Hydrogen Bonding

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Preparing Gold(I) for Interactions with Proton Donors: The Elusive [Au]···HO Hydrogen Bond

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Abstract: *MP2 and DFT calculations with correlation consistent basis sets indicate that isolated linear anionic dialkylgold(I) complexes form moderately strong (ca. 10 kcal mol*$^{-1}$*) Au···H hydrogen bonds with single* H_2O *molecules as donors in the absence of sterically demanding substituents. Relativistic effects are critically important in the attraction. Such bonds are significantly weaker in neutral, strong σ-donor N-heterocyclic carbene (NHC) complexes (ca. 5 kcal mol*$^{-1}$*). The overall association (> 11 kcal mol*$^{-1}$*), however, is strengthened by co-operative, synergistic classical hydrogen bonding when the NHC ligands bear NH units. Further manipulation of the interaction by ligands positioned trans to the carbene, is possible.*

The field of gold chemistry is expanding rapidly, with important discoveries in gold chemistry covering an extensive range of research areas being made unabatedly.[1] Associated with bonding themes of metal atoms and ions, free or present in complexes, are results elaborating weak interactions such as metal–metal and metal–H interactions that could play a role in the construction of supramolecular assemblies, in complex kinetics, and in influencing the electronic structure of the involved metals.[2–4] The former type of association is now well understood at both theoretical and heuristic levels.[5] Although the Pt^{II}···H interaction in complexes has been confirmed by a combination of experimental and theoretical means,[5–7] Au···H interactions, particularly in complexes, cannot be discussed with confidence as yet. The problem is that whereas interactions between proton donors and Au^- ions are accepted as genuine hydrogen bonds,[8] most of the Au···H contacts reported in gold(I) complexes are compromised by virtue of concomitantly occurring "classical" hydrogen bonds, conjugation influences, preferred ligand arrangements or packing effects in crystals that impose positioning of particular H-atoms.[3] Indeed, it has been indicated recently that in a carbene complex of gold(I) exhibiting a potential Au···H interaction, the ligand arrangement remains unchanged when the structure is computationally optimized with protons ignored.[9] A promising intermolecular Au···H contact situation has been found in gold(I) thione complexes, but again, other weak intermolecular interactions are also present, casting some doubt on the stabilizing influence of the claimed hydrogen bonding with gold.[10] Of particular interest is the fact that there appears to be "no particular preference for establishing [Au···H–O] interactions in the solid state",[3] hence we were interested to probe this apparent lack of evidence for Au···H–O hydrogen bonds further. For simplicity, we chose to focus on H_2O, which typically interacts with Au^I centers through the O,[11] rather than the H; we thus aimed to probe the ability of Au^I to act as a Lewis base, counter to its normal behavior as a Lewis acid. Taking our cues from comments by Brammer[12] and Martin[13] that a more negative charge on the metal center would favor stronger hydrogen bonds, we initially embarked on a fundamental theoretical investigation to establish the strength of Au···H interactions in known anionic gold(I) complexes with water molecules as compared to those in gaseous Au^- adducts; calculations were also carried out using neutral gold(I) complexes bearing electron-donating ligands as potential proton acceptors. The results destined as directive for future experimental work, also provide new bonding information and indicate estimates of stabilization achievable by variation of the ligand environment of gold. The electronic properties of the auride anion, Au^-, known as a strong proton acceptor in hydrogen bond formation,[3,12] were mimicked by anionic dihydride (**1**)[14] and dialkyl (**2**, **3**, **4**) complexes[15–17] of gold(I) as well as in neutral complexes (**5–8**)[18,19] having a strong σ-donor *N*-heterocyclic carbene (NHC) ligand installed at gold.

This strategy was largely successful for the anionic complexes **2** and **3**, and their optimized structures along with that of Au^- acting as proton acceptors towards H_2O, are shown in Figure 1 (for computational details and further data, see the Supporting Information). Note that **3** is not known in the condensed phase but $[MeAu\textit{t}Bu]^-$ is.[15] The interaction energies, $E_{\mathrm{Int}} = E_{\mathrm{AB}}^{\mathrm{BSSE}} - E_{\mathrm{A}} - E_{\mathrm{B}}$, for the adducts of **2** and **3** with water, also included in Figure 1, can be compared to those calculated for $\mathbf{Au^-{\cdot}H_2O}$ by us ($-11.6\ \mathrm{kcal\,mol^{-1}}$) and previously by others (-11.36 to $-12.43\ \mathrm{kcal\,mol^{-1}}$).[20–23] An experimental estimate for Au^-···HOH adduct formation is $10.38\ \mathrm{kcal\,mol^{-1}}$.[24] In a broader context, the bond strengths for our Au^I···HOH interactions in $\mathbf{2{\cdot}H_2O}$ and $\mathbf{3{\cdot}H_2O}$ fall between those calculated for the water dimer, H_2O···H_2O (ca. $-5\ \mathrm{kcal\,mol^{-1}}$)[25] and hydrogen bonded Cl^- in Cl^-···H_2O ($-13.5\ \mathrm{kcal\,mol^{-1}}$).[26] These newly calculated energies are also numerically significantly higher than that (-3.9 kcal $\mathrm{mol^{-1}}$) reported recently for a [Pt]···HOH interaction involving a neutral Pt^{II} complex.[6] Au···H–O bond angles range from 151.3 to 165.8° in $\mathbf{2{\cdot}H_2O}$ and $\mathbf{3{\cdot}H_2O}$, while Au···H separations measure 2.47 Å, which is much shorter than the sum of the applicable van der Waals radii (2.75 Å).[27]

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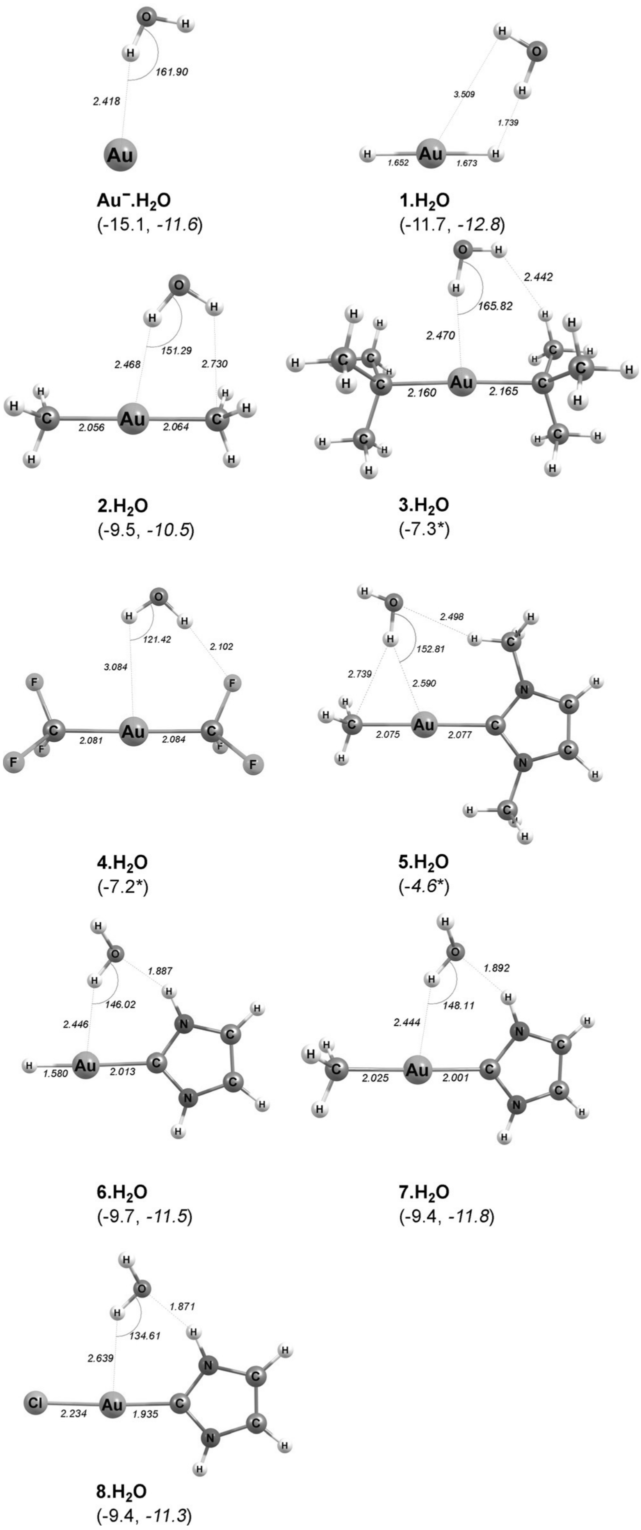

Au⁻.H₂O (-15.1, *-11.6*)

1.H₂O (-11.7, *-12.8*)

2.H₂O (-9.5, *-10.5*)

3.H₂O (-7.3*)

4.H₂O (-7.2*)

5.H₂O (*-4.6**)

6.H₂O (-9.7, *-11.5*)

7.H₂O (-9.4, *-11.8*)

8.H₂O (-9.4, *-11.3*)

Figure 1. Optimized structures of gold complexes **1**–**8** interacting with H_2O. Distances [Å], angles [°], and interaction energies calculated at the B3LYP/aug-cc-pVTZ-pp and MP2/aug-cc-pVTZ-pp (in italics) levels of theory [kcal mol^{-1}] are shown below in parenthesis. * Only the B3LYP/aug-cc-pVTZ-pp value is given for **4·H₂O** and **5·H₂O** owing to computational constraints of optimization at the MP2/aug-cc-pVTZ-pp level.

Surprisingly, the hydrogen bond in **3·H₂O** is weaker than in **2·H₂O**, despite the fact that the *tert*-butyl ligands in **3** are expected to be more electron donating than the methyl ligands in **2**. The better delocalization of the negative charge in complex **3** compared to **2** can be seen from the charges found on the Au, given in Table 1. The Au atom in **3** exhibits an unexpectedly lower negative charge than **2**, and is thus a poorer hydrogen bond acceptor. The most likely reason for this observation could be steric repulsion between the bulky *tert*-butyl ligands, which weakens the Au−C bonds (longer in **3** than in **2**, Figure 1) and thus reduces the electron donation to the Au atom. Similar results have been obtained for the isoelectronic and isostructural $Pd(PH_3)_2$ and $Pd(PMe_3)_2$ complexes,[28] where the steric repulsion occurring for the methyl substituted ligand leads to a more repulsive bonding potential energy surface than with the smaller hydrogen-containing counterpart.

Table 1: AIM derived charges on Au in the complexes prior to adduct formation and on the H_2O hydrogen involved in hydrogen bonding upon adduct formation, and BCP parameters, all in atomic units.

	q(Au) in complex	q(H) in adduct	Au···H BCP ρ	Au···H BCP $\nabla^2\rho$	O···H/ H···H BCP ρ	O···H/ H···H BCP $\nabla^2\rho$
Au⁻	−1.00	+0.64	0.0250	0.052	–	–
1	−0.33	+0.67[a]	–	–	0.021[a]	0.040[a]
2	−0.14 (−0.11)[b]	+0.65 (+0.65)[b]	0.017 (0.018)[b]	0.046 (0.038)[b]	–	–
3[b]	−0.07	+0.58	0.020	0.039	0.004[a]	0.012[a]
4[b]	+0.12	+0.58	0.006	0.017	0.014[c]	0.057[c]
5	+0.04	+0.58	0.014	0.035	0.008[d]	0.029
6	−0.08	+0.66	0.017	0.049	0.028	0.104
7	−0.001	+0.66	0.018	0.049	0.027	0.104
8	+0.17	+0.66	0.012	0.037	0.029	0.105

[a] Value for H···H interaction. [b] Value at B3LYP/aug-cc-pVTZ-pp level of theory. [c] Value for H···F interaction. [d] Value for CH···O interaction.

Complex **4** is not known but serves as a model for $[(C_6F_5)_2Au]^-$, which has been prepared.[29] Despite the relatively high positive charge on the central metal in **4** owing to the electron-withdrawing nature of the F atoms on the ligands (Table 1), an adduct with water is formed. Nevertheless, the very long Au···HO separation casts doubt on the existence of a hydrogen bond for this species (see below).

Strikingly, complex **1**, in comparison, does not form an Au···HO hydrogen bond with water, despite the large negative charge on the Au, choosing instead to undergo a H···H interaction (of very similar strength to the Au···H hydrogen bonds in **2·H₂O** and **3·H₂O**), which is the first example of a dihydrogen interaction in gold chemistry. Since our focus here is on the formation of Au···HO hydrogen bonds, this aspect of our investigation will not be discussed further, but is the subject of another paper.[30]

It is now realized that relativistic effects are probably not as important in dispersion-driven Au···Au aurophilic interactions as was previously accepted.[5,31,32] Nevertheless, consideration of the known greater availability of d-electrons as well as the possibility of a more efficient combination of outer s, p, and d orbitals in bonding on account of relativistic effects,[33] led us to hypothesize that relativistic influences could be beneficial and even dominant in the formation of the Au···H bond in gold(I) complexes. This prediction was indeed borne out by calculations.

The geometry of complex $\mathbf{2{\cdot}H_2O}$ was optimized using the non-relativistic ECP60MHF basis set (see the Supporting Information for details). The results (Figure 2 a) show that the Au···HO interaction is absent but is replaced by a slightly weaker (B3LYP: -8.82; MP2: -10.33 kcal mol^{-1}) $H_3C\cdots HO$ interaction when relativistic effects are not taken into account. No noncovalent stabilizing interaction is observed between Au and H_2O according to the NCI plot.[34] In contrast, a red region indicating a stabilizing interaction is clearly visible between a H_3C^- ligand and an HO unit of the water molecule (Figure 2 b).

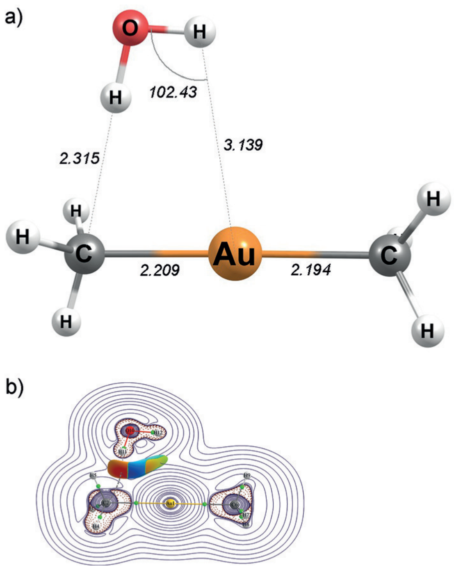

Figure 2. a) Optimized geometry of $\mathbf{2{\cdot}H_2O}$ with relativistic effects omitted, and b) the corresponding Laplacian and NCI plots. Red: attractive interaction, blue: repulsive interaction, green: no interaction.

The well-known inductive influence of the NHC ligand in neutral complex **5** (Figure 1; q(Au): $+0.035$, Table 1) is not sufficient to effect hydrogen bonding comparable in strength to that found in **2** and even **3** between the central gold atom and water, a result reflected in a relatively long Au···HO distance (2.590 Å) and an internal energy of only -4.6 kcal mol^{-1} for the adduct $\mathbf{5{\cdot}H_2O}$.

Employing neutral simplified model systems for Nolan's[19] and Baker's[18] carbene complexes, respectively (**6**–**8**, Figure 1), in 1:1 adduct formation with H_2O, a new and useful concept emerged. Note that variants of the ligand types, that is, thiazole- and imidazole-derived NHCs that contain N−H units,[35,36] have been reported previously. The small negative or even positive charges on the Au atoms in these adducts suggest that the hydrogen bonds when formed would be relatively weak (E_{Int} probably less for $\mathbf{8{\cdot}H_2O}$ than the 4.6 kcal mol^{-1} calculated for $\mathbf{5{\cdot}H_2O}$). Yet interaction energies for complexes **6**–**8** with water (Figure 1), again indicate moderately strong associations. Clearly, interactions between one of the H−N units of the NHC ligand and the water oxygen atoms acting as conventional hydrogen bond acceptors are also present, such that the water molecules are aligned to support maximum simultaneous interaction with both the Au atoms and NH fragments. No stable alternative geometries containing only one hydrogen bond could be identified. The energies indicated in Figure 1 are therefore associated with both Au···HO and O···HN bonding. Such interactions, leading to a different and stabilizing bonding motif for the water molecule, are reminiscent of Kryachko's coordination anchoring that theoretically enables Au···H association between neutral gold clusters and DNA bases.[37,38] Under the present circumstances, the proton donor is anchored at the NHC ligand while the two interactions are operating synergistically in tandem. Similar amphoteric behavior of the water molecules could be responsible for the observation that selective H···H association (see $\mathbf{1{\cdot}H_2O}$ above) is not an alternative, competitive and viable option for the hydride complex **6** when interacting with water.

Although the short Au···H distances of the optimized structures and interaction energies of products $\mathbf{6{\cdot}H_2O}$ and $\mathbf{7{\cdot}H_2O}$, and to a lesser extent, $\mathbf{8{\cdot}H_2O}$ suggest that Au···HO hydrogen bonds are present, these results alone do not confirm that such bonds provide stabilization to the systems. Such contacts could also appear owing to the presence of stronger directional O···HN bonds, as have been previously suggested for other examples.[3] To probe the potential interactions in greater depth, we turned to atoms in molecules (AIM) analysis, where the presence of bond critical points (BCPs) clearly indicates bonding between H_2O molecules and Au^- as well as in all complexes except **1** (see Table 1 and the Supporting Information for details). The presence of a BCP is one of the IUPAC requirements for the existence of hydrogen bonding,[39] although there has been some discussion regarding the validity of this approach, with Thakur and Desiraju cautioning against its use in discriminating between hydrogen bonding and agostic interactions if the charge-depleted metal center is positively charged.[40,41] However, these authors point out that a positive charge on the hydrogen atom in the adduct, as was found for all examples studied here (Table 1), serves as a useful indicator for hydrogen bonding. Comparison of various properties of the BCPs in all complexes (**2**, **3**, **6**, **7**) where the charge on the gold atom was negative prior to interacting with H_2O, namely the electron density ρ (see Table 1), the Laplacian of the electron density $\nabla^2\rho$ and the total electronic energy density H_b (see the Supporting Information), to the corresponding values published by Nakanishi et al.[42] indicate that these Au···HO close contacts unequivocally represent genuine hydrogen bonds, albeit weaker than the NH···O hydrogen bonds observed in $\mathbf{6{\cdot}H_2O}$–$\mathbf{8{\cdot}H_2O}$. The three complexes containing Au atoms with positive charges (**4**, **5**, and **8**), undergo weaker interactions as indicated by the BCP parameters, although the ρ values suggest that **5** and **8,** nevertheless, contain genuine, albeit weak hydrogen bonds. BCP parameters for $\mathbf{4{\cdot}H_2O}$ indicate only a van der Waals-type interaction, as also suggested by the abovementioned much longer Au···H distance (3.08 Å) as compared to the other adducts. The large interaction energy thus arises from a strong standard H···F hydrogen bond, rather than the Au···H interaction. The dependence of the strength of the interaction on the charge on the Au atom before adduct formation suggests that these hydrogen bonds are electrostatic in origin, although from the properties of the Au···H BCP in **4·H_2O** it appears that dispersion also plays a role. This was confirmed by undertaking energy decomposition analysis (EDA)[43] to analyze the nature of the interactions between the Au complex and water (with the gold species and H_2O chosen as the two fragments). The results shown in the Supporting Information, Section S4 confirm that the interactions are primarily electrostatic in nature (48.9 % of attractive interactions for **3·H_2O** to 61.3 % for **4·H_2O**), while dispersion plays a relatively small, but nevertheless significant role (at most 20.4 % for **5·H_2O**). In particular, as expected **Au$^-$·H_2O** exhibits the highest electrostatic component (−15.7 kcal mol^{-1}) concomitant with the lowest dispersion contribution (−1.5 kcal mol^{-1}), while the weak interaction observed for **5·H_2O** corresponds to the lowest electrostatic stabilization of −7.5 kcal mol^{-1}, as suggested by the atomic charges and AIM analysis.

NCI analysis[34] for **6·H_2O–8·H_2O** (Figure 3 and Supporting Information) is in accord with the AIM results, showing that the Au···HO hydrogen bonds provide less stabilization to the adducts than the O···HN interactions (indicated by lime/yellow regions between OH and Au, as opposed to red/yellow regions between O and HN). Most importantly, the NCI plots confirm that the Au···H contacts are attractive and provide added stabilization to the system. The steric repulsion indicated by the green areas in Figure 3 is also highlighted in the EDA results, where the steric repulsion within **6·H_2O–8·H_2O** is greater than for the other adducts.

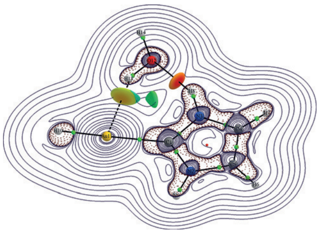

Figure 3. Two-dimensional contour plot of the electron density Laplacian for **6·H_2O** overlaid with the three-dimensional NCI plots at the MP2/aug-cc-pVTZ-pp level of theory. Red: attractive interaction, blue: repulsive interaction, green: no interaction.

According to our MP2 calculations, the strength of association (as shown directly related to the Au···HO interaction strength) in these adducts, depends upon the electron-donating character of the ligand positioned *trans* to the NHC ligand in the order $CH_3 > H > Cl$, although the differences are small. This result agrees with the variation in charge on the Au atom, while the Au···H distances suggest that the Au···H bonds in **6·H_2O** and **7·H_2O** are stronger than in **8·H_2O**. Note that very weak secondary interactions between one hydrogen atom of the water molecule and one of the coordinated carbon atoms in **2** or an H atom in **3** (at 2.7 and 2.4 Å, respectively), could also provide some extra stability during the "inverted hydration",[6] of the anionic complexes **2** and **3**.

We conclude that the interaction between gold(I) and a H_2O molecule in certain privileged complex structures is strong enough to warrant further theoretical and practical investigation. The latter, of course, is complicated by a variety of interactions in the condensed phase compared to the idealized and rather simple 1:1 association of isolated molecules described above.[44] Certain interaction energies and bonding analysis results, nevertheless, remain valid, important and even dominant. Initial Au···H bond formation could, for example, be followed by transition states during hydrolysis processes. Investigations are underway in our laboratory concentrating on the role played by both ligands in enhancing Au···H interactions, further probing the interaction with other proton donors or proton acceptors such as recently reported Au^0 complexes,[45] and characterizing in greater depth the Au−H···H dihydrogen bond, the first example of which was discovered during this investigation. Initial results indicate, as anticipated, that Au^I···HF hydrogen bonds in selected complexes are significantly stronger than those involving H_2O.

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