Bull. Chem. Soc. Jpn. Vol. 80, No. 3, 533–535 (2007)

Synthesis and Luminescence of Four-Coordinate Mononuclear Gold(I) Complex: $[Au(biphep)_2]PF_6$

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A tetrahedral four-coordinate bis-diphosphine gold(I) complex, $[Au(biphep)_2]PF_6$ (biphep = 2,2′-bis(diphenylphosphino)-1,1′-biphenyl), was prepared, and the structure was determined by X-ray structure analysis. The complex showed photoluminescence at room temperature in the solid state and in CH_2Cl_2.

There has been increasing interest in the design and construction of light-emitting diodes (LED) and employment of metal complexes as the emissive layer in electroluminescence (EL) devices.[1] Metal complexes with a d^{10} electronic configuration have become an important class of luminescent complexes.[2] Recently, we have been studying Pt^0 and Cu^I complexes containing arylphosphines,[3] which show relatively strong luminescence in solution.

Many emissive gold compounds have been reported; however, most of them are dinuclear, multinuclear, or cluster compounds.[4] This is partly because luminescent properties of many gold compounds are strongly related to gold–gold interactions, which are called "Aurophilic interactions." Most gold(I) complexes adopt a two-coordinate linear geometry, unlike other d^{10} transition-metal complexes containing Ag^I and Cu^I. In these metal complexes, coordination numbers greater than two are commonly observed. Photophysical studies on the mononuclear gold(I) complexes of four-coordinate bis-diphosphine geometry are rare.[5]

In this study, we synthesized a gold(I) complex containing the diphosphine ligand, 2,2′-bis(diphenylphosphino)-1,1′-biphenyl (biphep). The structure of $[Au(biphep)_2]PF_6$ was studied by X-ray structure analysis. The photophysical properties of the complex have been compared with the dinuclear gold(I) complex $[Au_2(biphep)Cl_2]$ the luminescent properties of the dinuclear complex were already published by Vogler et al.[6]

The asymmetric unit of the crystal consists of a $[Au(biphep)_2]^+$ cation (Fig. 1) and a PF_6^- anion. The geometry of the four-coordinate gold(I) is a distorted tetrahedron. The Au–P distances (2.446(3)–2.459(2) Å) are comparable to those found in other four-coordinate gold(I) complexes containing diphosphine ligands, e.g., 2.39–2.42 Å for [Au(1,2-bis(diphenylphosphino)ethane)$_2$]PF_6[7] and 2.47–2.48 Å for [Au(9,9-dimethyl-4,5-bis(diphenylphosphino)xanthene)$_2$](SbF_6),[5c] but are longer than those of two-coordinated gold(I) complexes (2.23–2.28 Å for $[Au_2I_2$(1,2-bis(diethylphosphino)-1,1′-biphenyl)]).[8]

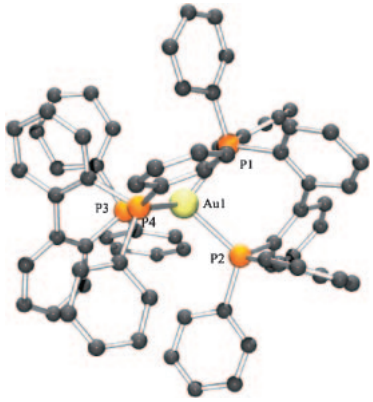

Fig. 1. Molecular structure of $[Au(biphep)_2]PF_6$ (the counter ion and hydrogen atoms have been omitted). Selected bond lengths (Å) and angles (°): Au–P1 = 2.451(3) Å, Au–P2 = 2.459(2) Å, Au–P3 = 2.449(3) Å, Au–P4 = 2.446(3) Å, P1–Au–P2 = 95.53(9)°, P3–Cu–P4 = 92.19(9)°.

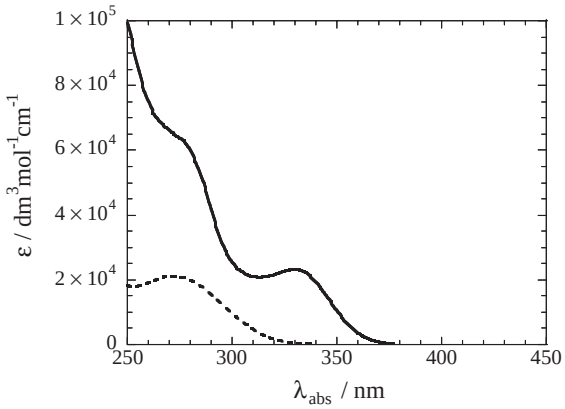

Fig. 2. Room temperature electronic absorption spectra of $[Au(biphep)_2]^+$ (1×10^{-5} M) (solid line) and free biphep ligand (0.67×10^{-4} M) (dotted line) in degassed CH_2Cl_2.

The UV spectrum of the $[Au(biphep)_2]^+$ complex in CH_2Cl_2 solution is presented in Fig. 2. There are two distinct absorption bands at 280 and 330 nm. Since a similar absorption band at 280 nm is also found for $[Au_2(biphep)Cl_2]$ and the free biphep ligand, the band is reasonably assigned to $^1\pi$–π^* transition of the ligand. An additional absorption band is seen for $[Au(biphep)_2]^+$ at 330 nm, which is tentatively assigned to the $^1\sigma$–π^* transition. Similar bands have been found in other four-coordinate bis-diphosphine gold(I) complexes and have been assigned to the σ–π^* transition by Yam et al.[5a] and Lagunas et al.[5c]

The emission spectrum of $[Au(biphep)_2]PF_6$ in the solid state is presented in Fig. 3. The emission maximum of the complex was 520 nm, and the band is blue-shifted by about 60 nm from that of $[Au_2(biphep)Cl_2]$. Vogler et al. have reported that the emissive excited state of the dinuclear complex is a metal-centered (MC) ds → dp state. The MC state should be a high energy state for mononuclear complexes. By analogy

Published on the web March 13, 2007; doi:10.1246/bcsj.80.533

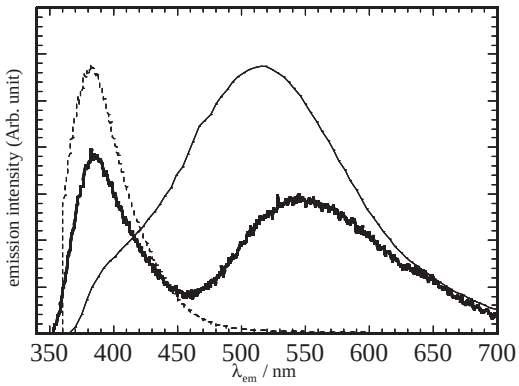

Fig. 3. Room temperature solid-state emission spectrum of $[Au(biphep)_2]PF_6$ (narrow solid line), solution-state emission spectra of $[Au(biphep)_2]^+$ (1×10^{-4} M) (solid line) and free biphep ligand (1×10^{-4} M) (narrow dotted line) measured in degassed CH_2Cl_2 ($\lambda_{ex} = 280$ nm).

to other bis(diphosphine)gold(I) complexes, the emission of $[Au(biphep)_2]^+$ might originate from $^3\sigma$–π^* excited state. The shoulder seen at ca. 390 nm may be due to $^1\pi$–π^* luminescence, vide infra.

We observed the emission spectrum of the gold(I) complex in the CH_2Cl_2 solution at room temperature, although no emission was reported for $[Au_2(biphep)Cl_2]$ in solution. In contrast to the solid-state emission spectrum, two distinct bands at 390 and 550 nm were found as shown in Fig. 3. Both decay curves measured at 400 and 540 nm were fitted to a single exponential. The lifetimes are $\leq$20 and 110 ns, respectively.

It is possible that the two emission bands are due to the presence of more than one emission species present in solution. However, the ^{31}P NMR spectrum of the complex in $CDCl_3$ shows a single signal at 21.70 ppm (Supporting Infomation). Similar emission spectra have been reported for some d^{10} metal–phosphine systems. The near UV and visible emission bands were assigned to π–π^* and σ–π^*, respectively.[5c,9]

For the emission of $[Au(biphep)_2]^+$, the band at 390 nm was thought to originate from the intra-ligand (IL) state of biphep, since the luminescence appears at an energy very close to that of the luminescence of the free biphep ligand. The longer wavelength emission of the complex at 550 nm was presumed to come from the $^3\sigma$–π^* transition state.

In conclusion, the four-coordinate bis-diphosphine gold(I) complex, $[Au(biphep)_2]PF_6$, showed room temperature luminescence in both the solid state and the CH_2Cl_2 solution. The luminescence originates from $^1\pi$–π^* and $^3\sigma$–π^* transition state.

Experimental

General. All reagents were obtained from commercial suppliers and used without further purification.

The spectroscopic properties of the complex in the CH_2Cl_2 solution were measured using a quartz cell connected to a glass tube and a Teflon stop cock. All samples were thoroughly deoxygenated by successive freeze–pump–thaw cycles. Absorption and luminescence spectra were measured with a Shimadzu UV-2100 spectrophotometer and a Shimadzu RF-5000 fluorometer, respectively. Luminescence decay-curves were measured on a laboratory-made apparatus. The sample was excited using a nitrogen laser (USHO AN-200), and the emission light was focused into a Jobin-Yvon H-20 monochromator equipped with a Hamamatsu R955 photomultiplier. The output of the photomultiplier was digitized by a Tektronix TDS 5034 digital oscilloscope and then downloaded to a PC.

Synthetic Procedure and Characterization of $[Au(biphep)_2]PF_6$. $[Au(tht)Cl]$[10] (0.286 g, 1 mmol) (tht = tetrahydrothiophene) and biphep (1.43 g, 2 mmol) were dissolved in hot acetone (50 mL). After stirring overnight at room temperature, the solution was taken to near dryness on a rotary evaporator and redissolved with water (ca. 20 mL). To this solution was added NH_4PF_6 (0.163 g, 1 mmol) in water (ca. 7 mL). After stirring for 2 h, a white precipitate was filtered off, washed with acetone–water (2:3) and dried in vacuo. Yield, 80%. Anal. Calcd for $C_{72}H_{56}AuF_6P_5$: C, 62.35; H, 4.07%. Found: C, 62.18; H, 4.08%.

Data Collection and Reduction for X-ray Crystallographic Analyses of $[Au(biphep)_2]PF_6$. The single crystals for X-ray structural analysis were obtained by slow diffusion of *n*-heptane into the CH_2Cl_2 solution of the complex. All measurements were made on a Rigaku Saturn CCD area detector with graphite monochromated Mo Kα radiation. The crystal-to-detector distance was 54.90 mm. The data were collected at a temperature of -150 ± 1 °C to a maximum 2θ value of 55.0°. 1800 oscillation images were collected. Of the 60358 reflections that were collected, 14140 were unique ($R_{int} = 0.048$); equivalent reflections were merged. Data were collected and processed using CrystalClear (Rigaku).[11] A numerical absorption correction was applied which resulted in transmission factors ranging from 0.62 to 0.93. The structure was solved by direct methods[12] and was expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically and the rest were refined using the riding model. All calculations were performed using the CrystalStructure[13] crystallographic software package except for refinement, which was performed using SHELXL-97.[14]

$[Au(biphep)_2]PF_6$: $C_{72}H_{56}AuF_6P_5$ (fw: 1387.06) $a = 13.368(4)$ Å, $b = 23.209(7)$ Å, $c = 20.614(6)$ Å, $\alpha = 90°$, $\beta = 99.584(1)°$, $\gamma = 90°$, $V = 6306.6(34)$ Å^3, $\mu = 2.527$ cm^{-1}, Space Group: $P2_1/n$ (#14), $Z = 4$, $D_{calcd} = 1.461$ g cm^{-3}, No. of unique reflections ($2\theta < 55°$) = 14140, $R_1 = 0.083$ ($I > 2\sigma(I)$), $wR_2 = 0.266$ (all data), GOF = 0.955.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-620172 for $[Au(biphep)_2]PF_6$. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

This work was financially supported by the Promotion and Mutual Aid Corporation for Private Schools of Japan through the High-tech Research Center project.

Supporting Information

The NMR spectrum of $[Au(biphep)_2]PF_6$. This material is available free of charge on the web at http://www.csj.jp/journals/bcsj/.

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