

Au(I)⋯Ag(I) Metallophilic Interactions between Anionic Units: Theoretical Studies on a AuAg₄ Square Pyramidal Arrangement

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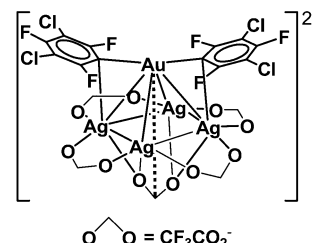
We have studied theoretically the organometallic compound (NBu₄)₂[Au(3,5-C₆F₃Cl₂)₂Ag₄(CF₃CO₂)₅], whose dianionic part displays a AuAg₄ square pyramidal arrangement based on closed-shell Au(I)⋯Ag(I) interactions between two monoanionic fragments. DFT/B3LYP, ab initio Hartree–Fock (HF), and second-order Møller Plesset perturbation theory (MP2) calculations have been carried out for simplified model systems. Model system [AuPh₂][−]⋯[Ag₄(CO₂H)₅][−] (**C1**) has been chosen from DFT results as an appropriate model for the study of the interactions. The four Au(I)⋯Ag(I) interactions and two additional C⋯Ag(I) interactions are observed when dispersion-type interactions are considered in the level of theory (MP2) displaying a metallophilic attraction between two anionic units. The study of model **C2** (similar to **C1** but with minimized C⋯Ag(I) interactions) permits the study of the Au(I)⋯Ag(I) interactions separately, which confirms the existence of stabilizing Au(I)⋯Ag(I) interactions around 13 kJ·mol^{−1} each.

Introduction

The attraction between two or more monovalent Au(I) ions in chemical structures has been studied for a long time.¹ This phenomenon was termed *aurophilic attraction*, and it usually occurs among formally cationic Au(I) centers.² If one follows classical bonding rules, two closed-shell metal cations would normally be expected to repel each other, but instead of that, attraction is observed due to electronic correlation effects strengthened by the large relativistic effects for gold³ as can be demonstrated for many structurally characterized compounds.⁴ This unique feature permits achievement of different structural dispositions and even rather uncommon situations such as, for instance, the + − − + arrangement reported by Schmidbaur et al.⁵ for the complex [Au(PPhMe₂)₂]⁺[Au(GeCl₃)₂][−], in which two anionic Au(I) fragments display a metal–metal interaction that is electrostatically compensated by one cationic external fragment. Moreover, complex [(C₁₂H₁₄N₂)Au₂I₄]⁶ is even more striking since the structure consists of an anionic gold(I) infinite chain of “crossed-stick” AuI₂[−] anions linked through Au(I)⋯Au(I) interactions between anionic counterparts, (− − −)_∞.

On the other hand, there is a growing theoretical and experimental interest in metallophilic interactions between Au(I) and different closed-shell metal centers such as, for example, silver(I).⁷ In principle, this type of interaction also permits the formation of different structural dispositions governed by the attractions among formally cationic Au(I) and Ag(I) centers, and examples of structurally characterized complexes go from dimers or polynuclear compounds to infinite chains in which the charges of the metallic units appear in a

SCHEME 1: Schematic Representation of the Dianionic Part of Complex (NBu₄)₂[Au(3,5-C₆F₃Cl₂)₂Ag₄(CF₃CO₂)₅]^a



^a The dashed line represents the monitored Au–C distance (*R*) in the theoretical analysis.

formal +1 oxidation state similar to those usually found for the aurophilic case. Nevertheless, as far as we are aware, no metallophilic Au–M interactions between anionic units have been described to date.

In this sense, we have recently reported the synthesis and structural characterization of the complex (NBu₄)₂[Au(3,5-C₆F₃Cl₂)₂Ag₄(CF₃CO₂)₅],⁸ where the anionic {AuAg₄}^{2−} moiety consists of a square pyramidal core in which the silver(I) atoms form the base of the pyramid, surrounded by five bridging trifluoroacetate ligands, and the gold center is in the apical position (see Scheme 1). The dianionic charge of this complex could be formed by the combination of two interacting monoanionic fragments: the [AuR₂][−] (R = 3,5-C₆F₃Cl₂) unit and the [Ag₄(CF₃CO₂)₅][−] unit, leading to four metallophilic Au(I)⋯Ag(I) interactions. This structural situation in which one Au(I) atom is able to interact with up to four Ag(I) Lewis acid centers, leading to a global interaction between two anionic fragments, is unprecedented. Hence, in this study, we investigate theoretically the stability of the square pyramidal {AuAg₄}^{2−} arrangement through DFT⁹ and ab initio (Hartree–Fock (HF) and second-order Møller–Plesset perturbation theory¹⁰ (MP2))

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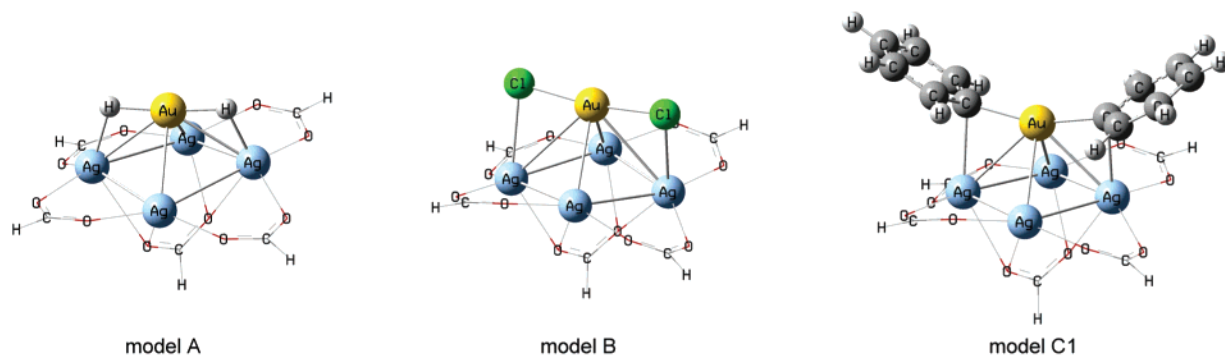


Figure 1. Optimized model systems A, B, and C1 (DFT/B3LYP level of theory).

TABLE 1: Interaction Energy (BSSE-Corrected) at the HF and MP2 Levels of Theory at Different $[\text{AuPh}_2]^- \cdots [\text{Ag}_4(\text{CO}_2\text{H})_5]^-$ Distances (Based on $\text{Au} \cdots \text{C}$ or the Corresponding $\text{Au} \cdots \text{Ag}$ Distances) for Model System C1

| $R(\text{Au} \cdots \text{C})^a$ | $R(\text{Au} \cdots \text{Ag})^a$ | $\Delta E_{\text{int}}(\text{HF})^b$ | $\Delta E_{\text{int}}(\text{MP2})^b$ |
|----------------------------------|-----------------------------------|--------------------------------------|---------------------------------------|
| 5.3 | 3.443, 3.541 | 0.03349 | 0.00271 |
| 5.0 | 3.210, 3.309 | 0.03107 | −0.01837 |
| 4.69 | 2.984, 3.084 | 0.03843 | −0.03432 |
| 4.5 | 2.851, 2.951 | 0.05576 | −0.03618 |
| 4.3 | 2.720, 2.820 | 0.09583 | −0.02112 |
| 4.0 | 2.540, 2.640 | 0.24640 | 0.08046 |
| 3.7 | 2.385, 2.482 | 0.66048 | 0.44259 |

^a Distance in angstroms. ^b Interaction energies in atomic units (1 au = 2.6255×10^3 kJ·mol^{−1}).

calculations, assessing the contribution of the $\text{Au(I)} \cdots \text{Ag(I)}$ or $\text{C}_{\text{ipso}} \cdots \text{Ag(I)}$ interactions to the stability of the system.

Theoretical Methods

All calculations were performed using the Gaussian 03 package program.¹¹ The molecular geometries of model systems $[\text{AuH}_2]^- \cdots [\text{Ag}_4(\text{CO}_2\text{H})_5]^-$ (A), $[\text{AuCl}_2]^- \cdots [\text{Ag}_4(\text{CO}_2\text{H})_5]^-$ (B), and $[\text{AuPh}_2]^- \cdots [\text{Ag}_4(\text{CO}_2\text{H})_5]^-$ (C1) were initially optimized at the DFT level of theory using the B3LYP functional. Electronic correlation effects, keeping the core orbitals frozen, were included in further single-point calculations at various Au–Ag distances by using second-order Møller–Plesset perturbation theory or Hartree–Fock calculations on model system C1. This model was chosen to represent the experimental geometry by substituting from the X-ray diffraction structure the 3,5- $\text{C}_6\text{F}_3\text{Cl}_2$ rings by C_6H_5 rings and the trifluoroacetate ligands by formate ligands, to keep the computational cost feasible. To modify all Au–Ag distances in the same way, we have modified the distance R , defined as the distance between the Au(I) center in the apical position of the square pyramid and the C atom of the fifth formate ligand opposite the gold center, both on the C_2 main axis. An analogous study has been carried out on model system C2, which is similar to C1 but with the $[\text{AuPh}_2]^-$ unit turned to minimize $\text{C} \cdots \text{Ag(I)}$ interactions and study only $\text{Au(I)} \cdots \text{Ag(I)}$ interactions. The interaction energy at the HF and MP2 levels of theory was obtained according to eq 1. A counterpoise correction for the basis set superposition

$$\Delta E = E_{\text{AB}}^{(\text{AB})} - E_{\text{A}}^{(\text{AB})} - E_{\text{B}}^{(\text{AB})} = V(R)$$

error (BSSE)¹² on ΔE was thereby performed. The optimized interaction energies (ΔE) and $\text{Au} \cdots \text{C}$ distances for models C1 and C2 are listed in Tables 1 and 2. We fitted the calculated points using the four-parameter eq 2, which had been previously

$$\Delta E = V(R) = A e^{-BR} - CR^{-n}$$

TABLE 2: Interaction Energy (BSSE-Corrected) at the HF and MP2 Levels of Theory at Different $[\text{AuPh}_2]^- \cdots [\text{Ag}_4(\text{CO}_2\text{H})_5]^-$ Distances (Based on $\text{Au} \cdots \text{C}$ or the Corresponding $\text{Au} \cdots \text{Ag}$ Distances) for Model System C2

| $R(\text{Au} \cdots \text{C})^a$ | $R(\text{Au} \cdots \text{Ag})^a$ | $\Delta E_{\text{int}}(\text{HF})^b$ | $\Delta E_{\text{int}}(\text{MP2})^b$ |
|----------------------------------|-----------------------------------|--------------------------------------|---------------------------------------|
| 5.3 | 3.443, 3.541 | 0.03816 | 0.00583 |
| 5.0 | 3.210, 3.309 | 0.03817 | −0.00903 |
| 4.69 | 2.984, 3.084 | 0.04814 | −0.01926 |
| 4.53 | 2.872, 2.892 | 0.06180 | −0.01849 |
| 4.3 | 2.720, 2.820 | 0.09989 | −0.00215 |
| 4.0 | 2.540, 2.640 | 0.20707 | 0.06935 |
| 3.7 | 2.385, 2.482 | 0.43383 | 0.24828 |

^a Distance in angstroms. ^b Interaction energies in atomic units (1 au = 2.6255×10^3 kJ·mol^{−1}).

used¹³ to derive the Herschbach–Laurie relation (see Figures 3 and 4).¹⁴ The following basis set combinations were employed: for the metals, the 19-VE pseudopotentials from Stuttgart and the corresponding basis sets¹⁵ augmented with two f polarization functions were used.¹⁶ The atoms C and O were treated by Stuttgart pseudopotentials,¹⁷ including only the valence electrons for each atom. For these atoms the double- ζ basis sets of ref 17 were used, augmented by d-type polarization functions.¹⁸ For the H atom, a double- ζ plus a p-type polarization function were used.¹⁹

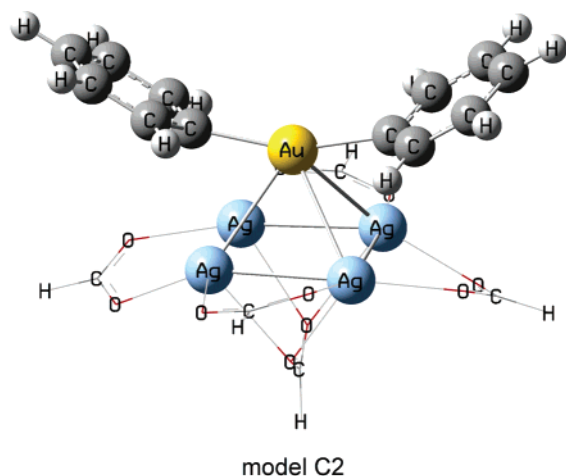
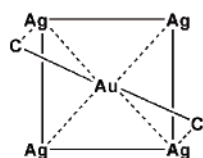
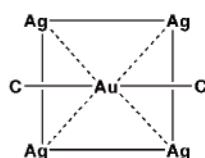
Results and Discussion

First, to save computational costs, we have fully optimized model systems A, B, and C1 (all C_2 symmetry) at the DFT/B3LYP level of theory, which includes some of the correlation energy at low cost (Figure 1). Then, to analyze the effects governing the aggregation of the AuAg_4 core due to interactions between anionic fragments, we have carried out ab initio calculations at the HF and MP2 levels of theory on models C1 and C2. We have studied the interaction energies (BSSE-corrected) between the anions in two different structural situations based on model C1 depending on the orientation of the $[\text{AuPh}_2]^-$ fragment relative to the $[\text{Ag}_4(\text{CO}_2\text{H})_5]^-$ pyramidal base. The first one (model C1) corresponds to the fully optimized situation at the DFT level, which is in very close agreement with the experimental one (only slightly larger metal–metal distances are theoretically obtained) in which both four metalphilic $\text{Au} \cdots \text{Ag}$ interactions and two $\text{Ag} \cdots \text{C}$ interactions are observed (see Figure 1). The second structural situation (model C2) corresponds to the same pyramidal arrangement but with the $[\text{AuPh}_2]^-$ unit turned to avoid the $\text{Ag} \cdots \text{C}$ interactions and to account only for the $\text{Au} \cdots \text{Ag}$ interactions (see Figure 2) In this way we can estimate the total interaction energy between $[\text{AuPh}_2]^-$ and $[\text{Ag}_4(\text{CO}_2\text{H})_5]^-$ anions with the first model system and the stabilization produced by the four metalphilic $\text{Au} \cdots \text{Ag}$ interactions with the second one.

TABLE 3: Selected Experimental Structural Parameters for Complex $(\text{NBu}_4)_2[\text{Au}(\text{3,5-C}_6\text{F}_3\text{Cl}_2)_2\text{Ag}_4(\text{CF}_3\text{CO}_2)_5]$ and Optimized Parameters for Model Systems A, B, and C1 at the DFT/B3LYP Level of Theory (Distances, Å; Angles, deg)

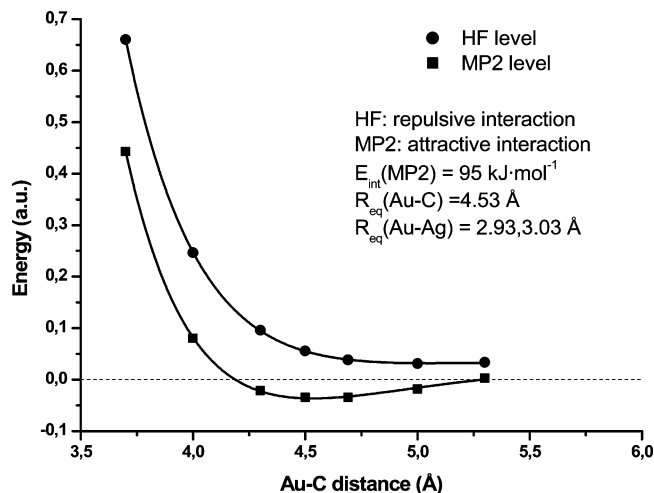
| | Au...Ag | X...Ag ^a | X-Au ^a | Ag...Ag | X-Au-X ^a |
|--------------|--------------|---------------------|-------------------|--------------|---------------------|
| experimental | 2.902, 3.013 | 2.439, 2.450 | 2.068, 2.067 | 2.843, 2.939 | 164.4 |
| model A | 2.866, 3.020 | 1.197 | 1.684 | 3.060, 3.357 | 174.1 |
| model B | 3.118, 3.444 | 2.827 | 2.340 | 3.037, 3.226 | 170.7 |
| model C1 | 2.984, 3.084 | 2.529 | 2.102 | 2.949, 3.105 | 159.2 |

^a X = C for experimental and model C1, X = H for model A, and X = Cl for model B.

**TOP VIEWS OF MODELS C1 AND C2****Model C1: 4 Au...Ag and 2 Ag...C interactions****Model C2: 4 Au...Ag interactions****Figure 2.** Model system C2 showing the $[\text{AuPh}_2]^-$ group turned with respect to the $[\text{Ag}_4(\text{CO}_2\text{H})_5]^-$ group.

In Table 3 we summarize some representative structural data for the dianion of complex $(\text{NBu}_4)_2[\text{Au}(\text{3,5-C}_6\text{F}_3\text{Cl}_2)_2\text{Ag}_4(\text{CF}_3\text{CO}_2)_5]$ and models A, B, and C1. The calculated metallophilic interaction distances (Au...Ag and Ag...Ag) are, in general, slightly larger than the experimental ones. This is probably due to the DFT method, which includes some of the correlation energy but not all. Nevertheless, the low computational cost of DFT/B3LYP permits rapid achievement of many results that are comparable with the experimental ones. In fact, if one compares carefully models A, B, and C1 with the experimental structure, model C1 displays, as expected, the closest data to the X-ray diffraction results. Model A leads to rather different Au...Ag interactions (Au-Ag = 2.866 and 3.020 Å) and too large Ag...Ag interactions (Ag-Ag = 3.060 and 3.357 Å), giving rise to a distorted square pyramidal arrangement. Model B displays better results, but metallophilic interactions are much too large (Au-Ag = 3.118 and 3.444 Å; Ag-Ag = 3.037 and 3.226 Å). Therefore, we can choose model C1 to study in more detail the interaction energies between the $[\text{AuPh}_2]^-$ and $[\text{Ag}_4(\text{CO}_2\text{H})_5]^-$ fragments.

As we have mentioned above, we have used the DFT/B3LYP-optimized model C1 as the starting point for the study of the interaction energy between anionic fragments at various Au...Ag₄ distances. At the MP2 level of theory the obtained Au-Ag equilibrium distances (2.93 and 3.03 Å) (see Table 4) are in excellent agreement with the experimental ones (2.90 and

**Figure 3.** Interaction energy values for the $[\text{AuPh}_2]^- \cdots [\text{Ag}_4(\text{CO}_2\text{H})_5]^-$ interaction in model C1 at the HF and MP2 levels of theory.**TABLE 4:** Experimental Au...Ag Distances, Optimized Equilibrium Au...Ag Distances (Å), and Interaction Energy (ΔE_{int} , kJ·mol⁻¹) at the MP2 Level of Theory for Model Systems C1 and C2

| | Au...Ag | ΔE_{int} |
|--------------|--------------|-------------------------|
| experimental | 2.902, 3.013 | |
| model C1 | 2.928, 3.027 | 95 |
| model C2 | 2.965, 3.065 | 52 |

3.01 Å). At the HF level of theory the $[\text{AuPh}_2]^- \cdots [\text{Ag}_4(\text{CO}_2\text{H})_5]^-$ interaction energy is repulsive for all distances. Thus, at the MP2 level the energy of the $[\text{AuPh}_2]^- \cdots [\text{Ag}_4(\text{CO}_2\text{H})_5]^-$ interaction at the equilibrium distance is 95 kJ·mol⁻¹ and includes four Au(I)···Ag(I) metallophilic interactions and two C_{ipso}···Ag(I) interactions. With the study of model C1, we conclude that dispersion-type interactions (van der Waals) are needed to describe the $\{\text{AuAg}_4\}^{2-}$ square pyramidal arrangement since the ionic component of the interaction, which is already included at the HF level, displays a repulsive behavior. These attractive (MP2) and repulsive (HF) trends at different anion···anion distances are depicted in Figure 3.

On the other hand, we have analyzed the electron density distributions for the optimized model C1 at the MP2 level of theory. Thus, Figure 4 shows the electrostatic potentials mapped on the electron density surfaces of model C1. The figure clearly displays negative values for the electrostatic potential for the whole system, showing the anionic character for both gold and silver fragments that form the square pyramidal arrangement.

The analysis of the metallophilic part of the interaction between Au(I) and four Ag(I) centers has been carried out using model C2 (Figure 2), which minimizes the interaction between the C_{ipso} of the C₆H₅ rings bonded to Au(I) and the Ag(I) center and accounts mostly for the metallophilic Au...Ag interactions. Again, we have analyzed the interaction energy between the ionic fragments $[\text{AuPh}_2]^-$ and $[\text{Ag}_4(\text{CO}_2\text{H})_5]^-$ at different Au...Ag₄ distances. The obtained result (see Table 4) shows very interesting features. First, although C...Ag interactions are

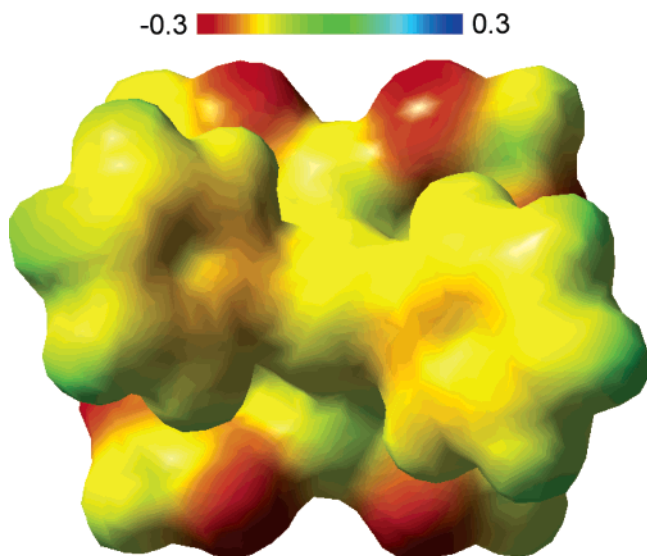


Figure 4. Electron density from the total SCF density (isoval = 0.02, mapped with the electrostatic potential (ESP)). The figure shows a top view of the AuAg₄ square pyramidal arrangement.

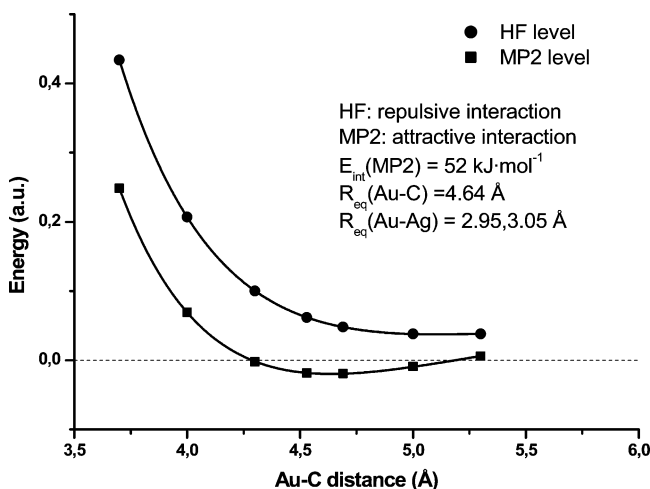


Figure 5. Interaction energy values for the [AuPh₂][−]···[Ag₄(CO₂H)₅][−] interaction in model C2 at the HF and MP2 levels of theory.

minimized for model C2, the obtained Au–Ag equilibrium distances (2.96 and 3.06 Å) are surprisingly closed to the experimental ones (2.90 and 3.01 Å) and to those of model C1 (2.93 and 3.03 Å) in which C···Ag interactions are present. This result shows the significance of the unsupported Au···Ag metallophilic interactions, whose contribution to the existence of the square pyramidal AuAg₄ arrangement is of basic importance. In fact, in Figure 5 it can be observed that, while the behavior of model C2 is also repulsive for all distances at the HF level of theory, at the MP2 level of theory we obtain an interaction energy of 52 kJ·mol^{−1} at the equilibrium distance, showing, again, the key role of dispersion-type interactions. At this point, if we assume as an approximation that model C2 displays the interaction energy of four Au···Ag interactions, we can estimate that the energy of each Au···Ag interaction is around 13 kJ·mol^{−1} (52 kJ·mol^{−1} divided by four interactions) and, from model C1, we can deduce that the energy of each C_{ipso}···Ag(I) interaction is 21.5 kJ·mol^{−1} since we can subtract the interaction energy of model C2 from that of model C1, leading to the energy of two C···Ag(I) interactions (43 kJ·mol^{−1}).

Conclusions

(1) Preliminary DFT/B3LYP calculations permit achievement at low cost of optimized parameters in agreement with the experimental ones but slightly larger for the square pyramidal arrangement in model C1.

(2) Hartree–Fock calculations on models C1 and C2 give rise to ionic repulsion between anionic fragments [AuPh₂][−] and [Ag₄(CO₂H)₅][−] as expected for two negatively charged fragments.

(3) MP2 calculations give rise to excellent agreement between theoretical results and experimental X-ray data, showing that dispersion-type interactions included in the correlation effects are needed for a correct description of the gold–silver square pyramidal arrangement. Indeed, the study of model C2 shows that, even without the support of C···Ag interactions, Au(I)···Ag(I) interactions would be enough to keep the square pyramidal arrangement.

(4) The interaction energies obtained for models C1 and C2 at the MP2 level permit estimation of the stabilization energy related to each Au(I)···Ag(I) interaction (13 kJ·mol^{−1}) and each C_{ipso}···Ag(I) interaction ((95 – 52)/2 = 21.5 kJ·mol^{−1}).

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Supporting Information Available: Theoretical results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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