b) Contour map of the electron localization function (ELF) in the region close to the Au atom, as calculated with the multiwfn utility program.[20] The dumbbell is vertically oriented in this plot, and the plane cuts through the gold atom of $[Au(C_{60})_2]^+$ and four neighboring C atoms. The white arrows point to zones between the Au atom and the nearest C atoms in each C_{60} molecule where ELF ≈ 0.75.

The discovery of $[C_{60}AuC_{60}]^{+/-}$ ions with stable dumbbell structures in the gas phase suggests the possibility that these complexes, and particularly the anion, might be synthesized in conventional wet chemistry. Such ions are new to chemistry and may prove to be useful tools in both gold and fullerene chemistry. Although not included in the current study, we flag the possibility that the corresponding neutral dumbbell species may also show particular stability. The applications of complexes built from these components are not clear at this juncture, but possibilities may exist in the development of new supramolecular architectures involving fullerenes. The potential also exists in molecular electronics given the ongoing interest in gold−fullerene contacts in nanoelectronics.[10−14] We therefore hope that the current study prompts a search for the $C_{60}AuC_{60}$ dumbbell moiety, both in solution chemistry and in the solid state.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpclett.8b01047.

Computational methodology employed; calculated ionization energies and electron affinities; and calculated dissociation energies for various ions (PDF)

Structural information for the species studied (ZIP)

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Notes

The authors declare no competing financial interest.

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