



# Mono- and dinuclear luminescent 1,1'-biisoquinoline gold(I) complexes

Manuel Bardají\*, Ana B. Miguel-Coello, Pablo Espinet\*

IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, E-47071 Valladolid, Spain

## ARTICLE INFO

### Article history:

Received 29 March 2012

Accepted 13 June 2012

Available online 23 June 2012

### Keywords:

Biisoquinoline

Gold

Gold–gold contact

Luminescence

Monodentate ligand

Bridging ligand

## ABSTRACT

Mono- and dinuclear, cationic or neutral gold(I) derivatives  $[(\text{biisoq})(\text{AuL})]^{n+}$  ( $\text{L} = \text{PPh}_3$ ,  $n = 1$ ;  $\text{L} = \text{C}_6\text{F}_5$ ,  $n = 0$ ), and  $[(\mu\text{-biisoq})(\text{AuL})_2]^{n+}$  ( $\text{biisoq} = 1,1'\text{-biisoquinoline}$ ;  $\text{L} = \text{PMe}_3$ ,  $\text{PPh}_3$ ,  $\text{PMePh}_2$ ,  $n = 2$ ;  $\text{L} = \text{C}_6\text{F}_5$ ,  $n = 0$ ) have been prepared. Auophilic interactions and steric requirements of the co-ligand L impose the torsion angle between the two isoquinoline units of the flexible, non-planar 1,1'-biisoquinoline ligand, affording different structures. The X-ray molecular structure of the mononuclear complex with  $\text{PPh}_3$  confirmed the monodentate mode for the biisoquinoline ligand. In the three X-ray structures solved for dinuclear compounds with bridging biisoquinoline, the torsion angles and the intramolecular gold–gold distances found are, respectively:  $65.2^\circ$  and  $3.0739(7) \text{ \AA}$  for  $\text{L} = \text{PMe}_3$ ;  $80.10^\circ$  and  $3.785 \text{ \AA}$  for  $\text{L} = \text{C}_6\text{F}_5$ ;  $95.6^\circ$  and  $4.505 \text{ \AA}$  for  $\text{L} = \text{PMePh}_2$ . All the phosphine derivatives are luminescent at room temperature in the solid state, with emission maxima in the range 390–422 nm, and emit from 370 to 438 nm at 77 K. They are also emissive in  $\text{CH}_2\text{Cl}_2$  at 298 K in the range 381–458 nm, whilst they are luminescent at 77 K in the range 382–550 nm. The fluoroaryl derivatives are not emissive.

© 2012 Elsevier B.V. All rights reserved.

## 1. Introduction

The study of closed shell gold(I) derivatives has revealed the frequent presence of short gold–gold distances, which have been attributed to correlation effects reinforced by relativistic effects and electrostatic contributions. The so-called auophilic interaction leads to gold–gold distances in the range 2.8–3.6 Å, with strength similar to some hydrogen bonds, in the order 20–50 kJ/mol [1]. Gold(I) usually forms two-coordinated complexes displaying linear geometry, which facilitates the formation of these gold–gold contacts, provided the steric requirements of the ligands do not hinder the interaction. Many gold(I) compounds, with or without gold–gold contacts, are luminescent in the visible region [2], and some of them have been proposed for applications as chemosensors for cations or anions, or as light-emitting diodes [3].

Ligands incorporating a 1,1'-binaphthyl unit, for instance chiral N-heterocyclic carbenes, have been receiving attention recently because of their application in catalytic asymmetric reactions [4]. These ligands can show optical activity based on the high barrier to rotation about the C–C  $\sigma$ -bond, which gives rise to atropisomers [5]. In particular, 1,1'-biisoquinoline is a diamine with a more extended  $\pi$ -acceptor system than 2,2'-bipyridine, while it has a comparable N  $\sigma$ -donor ability. 1,1'-Biisoquinoline is non-planar, as result of trans-annular steric hindrance between the hydrogen atoms in positions 8 and 8', one on each isoquinoline subunit (see labels in Scheme 1 below). Its lack of planarity might be

thought to disfavor its chelating coordination, but in fact this flexible ligand usually acts as chelate in metal complexes, as reported for square planar Rh(I) [6] and Pt(II) [7], or octahedral Os(II) [8], Ru(II) [8,9], and Ir(III) complexes [10]. Potentially 1,1'-biisoquinoline can also act as bridging bidentate and as monodentate ligand, although, among the many reported complexes, only two reports of 1,1'-biisoquinoline acting as a bridging ligand (a dinuclear palladium complex [11] and a series of silver(I) compounds recently described by us [12]), and only one complex where it is acting as monodentate ligand (the X-ray crystal structure of a platinum complex), are found [7a].

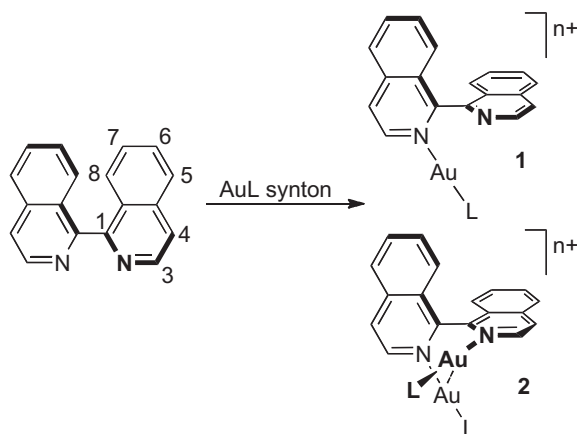
The predominant tendency of 1,1'-biisoquinoline to behave as a chelate ligand should be frustrated on metal centers with linear coordination, thus favoring the occurrence of the other bonding modes. In effect, in this paper we report mono- and dinuclear gold(I) compounds with the 1,1'-biisoquinoline ligand acting as monodentate or bridging bidentate, respectively. Most of the complexes are luminescent, both in solution and in the solid state.

## 2. Experimental

IR spectra were recorded on a FT 1720X Perkin-Elmer spectrophotometer ( $4000\text{--}400 \text{ cm}^{-1}$ ) using KBr pellets.  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on Bruker AC-300, ARX-300 or AV-400 instruments in  $\text{CDCl}_3$  solutions (if no other solvent is stated); chemical shifts are quoted relative to  $\text{SiMe}_4$  (external,  $^1\text{H}$ ),  $\text{CFCl}_3$  (external,  $^{19}\text{F}$ ) and 85%  $\text{H}_3\text{PO}_4$  (external,  $^{31}\text{P}$ ).  $^1\text{H}$  NMR labels are in Scheme 1. Elemental analyses were performed with a Perkin-Elmer 2400 microanalyzer. Emission and excitation spectra

\* Corresponding authors. Tel.: +34 983184624; fax: +34 983423013.

E-mail addresses: [bardaji@qi.uva.es](mailto:bardaji@qi.uva.es) (M. Bardají), [espinet@qi.uva.es](mailto:espinet@qi.uva.es) (P. Espinet).



Scheme 1.

at 298 and 77 K were measured in the solid state as finely pulverized KBr mixtures, and in deoxygenated  $\text{CH}_2\text{Cl}_2$  solutions in quartz tubes with a Perkin-Elmer LS-55 spectrofluorimeter. UV-Vis absorption spectra were recorded at 297 K on a Shimadzu UV-2550. Literature methods were used to prepare 1,1'-bisoquinoline [9f],  $[\text{AuCl}(\text{PRR}'_2)]$  [13], and  $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$  [14].

#### 2.1. Synthesis of $[(\mu\text{-bisoq})\{\text{Au}(\text{PRR}'_2)\}_2](\text{CF}_3\text{SO}_3)_2$ ; $R = R' = \text{Me}$ **2a**, $\text{Ph}$ **2b**; $R = \text{Me}$ , $R' = \text{Ph}$ **2c**

To an acetone solution (20 mL) of  $[\text{AuCl}(\text{PRR}'_2)]$  (0.17 mmol;  $R = R' = \text{Me}$  52 mg,  $\text{Ph}$  84 mg;  $R = \text{Me}$ ,  $R' = \text{Ph}$  74 mg) was added  $\text{Ag}(\text{CF}_3\text{SO}_3)$  (44 mg, 0.17 mmol), and the reaction stirred for 60 min protected from the light.  $\text{AgCl}$  was filtered off, and the corresponding bisoquinoline (22 mg, 0.085 mmol) was added to the solution. After stirring for 1 h, the suspension was concentrated to ca. 5 mL. Addition of diethyl ether afforded compounds **2a–2c** as white solids. Yield of **2a**: 61 mg, 65%. *Anal. Calc.* for C, 28.38; H, 2.75; N, 2.55. Found: C, 28.65; H, 2.67; N, 2.83%.  $^1\text{H NMR}$ :  $\delta$  1.45 (d,  $J_{\text{HP}} = 10.5$  Hz, 18H, Me), 7.48 (d,  $J_{\text{HH}} = 8.6$  Hz, 2H,  $\text{H}^8$ ), 7.65 (t,  $J_{\text{HH}} = 7.8$  Hz, 2H,  $\text{H}^7$ ), 8.11 (t,  $J_{\text{HH}} = 7.5$  Hz, 2H,  $\text{H}^6$ ), 8.13 (d,  $J_{\text{HH}} = 8.3$  Hz, 2H,  $\text{H}^5$ ), 8.20 (d,  $J_{\text{HH}} = 5.7$  Hz, 2H,  $\text{H}^4$ ), 8.95 (d,  $J_{\text{HH}} = 5.7$  Hz, 2H,  $\text{H}^3$ ).  $^{19}\text{F NMR}$ :  $\delta$   $-78.3$  (s).  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$   $-11.2$  (s). IR (KBr): 1274, 638 ( $\text{CF}_3\text{SO}_3$ )  $\text{cm}^{-1}$ . Yield of **2b**: 81 mg, 65%. *Anal. Calc.* for C, 45.66; H, 2.87; N, 1.90. Found: C, 45.32; H, 2.77; N, 1.80%.  $^1\text{H NMR}$ :  $\delta$  7.0–7.5 (m, 32H,  $\text{Ph} + \text{H}^8$ ), 7.75 (t,  $J_{\text{HH}} = 7.9$  Hz, 2H,  $\text{H}^7$ ), 8.11 (t,  $J_{\text{HH}} = 7.6$  Hz, 2H,  $\text{H}^6$ ), 8.08 (d,  $J_{\text{HH}} = 8.0$  Hz, 2H,  $\text{H}^5$ ), 8.27 (d,  $J_{\text{HH}} = 6.1$  Hz, 2H,  $\text{H}^4$ ), 9.15 (d,  $J_{\text{HH}} = 6.1$  Hz, 2H,  $\text{H}^3$ ).  $^{19}\text{F NMR}$ :  $\delta$   $-78.3$  (s).  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  28.5 (s). IR (KBr): 1260, 640 ( $\text{CF}_3\text{SO}_3$ )  $\text{cm}^{-1}$ . Yield of **2c**: 79 mg, 69%. *Anal. Calc.* for C, 40.96; H, 2.84; N, 2.08. Found: C, 40.61; H, 2.89; N, 2.0%.  $^1\text{H RMN}$ :  $\delta$  2.04 (d,  $J_{\text{HP}} = 11.3$  Hz, 6H, Me), 7.1–7.5 (m, 22H,  $\text{Ph} + \text{H}^8$ ), 7.70 (t,  $J_{\text{HH}} = 7.6$  Hz, 2H,  $\text{H}^7$ ), 7.95 (t,  $J_{\text{HH}} = 7.8$  Hz, 2H,  $\text{H}^6$ ), 8.08 (d,  $J_{\text{HH}} = 8.4$  Hz, 2H,  $\text{H}^5$ ), 8.26 (d,  $J_{\text{HH}} = 6.2$  Hz, 2H,  $\text{H}^4$ ), 9.2 (d,  $J_{\text{HH}} = 6.2$  Hz, 2H,  $\text{H}^3$ ).  $^{19}\text{F NMR}$ :  $\delta$   $-78.3$  (s).  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  13.9 (s). IR (KBr): 1260, 637 ( $\text{CF}_3\text{SO}_3$ )  $\text{cm}^{-1}$ .

#### 2.2. Synthesis of $[(\text{bisoq})\{\text{Au}(\text{PPh}_3)\}](\text{CF}_3\text{SO}_3)$ **1b**

To an acetone solution (20 mL) of  $[\text{AuCl}(\text{PR}_3)]$  (84 mg, 0.17 mmol) was added  $\text{Ag}(\text{CF}_3\text{SO}_3)$  (44 mg, 0.17 mmol), and the reaction stirred for 90 min protected from the light.  $\text{AgCl}$  was filtered off, and the corresponding bisoquinoline (44 mg, 0.17 mmol) was added to the solution. After stirring for 1 h, the suspension was concentrated to ca. 5 mL. Addition of hexane afforded compounds **1b** as a white solid. Yield of **1b**: 118 mg, 80%. *Anal. Calc.* for C,

51.40; H, 3.15; N, 3.24. Found: C, 51.08; H, 3.27; N, 2.92%.  $^1\text{H NMR}$ :  $\delta$  6.9–7.6 (m, 17H,  $\text{Ph} + \text{H}^8$ ), 7.63 (t,  $J_{\text{HH}} = 7.9$  Hz, 2H,  $\text{H}^7$ ), 7.87 (t,  $J_{\text{HH}} = 7.6$  Hz, 2H,  $\text{H}^6$ ), 8.05 (d,  $J_{\text{HH}} = 8.0$  Hz, 2H,  $\text{H}^5$ ), 8.10 (d,  $J_{\text{HH}} = 6.2$  Hz, 2H,  $\text{H}^4$ ), 8.75 (d,  $J_{\text{HH}} = 6.2$  Hz, 2H,  $\text{H}^3$ ).  $^{19}\text{F NMR}$ :  $\delta$   $-78.3$  (s).  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  29.7 (s). IR (KBr): 1266, 639 ( $\text{CF}_3\text{SO}_3$ )  $\text{cm}^{-1}$ .

#### 2.3. Synthesis of $[(\mu\text{-bisoq})\{\text{Au}(\text{C}_6\text{F}_5)_2\}]$ **2d** and $[(\text{bisoq})\{\text{Au}(\text{C}_6\text{F}_5)\}]$ **1d**

To a dichloromethane solution (20 mL) of  $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$  (81 mg, 0.18 mmol) was added the stoichiometric amount of the bisoquinoline (23 mg, 0.09 mmol). The resulting solution was stirred for 1 h and concentrated to ca. 5 mL. Addition of hexane afforded the mixture of compounds **2d–1d** as a light yellow solid in 1:2 M ratio.  $^1\text{H NMR}$  of **2d**:  $\delta$  7.41 (d,  $J_{\text{HH}} = 8.6$  Hz, 2H,  $\text{H}^8$ ), 7.69 (t,  $J_{\text{HH}} = 7.8$  Hz, 2H,  $\text{H}^7$ ), 8.00 (t,  $J_{\text{HH}} = 7.5$  Hz, 2H,  $\text{H}^6$ ), 8.18 (d,  $J_{\text{HH}} = 8.3$  Hz, 2H,  $\text{H}^5$ ), 8.29 (d,  $J_{\text{HH}} = 5.7$  Hz, 2H,  $\text{H}^4$ ), 8.82 (d,  $J_{\text{HH}} = 5.7$  Hz, 2H,  $\text{H}^3$ ).  $^{19}\text{F NMR}$  of **2d**:  $\delta$   $-116.59$  (m, 4F,  $\text{F}_o\text{-Au}$ ),  $-159.87$  (t,  $N = 18.1$  Hz, 2F,  $\text{F}_p\text{-Au}$ ),  $-163.53$  (m, 4F,  $\text{F}_m\text{-Au}$ ).  $^1\text{H NMR}$  of **1d**:  $\delta$  7.48 (d,  $J_{\text{HH}} = 8.6$  Hz, 2H,  $\text{H}^8$ ), 7.56 (t,  $J_{\text{HH}} = 7.8$  Hz, 2H,  $\text{H}^7$ ), 7.85 (t,  $J_{\text{HH}} = 7.5$  Hz, 2H,  $\text{H}^6$ ), 8.04 (d,  $J_{\text{HH}} = 5.7$  Hz, 2H,  $\text{H}^4$ ), 8.06 (d,  $J_{\text{HH}} = 8.3$  Hz, 2H,  $\text{H}^5$ ), 8.74 (d,  $J_{\text{HH}} = 5.7$  Hz, 2H,  $\text{H}^3$ ).  $^{19}\text{F NMR}$  of **1d**:  $\delta$   $-116.59$  (m, 4F,  $\text{F}_o\text{-Au}$ ),  $-160.50$  (t,  $N = 18.1$  Hz, 2F,  $\text{F}_p\text{-Au}$ ),  $-163.86$  (m, 4F,  $\text{F}_m\text{-Au}$ ).

#### 2.4. Crystal structure determination of compounds **1b**, **2a**, **2c** and **2d**

Crystals of **1b**, **2c** and **2d** were obtained by slow diffusion of hexane into a dichloromethane solution, whilst crystals of **2a** were obtained by slow diffusion of diethyl ether/ethanol into a chloroform solution, always at  $-18$  °C. The crystal was mounted on a glass fiber and transferred to a Bruker SMART CCD diffractometer. Crystal data and details of data collection and structure refinement are given in Table 1. Cell parameters were retrieved using SMART [15] software and refined with SAINT [16] on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were based on multiple scans (program SADABS) [17]. The structure was refined anisotropically on  $F^2$  [18]. All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. The hydrogen atoms were placed in their geometrically generated positions. In the structure of **2c** a water molecule between two positions was included (their H were not added); the  $\text{CF}_3$  of one anion is incipiently disordered. The structure of **2d** contains some disordered solvent in the channels, and we were unable to properly model it.

### 3. Results and discussion

#### 3.1. Synthesis and characterization

The reaction of the 1,1'-bisoquinoline with appropriate gold(I) precursors, prepared in situ, yielded compounds of the types **1** or **2**, according to Scheme 1.

Thus, using  $[\text{Au}(\text{CF}_3\text{SO}_3)(\text{PR}_2\text{R}')]_2$ , prepared in situ from  $[\text{AuCl}(\text{PR}_2\text{R}')]_2$  and  $\text{Ag}(\text{CF}_3\text{SO}_3)$ , and an Au:1,1'-bisoquinoline 2:1 ratio, the dicationic complexes **2a–c**, with  $\text{CF}_3\text{SO}_3$  as counter-anion (**2a**:  $R = R' = \text{Me}$ ; **2b**:  $R = R' = \text{Ph}$ ; **2c**:  $R = \text{Ph}$ ,  $R' = \text{Me}$ ), were obtained. Using an Au:1,1'-bisoquinoline 1:1 ratio, the monocationic complex **1b** was obtained. Compounds **1b** and **2a–c** are air-stable white solids at room temperature and were characterized by elemental analysis, and by IR and NMR spectroscopy.

The dicationic complexes **2a–c** show in their  $^1\text{H NMR}$  spectra a phosphine:bisoquinoline 2:1 ratio, and only six chemically non-equivalent bisoquinoline protons, as expected for two equivalent

Download English Version:

<https://daneshyari.com/en/article/1305986>

Download Persian Version:

<https://daneshyari.com/article/1305986>

[Daneshyari.com](https://daneshyari.com)