Aggregation through the Quadrupole Interactions of Gold(I) Complex with Triphenylphosphine and Pentafluorobenzenethiolate

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A new class of the aggregation of the gold(I) phosphine complex with pentafluorobenzenethiolate ligand through intermolecular quadrupole interactions was designed and characterized both by X-ray crystallography in solid state and by electrospray ionization mass spectroscopy in solution.

A great deal of research has focused on the structural chemistry of gold(I) complexes with d^{10} closed-shell electronic structure, since various types of supramolecules, which have 1-D chain or 2-D sheet structure, have been constructed through intermolecular interactions such as the aurophilic interaction.[1,2] Noncovalent interactions, namely, the hydrogen bonding and the π–π stacking also contribute largely to the construction of the solid-state structure and packing arrangements of gold(I) complexes as well as the aurophilic interaction.[2,3] It is well known that the cooperation with electron-deficient fluorinated aromatics and electron-rich aromatics can induce the electrostatic quadrupole stacking interaction and contribute to the architecture of extended structures in crystal.[4,5] A gold(I) phosphine thiolate complex, $Ph_3PAu(SC_6F_5)$,[6] is a potential example of the formation of such an electrostatic quadrupole interaction in crystal, since this complex contains both aromatics in the phosphine and fluorinated aromatic in the thiolate ligand in its molecular system, but the crystal structure has not been determined. We report here a new class of supramolecular aggregation of the gold(I) thiolate complex through the quadrupole interaction not only in crystal but also in diluted solution.

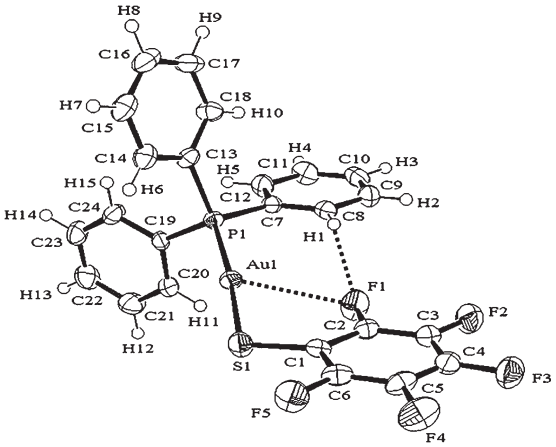

Figure 1. ORTEP[9] drawing of **1** at 50% probability level. Dotted lines show possible intramolecular close contacts. Selected bond distances (Å) and angles (°): Au1–S1, 2.310(2); Au1–P1, 2.251(2); S1–C1, 1.765(8); Au1–F1, 2.908(5); F1–H1, 2.585; P1–Au–S1, 174.44(8); Au1–S1–C1, 108.4(3).

The crystal structure of the present complex, $Ph_3PAuSC_6F_5$ (**1**) was determined by X-ray diffraction method for the first time.[7,8] The gold centre of **1** has linear two-coordinate geometry with tertiary phosphine and thiolate ligands, the P1–Au1–S1 axis deviates slightly from the linearity (Figure 1). The P1–Au1–S1 angle, the Au1–S1 and the Au1–P1 bonds correspond to those of a series of gold(I) phosphine thiolate complexes [P–Au–S: 171.01–176.53°, Au–S: 2.285–2.303 Å, Au–P: 2.253–2.269 Å].[2,10] The S1–C1 bond distance and the Au1–S1–C1 angle are also consistent with those of the analogous complexes and reveal the single bond character as a thiolate [S–C: 1.739–1.801 Å, Au–S–C: 96.35–110.82°].[2,10] The most remarkable structural feature is the almost parallel orientation of the fluorinated phenyl ring (C1 ring) of the thiolate ligand and one of the phenyl rings (C7 ring) of phosphine ligand in the molecule, where the dihedral angle between them is 1.8(3)° (Figure 1). The Au1–S1–C1–C2 torsion angle of 19.4(9)°, which is the smallest value in this type of gold(I) complexes [Au–S–C–C: 22.27–77.29°],[2,10] reveals that the C1 ring and the C7 ring are not on an identical plane. The F1 and the H1 atoms show close contact (C–H distance is fixed at 0.95 Å), where the F1–H1 distance (2.585 Å) is slightly shorter than the sum of the van der Waals radii (2.67 Å) of the H (1.20 Å) and F (1.47 Å) atoms.[11] The distance of Au1–F1 of 2.908(5) Å, is also shorter than the sum of the van der Waals radii (3.13 Å) of the Au (1.66 Å) and F atoms.[11] This relatively short interatomic distance is consistent with those of gold complexes, $[Au_4(\mu_3\text{-}SC_6F_5)_2(C_6F_5)_6(\mu\text{-dppf})]$[12] (2.90 Å), $[Au_2(\mu\text{-}SC_6F_5)(\mu\text{-dppf})]ClO_4$[12] (3.10 Å) and values of the F–Ag distances of various silver complexes [2.602(10)–2.982(6) Å].[12] These intramolecular close contacts

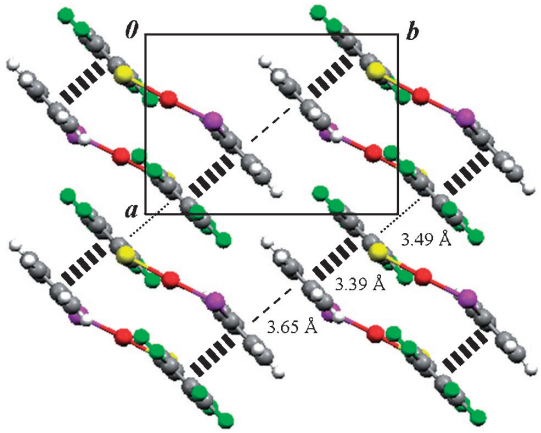

Figure 2. 2-D network through C_6F_5–C_6H_5 (▮▮▮▮), C_6F_5–C_6F_5 (·····), and C_6H_5–C_6H_5 (-----). Unrelated phenyl rings of phosphine ligands are omitted for clarity.

can play a role to increase in structural rigidity, and may facilitate intermolecular contacts.

No intermolecular aurophilic interaction was observed, but the molecules were stacked each other in crystal through various types of intermolecular π–π interactions. The fluorinated phenyl ring of the thiolate ligand and the phenyl ring of the phosphine ligand of the neighboring molecule show parallel displaced close contact. The least-square distance is 3.39(1) Å, and an intermolecular quadrupole interaction can exist, resulting in forming a pseudocyclic dimer (Figure 2). The dimer also alternatively stacks to form sheet-like structure in *ab* plane (Figure 2). The π–π interaction based on the fluorinated phenyl rings shows out of alignment as with the quadrupole interaction, where the distance between the mean planes [3.49(1) Å] corresponds to those of the $(n\text{-}Bu_4N)[Au(SC_6F_5)_4]$.[3] The π–π interaction through the phenyl rings also shows the parallel displaced structure, where the distance between the mean planes [3.65(1) Å] is longer than that of the fluorinated phenyl rings. These interactions must be responsible for the further assembly of the complex dimer and the stabilization of the crystal structure. As the result of assembly, the complex **1** shows 2-D sheet-like molecular network in the crystal. The packing structure is layered and 2-D sheets pile up along *c* axis with orthogonal rotation through the weak edge-to-face C–H$\cdots\pi$ intermolecular interactions [2.765(5) Å] between the phenyl rings of the phosphine ligand (H13 of C19 ring and C13 ring of adjacent molecule). Thus, the molecule is tightly packed in the crystal through the 3-D linkage.

Electrospray ionization mass spectroscopy (ESIMS) was conducted to the dilute acetonitrile solution (2.4×10^{-5} mol dm^{-3}).[13] The positive-ion spectrum of the complex displayed significant peaks at m/z 1338.7 (relative intensity: 38), 1117.2 (100), and 721.4 (20) as shown in Figure 3. These m/z values correspond to $[Ph_3PAu(SC_6F_5)]_2 + Na^+$, $[(Ph_3PAu)_2(SC_6F_5)]^+$, and $[(Ph_3P)_2Au]^+$, respectively. However, no peaks corresponding to monomeric species such as $Ph_3PAu(SC_6F_5) + H^+$ at m/z 659 or $Ph_3PAu(SC_6F_5) + Na^+$ at m/z 681 were detected. In the previous report of the FABMS measurement for the same complex, the peaks due to the dimer were absent but those of the monomer were present.[6] However, the "softness" of the ESI method provides direct evidence of the existence of the dimeric species in diluted solution without fragmentation. In addition, MS/MS measurement to the selected precursor ion (m/z 1338.7) gave new peak at m/z 681.0 (0.3)

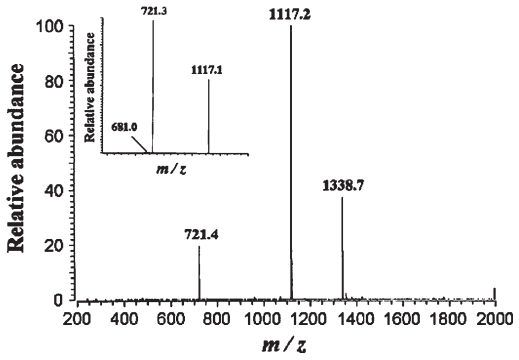

Figure 3. ESI mass spectrum of the complex **1** in 2.4×10^{-5} mol dm^{-3} acetonitrile solution. The inset shows MS/MS of the selected precursor ion (m/z 1338.7).

which corresponds to the monomer species obtained by the collision-induced dissociation of the dimer, together with 1117.1 (56) and 721.3 (100) (the inset of the Figure 3). Thus, these results can be explained by the fact that the complex still exists in the dimeric form even in the diluted solution and the dual electrostatic quadrupole interaction which may be responsible for this dimeric aggregation, suggesting that the quadrupole interaction[5] should be more stable than the other interactions in this molecular system. In other words, $[Ph_3PAu(SC_6F_5)]_2$ as a dimeric form is reasonable for the chemical formula of this complex rather than $Ph_3PAu(SC_6F_5)$ as a monomeric form. In conclusion, the gold(I) phosphine thiolate complex, $Ph_3PAu(SC_6F_5)$ shows molecular aggregation through the electrostatic quadrupole interaction between the phenyl and fluorinated phenyl rings in the solid state and even in solution, leading to the new class of supramolecular aggregation.

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7 The colorless crystal was obtained from dichloromethane/pentane (isolated yield 89%). Anal. Calcd for $C_{24}H_{15}AuF_5PS$: C, 43.78; H, 2.30%. Found: C, 43.98; H, 2.13%.
8 Crystal data for 1: $C_{24}H_{15}AuF_5PS$, $M_r = 658.37$, monoclinic, space group $P2_1/n$, $a = 8.2721(2)$, $b = 11.3627(2)$, $c = 23.6798(5)$ Å, $\beta = 97.1292(6)^\circ$, $V = 2208.54(8)$ Å^3, $\lambda = 0.71069$ Å, $Z = 4$, $D_{calcd} = 1.980$ g cm^{-3}, $T = 296$ K, μ(Mo $K\alpha$) $= 69.03$ cm^{-1}. The structure was solved by a direct method (SIR92). 3537 reflections ($I > 3.0\sigma(I)$, $2\theta_{max} = 55.0^\circ$) converged at $R_1 = 0.039$ ($R = 0.053$ and $R_w = 0.104$). Hydrogen atoms were placed in calculated positions (C–H = 0.95 Å).
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13 ESI mass spectra were obtained with an LCQ^{DECA} mass spectrometer (Thermo Quest) and analyzed by Xcaliber software. The sample was infused via a syringe pump. The measurement conditions: spray voltage: 2 kV; sheath gas flow rate: 50 units (roughly 1.25 L min^{-1}); capillary voltage, 5 V; capillary temperature, 150 °C; ion gauge pressure, ca. 1.3×10^{-5} Torr; syringe pump flow rate, 3 μL min^{-1}; mass range, m/z 50–2000. MS/MS was achieved by collisions of the isolated clusters with buffer gas (He) during an excitation period of 30 ms. Data were obtained at a collision energy chosen such that total fragment ion abundances amounted to about 22% of that of the selected precursor ions (m/z 1338.7).

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