

The Smallest “Aurophilic Species”

Raphael J. F. Berger

Anorganische Chemie und Strukturchemie, Universität Bielefeld, D-33615 Bielefeld, Germany

Reprint requests to Dr. R. J. F. Berger. E-mail: Raphael.Berger@uni-bielefeld.de

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The existence of the C_{2v} symmetric closed-shell di[gold(I)]hydronium cation $[\text{Au}_2\text{H}]^+$ (**1**), is predicted. It is shown that **1** is the smallest possible molecular species containing aurophilic contacts. Equilibrium structural parameters, vibrational frequencies and formation energies of **1** from Au^+ and AuH , have been calculated, employing a series of highly correlated but available standard relativistic *ab initio* methods up to CCSD(T) level of theory and all-electron basis sets of quadruple- ζ quality with double polarizations. Relativistic effects have been taken into account by employing pseudo-relativistic electron core potentials (ECP) or a scalar relativistic treatment using a Douglas-Kroll-Heß Hamiltonian of 2nd, 3rd and 4th order (DKH2, DKH3, DKH4).

Key words: Au(I)–Au(I) Interaction, Metallophilic Interaction, Gold Hydride, Quantum Chemical Calculation

Introduction

Gold is not only appealing for aesthetical and economical reasons, it has also been the subject of intense research activities in chemistry, from the early days of alchemy to the present day. An overview of modern gold chemistry is contained, for example, in [1]. One of the most “attractive” chemical properties of gold in its compounds is the fact that two formally positively charged Au(I) atoms tend to aggregate and form contacts almost as short as in metallic gold. The terms “aurophilicity” and “aurophilic attraction” were coined for this effect by Schmidbaur [2]. The theoretical literature on this subject is vast – two recent review articles have appeared [3, 4] and a list of earlier summaries is compiled in Table 4 in [5].

The nature of the aurophilic attraction is closely related to both dispersion interactions (the attractive part of correlation interactions) and relativistic effects [5]. Hence, a proper quantum chemical description of aurophilicity is still a challenging task. For the consideration of relativistic effects there exist several competing schemes of different flavors, as summarized in section 2.2 in [5]. A very recent work of Bühl *et al.* has analyzed the performance of different DFT functionals to describe gas-phase equilibrium structures of third row transition metal complexes under explicit consideration of relativistic methods [6].

Despite the great effort currently spent exploring the quantum-chemical methods required to describe au-

rophilicity, a literature search reveals a surprising fact: The smallest chemical species containing an aurophilic interaction have not yet been identified in the literature. While the linear anions $[\text{AuAuH}]^-$ and $[\text{AuHAu}]^-$ are both theoretically and experimentally well documented [7], to the best of our knowledge **1** has been mentioned only twice in the scientific primary literature as yet. Gaspar and Tamassy-Lentai studied related reactions computationally, involving alkali metals and as an extension also coinage metals in 1981 and 1982, respectively, half a dozen of years before the formulation of the concept of “aurophilicity” [8]. In their work they used the analytical Hellmann pseudopotential [9] in a form modified semi-empirically according to Landányi for the description of the core electrons of the Au atom but without explicit consideration of relativistic effects [10]:

$$V_{H'} = -Z/r + A \exp(-2\kappa r)/r + B \exp(-2\lambda r)/r,$$

with A , κ , B and λ as adjustable parameters. They calculated the equilibrium geometry parameters of **1** to $\text{Au-H} = 113.0$ pm and $\text{Au-Au} = 227.5$ pm.

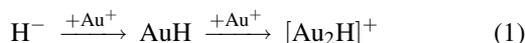
We will show in this work, that the di[gold(I)]hydronium cation $[\text{Au}_2\text{H}]^+$ (**1**) is in this sense the smallest possible species with its bonding affected by aurophilic interactions, referred to here as an “aurophilic species”. The C_{2v} symmetric, closed-shell cation **1** (*v. i.*) seems to be ideally suited as a benchmark sys-

tem for standard quantum-chemical methods, trying to explore the limits of approximations. A collection of results from correlated *ab initio* methods, up to CCSD(T), and different scalar relativistic approaches, which are available standards in commercial programs, are presented. The dependence of the structural parameters, vibrational frequencies and energies on the level of theory is discussed, and the possible existence of **1** and its stability are investigated on the basis of its calculated properties.

Results and Discussion

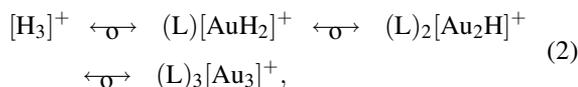
Heuristics

The concept of “aurophilicity” in the originally formulated [2] stricter sense, only deals with interactions between gold centers in the formal oxidation state +I (for a recent critical review see also [11]) and thus does not apply *e.g.* to the gold dimer Au₂ (a thoroughly investigated reference system [12–14]) with the atoms in formal oxidation state of 0. On the other hand, the digold dication [Au₂]²⁺, appears to be an unstable species in its ground state [15], with a purely repulsive interatomic potential [16]. However, our own results have shown now that the [Au₂]²⁺ fragment can be stabilized by adding a hydride anion, which is the simplest possible anion, to formally yield **1**. From a different perspective, **1** can be also regarded as the formal product of the double auration of a hydride anion,



yielding an aurophilically stabilized, positively polarized hydride anion (or “hydronium cation” as the term is used in this context). In this view **1** is an analog of the well known bis-gold halogenonium cations [17].

Since (phosphino)gold(I) cations [(L)Au]⁺ are isolobal analogs of H⁺ [18], from again a different perspective, **1** (or its ligand stabilized derivatives) can be regarded as an isolobal analog of the H₃⁺ cation, a textbook example for 2-electron-3-center (2e⁻3c) bonding and one of the most abundant molecular ions in the universe [19]. H₃⁺ is formally transformed in two isolobal substitution steps



via [AuH₂]⁺ (**2**) into **1** and furthermore to [Au₃]⁺ (**3**) or their respective ligand coordinated forms. The

isolobal analogy of **1** and H₃⁺ is also noted in a recent report about the isolation and structural characterization of carbene ligand-coordinated forms of both the gold(I)hydride AuH and **1** [20].

For cation **2** aurophilicity is not an issue, but the cation is an interesting case of dihydrogen complexation. This is not considered here, but will be examined in a separate study, which is currently in progress.

For the sake of completeness, the radical species [HAu₂]^{2+•} (**4**) was considered as a potentially even smaller aurophilic system than **1**, although the formal oxidation state of the gold atoms in **4** is not +I. A structure optimization at the DFT level of theory [21] results in an almost linear equilibrium structure, showing no indication of an intramolecular Au···Au attraction [Au–H = 169.1 pm, Au–Au = 338.3 pm, ∠(Au–H–Au) = 177.5°]. For these reasons **1** is the “smallest possible aurophilic species”.

Properties of **1**

In this section only the results of the calculations at the highest employed level of theory [22] are discussed.

Molecular geometry

All attempted structure optimizations of **1** yielded C_{2v} symmetrical equilibrium geometries (Fig. 1). The Au–Au distance was calculated to be 260.1 pm, which

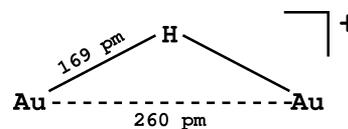


Fig. 1. Equilibrium structure of **1** at the DF-LCCSD(T0)/TZVPP/DKH3 level of theory.

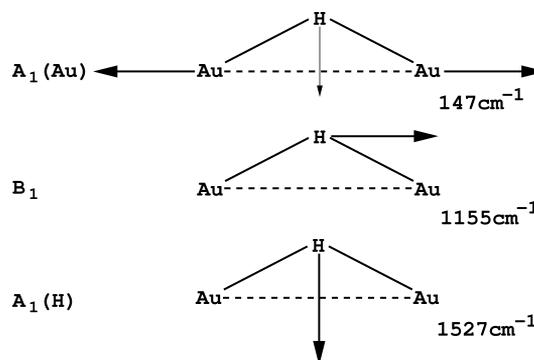


Fig. 2. Normal modes of vibration of **1**, labeled according to symmetry and atoms involved.

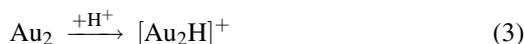
is generally shorter than aurophilic Au(I)··Au(I) contacts (in the solid state) which, as a rule of thumb, are in the order of 300(25) pm [23]. This effect may be assigned in part to the unsaturated coordination sphere of the Au atoms, and to the bonding situation at the small hydrogen atom. The Au–Au bond length in **1** is 12.9 pm longer than in Au₂ [24], while the Au–H distance of 169.0 pm is 16.6 pm longer than that in AuH [5].

Vibrational frequencies

The three fundamental vibrational frequencies are calculated as 147, 1155, and 1527 cm⁻¹. The modes are depicted in Fig. 2. As expected, the mode containing the Au–Au stretch is lower in frequency than the corresponding one in Au₂ of 191 cm⁻¹ [24]. Due to the relative masses of gold and hydrogen, the other two normal modes show almost no contributions of Au atom motions in the harmonic approximation. Hence, they are represented by two exactly perpendicular motions of the bridging hydrogen atom.

Energetics and thermochemistry

The energy balance of the exothermal second step in reaction (1), AuH + Au⁺ → [Au₂H]⁺, amounts to -59.0 kcal mol⁻¹ (including a counterpoise correction for the BSSE of 0.5 kcal mol⁻¹). The zero point vibrational energy correction to this value is 0.6 kcal mol⁻¹ ($\Delta H^0 = -58.4$ kcal mol⁻¹). The protonation of Au₂ may be regarded as an alternative route to obtain **1**,



Using ΔE of reaction (1), the experimentally determined dissociation energies of Au₂ and AuH [5] and the (first) ionization energies of H and Au [25] in a Born-Haber cycle, ΔE of the highly exothermal reaction (3) is determined to amount to -179.0 kcal mol⁻¹.

Bonding

The considerable elongation of the Au–Au distance when changing from MP2 to HF level of theory (254.2 → 286.4 pm, see Table 1) demonstrates clearly the dominance of aurophilicity in the Au··Au interactions in **1**. This interpretation is reinforced by an NBO charge decomposition, which assigns partial charges of $\approx +0.6$ to the Au atoms and ≈ -0.2

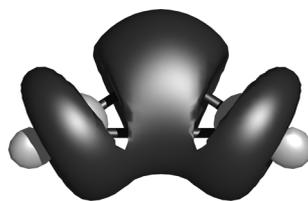


Fig. 3. Valence orbital of **1** (HF/TZVPP/ECP). The small positive overlap region between the gold atoms at the basis of the triangle hints to a covalent $2e^-3c$ bonding contribution to the Au··Au interaction in **1**.

to the H atom. However, a glance at the valence orbital of **1** (Fig. 3) also hints at a possibly small covalent $2e^-3c$ bonding contribution to the Au–Au contact. Both types of interactions may collude in a synergism resulting in the remarkably short Au(I)··Au(I) distance of 260.1 pm [26]. A more detailed analysis of the bonding situation in **1** is beyond the scope of this work and shall be presented in a comparative study of **1**, **2** and **3** elsewhere.

Computational Remarks

General

Heß and Kaldor showed for the gold dimer [12] that in order to obtain results which do not rely on systematic error cancellation in conjunction with an all-electron scalar relativistic treatment, the following criteria are critical: the inclusion of *h*- and even *i*-type basis set functions; the correction of the dissociation potential for the basis set superposition error (BSSE), and the inclusion of at least 34 electron pairs into the correlation space [12]. In this way inaccuracies of less than 1 pm in geometries, and less than 20 wave numbers in vibrational frequencies can be achieved without having to rely on systematic error cancellations. Moreover, these authors have shown that a correlation treatment of at least CCSD(T) is necessary, since double excitation schemes (CCSD, MP2) in general turn out to overestimate Au–Au interactions.

For various reasons it is still not possible to improve such accuracies using only available standard low-order scaling methods. Two main reasons may be mentioned. Firstly, optimized and efficient RI-auxiliary basis sets for basis sets which include *h* and *i* functions are not yet available. Secondly, there is no concise standardized scheme to correct for an intramolecular BSSE in molecules containing more than two atoms. In this work we do not aim to get beyond these limits for [HAu₂]⁺ either, but we rather want to show the trends

Table 1. Comparison of equilibrium structural parameters and frequencies of vibrational normal modes (see Fig. 2) of **1** and AuH calculated at different levels of theory. Bond lengths are given in pm, angles in degrees and frequencies in cm^{-1} . To display trends clearly, redundant entries have been added into the table.

Wave func.	— Method —		— [HAu ₂] ⁺ —				— AuH —		
	Basis	Relativ.	Au–Au [pm]	Au–H [pm]	A ₁ (H) [cm^{-1}]	B ₁ [cm^{-1}]	A ₁ (Au) [cm^{-1}]	Au–H [pm]	ν [cm^{-1}]
HF	def2-TZVPP	ECP	286.4	172.2	–	–	–	–	–
MP2	def2-TZVPP	ECP	254.2	165.6	1654	1225	160	149.2	2473
SCS-MP2	def2-TZVPP	ECP	258.3	166.7	1595	1219	148	150.3	2407
LCCSD(T0)	def2-TZVPP	ECP	261.1	168.9	1502	1155	143	152.6	2262
SCS-MP2	def2-TZVP	ECP	260.5	167.2	1585	1216	145	151.9	2358
SCS-MP2	def2-TZVPP	ECP	258.3	166.7	1595	1219	148	150.3	2407
SCS-MP2	def2-QZVPP	ECP	256.9	166.2	1610	1226	152	149.6	2417
LCCSD(T0)	def2-TZVP	ECP	263.5	169.2	1508	1196	135	153.6	2254
LCCSD(T0)	def2-TZVPP	ECP	261.1	168.9	1502	1155	143	152.6	2262
LCCSD(T0)	def2-QZVPP	ECP	259.2	168.9	1527	1155	147	152.6	2285
LMP2	SARC-TZVPP	DKH3	257.0	167.1	1598	1180	155	150.6	2425
SCS-LMP2	SARC-TZVPP	DKH3	260.5	167.5	1550	1180	145	150.8	2400
LCCSD(T0)	SARC-TZVPP	DKH3	260.1	169.0	–	–	–	152.7	2291
SCS-LMP2	SARC-TZVP	DKH2	261.7	168.6	1527	1125	143	151.5	2386
SCS-LMP2	SARC-TZVPP	DKH2	260.8	167.6	1545	1181	144	150.9	2391
SCS-LMP2	SARC-QZVPP	DKH2	259.9	167.3	1555	1204	146	150.7	2386
SCS-LMP2	SARC-TZVPP	DKH2	260.8	167.6	1545	1181	144	150.9	2391
SCS-LMP2	SARC-TZVPP	DKH3	260.5	167.5	1550	1180	145	150.8	2400
SCS-LMP2	SARC-TZVPP	DKH4	260.5	167.5	1550	1180	145	150.8	2399
	CCSD(T)/AE [30]							152.5	2288
	exp							152.5	2305

in approximating these limits as closely as possible, using the available standard methods only.

For the CCSD method and all scalar relativistic methods (MP2, SCS-MP2 using DKH n , $n = 2, 3, 4$) in addition to the RI approximation, the local approximation implemented in MOLPRO [27–29] was also used. However, due to the small size of the system no “distant” or “very distant” pairs occurred and full advantage of the low-order scaling of the method may not have been achieved.

In the CCSD(T) method the non-iterative-triples treatment (T0) was used, since test calculations for AuH showed that the influence of a full iterative triples treatment (TF) on the geometrical parameters is negligible, and the efficiency, at least for the large SARC type basis sets, is drastically improved using T0.

In all calculations a frozen core treatment was employed, since for both the TURBOMOLE basis and auxiliary basis sets, as well as for the SARC basis sets (which have been developed in the first place for uncorrelated methods) [14], this is recommended in connection with MP2 or CC methods.

Correlation treatment

Table 1 gives an overview of the calculated structural and spectroscopic properties of **1** at the different

levels of theory employed. Additionally, the same calculations on AuH, for which experimental reference values exist, were included in this Table. Three different types of correlated wavefunctions were used in this work: MP2, SCS-MP2 and CCSD(T). It is well known that SCS-MP2, especially for molecules with strong correlation interactions, gives a more balanced description of attractive and repulsive contributions than MP2, and in this respect may give results which are close to coupled cluster methods including triple excitations [31]. For that reason we chose SCS-MP2 as a correlated method which is, in terms of approximation, in between MP2 and CCSD(T).

In both the relativistic ECP treatments and the scalar relativistic approximations, the correlation level has the biggest influence on the Au–Au distance in **1**, which turns out to be the most sensitive parameter [along with the A₁(H) vibrational mode] in this study. Also, in both treatments the SCS-MP2 value is closer to the CCSD(T) than to the MP2 value, albeit more pronounced in the DKH3 treatment. Here especially, it seems likely that the CCSD(T) values for the Au–Au distance of 261.1 and 260.1 pm are close to the correlation limit. This observation is confirmed by the respective parameters of AuH, for which experimental values are available (see Table 1).

In the case of the parameters which involve the hydrogen atoms [Au–H, $A_1(H)$, B_1], it has to be noted that there is a much larger gap between the results of SCS-MP2 and CCSD(T) than between the results of the two MP2 methods. This again holds true for both relativity treatments (ECP/DKHn). However, a comparison with the results of the calculations on AuH shows that this is more likely due to the errors of the SCS-MP2 approximation and not due to the errors of the CCSD(T) calculation.

Still, the close match of parameters from both levels [DF-LCCSD(T0)/TZVPP with ECP or DKH2] with the experimental values should be taken with caution, since neither *h*- or *i*-type basis functions, nor BSSE corrections have been applied in these cases (as recommended in [12] for Au₂), although according to the expected trends, both effects should cancel to some extent [counterpoise (cp) correction elongates the Au–Au distance, while it shrinks with an increasing basis set (*v. i.*)].

Basis set

As mentioned before, the Au–Au distance is reduced when going from TZVP to TZVPP and from TZVPP to QZVPP basis sets. However, this trend is more pronounced in case of the ECP treatments [–2.2, –1.4 pm for SCS-LMP2 and –2.4, –1.9 pm for LCCSD(T0)] than for the scalar relativistic approximations (–0.9, –0.9 pm for SCS-LMP2). This might be related to the fact that the relative differences in terms of “space exhaustion” between the SARC basis sets are considerably smaller than those between the def2 basis sets [32]. The conclusion has to be that a basis set saturation is not guaranteed even in case of the QZVPP sets, but may be closer-by in case of the SARC-QZVPP basis sets.

Basis set superposition error

1 cannot be decomposed into two monomers that interact only “weakly”, hence no advantage could be taken of the BSSE elimination properties of the local-MP2 and local-CCSD approximations. To estimate the size of the BSSE in case of the highest employed level of theory, a cp correction for the potential energy of the Au–H–Au angle deformation around the (not cp-corrected) equilibrium structure of **1** was made [33]. Both the normal potential and the cp-corrected potential are shown in Fig. 4. The effect of the cp correction on the equilibrium distance (r_e) is an increase

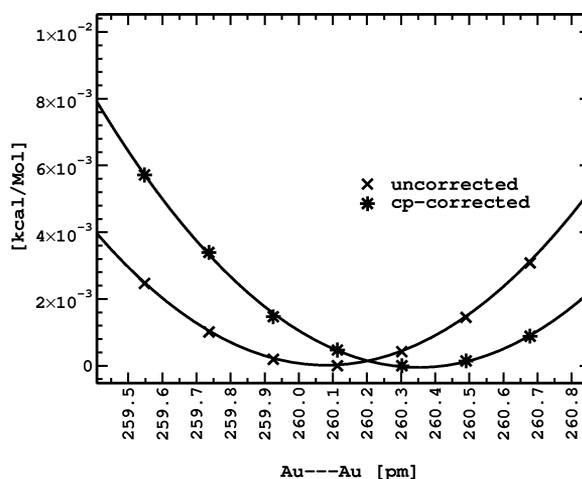


Fig. 4. Relative Au–Au stretching potentials of **1** at Au–H = 169.0 pm, with and without cp correction, which shifts r_e by $\approx +0.25$ pm. The absolute energy difference between cp-corrected and non-corrected minimum energies is $8.2083 \cdot 10^{-4}$ eV.

by 0.25 pm (interpolated), while the total cp correction to the minimum energy amounts $+8.2083 \cdot 10^{-4}$ eV (+0.53 kcal/mol).

Relativity treatment

While the DKH2 and the DKH3 treatments in general give very similar results, and the DKH3 and DKH4 results are virtually equal, the difference between the ECP treatment and DKH at the same basis set hierarchy is not negligible. Still, at the highest level of theory [LCCSD(T0)/QZVPP] the results of the different treatments are approaching one another and deviations of structural parameters are only about 1 pm, and 6 cm^{-1} for vibrational frequencies.

Conclusion

The molecular ion **1** has been identified as the smallest molecular species which contains aurophilic contacts in the stricter sense of this concept. It can be interpreted as a doubly aurophilic hydride anion. A synergism of aurophilic attraction and a small covalent $2e^-3c$ bonding contribution results in the extremely short Au–Au contact of 260.1 pm (*ab initio*). Based on calculated properties, the existence of **1**, for instance under mass spectrometrical conditions, appears to be possible.

In a series of available standard high-level *ab initio* methods, the limits of computationally achiev-

able accuracies for medium sized molecules containing Au(I)··Au(I) interactions were investigated. While an accuracy as achieved with standard experimental methods is still out of reach without making use of some systematic error cancellation, values with only slightly lower accuracy are already obtainable with low-order scaling methods, even for problematic cases such as molecules exhibiting auophilic interactions.

Computational Section

All calculations, except the DFT calculation on **4** and the HF calculation on **1**, were carried out using the RI- or, equivalently, the DF-approximation. Hence, this work does not deal with the accuracy problem and with errors introduced by this scheme of an approximation of multi-orbital integrals by three center terms.

The calculations for the computational levels termed MP2/TZVP/ECP, MP2/TZVPP/ECP, SCS-MP2/TZVPP/ECP, MP2/QZVPP/ECP, SCS-MP2/QZVPP/ECP were carried out with the TURBOMOLE program package, version 5.10 [34, 35] using the RI-MP2 [36–39] routine as it is implemented in the *ricc2* program deck [40, 41]. For the SCS methods, Grimme’s spin-component scaled approach was used in combination with the standard parameters $\cos = 6/5$ and $\text{css} = 1/3$ [42]. TURBOMOLEs def2 basis sets [43, 44] including the corresponding relativistic pseudo potential on Au [45] from Andrae *et al.* were used throughout in connection with the corresponding auxiliary basis sets for

the RI fit [38, 46, 47]. All frequency analyses at this level were carried out numerically [48].

The calculations for the remaining methods were performed using MOLPRO (version 2008.1) [27].

For RI-LMP2 [28] with pseudo-relativistic electron core potential treatments, analytical gradients [49] are available for the geometry optimization in MOLPRO. Coupled cluster optimizations were carried out using also a local correlation treatment, CCSD(T0) [29], with non-iterative local triples (T0) and numerical gradients. For the methods using ECPs, the same basis and auxiliary basis sets as for the TURBOMOLE methods were employed. All methods using explicitly scalar relativistic treatments with Douglas-Kroll-Heß Hamiltonians of 2nd, 3rd or 4th order (DKH2, DKH3 and DKH4, respectively [50, 51]) were used in conjunction with segmented all-electron relativistically contracted (SARC) TZV and QZV quality basis sets [14] augmented with (one or two) polarization functions from the TURBOMOLE def2 basis set library.

All correlated calculations were performed using a “frozen core” of electron pairs, which were not taken into the correlation space. For $[\text{AuH}_2]^+$ 11 electron pairs were taken into the correlation space, and 6 for AuH and Au^+ .

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