

Influence of the Substitution Pattern (ortho vs para) on the Structure and Luminescence of Silver(I) Complexes Ligated by Diphenylphosphinobenzoic Acids

Ana B. Miguel-Coello and Manuel Bardají*

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

Valladolid, Spain.

* Author to whom correspondence should be addressed: M. B. e-mail: bardaji@qi.uva.es

ABSTRACT

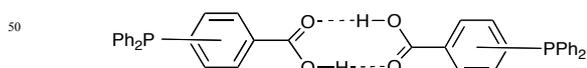
The reaction of AgCF_3SO_3 with diphenylphosphinobenzoic acids leads to a cyclic dinuclear or a polynuclear silver(I) compound, depending on the relative position of phosphine versus carboxylic functional group. The dimers $[\text{Ag}_2(\text{OSO}_2\text{CF}_3)_2(\mu\text{-O,P-PPh}_2\text{C}_6\text{H}_4\text{COOH-o})_2]$ **1** or $[\{\text{Ag}(\mu\text{-O,P-PPh}_2\text{C}_6\text{H}_4\text{COOH-o})(\text{OH}_2)_2\}_2](\text{CF}_3\text{SO}_3)_2 \cdot 2\text{CH}_2\text{Cl}_2$ **1a** are 12-membered diargentacycles with a silver-silver distance of 3.982 or 3.754 Å, while the polymer $[\text{Ag}_n(\text{OSO}_2\text{CF}_3)_n(\mu\text{-O,P-PPh}_2\text{C}_6\text{H}_4\text{COOH-p})_n]$ **2** is a 1D type. The ligand is always acting as non-chelating bridge, being the silver center coordinated to the phosphine phosphorous, and one oxygen (carbonyl) of the carboxylic acid of next fragment. One oxygen of the triflate anion or two water molecules complete the coordination sphere. Besides, *p*-(diphenylphosphino)benzoic acid compound is emissive in solution and in the solid state at 298 and 77 K, while compound with the *ortho* ligand is not. At 298 K, the emissions are centered at 471 nm in the solid state and at 416 nm in solution.

Keywords: 2-(diphenylphosphino)benzoic acid, 4-(diphenylphosphino)benzoic acid, silver complexes, bridging ligand, luminescence, X-ray crystal structure.

1. Introduction

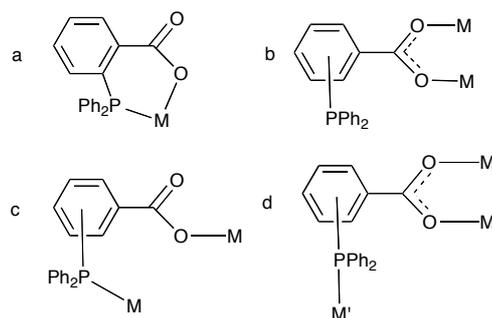
A key strategy in the design and synthesis of metal-organic frameworks (MOF's) and other hybrid organic-inorganic molecular materials is the utilization of simple multifunctional building blocks that induce the formation of complex molecular structures by self-assembly [1]. Silver (I) centers are particularly versatile as components of such building blocks because of their flexible coordination number and geometry [2], and the tendency to form $\text{Ag}\cdots\text{Ag}$ weak interactions [3]. Although there are many reports on other luminescent d^{10} -metal complexes, emissive Ag^I complexes have been less studied because of their potential photosensitivity and limited luminescence [4]. In this respect, the potentially polydentate *o*- and *p*-(diphenylphosphino)benzoic acids are interesting ligands combining soft (P) with hard (O) donor atoms. Moreover, the carboxylic group is suitable to produce hydrogen bonds. In

fact 2-diphenylphosphinobenzoic acid is a dimer with the typical H-bonds of carboxylic acids (Scheme 1) [5].



Scheme 1. H-bonds between two carboxylic groups.

The *ortho* or *para* relative position of the phosphine versus the carboxylic acid can be used to engineer different three-dimensional geometries. For instance, the homoleptic gold complex of 2-(diphenylphosphino)benzoate is a mixture of a dimer and a trimer (a trimer is isolated as crystal), while the corresponding 4-(diphenylphosphino)benzoate complex is a polymer; in both cases, the ligands are working as O, P-bridges [6]. Homoleptic silver complex of 2-(diphenylphosphino)benzoate is a hexanuclear compound with the ligand acting as tri- and tetradentate bridge [7]. Depending on the metal center, 2-(diphenylphosphino)benzoate ligand leads to dimers via carboxylate or O, P-bridges, or to mononuclear compounds acting as O, P-chelate (Scheme 2) [8]. 4-(diphenylphosphino)benzoate evolves again to a dimer with carboxylate bridges, which can be additionally bonded through the phosphorus atom; besides, polynuclear derivatives can be obtained by O, P-bridges (Scheme 2) [9].



Scheme 2. a) Chelate for 2-(diphenylphosphino)benzoate; b) carboxylate bridges; c) O, P-bridges; d) more complex coordination mode (M' can be the same metal fragment).

The related chloro gold(I) derivatives of 2- or 4-(diphenylphosphino)benzoic acid are dimers, by a

symmetrical double H–bond between the two carboxylic groups [6, 10]. Similarly, Cu(I) complexes become dimers by a typical double carboxylic H–bond [11]. However, chloro palladium(II) compounds with 4–(diphenylphosphinobenzoic) acid are mononuclear with the carboxylic group making H–bonds with solvent crystallization molecules [12].

Here we report the synthesis and structural characterization of silver(I) compounds with 2– and 4–(diphenylphosphino)benzoic acids, where the substitution pattern on the ligand leads to different nuclearities and luminescence properties on the complexes.

2. Experimental

For general procedures see Supplementary data.

2.1. Synthesis of [Ag(OSO₂CF₃)(PPh₂C₆H₄COOH)]; *ortho* (1), *para* (2).

To a diethyl ether solution (20 mL) of AgCF₃SO₃ (51 mg, 0.2 mmol) was added the corresponding phosphinobenzoic acid (61 mg, 0.2 mmol), and the reaction stirred for 2 h protected from the light. The insoluble compounds were filtered off, washed and dried. A second fraction was obtained by

evaporation *ca.* 2 ml and addition of hexane. Compounds 1–2 were obtained as white solids. Yield of 1: 78 mg, 70 %. Anal. Calc. for C₄₀H₃₀Ag₂F₆O₁₀P₂S₂: C, 42.65; H, 2.68; N, 0. Found: C, 42.37; H, 2.75; N, 0%. ¹H NMR (d₆-acetone): δ 8.37 (d, J_{HH} = 7.6 Hz, 1H, H⁶), 7.76 (td, J_{HH} = 7.6 Hz, J_{HP} = 1.4 Hz, 1H, H⁵), 7.70 (td, J_{HH} = 7.6 Hz, J_{HP} = 1.4 Hz, 1H, H⁴), 7.59–7.45 (m, 10H, Ph), 7.04 (t, J_{HP} = J_{HH} = 7.8 Hz, 1H, H³). ¹H NMR (–50°C, d₆-acetone): δ 12.49 (brs, 1H, COOH), 8.40 (ddd, J_{HH} = 7.5 and 1.5 Hz, J_{HP} = 4.4 Hz, 1H, H⁶), 7.82 (t, J_{HH} = 7.5 Hz, 1H, H⁵), 7.77 (t, J_{HH} = 7.5 Hz, 1H, H⁴), 7.60–7.43 (m, 10H, Ph), 6.94 (ddd, J_{HP} = 9.2 and 1.2 Hz, J_{HH} = 7.5 Hz, 1H, H³). ¹⁹F NMR (d₆-acetone): –77.58 (s). ³¹P NMR (d₆-acetone): 15.6 (brs). ³¹P NMR (–50°C, d₆-acetone): 15.5 (d, ¹J_{107Ag–31P} = 736 and ¹J_{109Ag–31P} = 849 Hz). IR (KBr): 3060 ν(O–H), 1673 ν(C=O), 1257, 1223, 1209, 635 (CF₃SO₃) cm^{–1}. Yield of 2: 91 mg, 81 %. Anal. Calc. for C₂₀H₁₅AgF₃O₅PS: C, 42.65; H, 2.68; N, 0. Found: C, 42.60; H, 2.84; N, 0%. ¹H NMR (d₆-acetone): δ 11.5 (brs, 1H, COOH), 8.13 (d, J_{HH} = 8.0 Hz, 2H, H²), 7.68–7.55 (m, 12H, H³ + Ph). ¹H NMR (–50°C, d₆-acetone): δ 12.54 (brs, 1H, COOH), 8.15 (dd, J_{HP} = 1.6 Hz, J_{HH} = 8.4 Hz, 2H, H²), 7.68–7.53 (m, 12H, H³ + Ph). ¹⁹F NMR (d₆-acetone): –77.6 (s). ³¹P NMR (d₆-acetone): 14.5 (d, ¹J_{Ag–P} = 721 Hz). ³¹P NMR (–50°C, d₆-acetone): 13.8 (d, ¹J_{107Ag–31P} = 690 and ¹J_{109Ag–31P} = 795 Hz). IR (KBr): 3054 ν(O–H), 1687 ν(C=O), 1223, 635 (CF₃SO₃) cm^{–1}.

Table 1. Details of Crystal Data and Structure Refinement for Complexes 1, 1a and 2

Compound	1	1a	2
Empirical formula	C ₄₀ H ₃₀ Ag ₂ F ₆ O ₁₀ P ₂ S ₂	C ₄₂ H ₄₂ Ag ₂ Cl ₄ F ₆ O ₁₄ P ₂ S ₂	C ₂₀ H ₁₅ AgF ₃ O ₅ PS
Formula weight	1126.44	1368.36	563.22
T (K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P 2 ₁ /n
Unit cell dim.: a (Å)	7.8319(5)	10.5574(17)	12.8706(11)
b (Å)	11.8958(10)	11.4142(18)	10.4407(5)
c (Å)	12.1326(11)	13.1871(11)	16.3978(10)
α (°)	104.153(7)	100.856(10)	90
β (°)	94.333(6)	104.094(10)	103.466(7)
γ (°)	104.957(7)	113.623(16)	90
V (Å ³)	1047.25(14)	1337.0(3)	2142.9(3)
Z	1	1	4
D _{calc} (Mg/m ³)	1.786	1.699	1.746
Abs. coeff. (mm ^{–1})	1.195	1.151	1.168
F(000)	560	684	1120
Crystal habit	Prism	Tablet	Plate
Crystal size (mm)	0.22 x 0.09 x 0.09	0.33 x 0.08 x 0.06	0.26 x 0.17 x 0.07
Θ range for data colln	2.72 to 28.62	2.06 to 27.83	2.29 to 28.76
Index ranges	–10 ≤ h ≤ 6, –15 ≤ k ≤ 15, –14 ≤ l ≤ 16	–12 ≤ h ≤ 13, –11 ≤ k ≤ 13, –17 ≤ l ≤ 15	–11 ≤ h ≤ 16, –12 ≤ k ≤ 13, –21 ≤ l ≤ 16
Reflections collected	7061	7344	8575
Independent reflections	4310 [R(int) = 0.0196]	5341 [R(int) = 0.0256]	4474 [R(int) = 0.0226]
Maximum and minimum transmissions	1.000 and 0.707	0.943 and 0.803	0.933 and 0.797
Data/restraints/parameters	4310 / 0 / 290	5341 / 1 / 325	4474 / 0 / 280
Goodness-of-fit on F ²	1.047	1.022	1.024
Final R indices [I > 2σ(I)]	R1 = 0.0384, wR2 = 0.0704	R1 = 0.0669, wR2 = 0.1428	R1 = 0.0480, wR2 = 0.1083
R indices (all data)	R1 = 0.0566, wR2 = 0.0786	R1 = 0.1243, wR2 = 0.1801	R1 = 0.0699, wR2 = 0.1204
Largest difference in peak and hole (e Å ^{–3})	0.682 and –0.470	0.823 and –0.716	0.603 and –0.598

2.2. Crystal structure determination of compounds 1, 1a and 2.

The crystal was mounted on a glass fiber and transferred to

the SuperNova Oxford Diffraction diffractometer. Crystal data and details of data collection and structure refinement are given in Table 1. Cell parameters, data reduction and absorption corrections were carried out with the Crysalis

system software [13]. The structure was refined anisotropically on F^2 [14]. All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. The hydrogen atoms were placed in their geometrically generated positions. The presence of residual electronic density in monocrystal **1** that cannot be taken into account by displacement parameters shows some delocalisation of the silver ions around the main site. To describe it, a second position (Ag1B) is introduced. The refinement of the occupancy of both sites leads to an overall composition of 0.935 mainly located on the first one. H of water in **1a** were localized in Fourier maps, then the water molecules were refined as rigid units (**1a** is: $[\{Ag(\mu-O,P-PPh_2C_6H_4COOH-o)(OH_2)_2\}_2](CF_3SO_3)_2 \cdot 2CH_2Cl_2$). The triflate anion of monocrystal **2** is ‘incipiently’ disordered.

Table 1. Details of Crystal Data and Structure Refinement for Complexes **1**, **1a** and **2**.

Compound	1	1a	2
Empirical formula	C ₄₀ H ₃₀ Ag ₂ F ₆ O ₁₀ P ₂ S ₂	C ₄₂ H ₄₂ Ag ₂ Cl ₄ F ₆ O ₁₄ P ₂ S ₂	C ₂₀ H ₁₅ AgF ₃ O ₅ PS
Formula weight	1126.44	1368.36	563.22
T (K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P 2 ₁ /n
Unit cell dim.: <i>a</i> (Å)	7.8319(5)	10.5574(17)	12.8706(11)
<i>b</i> (Å)	11.8958(10)	11.4142(18)	10.4407(5)
<i>c</i> (Å)	12.1326(11)	13.1871(11)	16.3978(10)
α (°)	104.153(7)	100.856(10)	90
β (°)	94.333(6)	104.094(10)	103.466(7)
χ (°)	104.957(7)	113.623(16)	90
V (Å ³)	1047.25(14)	1337.0(3)	2142.9(3)
Z	1	1	4
D _{calc} (Mg/m ³)	1.786	1.699	1.746
Abs. coeff. (mm ⁻¹)	1.195	1.151	1.168
F(000)	560	684	1120
Crystal habit	Prism	Tablet	Plate
Crystal size (mm)	0.22 x 0.09 x 0.09	0.33 x 0.08 x 0.06	0.26 x 0.17 x 0.07
Θ range for data colln	2.72 to 28.62	2.06 to 27.83	2.29 to 28.76
Index ranges	-10 $\leq h \leq 6$, -15 $\leq k \leq 15$, -14 $\leq l \leq 16$	-12 $\leq h \leq 13$, -11 $\leq k \leq 13$, -17 $\leq l \leq 15$	-11 $\leq h \leq 16$, -12 $\leq k \leq 13$, -21 $\leq l \leq 16$
Reflections collected	7061	7344	8575
Independent reflections	4310 [R(int) = 0.0196]	5341 [R(int) = 0.0256]	4474 [R(int) = 0.0226]
Maximum and minimum transmissions	1.000 and 0.707	0.943 and 0.803	0.933 and 0.797
Data/restraints/parameters	4310 / 0 / 290	5341 / 1 / 325	4474 / 0 / 280
Goodness-of-fit on F^2	1.047	1.022	1.024
Final <i>R</i> indices [$I > 2\sigma(I)$]	R1 = 0.0384, wR2 = 0.0704	R1 = 0.0669, wR2 = 0.1428	R1 = 0.0480, wR2 = 0.1083
<i>R</i> indices (all data)	R1 = 0.0566, wR2 = 0.0786	R1 = 0.1243, wR2 = 0.1801	R1 = 0.0699, wR2 = 0.1204
Largest difference in peak and hole (e Å ⁻³)	0.682 and -0.470	0.823 and -0.716	0.603 and -0.598

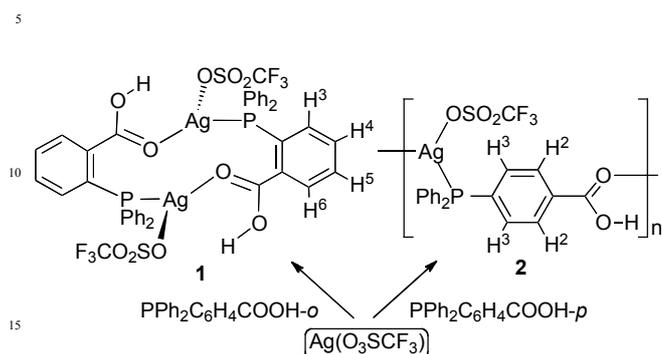
30

text.

3. Results and discussion

3.1. Synthesis and characterization

The reaction of silver(I) triflate with 2- and 4-(diphenylphosphino)benzoic acid in a 1:1 molar ratio (Scheme 3) yields [Ag(OSO₂CF₃)(PPh₂C₆H₄COOH)].



Scheme 3. Preparation of compounds.

Compounds **1** – **2** are air-stable white solids at room temperature, and were characterized by elemental analysis, IR and NMR spectroscopy. The complexes display one $\nu(\text{C}=\text{O})$ band from the carboxylic group at about 1680 cm⁻¹, and a broad $\nu(\text{O}-\text{H})$ band at about 3060 cm⁻¹. In their ¹H NMR spectra, the aromatic benzoic protons are slightly shifted compared to the free phosphine ligand. The largest shifts are about +0.27 ppm for H⁵ in the *ortho* ligand, and +0.28 ppm for H³ in the *para* ligand. The assignment was confirmed by COSY and ¹H {³¹P} NMR spectra. The ¹⁹F NMR spectra show a singlet at about -78 ppm because of the triflate anion. A broad resonance for the coordinated phosphine, because of unresolved coupling to the two silver isotopes, was observed in the ³¹P{¹H} NMR spectra of compound **1**, while for compound **2** a doublet is seen. The resonance is low-field shifted about 19 ppm for compounds compared to the free phosphine ligand. At -50 °C, the two Ag-P couplings are resolved and two doublets are observed centered at 15.5 ppm (¹J_{107Ag-31P} = 736 Hz, ¹J_{109Ag-31P} = 849 Hz) for complex **1**, and 13.8 (¹J_{107Ag-31P} = 690 Hz, ¹J_{109Ag-31P} = 795 Hz) for **2**.

3.2. Solid-state structures

The solid-state structures of compounds **1** and **2** were solved by single-crystal X-ray diffraction studies and confirmed the bridging coordination of diphenylphosphinobenzoic acid. The crystals studied were obtained by slow diffusion of petroleum ether (60–95°) into a solution of **1** in acetone/toluene or **2** in acetone at -18°C. By slow evaporation of a diethyl ether solution of **1**, the same single crystals were obtained, which was verified by determining the unit cell. Slow diffusion of hexane into a solution of **1** in dichloromethane at -18°C led to a different complex, denoted as **1a** and being its formula: [Ag(2-PPh₂C₆H₄COOH)(OH₂)₂]₂(CF₃SO₃)₂·2CH₂Cl₂. Compounds **1** and **1a** crystallized as a P-1 triclinic single crystal, while compound **2** crystallized as a P2₁/n monoclinic single crystal. The structures are shown in Figures 1–3, with selected bond lengths and angles in Table 2. The asymmetric unit of **1** and **2** contained the fragment Ag(OSO₂CF₃)(PPh₂C₆H₄COOH), with the silver center coordinated to the phosphine through the P atom and to the

triflate anion via an oxygen. On the other hand, the asymmetric unit of **1a** displayed the fragment [Ag(OH₂)₂(PPh₂C₆H₄COOH)](CF₃SO₃), again with the silver center coordinated to the phosphine through the P atom, but now is coordinated to two water molecules (loosely to one) via their oxygen atom and with free triflate anion. The silver center is coordinated to another oxygen atom in the three structures: the carbonyl of the carboxylic acid of another equal fragment. Therefore, the ligand is always acting as a bidentate non-chelating bridge. In that way the *ortho* benzoic acid leads to a cyclic dimer, which consists of a 12-membered dimetallacycle with tri- or tetracoordinated silver centers. On the other hand, the *para* benzoic acid leads to a 1D-polymer because of the relative position of the carboxylic and the phosphine functional groups. The close compound [Ag₆(*o*-PPh₂C₆H₄COO)₆] shows two silver triangles (Ag-Ag distances of 3.244, 3.756 and 3.805 Å) related by a symmetry center, with the anionic ligand acting as tri- or tetradentate non-chelating bridge [7].

Table 2. Selected Bond Lengths [Å] and Angles [deg] for Complexes **1**, **1a** and **2**.

	1	1a	2
Ag-P	2.4127(9)	2.3623(16)	2.3617(11)
Ag-O (carbox.)	2.482(2)	2.362(5)	2.272(3)
Ag-O (triflate)	2.318(3)	–	2.398(5)
Ag-O (water)	–	2.2474(18)	–
O=C	1.211(4)	1.207(8)	1.200(5)
O-C	1.308(4)	1.315(8)	1.308(5)
P-Ag-O (triflate)	129.09(8)	–	129.77(12)
P-Ag-O (water)	–	136.18(8)	–
P-Ag-O (carbox.)	112.49(6)	138.09(13)	146.08(11)
O-Ag-O	97.07(9)	80.02(13)	78.34(17)
		84.46(6)	
		85.74(13)	
C-O-C	123.6(3)	122.8(6)	123.1(4)
C-P-Ag	108.65(10)	107.3(2)	112.05(12)
	114.49(10)	116.7(2)	114.52(14)
	118.66(10)	119.92(19)	116.51(14)

The silver atom of compound **1** displays a distorted trigonal geometry, with a large P-Ag-O (triflate) angle of 129.09(8)°, and smaller P-Ag-O (carboxylic) and O-Ag-O angles of 112.49(6) and 97.07(9)°, respectively. However, the silver atom of compound **1a** displays a highly distorted tetrahedral geometry, with a large P-Ag-O (carboxylic) angle of 138.09(13)°, smaller P-Ag-O (water) angles of 136.18 (8) and 100.46 (6)°, and the smallest angles are O-Ag-O: 80.02(13), 84.46(6) and 85.74(13)°. On the other hand, the silver atom of compound **2** shows a highly distorted trigonal geometry, being the largest angle of 146.08(11)° corresponding to P-Ag-O (carboxylic); there is an intermediate angle P-Ag-O (triflate) of 129.77(12)°, and a small angle of 78.34(17)° for O-Ag-O. The Ag-O (triflate) distance found for **1** (2.318(3) Å) is slightly shorter than found for **2** (2.398(5) Å). However, the Ag-O (carboxylic) distance of **1** (2.482(2) Å) is slightly longer than found for **1a** (2.362(5) Å), and both are longer than found for **2** (2.272(3) Å). For **1a** there is a short and a

Figure 3. Polymeric structure of compound **2**. Additional black lines to show the polymer growth. Ellipsoids are at 25% probability (most H atoms omitted for clarity): **above**, two consecutive units of the 1D chain (Ag–O bonds); **below**, fragment showing inter-chains H–bonds, giving rise to double chains.

Table 3. Hydrogen Bonds for Dimers **1** and **1a** and polymer **2** [Å and deg] involving the carboxylic group.

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
Compound 1				
O(2)–H(2)···O(4A)	0.820	1.839	2.646	168.39
O(2A)–H(2A)···O(4)	0.820	1.839	2.646	168.39
Compound 1a				
O(2)–H(2)···O(7A)	0.820	1.819	2.610	161.69
O(2A)–H(2A)···O(7)	0.820	1.819	2.610	161.69
Compound 2				
O(1)–H(1)···O(4A)	0.820	1.828	2.626	164.09
O(1A)–H(1A)···O(4)	0.820	1.828	2.626	164.09

Symmetry transformations used to generate equivalent atoms: for compound **1** are 1–x, 2–y, 1–z; for compound **1a** are –x, –y, 1–z; for compound **2** are 1–x, 2–y, 1–z.

The powder X–ray diffraction (XRD) patterns of compounds **1** and **2** are in good agreement with that simulated from the corresponding single–crystal diffraction data (see Supplementary Information) confirming that the latter accurately represents the structure of the bulk solid (and not **1a**).

3.3. Luminescence studies

The emission and excitation spectra of the free ligands and the silver complexes were recorded in the solid–state and in CH₂Cl₂ solution, at 298 K and 77 K. The spectra of compound **2** at 298 K are shown in Figure 4. The 4–(diphenylphosphino)benzoic compound **2** and the corresponding free ligand emit, while the 2–(diphenylphosphino)benzoic acid and its derivative **1** are non–emissive. The emission maximum in the solid state is at 471 nm at 298 K, similar to the free ligand (474 nm), but at 457 nm at 77 K, blue–shifted compared to the free ligand (479 nm) and to 298 K emission. This emission could be assigned as ligand centered, although slightly modified by the metal fragment. Compound **2** shows an emission in CH₂Cl₂ solution at 298 K centered at 416 nm, while compound **1** and the two free ligands are non–emissive. At 77 K the emission maximum show little change, and is observed at 420 nm, blue–shifted compared to the corresponding free ligand emission (486 nm). Emission peaks of compound **2** are strongly blue–shifted compared to these observed in the solid state. Again, the emission could be assigned as ligand centered modified by the silver fragment.

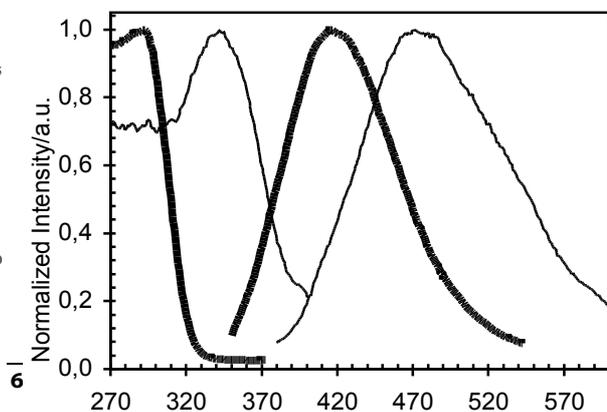


Figure 4. Solid state (regular line) and dichloromethane solution (bold line) excitation and emission spectra of compound **2** at 298K.

4. Conclusions

2– or 4–(diphenylphosphino)benzoic acids act as non–chelating bridge to give di– or polymeric silver(I) compounds, respectively, demonstrating that different geometrical orientation of the substituent induces entirely different connectivity patterns. The triflate anion or water molecules complete the coordination sphere. On the one hand, the carboxylic functional group is bridging monomers, on the other hand is making H–bonds: intramolecularly for the dimer, and associating 1D chains in pairs for the polymer. Besides, the *p*–(diphenylphosphino) benzoic ligand and its corresponding silver complex are emissive, while the *ortho* ligand and complex are non–emissive.

Acknowledgements

We thank the Spanish Comisión Interministerial de Ciencia y Tecnología (Project CTQ2011–25137) and the Junta de Castilla y León (Project VA302U13) for financial support.

Appendix A. Supplementary material

CCDC 1004945–1004947 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi: xxx.

References

- [1] (a) S. Leininger, B. Olenyuk, P. J. Stang, *Chem. Rev.* 100 (2000) 853; (b) G. Ferey, *Chem. Soc. Rev.* 37 (2008) 191. (c) G. A. Santillan, C. J. Carrano, *Cryst. Growth Des.* 9 (2009) 1590; (d) J. Ni, K.–J. Wei, Y. Liu, X.–C. Huang, D. Li, *Cryst. Growth Des.* 10 (2010) 3964; (e) A. M. Kirillov, S. W. Wieczorek, M. F. C. Guedes da Silva, J. Krol, Z. Staroniewicz, P. Smolenski, A. J. L. Pombeiro, *Cryst. Growth Des.* 11 (2011) 2711; (f) X.–L. Wang, Q. Gao, A.–X. Tian, G.–C. Liu, *Cryst. Growth Des.* 12 (2012) 2346; (g) L. Cunha–Silva, M. J. Carr, J. D. Kennedy, M. J. Hardie, *Cryst. Growth Des.* 13 (2013) 3162.
- [2] (a) A. Laguna, M. C. Gimeno, *Silver and Gold In Comprehensive Coordination Chemistry II: From Biology to Nanotechnology* McCleverty, J. A., Meyer, T. J., Eds.; Elsevier, Oxford, UK, 2003; Vol. 6, Transition Metal Groups 9–12, Fenton, D. E., ed. Chapter 6.7, p. 911; (b) J.–R. Li, R.–H. Zhang, X.–H. Bu, *Cryst. Growth Des.* 3 (2003) 829; (c) C. S. Liu, P. Q. Chen, E. C. Yang, J. L. Tian, X. H. Bu, Z. M. Li, H. W. Sun, Z. Lin, *Inorg. Chem.* 45 (2006) 5812; (d) P. Yang, F. Cui, X.–J. Yang, B. Wu, *Cryst. Growth Des.* 13 (2013) 186; (e) X. Ma, L.–H. Huo, Z.–P. Deng, T.–P. Liu, H. Zhao, S. Gao, *Inorg. Chem. Commun.* 43 (2014) 94.
- [3] (a) K. Singh, J.R. Long, P. Stavropoulos, *J. Am. Chem. Soc.* 119 (1997) 2942; (b) Q. M. Wang, T. C. W. Mak, *J. Am. Chem. Soc.* 123 (2001) 7594; (c) B. Liu, W. Chen, S. Jin, *Organometallics* 26 (2007) 3660; (d) L. Ray, M. M. Shaikh, P. Ghosh, *Inorg. Chem.* 47 (2008) 230; (e) X. D. Zheng, L. Jiang, X. L. Feng, T. B. Lu, *Inorg. Chem.* 47 (2008) 10858; (f) R. Santra, K. Biradha, *Cryst. Growth Des.* 10 (2010) 3315; (g) B. Li, S. Q. Zang, R. Liang, Y. J. Wu, T. C. W. Mak, *Organometallics* 30 (2011) 1710; (h) A. Serpe, F. Artizzu, L. Marchio, M. L. Mercuri, L. Pilia, P. Deplano, *Cryst. Growth Des.* 11

-
- (2011) 1278; (i) P.-S. Cheng, S. Marivel, S.-Q. Zang, G.-G. Gao, T. C. W. Mak, *Cryst. Growth Des.* 12 (2012) 4519.
- [4] (a) M. A. Omary, H. H. Patterson, *Inorg. Chem.* 37 (1998) 1060; (b) M. L. Tong, B. H. Ye, X. M. Chen, L. N. Ji, *Angew. Chem. Int. Ed.* 38 (1999) 2237; (c) X. H. Bu, H. Liu, M. Du, K. M. Wong, V. W. Yam, M. Shionoya, *Inorg. Chem.* 40 (2001) 4143; (d) T.-L. Hu, J.-R. Li, Y.-B. Xie, X.-H. Bu, *Cryst. Growth Des.* 6 (2006) 648; (e) M.-S. Wang, S.-P. Guo, Y. Li, L.-Z. Cai, J.-P. Zou, G. Xu, W.-W. Zhou, F.-K. Zheng, G.-C. Guo, *J. Am. Chem. Soc.* 131 (2009) 13572; (f) K. Matsumoto, T. Shindo, N. Mukasa, T. Tsukuda, T. Tsubomura, *Inorg. Chem.* 49 (2010) 805; (g) M. Bardaji, M. Barrio, P. Espinet, *Dalton Trans.* 40 (2011) 2570; (h) D. Pucci, A. Crispini, M. Ghedini, E.I. Szerb, M. La Deda, *Dalton Trans.* 40 (2011) 4614; (i) M. G. Babashkina, D. A. Safin, M. Bolte, Y. Garcia, *Dalton Trans.* 40 (2011) 8523; (j) A. Hameau, F. Guyon, A. Khatyr, M. Knorr, C. Strohmman, *Inorg. Chim. Acta* 388 (2012) 60; (k) M. Bardaji, A. B. Miguel-Coello, P. Espinet, *Inorg. Chim. Acta* 386 (2012) 93; (l) C.-F. Yan, Y.-X. Lin, F.-L. Jiang, M.-C. Hong, *Inorg. Chem. Commun.* 43 (2014) 19.
- [5] A. Chandrasekaran, R. O. Day, R. R. Holmes, *Inorg. Chem.* 40 (2001) 6229.
- [6] F. Mohr, M. C. Jennings, R. J. Puddephatt, *Angew. Chem. Int. Ed.* 43 (2004) 969.
- [7] W.-K. Wong, L. Zhang, W.-T. Wong, *Chem. Commun.* (1998) 673.
- [8] (a) Z. J. A. Komon, X. Bu, G. C. Bazan, *J. Am. Chem. Soc.* 122 (2000) 12379; (b) P. Barbaro, C. A. Ghilardi, S. Midollini, A. Orlandini, J. A. Ramirez, G. Scapacci, *J. Organomet. Chem.* 555 (1998) 255; (c) S.-M. Kuang, P. E. Fanwick, R. A. Walton, *Inorg. Chem.* (41) 2002 405; (d) S.-M. Kuang, P. E. Fanwick, R. A. Walton, *Inorg. Chem. Commun.* 5 (2002) 134; (e) W. Uhl, H. R. Bock, J. Kosters, M. Voss, *Z. Anorg. Allg. Chem.* 636 (2010) 1851; (f) G. Sanchez, J. Garcia, D. Meseguer, J. L. Serrano, L. Garcia, J. Perez, G. Lopez, *Dalton Trans.* (2003) 4709; (g) T. Schultz, A. Pfaltz, *Synthesis* (2005) 1005; (h) P. P. Phadnis, S. Dey, V. K. Jain, M. Nethaji, R. J. Butcher, *Polyhedron* 25 (2006) 87; (i) H. Schumann, H. Hemling, V. Ravindar, Y. Badrieh, J. Blum, *J. Organomet. Chem.* 469 (1994) 213. (j) J. S. M. Samec, R. H. Grubbs, *Chem. Eur. J.* 14 (2008) 2686; (k) M. Kawatsura, F. Ata, S. Wada, S. Hayase, H. Uno, T. Itoh, *Chem. Commun.* (2007) 298; (l) J. D. G. Correia, A. Domingos, I. Santos, C. Bolzati, F. Refosco, F. Tisato, *Inorg. Chim. Acta* 315 (2001) 213.
- [9] (a) S.-M. Kuang, P. E. Fanwick, R. A. Walton, *Inorg. Chem.* 41 (2002) 1036; (b) S.-M. Kuang, P. E. Fanwick, R. A. Walton, *Inorg. Chim. Acta* 338 (2002) 219; (c) W. Uhl, H. R. Bock, A. Hepp, F. Rogel, M. Voss, *Z. Anorg. Allg. Chem.* 636 (2010) 1255; (d) J.-M. Rueff, O. Perez, A. Leclaire, H. Couthon-Gourves, P.-A. Jaffres, *Eur. J. Inorg. Chem.* (2009) 4870.
- [10] B. P. Howe, R. V. Parish, R. G. Pritchard, *Quim. Nova* 21 (1998) 564.
- [11] M. Pellei, G. G. Lobbia, C. Santini, R. Spagna, M. Camalli, D. Fedeli, G. Falcioni, *Dalton Trans.* (2004) 2822.
- [12] S. J. Carlson, T. Lu, R. L. Luck, *Inorg. Chem. Commun.* 6 (2003) 455.
- [13] CrysAlisPro Software system, Version 1.171.32; Oxford Diffraction; Oxford Ltd., Xcalibur CCD system, 2007.
- [14] SHELXTL program system version 5.1; Bruker Analytical X-ray Instruments Inc.: Madison, WI, USA, 1998.