Inorganic Chemistry
Communication
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# Experimental and Theoretical Comparison of the Metallophilicity between $d^{10}$–$d^{10}$ $Au^{I}$–$Hg^{II}$ and $d^{8}$–$d^{10}$ $Au^{III}$–$Hg^{II}$ Interactions

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Supporting Information

**ABSTRACT:** The heteronuclear $Au^{I}/Hg^{II}$ complexes $[Hg\{AuR(\mu\text{-}2\text{-}C_6H_4PPh_2)\}_2]$ [R = $C_6F_5$ (**1**), $C_6Cl_2F_3$ (**2**)] were prepared by reacting $[Hg(2\text{-}C_6H_4PPh_2)_2]$ with $[AuR(tht)]$ (1:2) and further transformed into the $Au^{III}/Hg^{II}$ species $[Hg\{Au(C_6F_5)Cl_2(\mu\text{-}2\text{-}C_6H_4PPh_2)\}_2]$ [R = $C_6F_5$ (**3**), $C_6Cl_2F_3$ (**4**)] by the addition of 2 equiv of $PhI{\cdot}Cl_2$. The crystal structures of **1**–**3** display $Au{\cdots}Hg^{II}$ interactions, which in the case of **3** is the first $Au^{III}{\cdots}Hg$ contact described to date. Theoretical calculations on model systems of the $C_6F_5$ derivatives evidence that the attraction between $Au^{I}$ or $Au^{III}$ and $Hg^{II}$ arise from dispersion-type interactions and that both contacts are of the same strength.

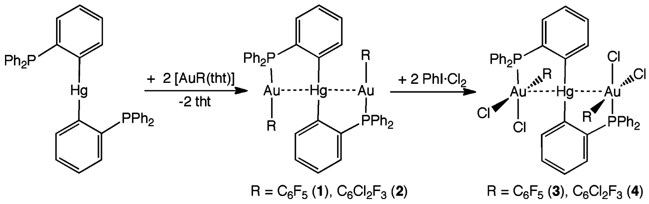
The construction of molecular architectures based on metallophilic interactions between $Au^{I}$ and closed-shell centers has been the subject of many investigations because the resulting materials present a rich solid-state chemistry, often showing unusual stoichiometries and structures, and also because they usually exhibit an impressive display of tunable photoluminescent, piezochromic, or vapochromic properties of relevance for applications in luminescence signaling and vapochemical sensing[1] or are applicable in electronics or catalysis.[2]

Our group has contributed a number of examples of interactions of $Au^{I}$ with $Ag^{I}$, $Tl^{I}$, or $Bi^{III}$, using the acid–base strategy,[3] $Cu^{I}$, through transmetalation reactions,[4] $Pd^{II}$, using heterobidentate ligands,[5] or very recently, $Hg^{II}$, taking advantage of the strong acidity of $[Hg(C_6F_5)_2]$ and of the resemblance of the $[Au(PR_3)]$ unit with hydrogen, using the isolobality concept.[6] Theoretical calculations on these interactions have allowed us to describe their nature and quantify their strength, being very helpful in the rational design of the synthesis of these types of complexes. Thus, the energy of these contacts range from 35 ($Au^{I}{\cdots}Pd^{II}$)[5] to 276 kJ $mol^{-1}$ ($Au^{I}{\cdots}Tl^{I}$),[7] and they include different contributions: dispersive in the weakest interactions and ionic plus dispersive in the strongest ones. In particular, gold and mercury, with the largest relativistic effects, display the strongest correlation effects.

Continuing with these studies, our aim was to gain insight into the influence of the oxidation states on the metallophilicity by comparing the strength of $d^{10}$–$d^{10}$ contacts with that of $d^{10}$-$d^{8}$ ones in species with the same counterparts. Thus, we prepared heterometallic complexes containing $Au^{I}$ or $Au^{III}$ as $d^{10}$ or $d^{8}$ centers and a heterometal that showed higher dispersive forces with gold and significant contributions from relativistic effects ($Hg^{II}$). Therefore, here we report the synthesis, structural characterization, and theoretical studies of $Au^{I}$–$Hg^{II}$ and $Au^{III}$–$Hg^{II}$ complexes with diphenylphosphino-2-phenyl bridging ligands.

The synthesis of heterotermetallic $Au^{I}$–$Hg^{II}$ complexes $[Hg\{AuR(\mu\text{-}2\text{-}C_6H_4PPh_2)\}_2]$ [R = $C_6F_5$ (**1**), $C_6Cl_2F_3$ (**2**)] was achieved by the reaction of $[Hg(2\text{-}C_6H_4PPh_2)_2]$ with 2 equiv of $[AuR(tht)]$ (tht = tetrahydrotiophene; Scheme 1) in dichloromethane. The labile tht ligands are displaced by the P atoms of the bidentate ligands, and both products are obtained as white solids with analytical and spectroscopic data in agreement with the proposed stoichiometries [see the Supporting Information (SI) for details].

**Scheme 1**



By reacting suspensions of **1** and **2** with 2 equiv of the adduct $PhI{\cdot}Cl_2$ in dichloromethane, colorless solutions are formed, from which complexes $[Hg\{AuRCl_2(\mu\text{-}2\text{-}C_6H_4PPh_2)\}_2]$ [R = $C_6F_5$ (**3**), $C_6Cl_2F_3$ (**4**)] are obtained as pale-yellow solids (see Scheme 1), with analytical and spectroscopic data in agreement with the proposed stoichiometry (see the SI).

The crystal structures of **1**–**3** were determined by X-ray diffraction (see the SI) from single crystals obtained by the slow diffusion of *n*-hexane into a solution of the complex in tetrahydrofuran (**1**) or dichloromethane (**2** and **3**). The three crystal structures consist of a central $Hg^{II}$ center linked to two $[Au^{I}R]$ (**1** and **2**) or *cis*-$[Au^{III}RCl_2]$ (**3**) moieties via metallophilic interactions reinforced by the presence of two $2\text{-}C_6H_4PPh_2$ bridging ligands (Figures 1 and 2). These types of intermetallic contacts are rather uncommon because there are only a few examples of complexes displaying $Au^{I}{\cdots}Hg^{II}$ contacts,[6,8] and they are usually supported by ancillary ligands.[8a−c]

It is worth noting that complex **3** contains the first $Au^{III}{\cdots}Hg^{II}$ contact described to date. Although a couple of Au/Hg

**Received:** December 10, 2013
**Published:** January 14, 2014

dx.doi.org/10.1021/ic403036s | *Inorg. Chem.* 2014, 53, 1275−1277

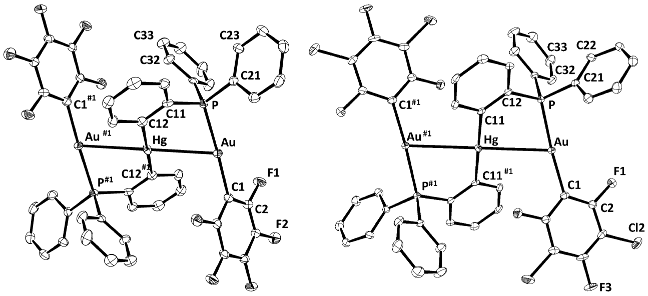


**Figure 1.** Crystal structures of **1** (left) and **2** (right). Selected bond lengths [Å] for **1**: Hg−Au 3.1222(3), Hg−C12 2.122(8), Au−C1 2.048(8), Au−P 2.2813(18). Selected bond lengths [Å] for **2**: Au−Hg 3.1950(3), Hg−C11 2.107(4), Au−C1 2.061(5), Au−P 2.2864(12).

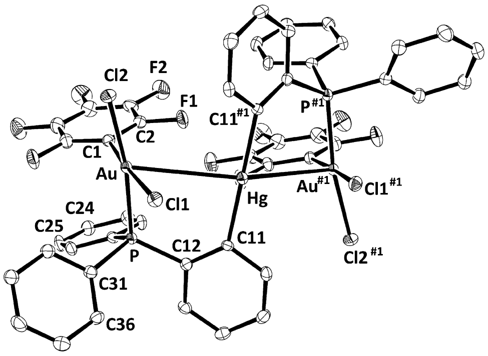


**Figure 2.** Crystal structure of **3**. Selected bond lengths [Å]: Hg−Au 3.3973(3), Hg−C11 2.096(5), Au−C1 2.027(6), Au−P 2.3093(15), Au−Cl2 2.3194(15), Au−Cl1 2.3430(15).

complexes previously reported contain $Au^{III}$ and $Hg^{II}$ centers in the same molecule,[8a,b] no interaction between them is observed, and only a weak $Au^{I}\cdots Au^{III}$ contact of 3.404(2) Å appears in one of them.[8a] By contrast, complex **3** displays a Au−Hg distance of 3.3973(3) Å, indicative of an unprecedented $Au^{III}\cdots Hg^{II}$ interaction. In spite of the smaller size of $Au^{III}$ compared to $Au^{I}$, this distance is even shorter than some of the $Au^{I}-Hg^{II}$ separations observed in other compounds that display such contacts, which vary from 3.4983(3) to 3.6531 Å.[6b,8d] Nevertheless, the Au−Hg distances in both **1** and **2** [3.1950(3) and 3.1222(3) Å, respectively], as well as the rest of the Au−Hg distances reported to date,[6,8] are shorter than those in complex **3**.

The Hg−C bond distances are similar in the three compounds, lying in the range of Hg−C bond lengths previously described for related Au/Hg compounds [from 2.068(11)[6b] to 2.161(17) Å[8a]]. As for the Au−Hg distances, the Au−P bond length in **3** is longer than those in **1** and **2**, and it is also longer than those in related Au/Hg systems.[6] Nevertheless, the Au−C bond distances are all of the same order and similar to those in the heterometallic compounds cited above [from 2.052(6) to 2.081(6) Å].[6] If the Au···Hg interactions are considered, a perfect square-planar environment is found for the Hg atoms in **1** and **2**, while the Au−Hg−Au angle in **3** is only of 145.562(13)°, a value similar to that previously described in $[Hg\{CH_2P(S)Ph_2\}_2(AuCl)_2]$ (151.8°).[8a]

To explain the nature of the $Au^{I}\cdots Hg^{II}$ and unprecedented $Au^{III}\cdots Hg^{II}$ interactions, we carried out theoretical calculations at density functional theory (DFT), Hartree−Fock (HF), and Moeller−Plesset second-order perturbation theory (MP2) levels of theory. We optimized the simplified dinuclear model systems $[HgAu(C_6F_5)(C_6H_5)(2\text{-}C_6H_4PH_2)]$ (**1a**) and $[HgAu(C_6F_5)Cl_2(C_6H_5)(2\text{-}C_6H_4PH_2)]$ (**3a**), which represent one of the metallophilic Au···Hg interactions observed in each case. Figure 3 depicts the optimized models **1a** and **3a** at HF and MP2. At the HF level, none of the models display intermetallic interactions, in contrast with the experimental structural disposition. However, when correlation effects are included at the MP2 level the $Au^{I}\cdots Hg^{II}$ and $Au^{III}\cdots Hg^{II}$ interactions are observed at distances slightly shorter than the experimental ones: 2.93 vs 3.12 Å (**1a**) and 2.99 vs 3.40 Å (**3a**). Note that the MP2 level exaggerates the metallophilicity,[9] but we can conclude that the attraction between $Au^{I}$ or $Au^{III}$ and $Hg^{II}$ arises from dispersion-type interactions.

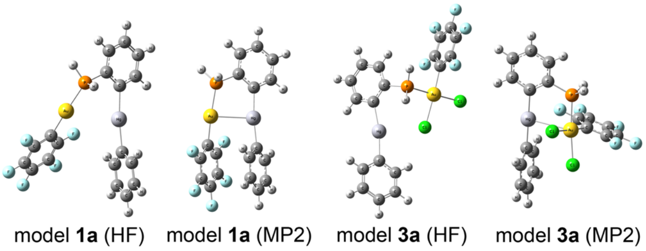


**Figure 3.** Optimized model systems **1a** and **3a** at the HF and MP2 levels of theory.

Two unbridged model systems, $[Hg(C_6H_5)_2]\cdots[Au(C_6F_5)(PH_3)]$ (**1b**) and $[Hg(C_6H_5)_2]\cdots[Au(C_6F_5)Cl_2(PH_3)]$ (**3b**), were built up to account for the $Au^{I}\cdots Hg^{II}$ and $Hg^{II}\cdots Au^{III}$ interaction strengths, making use of the counterpoise correction of the basis-set superposition error (BSSE; see the SI). In model **1b**, the mononuclear fragments were forced to be perpendicular to each other in order to exclusively study the metallophilicity, and the interaction energy was evaluated at different intermetallic distances at the HF and MP2 levels of theory (Figure 4). The HF curve is repulsive, whereas the MP2 curve displays a minimum at 3.11 Å (exp. 3.12 Å) with an interaction energy of −38.9 kJ $mol^{-1}$. This interaction is of similar nature but weaker than the one previously described in model $[Hg(C_6F_5)_2]\cdots[Au(C_6F_5)(PH_3)]$, which led to a stabilization energy for the $Au^{I}\cdots Hg^{II}$ contact of −73.3 kJ $mol^{-1}$.[6a] If we assume that the dispersion-type component is obtained when correlation effects are included at the MP2 level, we conclude that the $Au^{I}\cdots Hg^{II}$ interaction in **1b** arises from dispersive forces. In model **3b**, ligand disposition in the optimized fragments made analysis of the $Au^{III}\cdots Hg^{II}$ interaction very difficult, and we used a fully optimized model **3b** at the MP2 level of theory. The local minimum includes $Au^{III}\cdots Hg^{II}$ and a weak C−H···F hydrogen bond, which seems to be

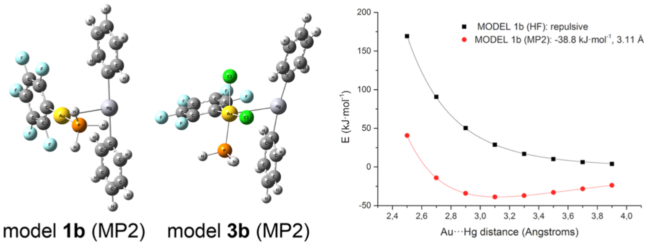


**Figure 4.** Model system **1b** (left) displaying the DFT-optimized monomers at the MP2-optimized equilibrium distance. Model system **3b** (center) fully optimized at the MP2 level of theory. Interaction energy curves for model **1b** at the HF and MP2 levels of theory (bottom). The curves represent the BSSE-corrected interaction energies with respect to the Au−Hg distance.

favored when the supporting ligand is broken. In order to account for the isolated $Au^{III}\cdots Hg^{II}$ interaction, we built up a third model of complex **3**, $[Hg(C_6H_5)_2]\cdots[Au(C_6F_5)Cl_2(PH_3)]$ (**3c**), in which the metallophilic $Au^{III}\cdots Hg^{II}$ interaction is avoided and C−H···F is estimated (see the SI). If we subtract the interaction energy obtained from model **3c** from that obtained for model **3b**, we can approximately account for the $Au^{III}\cdots Hg^{II}$ interaction. This strategy has previously been employed by some of us, leading to good results.[6] The overall MP2 stabilization energy obtained at the equilibrium distance of 3.09 Å (exp. 3.40 Å) for model **3b** was −60.6 kJ mol$^{-1}$, while at the HF level, a repulsive behavior was found. The MP2 stabilization energy obtained at the equilibrium distance of 2.53 Å (exp. 2.39 Å) for model **3c** was −13.8 kJ mol$^{-1}$, corresponding to the stabilization energy produced by the C−H···F hydrogen bond. Thus, the energy difference between **3b** and **3c** of −46.8 kJ mol$^{-1}$ corresponds to the energy estimated for the $Au^{III}\cdots Hg^{II}$ contact, which is slightly stronger than the $Au^{I}\cdots Hg^{II}$ contact (−38.9 kJ mol$^{-1}$) with a similar dispersive origin.

Because the stabilization energies obtained for the $Au^{I}\cdots Hg^{II}$ and $Au^{III}\cdots Hg^{II}$ interactions are quite similar, although the interactions are formally different ($d^{10}-d^{10}$ and $d^{10}-d^{8}$, respectively), we carried out analysis of the natural bond order (NBO) charges (MP2 density) for models **1b** and **3b** and for the corresponding monometallic fragments (see the SI). The $[Hg(C_6H_5)_2]$ fragment displays a similar charge on the $Hg^{II}$ center for model **1b** (1.121+) and model **3b** (1.185+), indicating that the charge of the $Hg^{II}$ center is similarly affected upon interaction with the formally $Au^{I}$ or $Au^{III}$ centers. Analysis of the separated $[Hg(C_6H_5)_2]$ fragment for each model displays a similar charge on the $Hg^{II}$ center for model **1b** (1.115+) and model **3b** (1.151+), indicating that the NBO charge on $Hg^{II}$ is very similar to the one obtained when this metal ion interacts with the Au centers in the corresponding models. If we analyze the $Au^{I}$ or $Au^{III}$ centers, the results of the NBO charges are different. While the $Au^{I}$ charge in model **1b** (0.318+) is very similar to the one in the mononuclear fragment (0.328+), in model **3b** the $Au^{III}$ center displays a charge of 0.384+, lower than that obtained in the free $Au^{III}$ fragment (0.491+). These results would indicate that when the $Au^{III}$ fragment interacts with the $Hg^{II}$ center in model **3b**, the charge on the $Au^{III}$ atom is close to that observed in model **1b**. If we compare the NBO charges of model **3b** with the ones obtained for the free $Au^{III}$ fragment, we observe that the Au center, in the absence of $Hg^{II}$, displays a higher positive charge but that, upon interaction with $Hg^{II}$, the $Au^{III}$ center becomes very similar to $Au^{I}$ through a transfer of electron density, mainly from the P-donor ligand.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

X-ray crystallographic data in CIF format for **1**−**3** and experimental and theoretical details. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by the DGI Project (MINECO)/FEDER (CTQ2010-20500-C02-02). D.P. thanks the C.A.R. for a grant. The Centro de Supercomputación de Galicia is acknowledged for computational resources.

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