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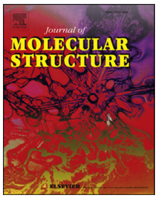

Higher coordinate gold(I) complexes with the weak Lewis base tri(4-fluorophenyl) phosphine. Synthesis, structural, luminescence, and DFT studies☆

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ABSTRACT

The structures and spectroscopic properties of two high coordinate gold(I) phosphine complexes with the TFFPP=tri(4-fluorophenyl)phosphine ligand are reported. Synthesis in a 1:3 metal to ligand ratio provided the compound [AuCl(TFFPP)$_3$] (**2**) that crystallize in the P$\overline{1}$ space group, where the asymmetric unit consists of three independent molecules. In all three sites, two sets of bond angles display distinctly different ranges. The three P–Au–P angles have average values of 117.92°, 117.57°, and 114.78° for sites A, B, and C, with the corresponding P–Au–Cl angles of 98.31°, 99.05°, and 103.38°, respectively. The chloride ion coordinates as the fourth ligand, at the corresponding Au–Cl distance of 2.7337, 2.6825, and 2.6951 Å for the three sites. This distance is longer by 0.40–0.45 Å than the Au–Cl distance found in the mono TFFPP complex **1** (2.285 Å) indicating a weakening of the Au–Cl interaction as the coordination number increases. In compound **3**, [Au(TFFPP)$_3$]Cl·½CH$_2$Cl$_2$.H$_2$O, the structure consists of three phosphine ligands bound to the gold(I) atom, but the Cl$^-$ exists as uncoordinated counter anion. The structural differences observed in the two complexes are attributable to crystal-packing effects caused by the introduction of H-bonding as well as enhanced intra and inter-molecular π-interaction in **3**. The photoluminescence of the complexes compared with that of the ligand show ligand centered emission perturbed by the metal coordination. Theoretical DFT studies conducted on these complexes supports assignments of the electronic transitions observed in these systems.

1. Introduction

Although molecular gold(I) compounds with a closed shell d^{10} electronic configuration are in most cases characterized by linear coordination [1–3], complexes possessing higher coordination numbers are also known to a lesser degree. Several factors influence the level of coordination at the gold(I) center including electronic factors and steric hindrances of the coordinating ligands. For example, recent work [4] in the use of ferrocene dithiocarboxylates showed that the ligand coordination to gold(I) center follows versatile modes including monodentate, chelating, or bridging modes with coordination numbers ranging from two to four. This result contrasts with the previously known coordination of sulfur containing ligands as reported for similar systems of dithiocarbamates [5,6] and xanthates [7], where monodentate coordination modes were dominant [8,9].

Overall only a small number of ligands have been found capable of providing high coordination geometries about the gold(I), with most reports to date involving either bidentate phosphines [10,11] and/or thiolate ligands [12,13]. Recent progress in four-coordinate gold(I) chemistry involves bridged diphosphine ligands that have been characterized structurally and studied computationally [14]. The solid state, vapor induced interconversion of high coordinate Au(I) complexes has also been observed recently [15,16]. Structurally characterized three- and specifically four-coordinate gold(I) complexes with monodentate phosphine ligands are still limited. The tris-2-furyl phosphine [17] and the 1,3,5-triaza-7phosphaadamantane (TPA) [18] ligands are noteworthy to mention as they

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provided a regular tetrahedral geometry.

A particularly interesting application of high coordination gold(I) complexes is related to the fact that three-coordinate species generally have luminescent properties that can be exploited for light-emitting diodes [19]. For example, tertiary phosphines with aromatic substituents have attracted a great deal of attention in the design and development of chemosensing applications [20]. The photoluminescent properties of several types of three-coordinate gold(I) complexes with aromatic substituents in organic solvents and in the solid state have been reported [21–23].

We have been interested in the coordination of aromatic tertiary phosphines including tri(4-fluorophenyl)phosphine (TFFPP) ligands to gold(I) centers. The steric properties of the TFFPP ligand are comparable to triphenylphosphine (PPh_3) since both have a similar cone angle of 145° [24]. Although the two ligands appear similar sterically, their electronic properties are different because of the presence of the strong electron withdrawing fluorine groups on the phenyl ring of the TFFPP ligand. Due to its unique electronic behavior TFFPP has been used as a flame-retarding additive in Li–ion battery electrolytes [25]. While the electronic properties of the TFFPP ligand might be interesting, its coordination chemistry with gold(I) has not been detailed extensively beyond the monocoordinated gold(I) chloride system [26].

The focus of the current work involves the nature of two structures containing three TFFPP ligands which show a geometrical transition from a pseudo trigonal pyramidal to a trigonal planar geometry as a result of inner/outer-sphere complexation of the fourth Cl^- ligand. These structural changes are collaborated with luminescence, ^1H NMR, ^{31}P NMR, UV–Vis, IR spectroscopy, and theoretical DFT studies.

2. Experimental

2.1. General method

All reactions were carried out under a modified Schlenk technique at room temperature. Tetrahydrothiophene gold(I) chloride [AuCl(tht)] is prepared according to literature [10]. All infrared spectra were collected with Ge coated on potassium bromide (KBr) on a Shimadzu IR Affinity-1 Fourier-transform infrared spectrophotometer, over the range 4000–300 cm^{-1}. ^1H and ^{31}P NMR spectra were recorded on a 300 MHz Varian NMR 300 – 411149 FT-NMR spectrometer. Chemical shifts (δ ppm) were reported relative to Me_4Si and 0.0485M triphenylphosphate in $CDCl_3$.

2.2. Spectroscopic studies

The UV–Vis spectra were collected on a Shimadzu UV-2401 PC UV–Vis recording spectrometer. The luminescence studies were conducted with a Photon Technology International (PTI) spectrometer model QM-7/SE, equipped with a Hamamatsu R928P photomultiplier. The instrument uses an Ushio 75 W Xe xenon arc lamp, and a model 101M f/4 0.2-m Czerny Turner with a 4 nm/mm bandpass monochromator. The instrument operation, data collection, and handling were all controlled using the advanced FeliX32 software. All samples for the luminescent studies were loaded in borosilicate capillary tubes and were sealed from the atmosphere using a micro torch.

2.3. X-ray crystallography studies

Single crystals of the complexes were selected, mounted on quartz fibers, and aligned with a digital camera on a Varian Oxford Xcalibur E single-crystal X-ray diffractometer. Intensity measurements were performed using Mo Kα radiation, from a sealed-tube Enhance X-ray source, and an Eos area detector. CrysAlisPro [27] was used for preliminary determination of the cell constants, data collection strategy, and for data collection control. Following data collection, CrysAlisPro was also used to integrate the reflection intensities, apply absorption corrections to the data (semi-empirical), and perform a global cell refinement, while Mercury 3.6 utility was used for structure visualization and exploration.

The program suite SHELX was used for structure solution (XS) and least-squares refinement (XL) [28]. The initial structure solutions were carried out using direct methods and the remaining heavy atom positions were located in difference maps. The final refinement included anisotropic displacement parameters for all non-hydrogen atoms. Refinement was performed against F^2 by weighted full-matrix least squares. The molecular structures for **2** and **3** are presented in Figs. 1 and 2, respectively. The crystallographic and structural refinement data for **2** and **3** are summarized in Table 1.

2.4. Computational studies

All of the theoretical calculations for the TFFPP ligand and the complexes **1**, **2**, and **3** were completed using the GAUSSIAN'09 software package [29]. Geometry optimization and vibration frequency calculations were performed with the Becke [30] three-parameter hybrid functional using the Perdew–Wang correlation functional (B3PW91) [31] level of density functional theory (DFT). The 6–311 G(d, p) basis set was utilized for C, P, Cl, H and F. The LANL2DZ basis set [32] was used in conjunction with two f-type polarization functions [33] and p-type functions [34] for the $5s^25p^6 5d^{10}6s^1$ valence electrons of gold, and one d-type polarization function for phosphorus. The predicted absorption spectra of the optimized structures were accomplished by time-dependent density functional theory (TD-DFT) without consideration of any solvent effects. Molecular orbitals iso-density diagrams (iso-values: 0.02 atomic units) of molecular orbitals were created using the GaussView 5 software (Gaussian Inc.)

2.5. Synthesis

2.5.1. Chloro(tri (4-fluorophenyl)phosphine)gold(I), [AuCl(TFFPP)] (1)

TFFPP (0.0200 g, 0.063 mmol) was added to a solution of $[AuCl(C_4H_8S)]$ (0.0146 g, 0.063 mmol) in dichloromethane (20 mL)

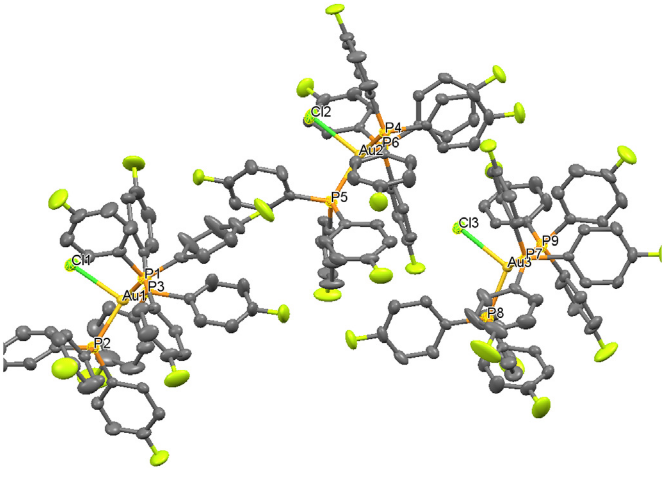

Fig. 1. Thermal ellipsoid diagram of $[AuCl(TFFPP)_3]$ (**2**) showing the asymmetric unit components consisting of the three independent molecules at sites A, B, and C. The independent molecules at each site consist of Au1, Au2, and Au3, respectively.