Fluxionality and σ-Aromaticity in Small Yttrium-Doped Gold Clusters


Aromativity is a qualitative concept which has been applied in organic chemistry very successfully. Recently, it has been extended to compounds containing different metallic elements. Reported examples of aromatic binary clusters of transition metals include the Au₅Zn⁺ cation[4] and the neutral Cu₅Sc molecule.[5] In Au₅Zn⁺, the six delocalized σ-electrons satisfy the Hückel (4n+2) rule, and it is a σ-aromatic five-membered ring.[6] The ten σ-electrons in Cu₅Sc are also fully delocalized, and on the basis of electron count and a partition of its electron density, this seven-membered ring was shown to be σ-aromatic.[5] We now present experimental evidence for the geometrical structure of the small neutral yttrium-doped gold clusters Au₅₋₆Y in the gas phase, and demonstrate theoretically that the anion Au₆⁻Y constitutes a new bimetallic aromatic six-membered cycle.

Structural information on neutral Y-doped Au clusters is obtained by means of vibrational spectroscopy. To record the vibrational spectra of the clusters in the gas phase, we employ the infrared multiple photon dissociation (IR–MPD) technique using action spectroscopy with Xe as the messenger atom.[6] The Free Electron Laser for Infrared Experiments (FELIX) provides intense radiation in the far IR.[7] Details are provided in the Supporting Information.

Let us first consider the IR spectroscopic results of the smaller clusters Au₄Y and Au₅Y. Their experimental spectra are displayed in Figures 1a and b together with the calculated vibrational spectra of the Xe complexes. Quantum chemical calculations were carried out using the DFT method with the pure BP86 functional, and the MO coupled-cluster theory CCSD(T) method (computational details and a table with experimental and scaled calculated IR frequencies are given in the Supporting Information). An initial calibration of DFT methods points out that the BP86 functional leads to reliable predictions of the vibrational frequencies for transition-metal-doped clusters.[8] Relative energies given hereafter include the zero-point energy corrections. Note that Au₄Y has a slightly bent Au–Y–Au structure (C₂v) and Au₅Y exhibits a D₃h form in which the Y atom occupies the central position. Attachment of an additional gold atom destroys the high symmetry, giving rise to a non-planar (C₃) Au₅Y cluster, with a central Y atom but a fourth axial Au atom. The Xe atom prefers to attach to Y in a trans position to the fourth Au atom with respect to the central AuY axis. The observed IR spectrum of Au₅Y features an intense peak centred at 228 cm⁻¹, which is reproduced well by DFT calculations (221 cm⁻¹, Figure 1a). Addition of the fifth gold atom leads to two distinct lower-lying Au₆Y forms nearly having the same energy at both BP86 and CCSD(T) levels. While Au₆Y-I is planar (C₂v), Au₆Y-II still maintains a non-planar C₃v form. In both cases, an attachment of Xe to Y is preferred. The IR spectra of both isomers in the region of 150–225 cm⁻¹ turn out to be similar, and both compare relatively well with the observed spectrum, whose peaks are centered at 185 and 211 cm⁻¹ (Figure 1b). Therefore, the isomers of Au₆Y cannot be discriminated based...
on their vibrational spectra alone, and might coexist in the experiment.

The experimental spectrum shown in the upper panel of Figure 1c has been obtained by IR–MPD of the Xe complex of Au$_6$Y.[7c] Among the numerous structures of Au$_6$Y possessing a doublet ground state, the two shown in Figure 2 are the lowest-lying isomers. Both forms have a Y centre, but are non-planar. A correspondence between Au$_6$Y-I and Au$_6$Y-II with Au$_{1-}$-Y-I and Au$_{1-}$-Y-II, respectively, can be established. Au$_6$Y-II arises from Au$_6$Y-I by a strong out-of-plane motion of one Au atom. The non-planarity and low-spin state of Au$_6$Y make it markedly different from other Au$_6$M clusters with M = Ti, V and Cr.[10] Au$_6$Y-I (2$^\text{A}_1$, C$_{2v}$) is more stable than Au$_6$Y-II (2$^\text{A}''$, C$_2$) by 0.24 eV with CCSD(T) and 0.35 eV with BP86 calculations.

For Au$_6$Y, the Xe atom also prefers to attach to Y, and the same energy ordering of the two isomers is also found for Xe complexes, but the energy difference between them is increased to 0.49 eV (BP86). Figure 1c compares the calculated and observed IR spectra of Xe complexes of the two lowest Au$_6$Y isomers. Interestingly, the experimental IR spectrum is characterized by unusually broad bands—much broader than observed for Au$_6$Y and Au$_6$Y—which are not reproduced in the calculated spectra of Au$_6$Y-I-Xe and Au$_6$Y-II-Xe.

We now consider the IR spectrum of the lower-lying Au$_6$Y-I-Xe. The Y–Xe stretch vibration corresponds to a peak at 76 cm$^{-1}$, which seemingly corresponds to the observed outermost left band. The observed band ranging from 100 to 150 cm$^{-1}$ is attributed to Au–Au and Y–Au stretch vibrations. The observed band at ~200 cm$^{-1}$ is a combination of two Au–Y stretch modes, one calculated at 183 and the other at 196 cm$^{-1}$. The observed strong broadening of the IR bands of Au$_6$Y needs further consideration. A rationalization would be to attribute this observation to a size-specific highly fluxional character. Indeed, broadening of vibrational bands of various species has been discussed before in terms of very rapid rearrangements. In the case of tricarbonyl (η$^3$-norbornadiene) iron, fast interwell dynamical processes have been invoked.[11] For the methionium cation CH$_3$$^+$, large-amplitude vibrations observed as broad features in the infrared spectrum have been explained through a dynamical mechanism for hydrogen exchange and eventually full hydrogen scrambling.[12] Also for Si and Au clusters fluxional characteristics have been described for specific sizes.[13] In the present case, as is illustrated in the potential energy curves shown in Figure 3, the neutral Au$_6$Y-I species is highly fluxional; it distorts along different axes extremely easily. In fact, the barrier of inversion through a planar transition structure (Figure 3a) amounts to only 1.9 kJ mol$^{-1}$ (BP86 level). More interestingly, the bond stretching isomerization (Figure 3b) is also a highly facile process, as the corresponding energy barrier amounts to only ~0.5 kJ mol$^{-1}$ at the same level. The existence of the different bond stretching isomers is a consequence of the partially filled quasi-degenerate SOMO and SOMO–1 orbitals. In $D_{5h}$ symmetry these orbitals are perfectly degenerate, which then yield the three bond-stretching isomers by Jahn–Teller distortions. This highly anharmonic potential with several degenerate minima in the PES separated by very low barriers is expected to yield fluxional behaviour of the cluster on picosecond timescales, which in turn would explain the broadening of the IR peaks of Au$_6$Y. Such a broadening was not observed for Au$_6$Y and Au$_6$Y, which do not possess similar electronic structures.

Overall, the good agreement for Au$_6$Y and Au$_6$Y (Figures 1a–b), and the relatively good agreement for Au$_6$Y (Figure 1c), taking into account the fluxionality-induced broadening, provides structural identification of the neutral Au$_6$Y cluster.

The observed structure of Au$_6$Y can be understood based on its electronic structure. According to the phenomenological shell model,[14] MOs composed of the valence s orbitals determine the properties and electronic structure of alkaline and metallic clusters such as Cu$_6$Sc to a great extent.[15] In planar (nearly) cylindrical clusters, shell closing occurs at ten electrons, which correspond to the $(1s)^2(1p_x)^2(1p_y)^2(1d_{z^2})^2(1d_{x^2-y^2})^2$ configuration.

![Figure 2. BP86/cc-pVQZ-PP structures (bond lengths in Å) of the two lowest-energy neutral isomers Au$_6$Y-I and Au$_6$Y-II, and the anion Au$_6$Y-I-I. Relative energies given in parentheses (eV) were obtained from CCSD(T)/cc-pVTZ-PP using BP86 geometries.](image)

![Figure 3. Potential energy curves corresponding to a) the inversion, and b) the bond stretching isomerization of the neutral Au$_6$Y-I obtained at the BP86/cc-pVQZ-PP level.](image)
The partial density of states (DOS) of Au_6Y-I indicates that other MOs with large contributions from s orbitals exist. Together with the three electrons of Y, Au_6Y-I has nine electrons in the shell model MOs. The electron localization indicator (ELI–D)[16] isosurface of Au_6Y-I, given in Figure 4a, demonstrates that there are localization domains only around the nuclei. The partial ELI–D function for the shell model MOs of Au_6Y-I (Figure 4b) is similar to the result for Cu_7Sc, which thus suggests that MOs with high contributions from valence s orbitals are mainly responsible for the chemical bonding in these clusters. The ELI–D function is much less important in the longer Au–Au bonds, suggesting that the electron distribution in these MOs is responsible for the elongation of these distances.

Attachment of an extra electron to the neutral cluster Au_6Y-I yields the anion Au_6Y^-I (Figure 2). Figure 5 shows the total and partial DOS of the s orbitals of the anion Au_6Y^-I, where the MOs corresponding to the shell model are also assigned. Au_6Y^-I behaves like a 10-electron system satisfying both the shell model and Hückel’s rule. Such an electronic configuration belongs to a perfect six-membered ring shape, and induces a strong stabilization effect. Indeed, Au_6Y^-I is calculated to have a planar D_6h symmetry and exhibits a particularly strong binding of the extra electron. The electron affinity of Au_6Y-I amounts to 3.12 eV (Figure 2). The HOMO–LUMO gap of 2.07 eV for Au_6Y^-I is comparable to that of, for example, Au_6Sc.[17] Both calculated energetic parameters suggest a high stability of the Au_6Y^-I anion. Consistently, as shown in Figure 4d, there are equivalent domains for Au_6Y^-I in the partial ELI–D function for the shell model MOs.

To probe the electronic behaviour of the anion further, the nucleus-independent chemical shifts (NICS)[2,18] were calculated. Since the NICS(0) value is strongly influenced by core electrons of the atom in the center of the ring, we rather used the NICS(1) and NICS(2) values where the ghost atom is put 1.0 and 2.0 Å above the middle of the ring, respectively. The NICS(1) value computed above the center of the ring of −15.3 ppm for Au_6Y-I can be compared to the corresponding value previously calculated for Cu_7Sc. The NICS(2) value at the center of the three-membered Au–Y–Au rings (about −6.9 ppm) of this cluster can be compared to the previously reported value of about −5 ppm for the σ-aromatic five-membered cyclic cation Au_6Zn^+ (D_5h).[16] The distribution of NICS(1), NICS(2) and the corresponding η tensor are negative for Au_6Y^-I, thus lending further support for the aromatic character of the anion. Moreover, the NICS(1) and NICS(1)̂ of Au_6Y^-I are calculated to be more negative than NICS(2) and NICS(2)̂, which is an additional indication for its σ-aromaticity (cf. ESI).

In summary, we report the IR spectra of Au_6Y, Au_6Y, and Au_6Y, which represent the first experimental far-IR spectroscopic data on neutral doped metal clusters in the gas phase. Comparisons with DFT/BP86 calculations allow their ground state structures to be identified. Calculations show that the global minimum of Au_6Y possesses a non-planar C2 structure, while the highly fluxional behaviour of this structure accounts for the experimentally observed line broadening in the IR spectra.

The corresponding anion Au_6Y^- has a planar cyclic D_6h form and the distribution of its σ electrons complies with the electronic shell model. The anion is relatively stable with respect to electron detachment (IE = 3.1 ±0.1 eV). The stability, high symmetry, closed electronic structure and the magnetic properties suggest that it can be regarded as a new σ-aromatic six-membered all-metallic cycle. Its experimental characterization is envisaged by, among others, photoelectron spectroscopy-based techniques.

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