When Does Gold Behave as a Halogen? Predicted Uranium Tetraauride and Other MAu4 Tetrahedral Species, (M = Ti, Zr, Hf, Th)

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Abstract
Quantum chemical calculations suggest that a series of molecules with the general formula MAu4 are stable, where M = U, Th, and a group-4 atom. They correspond to Au in the formal valence state −1 and indicate that gold can act as a ligand similar to the halogen series. Of the MAu4 species studied, UAu4, the first predicted mixed gold uranium compound, has a short M−Au bond distance, 2.71 Å, which would locate Au between Br and I from the bond length point of view in the U-tetrahalide series. Energetically, the U−Au bond is weaker than the corresponding U−Br and U−I bonds.

Reference

DOI : 10.1021/ja035385a
Stable gold clusters are the subject of both experimental and theoretical studies, because of their potential use as building blocks of new materials and catalytic properties. In this work the existence of uranium-tetraauride, UAu₄, and group-4-tetragold single molecules, MAu₄, where M = Ti, Zr, Hf, and Th is predicted. In such species gold carries a formal charge of (−1) and acts as a ligand to the metallic center. Only a few Au (−1) compounds are known in bulk and in the gas phase. Cesium auride in bulk was discussed in a recent mini-review by Pyykkö. Goodman mentioned other auride species, such as RbAu. The compound BaAu₂ was made in 1938. CsAu ammonia (1/1), CsAu·NH₃, was recently studied. Elements such as Cs and Ba are expected to form ionic compounds with all elements in the periodic table, and the fact that they bind to Au is not an indication that Au is a good ligand. The situation is different if Au, behaving like a halogen, forms tetrahedral complexes with group 4 elements, and also with Th and U. The present quantum chemical calculations show that these molecules are stable, with all real frequencies and some covalent bond character. (For the main group tetraaurides at HF level the same was true for groups 13−15.)

In this work all species were studied using second-order perturbation theory, MBPT2, and density functional theory, DFT, with the B3LYP exchange-correlation functional. The open shell species UAu₄ was also studied using the complete active space (CAS) SCF method with dynamic correlation added by multi-configurational second-order perturbation theory (MS-CASPT2). For Ti a basis set of 6-31g* type (5s4p2d1f) was used. For Au and M = Zr, Hf, Th, U the energy-adjusted Stuttgart ECPs were used to take into account relativistic effects. The number of valence electrons is 19 for Au, 12 for Zr or Hf, 30 for Th, and 32 for U. The basis sets accompanying the ECPs 6s5p3d for Au, Zr, and Hf, and 8s7p6d4f for Th and U, were used. Some calculations were repeated with larger basis sets, namely the gold valence basis and the Th and U valence basis were increased with one g function, 8s7p6d4f1g. The first set of calculations will be indicated as BS1 calculations and the second set as BS2-calculations. Equilibrium geometries and harmonic frequencies were computed for all species at the DFT and MBPT2 level of theory. For UAu₄, the MS-CASPT2 equilibrium geometry was also computed. The programs MOLCAS-5.2 and Gaussian98 were employed.

All molecules were found to be local minima in Td symmetry in their singlet ground state, with the exception of UAu₄ which has a triplet ground state and a slightly distorted symmetry from Td (see below). The calculations were repeated with lowered D₅d symmetry but the molecules maintained the tetrahedral structure. The results for the closed shell species will be presented first, and then UAu₄ will be discussed. The energy of the lowest triplet state for TiAu₄ was calculated and found ca. 2.7 eV above the singlet. In Table 1, the values of the M−Au bond distances in the species studied are reported. The metal−gold bond distance increases along the Ti−Th series and is virtually identical in the Zr and Hf species. MBPT2 predicts shorter bond distances than B3LYP, as expected. Some calculations on TiAu₄, ThAu₄, and UAu₄ have been repeated with the larger basis set, BS2. The general trend due to basis set increase is a M−Au bond shortening, indicating that also with larger basis sets these compounds are bound. In TiAu₄, for example, the B3LYP bond distance decreases from 2.438 Å, with BS1, to 2.422 Å, with BS2. At the MBPT2 level the Ti−Au bond decreases from 2.386 Å, with BS1, to 2.285 Å, with BS2. The B3LYP calculations on the other species with the larger basis also give a bond shortening.

In Table 2 the Td harmonic frequencies of the MAu₄ species, are reported, together with their IR intensities. All frequencies are real, and they maintain the Td degeneracy, even when the calculations are performed in D₅d symmetry. The lowest vibrational motions occur at ca. 20−30 cm⁻¹ and they correspond to Au−M−Au bending modes. The only modes with sizable IR intensity correspond to M−Au asymmetric stretching and occur at ca. 150−300 cm⁻¹. The symmetric M−Au stretching mode occurs at 100−120 cm⁻¹. The Mulliken partial charges on M and Au have been calculated. The relative values are important, not the absolute values. Along the series, Ti, Zr, Hf, Th, and U carry a positive charge of 1.53, 2.75, 1.55, 2.44, and 1.31, respectively. Zr has the largest positive charge and the U and Ti compounds are least ionic.

Among the various species, UAu₄ certainly deserves more attention for several reasons. First, no other mixed uranium−gold species is known in the gas phase; second it does not have a closed shell ground state. UAu₄ presents a rather complicated electronic structure, by analogy with UF₆. The molecule has a triplet ground state, with the lowest singlet lying 1.60 eV above. It was decided to per-

Table 1. M−Au Bond Distance in Å with BS1 and BS2 in the MAu₄ Species

| Species | BS1 | BS2 | MBPT2
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>TiAu₄</td>
<td>2.438</td>
<td>2.422</td>
<td>2.386</td>
</tr>
<tr>
<td>ZrAu₄</td>
<td>2.608</td>
<td>2.589</td>
<td>2.580</td>
</tr>
<tr>
<td>HfAu₄</td>
<td>2.608</td>
<td>2.591</td>
<td>2.583</td>
</tr>
<tr>
<td>ThAu₄</td>
<td>2.798</td>
<td>2.778</td>
<td>2.757</td>
</tr>
<tr>
<td>UAu₄</td>
<td>2.741</td>
<td>2.723</td>
<td>2.678</td>
</tr>
</tbody>
</table>

Table 2. Harmonic Frequencies (cm⁻¹) and Their IR Intensities (km mol⁻¹) in Parenthesis with the BS1 Basis Set, for the MAu₄ Species

<table>
<thead>
<tr>
<th>Mode</th>
<th>TiAu₄</th>
<th>ZrAu₄</th>
<th>HfAu₄</th>
<th>ThAu₄</th>
<th>UAu₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>ν(e)</td>
<td>24.9(0)</td>
<td>27.0(0)</td>
<td>28.1(0)</td>
<td>24.1(0)</td>
<td>24.3(0)</td>
</tr>
<tr>
<td>ν(t₁)</td>
<td>34.4(0)</td>
<td>35.8(0)</td>
<td>36.1(0)</td>
<td>30.0(0)</td>
<td>35.9(0)</td>
</tr>
<tr>
<td>ν(t₂)</td>
<td>50.8(2)</td>
<td>35.0(0)</td>
<td>38.7(0)</td>
<td>26.2(0)</td>
<td>25.7(0)</td>
</tr>
<tr>
<td>ν(α)</td>
<td>112.8(0)</td>
<td>115.8(0)</td>
<td>117.4(0)</td>
<td>108.7(0)</td>
<td>110.5(0)</td>
</tr>
<tr>
<td>ν(β)</td>
<td>109.2(0)</td>
<td>120.5(0)</td>
<td>121.4(0)</td>
<td>115.1(0)</td>
<td>119.7(0)</td>
</tr>
<tr>
<td>ν(γ)</td>
<td>287.1(17)</td>
<td>226.4(22)</td>
<td>179.5(14)</td>
<td>150.2(19)</td>
<td>150.2(19)</td>
</tr>
</tbody>
</table>

"* All structures are tetrahedral with the Au−M−Au angle 109.5°, with the exception of UAu₄. MBPT2-BS2 2.285, "∠Au−U−Au 105.3−111.6°. " ∠Au−U 106.8−110.8°. " MS-CASPT2: BS1 2.709; BS2 2.716.

"* B3LYP results are on the first line, and MBPT2 on the second line.

J. AM. CHEM. SOC. 2003, 125, 7504−7505
Gold clusters are particularly stable for several reasons, such as the so-called aurophilic attraction and relativistic effects. As pointed out by Pykkö,\,²⁵ covalent bonding and the van der Waals bonding behind the metallophilic attraction may be comparable in systems such as Au₂⁺. Moreover the covalent Au–Au bonds among peripheral atoms are substantially strengthened by relativistic effects.¹ We have thus performed calculations on Au clusters such as Au₄ and Au₅ to estimate the relative stability of the MAu₄ species. In particular, UAu₄ turned out to be 59 kcal/mol (per U–Au bond) lower in energy than a U atom and four Au atoms, 38 kcal/mol (per U–Au bond) lower in energy than U atom and two Au₂ molecules. UAu₅ is also 37 kcal/mol lower than a U atom and Au₄, which is formed by two Au₂ moieties at a distance of 4 Å. A similar energy balance for UBr₂ versus U + 2Br₂ and for UI₂ versus U + 2I₂ gives 74 and 63 kcal/mol per U–X bond, respectively. Although from the bond-length point of view, gold is between Br and I, the uranium tetraauride is less strongly bound than the analogous tetrabromine and tetraiodine species.

The existence of uranium–tetrauride, UAu₄, and group-4–tetrاغold compounds, MAu₄, where M = Ti, Zr, Hf, and Th and has been predicted. In such species gold carries a formal charge of (–1) and acts as a ligand to the metallic center, by analogy with the halogen series. UAu₄, the first predicted mixed uranium–gold compound, presents a fairly short M–Au bond distance, which places Au between Br and I from the bond-length point of view. However, from energy considerations, the U–Au bond is weaker than the analogous U–Br and U–I bonds. One possible way of making UAu₄ would be to heat U and Au together in a flowing inert gas stream or to laser-evaporate them and investigate the products by laser spectroscopy.

Acknowledgment. This work was partially supported by Ministero dell’Universitá e Ricerca Scientifica.

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JA035385A