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Hydrides and Iodides of Gold

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The synthesis of gold hydrides in the solid state has long been desirable. Despite early investigations by Wiberg et al.,[1] to prepare AuH_3 utilizing a variety of reducing agents such as $LiAlH_4$, AlH_3, and $LiBH_4$, no direct evidence for the elusive AuH_3 could be obtained and only decomposition products, that is, Au and H_2 could be detected. Despite, or possibly because, of the lack of experimental evidence for gold hydrides in the solid state, a considerable number of theoretical studies have probed the structure of AuH and by using density functional methods.[2–6] Moreover, in the past few years, the chemistry of the gold halides and hydrides has received a great deal of attention, and utilizing a combination of computational and experimental techniques, the structures of many of the gold halides have been shown to agree with earlier structural predictions made by Schwerdtfeger et al.[5–7]

The similar electronegativities ($\chi_{AR}\,I = 2.2$; $\chi_{AR}\,H = 2.2$; $\chi_{AR}\,Au = 2.4$)[6b] of I and H, makes a comparison between gold hydride and iodide compounds relevant. Whereas AuH is a stable diatomic molecule that has been characterized in the gas phase, and although the analogous diatomic AuX species (X = F, Cl, Br) have been know in the gas phase for some time, it was only very recently that the gas-phase structure of AuI was determined by microwave spectroscopy.[8] However, whereas AuH was until very recently unknown in the solid state, AuI is a well-known and even commercially available (!) polymer, which is constructed of a zigzag chain with linear I-Au-I units (Figure 1).[9] The unusual chainlike structure found for AuI can be explained by relativistic effects (as opposed to correlation effects) which show an increased covalency in the Au–I interactions.[10] The structures of AuI_3 and AuH_3, however, were found to be a complex problem, not least because of the decreasing stability of the gold trihalides with increasing mass of the halide.[11–14] For AuH_3, the lowest-energy isomer was found not to be either the T-shaped or linear structure, but rather, a Y-shaped structure (singlet electronic state) which is better viewed as an adduct between AuH and H_2.

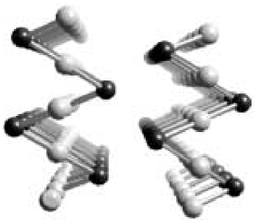
Figure 1. Solid state structure of gold(I) iodide.

Bayse recently reported detailed quantum-chemical DFT studies of the AuH_3/Au_2H_6 system, and suggested that in AuH_3 the AuH and H_2 units would be only loosely bound together [Eq. (1)].[3]

$$\mathrm{HAu}(\eta^2\text{-}\mathrm{H_2}) \xrightarrow{\Delta E_{\mathrm{diss}}=\mathrm{kJ\,mol^{-1}}} \mathrm{AuH} + \mathrm{H_2} \qquad (1)$$

Moreover, with respect to the dimerization of AuH_3 to form Au_2H_6, the “classical” square-planar, D_{2h} structure of Au_2H_6 was reported to be the only isomer located. The dimerization of both the Y- and T-shaped isomers of AuH_3, which formed D_{2h} Au_2H_6, was found in both cases to be an exothermic process by −84 and −305 kJ mol^{-1}, respectively (Figure 2). The bonding in the lowest-energy Y-shaped isomer of AuH_3

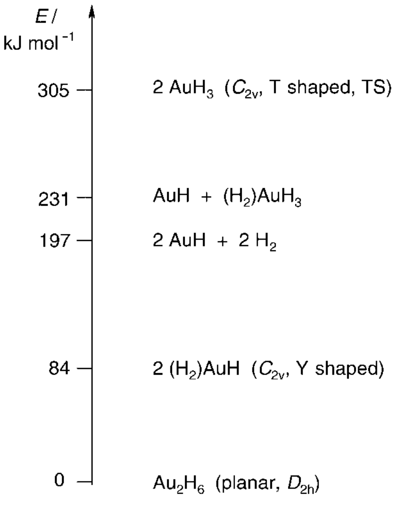

Figure 2. Relative energies of various gold hydride species (TS = transition state).

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can be rationalized as consisting of two major donor–acceptor interactions:[2]

a) donation of electron density from the bonding H_2 σ orbital into an empty orbital on the metal center (M),
b) back donation of electron density from a filled d_π metal orbital into the antibonding σ* H–H orbital.

The σ →M interaction results in both a decrease of the H–H bond strength, and an increase in the H–H bond length with respect to the free H_2 molecule. However, if the back donation M →σ* is particularly strong, the H_2 units can be cleaved by oxidative addition, which results in formal oxidation of the metal from M(n) to M($n+2$). However, in the case of AuH_3, oxidative addition does not occur, that is, the H–H bond in the H_2 ligand remains intact.

Recent ground-breaking solid-matrix investigations by Andrews and Wang,[15] have provided the first experimental evidence for not only $(H_2)AuH$, but also for AuH_5 and the corresponding deuterated analogues. The excellent agreement between calculated and experimentally observed vibrational spectra confirm the existence of the metal–hydride–dihydrogen complex for AuH_3 as opposed to the T-shaped C_{2v} structure which represents a first-order transition state, or the also postulated, but not observed, planar D_{3h} Y-shaped structure (also not a true minimum), or linear $C_{\infty v}$ form of AuH_3, with the triplet-electronic-state analogues being higher in energy in all cases than the singlet state. The effective stabilization of $(H_2)AuH$ by addition of H_2 forming $(H_2)AuH_3$, resulted in the experimental observation of a further, previously unknown gold hydride.

Certainly, establishing the first gold hydride in the condensed phase was a remarkable experimental achievement and now raises the question, as to whether the synthesis and characterization of one of the last missing members of the AuX/AuX_3 (X = H, F–I) series AuI_3 can be achieved. Recently, detailed computational investigations building on initial investigations by Schwerdtfeger et al.[12] have probed the question as to the structure and stability of gold iodides in the +III oxidation state.[14] The calculated isomers and their relative energies are shown in Figure 3. Whilst Au_2I_6 was calculated to adopt a D_{2h} gas-phase structure, the potential-energy surface for the monomer AuI_3 is particularly flat. Thus, the Y-shaped form of AuI_3 is a true minimum at B3LYP level of theory, but a first-order transition state at the MP2 level. In contrast to the lighter gold trihalide homologues, the Y-shaped structure is lower in energy than the T-shaped species (B3LYP level) which in turn corresponds to a first-order transition state (global minimum for AuF_3, $AuCl_3$, $AuBr_3$ is the T-shaped isomer; the Y-shaped form is a first-order transition state). The Y-shaped molecule (which is favored over the T-shaped form by 3–8 kJ mol^{-1}) in AuI_3 can best be described as $(I_2)AuI$ in an analogous manner to AuH_3, that is, an I_2 unit is loosely bound to an Au-I moiety. Again, the I–I bond length is only slightly longer than that found in free I_2, however, the dissociation energy of non-relativistic $(I_2)AuI$ (forming I_2 and AuI) is only +28 kJ mol^{-1}, and as for $(H_2)AuH$, the dissociation energy is only mildly endothermic. However, with relativistic considerations at the CCSD(T) level of theory this value is considerably higher at 97.3 kJ mol^{-1}. However, when a consideration of relativistic effects is taken into account, the Au–I bond length is considerably shortened (by ≈0.5 Å) and is rationalized as an increase in the oxidation state of the central Au atom from +I to +III, thus the higher oxidation state is stabilized by relativistic effects.

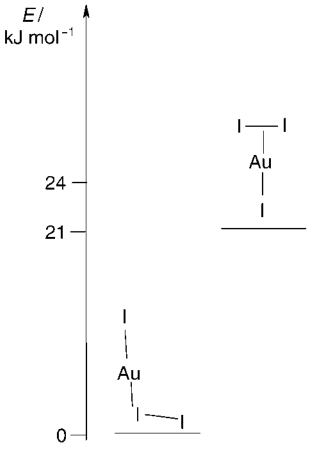

Figure 3. Relative energies of gold(III) iodide species.

Static and dynamic Jahn–Teller systems have been used to explain the paradox between the gold trihalides. In AuI_3 the difference in energy between the Y- and T-shaped species is considerably smaller than in AuF_3, thus making AuI_3 a dynamic Jahn–Teller system. Such distortions are, of course, further increased by relativistic effects. Recently, the global minimum for AuI_3 has been elucidated to be that of a further isomer, the L-shaped form (C_s symmetry), which is a true minimum for all AuX_3 (X = F–I) species, but only for AuI_3 is this the lowest energy form.[14] In the L-shaped isomer the charge transfer from the X_2 unit to the AuX moiety has been calculated to be most pronounced for AuI_3.

With the successful preparation of gold hydrides in the solid state for the first time, an obvious synthetic target must now be the solid state characterization of a free trialkyl gold compound, such compounds have been extensively investigated both theoretically and experimentally by Hoffmann et al. although never isolated in the solid state.[16] Finally, very exciting advances have also recently been made in gold chemistry by M. Jansen et al. in the chemistry of auride compounds with the synthesis, isolation, and characterization of cesiumauride ammonia, $CsAu\cdot NH_3$, a crystalline analogue of alkali metals dissolved in ammonia[17] and K. Seppelt and co-workers with the successful preparation of several binary and ternary gold-xenon complexes.[18, 19]

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