Cluster Compounds

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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.[1,2] The chemistry of gold, significantly different from that of its congeners (silver and copper), is mostly dominated by its extraordinarily strong relativistic effects,[3] 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).[4] The concept of gold–hydrogen analogy thus emerged[5] and has been extensively exploited in synthetic chemistry.[1,6] Since the isolobal analogy[7] between phosphine-ligated gold ($AuPR_3$) and hydrogen (H) was noticed by Mingos[5a] in mid 1970s, the use of the $AuPR_3$ synthon has brought out to a large number of Au-containing metal cluster compounds.[1,6] Key examples are $[O(AuPPh_3)_n]^{(n-2)+}$ (n = 3,4),[8] $[N(AuPPh_3)_n]^{(n-3)+}$ (n = 4, 5),[9] $[C(AuPPh_3)_n]^{(n-4)+}$ (n = 4–6),[10] and $[N_2(AuPR_3)_6]^{2+}$,[11] which are analogous to $[OH_n]^{(n-2)+}$ (n = 3,4), $[NH_n]^{(n-3)+}$ (n = 4, 5), $[CH_n]^{(n-4)+}$ (n = 4-6), and hydrazinium $[H_3N{-}NH_3]^{2+}$, respectively. On the other hand, a simple gold–hydrogen analogy was recently observed in a series of binary Si/Au clusters $[Si_mAu_n]$ (m = 1,2; n = 2–4) in the gas phase by Wang and co-workers.[12] Herein we report a joint experimental and theoretical investigation on a series of abundant Au/N binary cluster cations, $[AuN_4]^+$, $[Au_nN_{2n+1}]^+$ (n = 2–4), and $[Au_3N_6]^+$, which exist as dinitrogen-ligated aurodiazenylium $[(N_2(AuN_2)]^+$, auronitrenium $[N(AuN_2)_2]^+$, auroammonia radical cation $[N(AuN_2)_3]^+$, auroammonium $[N(AuN_2)_4]^+$, and triaurum cation $[(AuN_2)_3]^+$, and are structurally and electronically analogous to diazenylium ($[N_2H]^+$),[13] nitrenium ($[NH_2]^+$),[14] ammonia radical cation ($[NH_3]^+$),[15] ammonium ($[NH_4]^+$), and trihydrogen cation ($[H_3]^+$),[16] respectively, by following the isolobal analogy between N_2-ligated gold (AuN_2) and hydrogen. The chemical stability of these N_2-ligated complexes suggests that they might be viable in wet chemistry. Such a N_2-assisted gold–hydrogen analogy involving a $[AuN_2]^+$ synthon and covalent dative $Au^+{-}N_2$ bond is also relevant to the industrially important nitrogen fixation.

Figure 1 displays the mass spectrum ($180 < m/e < 1000$ amu) of $[Au_pN_q]^+$ clusters obtained by reactive collision of N_2 with laser-vaporized gold clusters. The strong mass

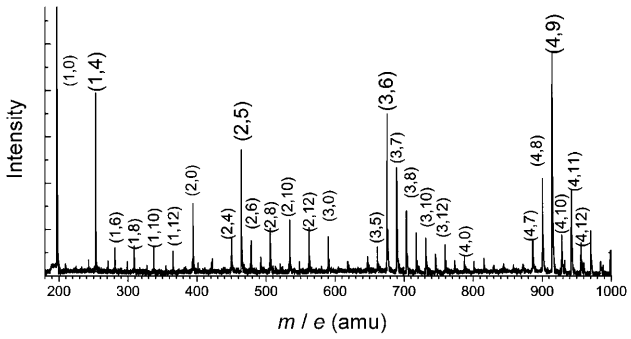

Figure 1. Mass spectrum of $[Au_pN_q]^+$ cluster cations produced by reactive collision of N_2 with laser-vaporized gold clusters. Peaks are labeled with values of p and q in parentheses as (p,q).

spectral peaks for $[AuN_4]^+$, $[Au_2N_5]^+$, $[Au_3N_6]^+$, and $[Au_4N_9]^+$ indicate that these "magic-number" cations are the most abundant for the positive cluster distribution. Furthermore, the signal intensity of $[Au_3N_7]^+$, a radical cation, is comparable to that of $[Au_2N_5]^+$, likely owing to the high stability of its neutral form, Au_3N_7. Moreover, the intense signals of $[Au_mN_{(2m+1)}]^+$ (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 N_2 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.

$[AuN_4]^+$ has a linear $D_{\infty h}$-symmetric ground-state structure, $[N_2\text{-Au-}N_2]^+$ (Figure 2a), isostructural to the isoelec-

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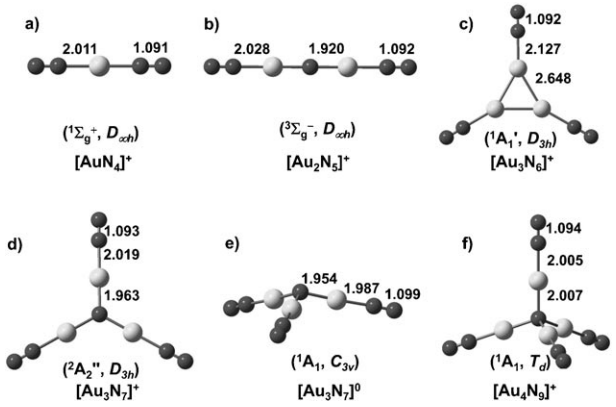

Figure 2. B3LYP/TZP-predicted ground-state structures of a) $[AuN_4]^+$, b) $[Au_2N_5]^+$, c) $[Au_3N_6]^+$, d) $[Au_3N_7]^+$, e) $[Au_3N_7]^0$, and f) $[Au_4N_9]^+$ (N black, Au gray; key bond lengths in Å).

tronic $[Au(CO)_2]^+$[17] and $[Au(CN)_2]^-$ [18a] complexes. $[Au_2N_5]^+$ has a triplet ground state $^3\Sigma_g^-$ with a linear $D_{\infty h}$-symmetric structure, $[N_2\text{-Au-N-Au-}N_2]^+$ (Figure 2b), which is 1.09 eV lower in energy than its singlet excited state, which has a C_{2v}-symmetric bent structure. Similarly, the interstellar species nitrenium $[NH_2]^+$ also has a triplet ground state ($^3B_1$) that is 2.12 eV lower than its singlet excited state.[14c]

$[Au_3N_6]^+$ has a planar D_{3h}-symmetric ground-state structure $[(AuN_2)_3]^+$ that contains a three-membered $[Au_3]^+$ ring (Figure 2c). Its Au–Au distance (2.648 Å) is slightly shorter than that of ligand-free $[Au_3]^+$ cluster (2.661 Å).[16d] Note that the central $[Au_3]^+$ unit has two skeletal valence electrons, akin to the trihydrogen cation.[16a]

$[Au_3N_7]^+$ has a $^2A_2''$ ground state with a planar D_{3h}-symmetric structure, $[N(AuN_2)_3]^+$ (Figure 2d). The neutral molecule $N(AuN_2)_3$ has a closed-shell singlet ground state with a C_{3v}-symmetric structure (Figure 2e). A similar structural change was found from $[NH_3]^+$ (D_{3h}) to NH_3 (C_{3v}).[15] $[Au_4N_9]^+$ has a T_d-symmetric ground-state structure $[N(AuN_2)_4]^+$ (Figure 2f), analogous to $[NH_4]^+$ and $[N(AuPPh_3)_4]^+$.[9]

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 $[(AuN_2)_3]^+$) are bi-coordinated. Second, they have a N_2-ligated central moiety X, $X = N_nAu_m^+$ ($n=0$, $m=3$; $n=1$, $m=2$–4; $n=2$, $m=1$), that is isostructural to the corresponding interstellar species $N_nH_m^+$ ($n=0$, $m=3$; $n=1$, $m=2$–4; $n=2$, $m=1$), implying a N_2-assisted gold–hydrogen analogy. Such a N_2-assisted gold–hydrogen analogy involves a N_2-ligated Au atom (i.e., AuN_2) as synthon, which is in effect similar to the widely exploited $AuPR_3$ synthon.[1,5] We will demonstrate such N_2-assisted gold–hydrogen analogy by analyzing the Au–N_2 bonding and by comparing the molecular orbitals (MOs) of these Au/N binary clusters with their N/H analogues.

We first consider the Au–N_2 bonding in $[Au(N_2)_2]^+$. The DFT-predicted Au^+–N_2 binding energy increases from 0.98 eV in $[AuN_2]^+$ to 1.17 eV in $[Au(N_2)_2]^+$. Further addition of a N_2 molecule to $[Au(N_2)_2]^+$ results in a van der Waals complex, with the third N_2 being weakly bound (see the Supporting Information). It is clear that Au^+ prefers a linear bi-coordinate environment, and the resultant Au^+–N_2 dative bond is covalent in nature.

The Au^+–N_2 bonding can be understood by using the Dewar–Chatt–Duncanson complexation model.[19] As shown in Figure 3, the 6σ MO in $[AuN_2]^+$ and the $5\sigma_g$ MO in $[Au(N_2)_2]^+$ account for the Au^+–N_2 σ bonding donation, whereas the 3π MOs in $[AuN_2]^+$ and the $2\pi_g$ MOs in

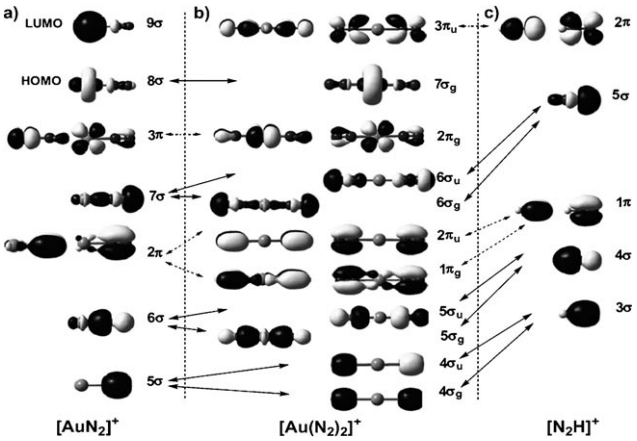

Figure 3. Selected valence orbitals (isosurface value ca. 0.04) of a) $[AuN_2]^+$, b) $[Au(N_2)_2]^+$, and c) $[N_2H]^+$. Solid and dash arrows indicate the correlation of σ- and π-type MOs, respectively, between them.

$[Au(N_2)_2]^+$ account for the Au^+–N_2 π bonding back-donation. Yet, further NBO analyses revealed that the Au^+–N_2 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 0.12 e and 0.06 e in $[AuN_2]^+$ and 0.21 e and 0.07 e per N_2 in $[Au(N_2)_2]^+$. The higher degree of σ donation in $[Au(N_2)_2]^+$ is a result of enhanced sd_σ hybridization of bi-coordinated Au (see the Supporting Information). For the same reason, even stronger and shorter Au^+–ligand bonding was previously found in $[Au(CO)_2]^+$ and $[Au(CN)_2]^-$ complexes.[17,18]

Besides $[Au(N_2)_2]^+$, other abundant Au/N binary clusters (now represented by the general formula $X(N_2)_n$) have similar Au–N_2 covalent dative bonds. As listed in Table 1, the average Au–N_2 binding energy ranges from 0.57 eV in

Table 1: B3LYP/TZP-predicted Wiberg bond order (WBO) and average binding energy E_{av} of Au–N_2 bond(s) in the $X(N_2)_n$ clusters (X = central moiety) and their HOMO–LUMO gap E_g.

$X(N_2)_n$	X	WBO	E_{av}[a] [eV]	E_g[b] [eV]
$[AuN_2]^+$	Au^+	0.30	0.98 (0.95)[c]	4.91 (4.37)
$[Au(N_2)_2]^+$	$[N_2Au]^+$	0.40	1.36 (1.42)[c]	6.77 (4.91)
$[(AuN_2)_3]^+$	$[Au_3]^+$	0.24	0.57	5.54 (3.79)
$[N(AuN_2)_2]^+$	$[NAu_2]^+$	0.36	1.12	1.09 (0.75)[d]
$[N(AuN_2)_3]^+$	$[NAu_3]^+$	0.38	1.05	–
$[N(AuN_2)_3]^0$	$[NAu_3]^0$	0.42	0.72	3.64 (3.07)
$[N(AuN_2)_4]^+$	$[NAu_4]^+$	0.40	1.04	5.19 (2.57)

[a] $E_{av}(Au-N_2) = \{E(X) + nE(N_2) - E[X(N_2)_n]\}/n$; [b] The E_g of central X moiety is given in parenthesis. [c] The CCSD(T)/TZP-predicted E_{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 $[N(AuN_2)_3]^0$. 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 $[Au_3]^+$ and 5.19 eV for $[N(AuN_2)_4]^+$ versus 2.57 eV for $[NAu_4]^+$ (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., 9σ 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 $[N_2H]^+$. As shown in Figure 3, while the occupied valence orbitals of $[N_2H]^+$ can find their equivalence in $[AuN_2]^+$ and $[Au(N_2)_2]^+$, its π-type LUMOs (i.e., the $2\pi^*$ 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 $[(AuN_2)_3]^+$, $[Au_3]^+$, 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

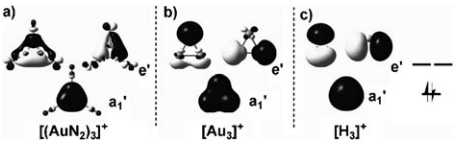

Figure 4. Skeletal valence orbitals (isosurface value ca. 0.04) of a) $[(AuN_2)_3]^+$, b) $[Au_3]^+$, and c) $[H_3]^+$.

$[AuN_2]^+$–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); $[Au_3]^+$ 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 Hückel rule of aromaticity. Consequently, they are σ-aromatic with predicted NICS values of $\delta = -42.8$, -33.4, and -33.8 ppm for $[(AuN_2)_3]^+$, $[Au_3]^+$, and $[H_3]^+$, respectively.

Figure 5 shows the selected valence orbitals of the $[NR_2]^+$, NR_3, 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 $[N(AuN_2)_4]^+$ to 0.85 in $N(AuN_2)_3$, showing the covalent nature of the N–R bonds. Although the N–(AuN_2) bond in $[N(AuN_2)_4]^+$ 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) bond.

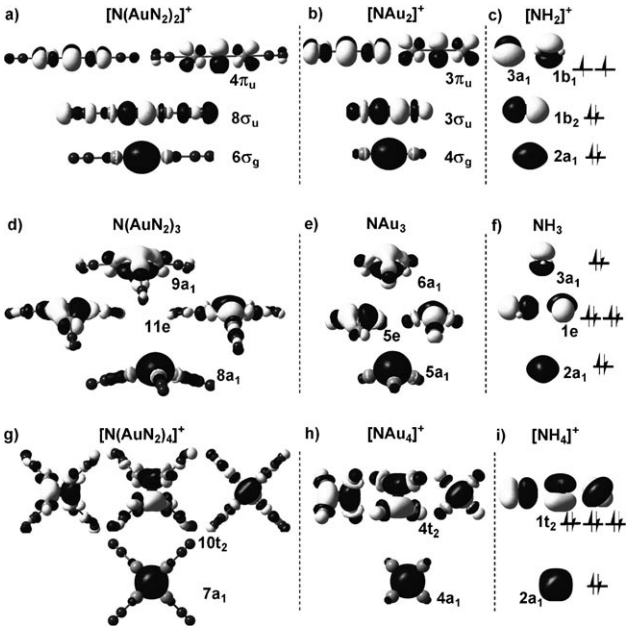

Figure 5. N-centered valence orbitals of $[NR_2]^+$, NR_3, and $[NR_4]^+$ (R = AuN_2, Au, and H).

Table 2: B3LYP/TZP-predicted Wiberg bond order of N–R bond(s) in the $[NR_2]^+$, NR_3, and $[NR_4]^+$ series of species (R = H, Au, and AuN_2).

	R = H	R = Au	R = AuN_2
$[NR_2]^+$	0.79	0.68	0.64
NR_3	0.88	0.85	0.59
$[NR_4]^+$	0.79	0.56	0.46

$$[N(AuN_2)_4]^+ \rightarrow N(AuN_2)_3 + [AuN_2]^+ \qquad \Delta E = 4.32\ \text{eV} \tag{1}$$

The ionization potential of N_2-ligated auroammonia N-$(AuN_2)_3$ 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 ($[AuN_4]^+$, $[Au_nN_{2n+1}]^+$ (n = 2–4), and $[Au_3N_6]^+$) produced by laser vaporization. We are looking forward to wet-chemistry synthesis[34] 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.

Experimental Section

Mass spectrometry: The experiments were carried out using a reflection time-of-flight mass spectrometer (RTOF) with a laser vaporization cluster source.[20] 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.[21] 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.[22] Geometry optimizations of various possible isomers of the Au/N binary clusters were performed using the hybrid density functional B3LYP[23] in combination with double-ξ basis set plus polarization (DZP), that is, the standard 6-31G* basis set[24] for N and Stuttgart/Dresden relativistic effective core potential plus valence double-ξ basis set (SDD)[25] for Au. The as-determined ground-state structures were re-optimized at the B3LYP/TZP level, in which TZP refers to Aug-cc-pVTZ basis set[26] for N and H as well as the scalar-relativistic effective 60-electron core potential[27] plus the 19-electron valence aug-cc-pVTZ-PP 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.[29] The natural bond orbital (NBO) method[30] was used for bonding analyses. Single-point CCSD(T)[31] calculations using the B3LYP-optimized geometries were performed for $[Au(N_2)_n]^+$ ($n = 1$–3) to justify the B3LYP-predicted Au^+–N_2 binding energy. Unless otherwise specified, reported binding energies are ZPE- and BSSE-corrected. The NICS (nucleus-independent chemical shift)[32] values were computed using the GIAO method[33] at the B3LYP/TZP level.

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