Au···H hydrogen bonds in ligand-coordinated gold clusters

Katsuaki Konishi, 1,2 M. Abu Bakar, 2 Yukatsu Shichibu. 1,2
1 Graduate School of Environmental Science, Hokkaido University, Sapporo, 060-0810, Japan
2 Faculty of Environmental Earth Science, Hokkaido University, Sapporo, 060-0810, Japan

For several decades, M···H interatomic forces, such as agostic and hydrogen-bonding interactions, have attracted continuing interest not only from the fundamental aspects but also in relation to their involvement in some catalysts. For gold, plenty of examples of close contacts with hydrogen atoms have been reported in the crystal structures of Au+, Au2+ and Au3+ complexes, but there has been limited decisive experimental evidence of such attractive interactions [1]. Especially, no examples of spectroscopically identified “hydrogen-bond-type” Au···H interactions have been reported. This is contrasted with the cases of the other transition metal complexes, which provide numerous examples of M···H hydrogen bonds.

Herein we demonstrate the first example of spectroscopically identified hydrogen bonding interaction of C–H units to Au atoms in divalent hexagold cluster (Au6)2+ decorated by diphosphine ligands [2]. Ligand-protected gold clusters have currently attracted attention as a class of molecule-like metal species residing between particles and simple complexes. We have recently reported some subnanometer-sized diphosphine-coordinated clusters and revealed their unique structures and optical properties [3]. The cluster we used here is core+exo type Au6 cluster carrying m-phenylene-bridged diphosphines (1), whose crystal structure showed close contacts of the gold framework to the bridging m-phenylene units (Fig. 1). The hydrogen atoms at the 2-position of the m-phenylene bridges (H-2) are located in proximity to the tetrahedral core with Au–H distances of 2.60 – 2.65 Å, which are fairly shorter than the sum of the van der Waals radii (2.86 Å). Accordingly, the distances to the nearest neighbour C atoms (3.641 – 3.699 Å) were explicitly shorter than when C, H and Au atoms are aligned with van der Waals Au-H contact (3.95 Å). The Au-H-C angles for the above short Au-H contacts were in the range of 162.0 – 171.0°. These observations imply the presence of hydrogen-bond-type interactions between the H-2 atoms and the Au cluster unit. It should be noted that the Au···H-C interactions were also observed in solution NMR, which showed 3H and 13C NMR signals of the C-H units at considerably downfield regions, indicating the hydrogen-bond character of the interactions. We also show the presence of electronic coupling between the Au6 moiety and bridged benzene rings in the absorption spectra. These results demonstrating the unique capability of small gold cluster to interact with unfunctionalized C-H groups may not only promote the further understanding of chemical bonding but also shed light on the elucidation / developments of recently emerging gold cluster catalysis, which would expand the scope of gold clusters.

Fig. 1. Schematic illustration of the structure of 1.

References

Corresponding author email: konishi@ees.hokudai.ac.jp