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COMMUNICATION

Does Aurophilicity Exist Beyond the Solid State?

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The first experimental gas-phase structure exhibiting aurophilic Au(I)···Au(I) interactions was determined by electron diffraction for the *o*-dimethylphosphanyl(perfluorophenylene)gold(I) dimer. The Au···Au contact is shorter than in the crystal structure, providing direct gas-phase evidence for an aurophilic attraction in a ligand-supported molecular system. High-level relativistic coupled-cluster calculations reproduce the experimental gas-phase value.

Aurophilicity, the attractive interaction between closed-shell Au(I) atoms, has played a central role in gold chemistry since its recognition by Schmidbaur in the 1970s.[1] Au(I)···Au(I) contacts are often substantially shorter than the sum of the van der Waals radii, approaching the distances in elemental gold.[2–7] Early theoretical studies attributed these interactions to electron correlation and relativistic effects,[9–11] while their quantitative description remains debated.[12–17] In particular, the balance between dispersion, relativistic contributions, and direct metal–metal interactions is still being discussed.[17]

Experimentally, structural evidence for aurophilicity relies almost exclusively on condensed-phase measurements. However, crystal packing and polarization effects can make direct comparisons with theoretical models for isolated molecules difficult.[18,19] Although early variable-temperature ^{31}P NMR studies by Schmidbaur and coworkers already provided indirect evidence for intramolecular Au(I)···Au(I) attraction in solution,[1] direct gas-phase structural characterisation has remained elusive. Even for lighter coinage metals, gas-phase metal–metal distances are exceedingly rare; a notable example is the copper(I) pivalate dimer.[20] No experimental gas-phase Au(I)···Au(I) distance has yet been reported.

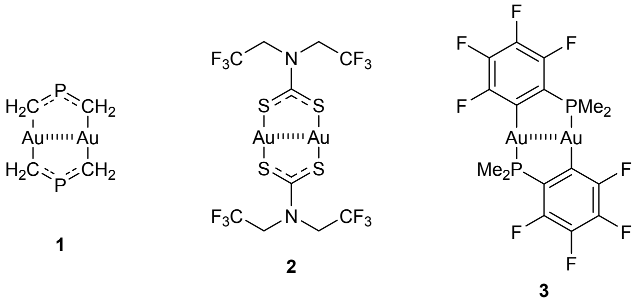

Fig. 1 Volatile compounds with Au···Au interactions. **1** and **2** are thermally too unstable for GED experiments, while **3** can be evaporated without decomposition.

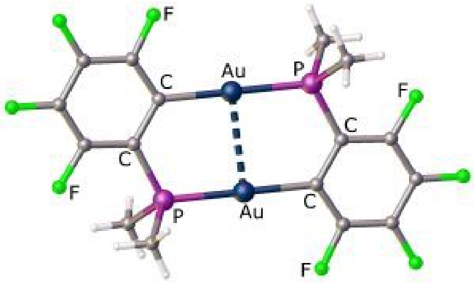

Fig. 2 Molecular structure of compound **3** with Au···Au interaction.

Gas electron diffraction (GED) is particularly suitable for studying heavy-atom interactions because of their strong scattering power.[21–24] However, identifying volatile and thermally robust Au(I) compounds remains challenging, since many decompose under evaporation conditions required for GED experiments. After numerous unsuccessful attempts involving simpler and ligand-supported Au(I) systems, we identified the dimer of *o*-dimethylphosphanyl(perfluorophenylene)gold(I) (**3**, Fig 1)[26] as sufficiently robust for undecomposed evaporation at 506 K, which was simultaneously monitored by mass spectrometry. In this way, GED patterns of good quality were obtained (see ESI).

We performed preliminary quantum-chemical calculations for first guesses of the structure and vibrational amplitudes for GED data interpretation (see ESI). Multiple low frequencies (<80 cm^{-1}) with the smallest value being only 14 cm^{-1} suggest that the molecule is highly floppy. Consequently, we performed molecular dynamics simulations to obtain accurate vibrational corrections, which enabled us to reliably determine of the most

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important semi-experimental equilibrium parameters of **3** (Table 1) in the structural refinement of the GED data. Figure 3 shows that the model radial distribution function (RDF) closely matches the experimental data points, resulting in a low total disagreement factor of R_f = 5.1 %. Notably, the Au···Au term makes a significant contribution to the total molecular diffraction intensity. This manifests as an intense and distinct peak at r_g = 2.85 Å in the radial distribution function, which makes GED especially suitable for studying aurophilic interactions.

The differences in the most relevant experimental gas and solid-state interatomic distances are statistically significant. The Au–P and Au–C bonds are 0.008 and 0.026 Å shorter, respectively, in the gas phase than in the solid state. Given their dative nature, it is interesting that they are expected to be shorter in the solid state due to the polar environment. Decreasing the bond length increases bond polarity. The resulting polar environment then stabilises this structural deformation.[18] However, in our case the overall packing effects are probably more complicated and cannot be described by this simple rule alone.

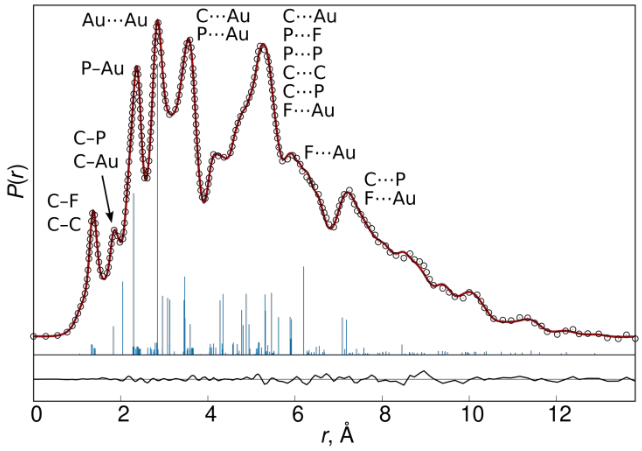

Fig 3 Semi-experimental (circles) and model (red solid line) GED radial distribution functions and their difference (lower curve) for **3**.

The parameter of central interest in this study is the Au···Au distance: It is 0.024 Å longer in the solid state than in the gas phase. In a recent review, we presented several cases of weak interactions governed by dispersion effects that exhibited this behaviour.[19] However, this has not been described before for metal–metal interactions. Although the body of experimental data is still too small to derive a general rule, these results demonstrate that weak, non-dative interactions can behave in this unexpected way. It should be noted that the crystal structure is vibrationally averaged and may also be affected by the asphericity of atomic scattering factors. However, these effects are expected to be much smaller than the differences between solid-state and gas-phase equilibrium parameters discussed here.

One of the largest factors influencing the refined distance r_e(Au···Au) is the corresponding vibrational correction. In the analysis of GED data there are two major options, how vibrational corrections can be calculated. Using perturbation theory (PBE0-D3/TZ,QZ(Au) force constants) we get a correction value dr = −0.002 A. However, the relatively high floppiness of **3** makes an alternative way for obtaining vibrational corrections preferable. This uses path-integral molecular dynamics (MD) simulations. We obtained an MD trajectory by calculating gradients at the PBE-D3BJ/DZ level of theory. Processing this trajectory resulted in dr = −0.014 A with a convergence level of 3%. Therefore, the difference of 0.012 A between the values obtained from perturbation theory and MD can be considered as a conservative estimate of the uncertainty arising from the ambiguity in the vibrational correction.

To see how well theory would be able to reproduce the experimental findings for the gas phase – and which theoretical method would perform best in describing such heavy-atom interactions – we undertook a large series of quantum chemical calculations. The results are listed in Table 1.

Table 1 Experimental and theoretical values for some interatomic distances in **3**.[a]

Method	**Au···Au**	**Au–P**	**Au–C**
GED[b,c]	2.827(2)	2.273(1)	2.034(1)
XRD[d,c]	2.851(1)	2.281(1)	2.060(2)
HF	2.980	2.369	2.121
VSXC	2.971	2.322	2.086
M05-D3	2.968	2.347	2.108
M05	2.955	2.352	2.107
B3LYP-D3	2.944	2.319	2.091
B97D	2.924	2.291	2.106
CAM-B3LYP-D3	2.923	2.307	2.080
M06	2.920	2.345	2.097
M06-D3	2.919	2.344	2.096
B3LYP	2.909	2.330	2.089
X3LYP	2.908	2.328	2.088
BMK	2.903	2.327	2.067
BP86-D3	2.901	2.304	2.076
CAM-B3LYP	2.898	2.313	2.079
M06HF	2.896	2.218	2.055
B98	2.891	2.322	2.078
LC-ωPBE-D3	2.890	2.284	2.067
PBE0-D3	2.879	2.295	2.067
PBE-D3	2.878	2.305	2.072
PBEh-3c[e]	2.878	2.330	2.065
BP86	2.867	2.314	2.075
PBE	2.866	2.309	2.072
LC-ωPBE	2.866	2.290	2.065
r^{2}SCAN-3c[e]	2.865	2.318	2.071
mPW1PW91	2.863	2.303	2.068
PBE0	2.862	2.300	2.066
B2PLYP-D4	2.859	2.296	2.064
PBE0-D3BJ	2.856	2.294	2.063
PBE0-D4	2.855	2.294	2.062
TPSSh	2.850	2.305	2.075
ωB97X-D4	2.843	2.292	2.068
SCS-MP2	2.834	2.266	2.037
X2C-SCS-MP2[f]	2.803	2.252	2.031
MP2	2.784	2.243	2.018

[a] Equilibrium distances in Å. Theoretical methods used def2-QZVPP basis sets, unless otherwise stated. Theoretical values are ordered by Au···Au distance value. [b] Semi-experimental equilibrium values determined by GED in this work. [c] 1σ least squares standard deviations are in parentheses. [d] Refined from single crystal X-ray diffraction data.[26] [e] A basis set specific for this approximation was used. [f] Relativistic (X2C) all-electron calculation with x2c-QZVPPall basis sets.

Correlated *ab initio* methods are the method of choice for describing aurophilic interactions,[17] because the d-shells at gold

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are formally closed for Au(I) and the distance dependence of $-1/r^6$ cannot be accurately described by single determinant methods, such as common DFT functionals. However, in recent years, the use of semi-empirical, dispersion-corrected DFT functionals has become increasingly popular. They have also been applied to systems involving aurophilic interactions,[16,27,28] but, no comprehensive, in-depth analysis of their performance in describing these effects has yet been reported. A second requirement for a suitable description of aurophilic attractions is the inclusion of relativistic effects (at least scalar), after providing a balanced description of dynamic correlation. In this case, it leads to spatial contraction and stronger effective nuclear charge shielding by the gold 5s shell.[11] This can easily be achieved using standard relativistic electronic core potentials (ECPs), which are widely used in most modern calculations. Including two additional diffuse f-functions (α = 0.2, α = 1.19)[10,29] into the gold basis set is crucial for obtaining accurate numerical results. Standard methods using basis sets such as those from the Karlsruhe def2-family fulfil this condition.

Based on these considerations, we performed a series of density functional theory (DFT) and *ab initio* structure optimizations of **3** – the latter under systematically increasing accuracy. These methods included Hartree-Fock[30,31] (HF, defining a correlation-free reference), second order Møller-Plesset perturbation theory[32] (MP2, the lowest-level theory that considers interelectronic correlation and is known to overestimate the attractive component of dispersion interactions), Grimme's spin-component scaled MP2[33] (SCSMP2, which partially compensates for the overestimation of dispersion achieved by classical MP2 and is termed "poor man's CCSD(T)"[34]) and finally the coupled cluster method CCSD(T).[35] Most of these methods were combined with the Karlsruhe def2-QZVPP basis sets.[36]

As expected, the transannular Au···Au distance is significantly longer (by 0.15 Å) at the uncorrelated HF level than in the experimental GED structure. As expected, the interelectronic correlation was overestimated by a second-order perturbation treatment (MP2) yielding a too short Au···Au distance of 2.784 Å. However, SCS-MP2 corrected this, resulting in a value that differed by only 0.007 Å from the semi-experimental GED value.

To go beyond the purely scalar relativistic description, we have also performed an SCS-MP2 optimization using the exact two-component theory (X2C)[37,38] and corresponding all-electron basis sets x2c-QZVPPall[39] instead of the standard relativistic electron core potential included in the def2-QZVPP basis set. Interestingly, this resulted in a value that was 0.024 Å too short, though not as dramatically as in the MP2 case, where the difference was 0.043 Å.

To elucidate the extremely flat potential energy surface for the Au···Au distance at the coupled cluster level of theory, we turned to the LNO-CCSD(T) approximation,[40] as only CCSD(T) at its basis set limit yields viable results. We extrapolated to the basis set and LNO space limits by combining the aug'-cc-pVXZ(-PP) [X = T, Q and 5] basis sets (see Supporting Information). Using this computational protocol, we scanned the potential energy surface along the Au···Au distance and found the minimum to be between 2.84 and 2.85 Å. We also investigated core correlation, which had no effect. However, going beyond scalar relativity results in a final best estimated *ab initio* distance of 2.830 Å, which is in excellent agreement with the GED value of 2.827(2) Å.

Studies investigating the performance of DFT methods are also shown in Table 1. We compared the results of a large range of functionals both with and without dispersion corrections, focusing on the Au···Au, Au–C and Au–P distances. We note:

- a relatively good performance of hybrid TPSSh and PBE0 (with D3BJ or D4 corrections) methods,
- the range-separated hybrid ωB97X-D4 approximation performs similarly well to SCS-MP2 and was the best among the tested DFT methods, however, with significantly lower computational requirements,
- D3 dispersion corrections without BJ dumping mostly worsen the results,
- D4 dispersion corrections do not lead to a significant improvement over D3BJ.

In summary, we emphasize the GED method's excellent suitability for studying aurophilicity in the gas phase, thanks to the high scattering power of gold atoms. Compound **3** studied in this work allowed us to determine the first experimental gas-phase structure involving an aurophilic Au(I)···Au(I) interaction. The aurophilic effect appeared to be significantly stronger in the gas phase than in the solid state.

However, we note that the Au···Au distance is observed in a ligand-supported dinuclear complex and therefore does not represent an unconstrained Au(I)···Au(I) pair. Such scaffold-supported systems are, however, the standard experimental setting for studying metallophilic interactions.[7] Within this molecular framework, the comparison between gas-phase, solid-state and theoretical structures provides direct evidence for a significant aurophilic contribution to the observed Au···Au contact.

Furthermore, this study provides a unique opportunity to validate a series of theoretical approaches. Specifically, the newly obtained structural parameters allow us to benchmark the accuracy of feasible theoretical methods, offering critical insights into the reliability of quantum chemical techniques – including CCSD(T), MP2, and dispersion-corrected DFT– in capturing the subtleties of these weak interactions between heavy metal atoms. Thus, this study fills a long-standing experimental gap and advances the theoretical understanding of aurophilicity by linking experiments and computations in an unprecedented manner.

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Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the Supplementary Information. Supplementary information: Experimental details of GED/MS experiment, data of structural analysis of GED data, quantum chemical calculations and references. See DOI: [URL – format https://doi.org/DOI].

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