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

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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.[1−7] 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.[8] Goodman[9] mentioned other auride species, such as RbAu. The compound BaAu₂ was made in 1938.[10] CsAu ammonia (1/1), CsAu·NH₃, was recently studied.[11] 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.[12])

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[13] with dynamic correlation added by multi-configurational second-order perturbation theory (MS-CASPT2).[14] For Ti a basis set of 6-31 g* 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.[15] The number of valence electrons is 19 for Au, 12 for Zr and 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.[16] Some calculations were repeated with larger basis sets, namely the gold valence basis set was increased by three f functions, 6s5p3d3f, the Zr and Hf valence basis set were increased with one f function, 6s5p3d1f, 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[17] and Gaussian98[18] were employed.

All molecules were found to be local minima in T_d symmetry in their singlet ground state, with the exception of UAu₄ which has a triplet ground state and a slightly distorted symmetry from T_d (see below). The calculations were repeated with lowered D_{2d} 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

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

	B3LYP-BS1	B3LYP-BS2	MBPT2-BS1
TiAu₄	2.438	2.422	2.386[b]
ZrAu₄	2.608	2.589	2.580
HfAu₄	2.608	2.591	2.583
ThAu₄	2.798	2.778	2.757
UAu₄	2.741[c]	2.723	2.687[d,e]

[a] All structures are tetrahedral with the Au−M−Au angle 109.5°, with the exception of UAu₄. [b] MBPT2-BS2 2.285. [c] ∠Au−U−Au 105.3−111.6°. [d] ∠Au−U−Au 106.8−110.8°. [e] MS-CASPT2: BS1 2.709; BS2 2.716.

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

mode	TiAu₄	ZrAu₄	HfAu₄	ThAu₄	UAu₄
ν_1(e)	24.9(0)	27.0(0)	28.1(0)	24.1(0)	24.3(0)
	42.5(0)	29.6(0)	31.2(0)	24.2(0)	22.2(0)
ν_2(t₂)	33.4(0)	35.8(0)	36.1(0)	30.0(0)	35.9(0)
	50.8(2)	35.0(0)	38.7(0)	26.2(0)	25.7(0)
ν_3(a₁)	112.8(0)	115.8(0)	117.4(0)	108.7(0)	110.5(0)
	109.2(0)	120.5(0)	122.4(0)	115.1(0)	119.7(0)
ν_4(t₂)	287.1(17)	226.4(22)	179.5(14)	150.2(19)	150.2(18)
	292.9(32)	235.5(21)	187.6(13)	164.0(17)	169.9(19)

[a] B3LYP results are on the first line, and MBPT2, on the second line.

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 BS-1, to 2.422 Å, with BS-2. At the MBPT2 level the Ti−Au bond decreases from 2.386 Å, with BS-1, to 2.285 Å, with BS-2. The B3LYP calculations on the other species with the larger basis also give a bond shortening. In Table 2 the T_d harmonic frequencies of the MAu₄ species, are reported, together with their IR intensities. All frequencies are real, and they maintain the T_d degeneracy, even when the calculations are performed in D_{2d} 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 UF₄. The molecule has a triplet ground state, with the lowest singlet lying 1.60 eV above. It was decided to per-

Table 3. M−X Bond Distance Å with BS1 in the M(X)$_4$ Species, M = Th, U; X = F, Cl, Br, Au, I

	exptl[a]	B3LYP[b]	MBPT2[b]		exptl[a]	B3LYP[c]
ThF$_4$	2.14	2.13	2.31	UF$_4$	2.06	2.09
ThCl$_4$	2.57	2.58	2.55	UCl$_4$	2.53	2.54
ThBr$_4$	2.73	2.74	2.71	UBr$_4$	2.69	2.68
ThAu$_4$		2.80[c]	2.76[c]	UAu$_4$		2.75
ThI$_4$	2.91	2.96	2.92	UI$_4$	2.85	2.90

[a] Reference 20. [b] Reference 21. [c] This work.

form MS-CASPT2 calculations, in addition to B3LYP and MBPT2 calculations. The active space in the MS-CASPT2 calculations comprises all the seven U 5f orbitals with two active electrons, without imposing any symmetry constraint. All the 21 electronic triplet states arising from the U 5f^5 configuration were studied. The ground-state geometry of UAu$_4$ was optimized at the B3LYP, MBPT2, and MS-CASPT2 level of theory, and the values of the U−Au bond distance obtained at these levels are reported in Table 1. The MS-CASPT2 calculation was repeated with the larger basis set BS2 and the U−Au bond distance is virtually unaffected. Unlike the closed shell species, UAu$_4$ is slightly distorted from T_d symmetry, toward D_{2d}, the Au−U−Au angles varying between 110 and 109°. The vibrational modes also lose the T_d degeneracy within a few cm^{-1}. A simple way to obtain insight into the U−Au bonding character is to compare the calculated U−Au bond length with the value resulting from a system of additive covalent radii. The particular system, based on Pauling's halogen radii proposed by Pyykkö[1] was used in this work. In Table 4 of Pyykkö's work[1] covalent radii of 128 pm and 153 pm are suggested for Au(I) and U(IV), respectively. These values add up to 281 pm, indicating that some multiple bonding character might be present in UAu$_4$, since the additive value of 281 pm is ca. 10 pm longer than the distance computed here. At the MS-CASPT2 optimized ground-state geometry, all the 21 triplet states lie within an energy range of 2.67 eV. The first five states are virtually degenerate, with an energy difference between the first and the fifth state of 80 cm^{-1}. Such a value is far below the accuracy of any present quantum chemical method in determining electronic excitation energies, and the five states are thus considered as degenerate. In UF$_4$[19] the 21 triplet states arising from the 5f^5 configuration lie within an energy range of 2.76 eV. The molecule has a well-defined $^3T_2$ ground state, with the $^3T_1$ and ^3E states lying 0.12 and 0.15 eV above the ground state, respectively. Spin−orbit coupling lowers the ground state by ca. 0.5 eV. A similar effect may be expected in UAu$_4$. A search for UAu$_4$ charge transfer (CT) states was made, and the lowest singlet state with some Au to U CT character was found to lie ca. 1.8 eV above the ground state. To discuss the behavior of Au as a halide, Th and U will be considered as particular partners of Au, and ThAu$_4$, and UAu$_4$ will be compared with the corresponding halogen series (see Table 3). Experimental values for the U−X bond distance in UX$_4$ are 2.06, 2.53, 2.69, 2.85 Å for X = F, Cl, Br, I respectively.[20] UAu$_4$ has a U−Au bond length of 2.74 Å at the B3LYP level (2.71 Å at MBPT2 level). B3LYP calculations on the uranium halide series were performed[21] and, from the bond-length point of view, Au is between Br and I. Experimental values for the Th−X bond distance in ThX$_4$ are 2.14, 2.57, 2.73, and 2.91 Å for X = F, Cl, Br, I, respectively. We have previously calculated the Th−X bond distances to be 2.13, 2.58, 2.74, 2.96 Å at the B3LYP level, and 2.31, 2.55, 2.71, 2.92 Å at the MBPT2 level, for X = F, Cl, Br, I respectively.[21] Also in this case, Au, with a Th−Au B3LYP bond distance of 2.80 Å (MBPT2 2.76 Å) is between Br and I.

Gold clusters are particularly stable for several reasons, such as the so-called aurophilic attraction and relativistic effects. As pointed out by Pyykkö,[2,5] covalent bonding and the van der Waals bonding behind the metallophilic attraction may be comparable in systems such as Au$_2$$^{2+}$. Moreover the covalent Au−Au bonds among peripheral atoms are substantially strengthened by relativistic effects.[1] We have thus performed calculations on Au clusters such as Au$_2$ and Au$_4$ to estimate the relative stability of the MAu$_4$ species. In particular, UAu$_4$ 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 Au$_2$ molecules. UAu$_4$ is also 37 kcal/mol lower than a U atom and Au$_4$, which is formed by two Au$_2$ moieties at a distance of 4 Å. A similar energy balance for UBr$_4$ versus U + 2Br$_2$ and for UI$_4$ versus U + 2I$_2$ 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−tetraauride, UAu$_4$, and group-4−tetragold compounds, MAu$_4$, where M = Ti, Zr, Hf, and Th 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. UAu$_4$, 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 UAu$_4$ 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.

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