The Dinitrogen-Ligated Triaurum Cation, Aurodiazenylium, Auronitrenium, Auroammonia, and Auroammonium**

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Gold complexes and nanoparticles exhibit fascinating properties and have found various applications recent years. The chemistry of gold, significantly different from that of its congeners (silver and copper), is mostly dominated by its extraordinarily strong relativistic effects, which impose a very small energy gap between its 5d and 6s valence orbitals and, consequently, a high degree of sd hybridization as well as an even higher electronegativity than that of the nonmetal monovalent hydrogen, that is, Au 2.54 versus H 2.20 (Pauling scale). The concept of gold–hydrogen analogy thus emerged and has been extensively exploited in synthetic chemistry. Since the isolobal analogy between phosphine-ligated gold (AuPR3) and hydrogen (H) was noticed by Mingos in mid 1970s, the use of the AuPR3 synthon has brought out to a large number of Au-containing metal cluster compounds. Key examples are [O(AuPPh3)n]2– (n = 3, 4), [N(AuPPh3)n]3– (n = 4, 5), [C(AuPPh3)n]1– (n = 4–6), and [N2(AuPR3)n]2– (n = 3, 4), which are analogous to [OH]2– (n = 3, 4), [NH]n3– (n = 4, 5), [CH]n4– (n = 4–6), and hydrazinium [H3N–NH2]+, respectively. On the other hand, a simple gold–hydrogen analogy was recently observed in a series of binary Si/Au clusters [Si4Au], [AuN4]+, [Au2N6]+ (n = 2–4), and [Au3N7]+, which exist as dinitrogen-ligated aurodiazenylium [N2(AuN3)+], auronitrenium [N2(AuN2)+], auroammonia radical cation [N2(AuN)+], auroammonium [N2(AuN)+], and aurotriazenylium cation [(AuN)3]+, and are structurally and electronically analogous to diazenylium ([N2H]+), nitrenium ([NH2]+), ammonia radical cation ([NH]+), and trihydrogen cation ([H]+), respectively, by following the isolobal analogy between N2-ligated gold (AuN2) and hydrogen. The chemical stability of these N2-ligated complexes suggests that they might be viable in wet chemistry. Such a N2-assisted gold–hydrogen analogy involving a [AuN]+ synthon and covalent dative Au–N bond is also relevant to the industrially important nitrogen fixation.

Figure 1 displays the mass spectrum (180 < m/e < 1000 amu) of [AuN4]+ clusters obtained by reactive collision of N2 with laser-vaporized gold clusters. The strong mass spectral peaks for [AuN4]+, [AuN8]2+, [Au3N4]+, and [AuN]+ indicate that these “magic-number” cations are the most abundant for the positive cluster distribution. Furthermore, the signal intensity of [AuN4]+, a radical cation, is comparable to that of [Au3N4]+, likely owing to the high stability of its neutral form, Au3N4. Moreover, the intense signals of [Au2N6m+1]+ (m = 2–4) with odd numbers of N atoms indicate that hot Au clusters produced by laser vaporization are capable of activating and cleaving the triple bond of the N2 molecule.

Density functional theory (DFT) calculations at the B3LYP/DZP level of theory (see the Supporting Information) were performed to search the ground-state structures of these abundant clusters. Figure 2 depicts the ground-state structures of these clusters re-optimized at the B3LYP/TZP level of theory. [AuN]+ has a linear D3h-symmetric ground-state structure, [N2-Au-N2] (Figure 2a), isostuctural to the isoelec-
tronic [Au(CO)]+ \cite{17} complex. [Au(N2)]+ has a triplet ground state in which the linear D∞h-symmetric structure, [N2-Au-N-Au-N2]+ (Figure 2b), is reported to be \SI{1.09}{eV} lower in energy than its singlet excited state, which has a C3v-symmetric bent structure. Similarly, the interstellar species nitrogen [NH3] has a triplet ground state \cite{15} that is \SI{2.12}{eV} lower than its singlet excited state \cite{14c}.

[Au(N2)]+ has a planar D∞h-symmetric ground-state structure (AuN2)4+ that contains a three-membered [AuN2]3+ ring (Figure 2c). Its Au–Au distance (2.648 Å) is slightly shorter than that of ligand-free [Au]+ cluster (2.661 Å) \cite{16d}. Note that the central [Au]+ unit has two skeletal valence electrons, akin to the trihydrogen cation \cite{16a}.

As discussed above, the ground states of these Au/N binary clusters exhibit two structural features. First, all Au atoms in these clusters (except in [(AuN2)3]+) are bi-coordinate. Second, they have a 3P2 ground state (3B1) that is \SI{1.09}{eV} lower than its singlet excited state. \cite{14c}

Figure 2. B3LYP/TZP-predicted ground-state structures of a) [AuN2]+, b) [Au2N5]+, c) [Au(N2)2]+, d) [Au(N2)3]+, e) [Au(N2)4]+, and f) [Au(N2)5]+ (N black, Au gray; key bond lengths in Å).

Besides [Au(N2)]+, other abundant Au/N binary clusters (now represented by the general formula X(N2)3) have similar Au–N2 covalent dative bonding. As listed in Table 1, the average Au–N2 binding energy ranges from 0.57 eV in [Au(N2)]+ account for the Au–N2 π bonding back-donation. Yet, further NBO analyses revealed that the Au–N2 bonding is dominated by σ bonding donation with marginal contribution from π bonding back-donation, as the estimated σ donation and π back-donation is \SI{0.12}{eV} and \SI{0.06}{eV} in [Au(N2)]+ and \SI{0.21}{eV} and \SI{0.07}{eV} per N in [Au(N2)]+. The higher degree of σ donation in [Au(N2)]+ is a result of enhanced sd hybridization of bi-coordinated Au (see the Supporting Information). For the same reason, even stronger and shorter Au–ligand bonding was previously found in [Au(CO)]+ and [Au(CN)]+ complexes.\cite{17,18}

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Bi-coordinate environment, and the resultant Au–N2 dative bond is covalent in nature.

The Au–N2 bonding can be understood by using the Dewar–Chatt–Duncanson complexation model.\cite{19} As shown in Figure 3, the 60 MO in [Au(N2)]+ and the 50g MO in [Au(N2)]3+ account for the Au–N2 0 bonding donation, whereas the 3σ MOs in [Au(N2)]+ and the 2πg MOs in

Table 1: B3LYP/TZP-predicted Wiberg bond order (WBO) and average binding energy \(E_{\text{av}}\) of Au–N2 bond(s) in the X(N2)3 clusters (X = central moiety) and their HOMO–LUMO gap \(E_G\).

\begin{tabular}{|c|c|c|c|}
\hline
X(N2)3 & X & WBO & \(E_{\text{av}}\) [eV] \(E_G\) [eV] \\
\hline
[AuN2]+ & Au+ & 0.30 & 0.98 (0.55) & 4.91 (4.37) \\
[Au(N2)]+ & [N-Au]+ & 0.40 & 1.36 (1.42) & 6.77 (4.91) \\
[Au(N2)]3+ & [Au]+ & 0.24 & 0.57 & 5.54 (3.79) \\
[N(AuN2)2]+ & [NaAu]+ & 0.36 & 1.12 & 1.09 (0.75) \\
[N(AuN2)3]+ & [NaAu]+ & 0.38 & 1.05 & – \\
[N(AuN2)4]+ & [NaAu]+ & 0.42 & 0.72 & 3.64 (3.07) \\
[N(AuN2)5]+ & [NaAu]+ & 0.40 & 1.04 & 5.19 (2.57) \\
\hline
\end{tabular}

[a] \(E_{\text{av}}(\text{Au–N}) = \langle E(X) + n \langle E(N) \rangle - \langle E(N_2) \rangle \rangle / n\); [b] The \(E_G\) of central X moiety is given in parenthesis. [c] The CCSD(T)/TZP-predicted \(E_{\text{av}}\) is given in parenthesis. [d] The energy gap between the triplet ground state and the singlet excited state.
[(AuN$_2$)$_3$]$^+$ to 1.12 eV in [N(AuN$_2$)$_2$]$^+$, and the Au–N$_2$ bond order is between 0.24 in [(AuN$_2$)$_3$]$^+$ and 0.42 in [N(AuN$_2$)$_2$]$^+$. Moreover, the gap between the highest occupied and lowest unoccupied MOs (HOMO–LUMO gap) of the X(N$_2$)$_n$ clusters is generally larger than that of the corresponding ligand-free X clusters, for example, 5.54 eV for [(AuN$_2$)$_3$]$^+$ versus 3.79 eV for [Au]$^+$ and 5.19 eV for [N(AuN$_2$)$_2$]$^+$ versus 2.57 eV for [NaAu]$^+$ (Table 1). Thus, ligation of N$_2$ molecules to the X species enhances not only their thermal stability but also their kinetic stability. That is why a N$_2$-assisted gold–hydrogen analogy, but not the simple gold–hydrogen analogy, is observed in the Au/N binary clusters.

Underlying the N$_2$-assisted gold–hydrogen analogy is the isolobal analogy between the [AuN$_2$]$^+$ synthon and H$^+$. Indeed, the LUMO (i.e., 90 MO) of [AuN$_2$]$^+$ (Figure 3a) is dominated by the Au 6s orbital, analogous to the empty 1s orbital of H$^+$. By following the [AuN$_2$]$^+$–H$^+$ isolobal analogy, it is [Au(N$_2$)$_2$]$^+$, rather than [AuN$_2$]$^+$, that is equivalent to [N$_2$H]$^+$. As shown in Figure 3, while the occupied valence orbitals of [N$_2$H]$^+$ can find their equivalence in [AuN$_2$]$^+$ and [Au(N$_2$)$_2$]$^+$, its π-type LUMOs (i.e., the 2s* antibonding orbitals of the N$_2$ moiety) are akin to the π-type LUMOs of [Au(N$_2$)$_2$]$^+$ but strikingly different from the σ-type LUMO of [AuN$_2$]$^+$.

Figure 4 shows the skeletal valence orbitals of [(AuN$_2$)$_3$]$^+$, [Au]$^+$, and [H$_3$]$^+$, consisting primarily of the 6s/1s-orbitals of the ring Au/H atoms. The resemblance in skeletal valence orbitals of these clusters gives evidence of the isolobal

\[ \text{[(AuN$_2$)$_3$]$^+} \rightarrow 1.12 \text{ eV in [N(AuN$_2$)$_2$]$^+}$, and the Au–N$_2$ bond order is between 0.24 in [(AuN$_2$)$_3$]$^+$ and 0.42 in [N(AuN$_2$)$_2$]$^+$. Moreover, the gap between the highest occupied and lowest unoccupied MOs (HOMO–LUMO gap) of the X(N$_2$)$_n$ clusters is generally larger than that of the corresponding ligand-free X clusters, for example, 5.54 eV for [(AuN$_2$)$_3$]$^+$ versus 3.79 eV for [Au]$^+$ and 5.19 eV for [N(AuN$_2$)$_2$]$^+$ versus 2.57 eV for [NaAu]$^+$ (Table 1). Thus, ligation of N$_2$ molecules to the X species enhances not only their thermal stability but also their kinetic stability. That is why a N$_2$-assisted gold–hydrogen analogy, but not the simple gold–hydrogen analogy, is observed in the Au/N binary clusters.

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Figure 4. Skeletal valence orbitals (isosurface value ca. 0.04) of a) [(AuN$_2$)$_3$]$^+$, b) [Au]$^+$, and c) [H$_3$]$^+$.

[(AuN$_2$)$_3$]$^+$–H$^+$ analogy as well as the simple Au–H analogy. The diatomic Wiberg bond order is 0.39 for Au–Au in [(AuN$_2$)$_3$]$^+$, close to that of [H$_3$]$^+$ (0.44); [Au]$^+$ has a slightly larger Au–Au bond order of 0.52. Moreover, all three of these species have an in-plane three-center-two-electron (3c-2e) bond (i.e., the occupied a’ MO) that conforms to the H/C$_2$ckel rule of aromaticity. Consequently, they are σ-aromatic with predicted NICS values of δ = −42.8, −33.4, and −33.8 ppm for [(AuN$_2$)$_3$]$^+$, [Au]$^+$, and [H$_3$]$^+$, respectively.

Figure 5 shows the selected valence orbitals of the [NR$_2$]$^+$, NR$_i$, and [NR$_4$]$^+$ series of clusters (R = AuN$_2$, Au, and H). These N-centered valence MOs are mainly composed of the valence 2s and 2p atomic orbitals of the central N atom and the 6s/1s orbitals of the surrounding Au/H atoms, except for the substantial sd-hybridization in Au. For each of the species, such N-centered MOs jointly account for its N–R covalent bonds and, if available, the lone-pair (or unpaired for the [NR$_2$]$^+$ series) electrons localized on the central N atom. For each series of species, the resemblance in the N-centered valence orbitals is terrific, evidencing the isolobal [AuN$_2$]$^+$–H$^+$ analogy and the simple Au–H analogy. The computed N–R bond orders are listed in Table 2. For R = Au or AuN$_2$, the computed N–R bond order ranges from 0.46 in [N(AuN$_2$)$_3$]$^+$ to 0.85 in N(AuN$_2$)$_3$, showing the covalent nature of the N–R bonds. Although the N–(AuN$_2$)$_3$ bond in [N(AuN$_2$)$_3$]$^+$ is the weakest, the loss of [AuN$_2$]$^+$ shown in Equation (1) is found to be highly endothermic by 4.32 eV, thus confirming the strong covalency of the N–(AuN$_2$)$_3$ bond.

\[ \text{N}(\text{AuN$_2$})_{3}^+ \rightleftharpoons \text{N}(\text{AuN$_2$})_{3} + \text{[AuN$_2$]}^+ \Delta E = 4.32 \text{ eV} (1) \]

The ionization potential of N$_2$-ligated auroammonia N-(AuN$_2$) is predicted to be 6.62 eV, which is 3.57 eV lower than that of ammonia. Therefore, N(AuN$_2$)$_3$ is much more electron-donating and could be a better ligand than ammonia.

In conclusion, we have shown that a N$_2$-assisted gold–hydrogen analogy, that is, the isolobal analogy between [AuN$_2$]$^+$ and H$^+$, underlies the remarkable chemical stability of a series of abundant Au/N binary cations ([AuN$_2$]$^+$, [AuN$_2$N$_{3n+1}$]$^+$ (n = 2–4), and [AuN$_2$]$^+$) produced by laser vaporization. We are looking forward to wet-chemistry synthesis[H] of these N$_2$-ligated auroammonia and auroammonium species and the σ-aromatic [[(AuN$_2$)$_3$]$^+$ complex. Such a dinitrogen-assisted gold–hydrogen analogy with involvement of a [AuN$_2$]$^+$ synthon and the relatively inert N$_2$ ligand opens a new way for exploring the chemistry of gold by either gas-phase dry chemistry or bench chemistry.

Table 2: B3LYP/TZP-predicted Wiberg bond order of N–R bond(s) in the [NR$_2$]$^+$, NR$_i$, and [NR$_4$]$^+$ series of species (R = H, Au, and AuN$_2$).

<table>
<thead>
<tr>
<th>R</th>
<th>[NR$_2$]$^+$</th>
<th>NR$_i$</th>
<th>[NR$_4$]$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.79</td>
<td>0.88</td>
<td>0.79</td>
</tr>
<tr>
<td>Au</td>
<td>0.68</td>
<td>0.85</td>
<td>0.56</td>
</tr>
<tr>
<td>AuN$_2$</td>
<td>0.64</td>
<td>0.59</td>
<td>0.46</td>
</tr>
</tbody>
</table>
Experimental Section

Mass spectrometry: The experiments were carried out using a reflection time-of-flight mass spectrometer (RTOF) with a laser vaporization cluster source. A vaporization laser beam (532 nm, Nd:YAG laser, about 5–10 mJ per pulse) was focused on the rotated gold target disk. The resulting ablation plasma plume crossed and was carried downstream by expanding 3–10 atm of a nitrogen gas packer from the pulsed valve. The positive ions were extracted by a high-voltage pulse (about 1.2 kV) and subjected to RTOF. The mass spectrum signals of RTOF were detected by a microchannel plate (MCP) detector. The total length of the flight tubes of RTOF is about 2.2 m, with a mass resolution better than 2800.

Theoretical calculations: All quantum chemical calculations were carried out using Gaussian03. Geometry optimizations of various possible isomers of the Au/N binary clusters were performed using the hybrid density functional B3LYP in combination with double-ζ basis set plus polarization (DZP), that is, the standard 6-31G* basis set [28] for Au. Vibrational frequencies were computed to characterize the nature of the stationary points and to get the zero-point energy (ZPE). Basis set superposition error (BSSE) was estimated by using the counterpoise method. The natural bond orbital (NBO) method [29] was used for bonding analyses. Single-point CCSD(T) calculations using the B3LYP-optimized geometries were performed for [Au(N2)]+(n = 1–3) to justify the B3LYP-predicted Au−N binding energy. Unless otherwise specified, reported binding energies are ZPE- and BSSE-corrected. The NICS (nucleus-independent chemical shift) values were computed using the GIAO method [30] at the B3LYP/TZP level.

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