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Predominance of bridging coordination in luminescent 1,1'-biisoquinoline silver(I) derivatives

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ABSTRACT

A series of di- and polynuclear silver(1) complexes of stoichiometry $[Ag(biisoq)_2]_n X_n$ and [AgX(biisoq)](biisoq = 1,1'-biisoquinoline, X = CF₃SO₃, BF₄), or $[(\mu$ -biisoq)_n(AgXL)₂] (n = 1, 2; L = PPh₃, PMePh₂; $X = CF_3SO_3$, ClO_4) have been prepared. During crystallization experiments to obtain single crystals the compounds can coordinate solvent or water giving the corresponding derivatives. Seven X-ray diffraction structures have been solved. Different roles of the biisoquinoline ligand are found, but all the structures have in common that it always acts as bridging ligand. Compound $[(\mu-biisoq){Ag(OSO_2CF_3)(PPh_3)}{Ag}]$ $(OH_2)(PPh_3)$](CF₃SO₃) (**3a**) shows a single biisoquinoline bridge and tricoordinated silver centres, whilst $derivatives \ [(\mu-biisoq)_2 \{Ag(acetone)(PPh_3)\}_2](ClO_4)_2 \ (\textbf{8a}), \ [(\mu-biisoq)_2 \{Ag(OClO_3)(PMePh_2)\}_2] \ (\textbf{9}), \ and \ [(\mu-biisoq)_2 \{Ag(Acetone)(PPh_3)\}_2](Ph_2)_2 \ (\textbf{8a}), \ [(\mu-biisoq)_2 \{Ag(Acetone)(Ph_2)\}_2](Ph_2)_2 \ (\textbf{8a}), \ [(\mu-biisoq)_2 (Ph_2)](Ph_2)_2 \ (\textbf{8a}), \ (\mu-biisoq)_2 \$ [(µ-biisoq)₂{Ag(OSO₂CF₃)(PMePh₂)}₂] (**10**) display double biisoquinoline bridging ligands and tetracoordinated silver centres, with intramolecular silver-silver distances in the range 3.684-4.434 Å. Compounds $[(\mu-biisoq)_2 \{Ag(OSO_2CF_3)(acetone)\}_2] \cdot 2acetone (6a), [(\mu-biisoq)_2 \{Ag(OSO_2CF_3)(acetone)\}_2] (6b), and [(\mu-biisoq)_2 \{Ag(OSO_2CF_3)(acetone)] (6b), and [(\mu-biisoq)] (6b), and [(\mu-biisoq)_2$ biisoq)Ag(OH₂)₂(μ -biisoq)Ag]_n(CF₃SO₃)_{2n}(**6c**), correspond either to a biisoquinoline-double bridged dimer with short intramolecular argentophilic silver-silver distances of 3.0737(6) Å (6a) or 3.1358(6) Å (6b), or to an infinite biisoquinoline-single bridged 1D polymer (6c). In these complexes, the silver centres are either linear 2-coordinate or distorted tetrahedral 4-coordinate. The silver coordination sphere is completed by the anion and in some cases by solvent (acetone, water). Complexes $[Ag(biisoq)_2]_n X_n$ (X = SO₃CF₃ (1); BF₄ (2)) are oligometric with bridging biisoquinoline, at least in solution. All the derivatives are luminescent at room temperature in the solid state with emission maxima in the range 397-519 nm; they emit at 77 K from 366 to 523 nm. They also emit in CH_2Cl_2 at 298 K in the range 376–490 nm, whilst they are luminescent at 77 K in the range 376-402 nm.

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1. Introduction

Polydentate nitrogen heterocycles play an important role in coordination chemistry and crystal engineering, because of their good coordinating properties and their ability to transmit electronic effects [1]. Systems containing silver(I) centres are specially interesting due to the high affinity of silver to N donor ligands, its flexible coordination number and geometry [2], and the possibility of forming Ag...Ag weak interaction in some cases [3]. Moreover, apparently small changes, for instance in the counter-anion or the solvent, can lead to significant changes in the structures obtained [4]. Although there are many reports on luminescent d¹⁰-metal complexes, emissive Ag(I) complexes have been less studied because of their potential photosensitivity and limited luminescence [5].

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Ligands incorporating a 1,l'-binaphthyl unit display helical structures, which gives rise to rotational isomers (atropisomers) associated to the high rotational barrier about the C1–C1' σ -bond [6]. This is the case of 1,1'-biisoquinoline, for which a DFT theoretical study concluded that the most stable structure is the anti-isomer (good to act as bridge) and displays a N-C-C'-N' torsional angle of 129.9°. Its atropisomer, the svn isomer (good to act as chelate), displays a torsional angle of 26.5°, and the calculated atropisomeric transition barrier is 123.09 kJ/mol [7]. In spite of this calculated barrier 1,1'-biisoquinoline behaves as a flexible ligand that can modify the torsion angle between the two isoquinoline halves allowing for monodentate, bidentate bridging and, most often, bidentate chelating modes of coordination [8]. This behavior is controlled mainly by the number of auxiliary ligands in the metallic fragment and by their steric requirements. Here we report the synthesis and characterization of mono-, di- and poly-nuclear 1,1'-biisoquinoline silver(I) compounds, where the versatility of coordination of Ag(I) allows for a variety of coordination modes of the biisoquinoline ligand. Most of the complexes are luminescent, both in solution and in the solid state.





2. Experimental

For general procedures see Supplementary data. Literature methods were used to prepare 1,1'-biisoquinoline [8k] [Ag(CF₃SO₃) (PRR'₂)] [9] and [Ag(OClO₃)(PRR'₂)] [10].

2.1. Synthesis of $[Ag(biisoq)_2]_n X_n$, $X = CF_3SO_3$ (1), $X = BF_4$ (2) and [AgX(biisoq)], $X = CF_3SO_3$ (6), $X = BF_4$ (7)

To a diethyl ether solution (20 mL) of AgX (0.2 mmol; $X = CF_3SO_3$ 51 mg, X = BF_4 39 mg) was added the corresponding biisoquinoline in the adequate molar ratio 1:2 (102 mg, 0.4 mmol) or 1:1 (51 mg, 0.2 mmol), and the reaction stirred for 60 min protected from the light. The insoluble compounds were filtered off, washed and dried. Compounds 1-2 and 6-7 were obtained as white solids. Yield of 1: 135 mg, 88%. Anal. Calc. for C, 57.75; H, 3.14; N, 7.28. Found: C, 57.44; H, 3.41; N, 7.16%. ¹H NMR (CDCl₃): δ 7.46 (d, J_{HH} = 8.3 Hz, 1H, H⁸), 7.50 (t, J_{HH} = 8.3 Hz, 1H, H⁷), 7.70 (d, J_{HH} = 5.7 Hz, 1H, H⁴), 7.77 (t, $J_{\rm HH}$ = 8.3 Hz, 1H, H⁶), 7.93 (d, $J_{\rm HH}$ = 8.3 Hz, 1H, H⁵), 8.40 (d, $I_{\rm HH} = 5.7$ Hz, 1H, H³). ¹⁹F NMR (CDCl₃): $\delta - 78.3$ (s). ¹H NMR (d₆-acetone): δ 7.49 (d, $J_{\rm HH}$ = 8.3 Hz, 1H, H⁸), 7.54 (t, $J_{\rm HH}$ = 7.7 Hz, 1H, H⁷), 7.88 (t, $J_{\rm HH}$ = 7.5 Hz, 1H, H⁶), 8.04 (d, $J_{\rm HH}$ = 5.7 Hz, 1H, H⁴), 8.14 (d, $J_{\rm HH}$ = 7.9 Hz, 1H, H⁵), 8.45 (d, $J_{\rm HH}$ = 5.7 Hz, 1H, H³). ¹H NMR $(-55 \text{ °C}, d_6\text{-acetone}): \delta 7.31 \text{ (d, } J_{\text{HH}} = 8.5 \text{ Hz}, 1\text{H}, \text{H}^8\text{)}, 7.52 \text{ (t,}$ $J_{\rm HH}$ = 7.7 Hz, 1H, H⁷), 7.93 (t, $J_{\rm HH}$ = 7.1 Hz, 1H, H⁶), 8.03–8.06 (br, 2H, $H^3 + H^4$), 8.23 (d, $J_{HH} = 8.3$ Hz, 1H, H^5). IR (KBr): 1254, 637 (CF₃SO₃) cm⁻¹. Yield of **2**: 106 mg, 75%. Anal. Calc. for C, 61.13; H, 3.42; N, 7.92. Found: C, 61.17; H, 3.71; N, 7.57%. ¹H NMR (CDCl₃): δ 7.35 (d, $J_{\rm HH}$ = 8.4 Hz, 1H, H⁸), 7.40 (t, $J_{\rm HH}$ = 8.3 Hz, 1H, H⁷), 7.73 (t, $J_{\rm HH}$ = 7.3 Hz, 1H, H⁶), 7.91 (d, $J_{\rm HH}$ = 5.7 Hz, 1H, H⁴), 8.01 (d, $J_{\rm HH}$ = 8.3 Hz, 1H, H⁵), 8.14 (d, $J_{\rm HH}$ = 5.7 Hz, 1H, H³). ¹⁹F NMR (CDCl₃): δ –152.9 (s). ¹H NMR (d₆-acetone): δ 7.41 (d, J_{HH} = 8.3 Hz, 1H, H⁸), 7.55 (t, $J_{\rm HH}$ = 7.3 Hz, 1H, H⁷), 7.87 (t, $J_{\rm HH}$ = 7.8 Hz, 1H, H⁶), 8.01 (d, $J_{\rm HH}$ = 5.7 Hz, 1H, H⁴), 8.14 (d, $J_{\rm HH}$ = 8.3 Hz, 1H, H⁵), 8.31 (d, $J_{\rm HH}$ = 5.7 Hz, 1H, H³). ¹H NMR (-55 °C, d₆-acetone): δ 7.30 (d, $J_{\rm HH}$ = 8.6 Hz, 1H, H⁸), 7.50 (t, $J_{\rm HH}$ = 7.4 Hz, 1H, H⁷), 7.91 (t, $J_{\rm HH}$ = 8.1 Hz, 1H, H⁶), 8.02 (br, 2H, H³ + H⁴), 8.21 (d, $J_{\rm HH}$ = 8.0 Hz, 1H, H⁵). IR (KBr): 1084, 1032 (BF₄) cm⁻¹. Yield of **6**: 87 mg, 85%. Anal. Calc. for C, 44.46; H, 2.36; N, 5.46. Found: C, 44.18; H, 2.71; N, 5.08%. ¹H NMR (CDCl₃): δ 7.31 (m, 1H, H⁸ + CDCl₃), 7.56 (t, J_{HH} = 8 Hz, 1H, H⁷), 7.91 (t, J_{HH} = 8.3 Hz, 1H, H⁶), 8.01 (d, J_{HH} = 5.7 Hz, 1H, H⁴), 8.10 (d, J_{HH} = 8.3 Hz, 1H, H⁵), 8.31 (d, J_{HH} = 5.7 Hz, 1H, H³). ¹⁹F NMR (CDCl₃): δ –78.3 (s). ¹H NMR (d₆-acetone): δ 7.45 (d, J_{HH} = 8.3 Hz, 1H, H⁸), 7.67 (t, J_{HH} = 7.9 Hz, 1H, H⁷), 8.01 (t, J_{HH} = 7.8 Hz, 1H, H⁶), 8.32 (d, $J_{\rm HH}$ = 8.3 Hz, 1H, H⁵), 8.35 (d, $J_{\rm HH}$ = 5.7 Hz, 1H, H⁴), 8.52 (d, $J_{\rm HH}$ = 5.7 Hz, 1H, H³). ¹H NMR (-55 °C, d₆-acetone): δ 7.57 (d, $J_{\rm HH}$ = 8.5 Hz, 1H, H⁸), 7.74 (t, $J_{\rm HH}$ = 7.3 Hz, 1H, H⁷), 8.1 (t, $J_{\rm HH}$ = 7.1 Hz, 1H, H⁶), 8.44 (d, J_{HH} = 8.3 Hz, 1H, H⁵), 8.53 (d, J_{HH} = 6.0 Hz, 1H, H⁴), $8.58 (d, J_{HH} = 6.0 \text{ Hz}, 1\text{H}, \text{H}^3)$. IR (KBr): 1252, 638 (CF₃SO₃) cm⁻¹. Yield of 7: 70 mg, 78%. Anal. Calc. for C, 47.94; H, 2.68; N, 6.21. Found: C, 47.65; H, 3.07; N, 6.13% N. ¹H NMR (CDCl₃): δ 7.26 (H⁸ under CDCl₃), 7.47 (t, $J_{\rm HH}$ = 8.1 Hz, 1H, H⁷), 7.80 (t, $J_{\rm HH}$ = 7.4 Hz, 1H, H⁶), 7.87 (brs, 1H, H⁴), 7.99 (d, $J_{\rm HH}$ = 8.1 Hz, 1H, H⁵), 8.29 (brs, 1H, H³). ¹⁹F NMR (CDCl₃): δ –153.1 (s). ¹H NMR (d₆-acetone): δ 7.50 (d, J_{HH} = 8.6 Hz, 1H, H⁸), 7.7 (t, J_{HH} = 7.4 Hz, 1H, H⁷), 8.03 (t, J_{HH} = 7.4 Hz, 1H, H⁶), 8.34 (d, $J_{\rm HH}$ = 8.3 Hz, 1H, H⁵), 8.37 (d, $J_{\rm HH}$ = 6.2 Hz, 1H, H⁴), 8.53 (d, $J_{\rm HH}$ = 6.2 Hz, 1H, H³). ¹H NMR (-55 °C, d₆-acetone): δ 7.57 (d, $J_{\rm HH}$ = 8.6 Hz, 1H, H⁸), 7.74 (t, $J_{\rm HH}$ = 7.1 Hz, 1H, H⁷), 8.1 (t, $J_{\rm HH}$ = 7.3 Hz, 1H, H⁶), 8.43 (d, J_{HH} = 8.6 Hz, 1H, H⁵), 8.53 (br, 2H, H⁴ + H³). IR (KBr): 1084, 1034 (BF₄) cm⁻¹.

2.2. Synthesis of $[(\mu-biisoq){AgX(PRR'_2)}_2]$, $X = CF_3SO_3$; R = R' = Ph (**3**), R = Me, R' = Ph (**4**). $X = CIO_4$, R = Me, R' = Ph (**5**)

To a dichloromethane solution (20 mL) of $[AgX(PRR'_2)]$ (0.2 mmol; X = CF₃SO₃, R = R' = Ph 104 mg, R = Me, R' = Ph 91 mg,

 $X = ClO_4$, R = Me, R' = Ph 82 mg) was added biisoquinoline (0.1 mmol, 26 mg). The mixture was stirred for 1 h protected from the light. The solution was concentrated to *ca*. 5 mL. The addition of diethyl ether afforded compounds 3-5 as white solids. Yield of 3: 92 mg, 71%. Anal. Calc. for C, 51.95; H, 3.27; N, 2.16. Found: C, 51.65; H, 3.1; N, 2.38%. ¹H NMR (CDCl₃): δ 7.03-7.42 (m, 30H, Ph), 7.50 (d, $J_{\rm HH}$ = 8.2 Hz, 2H, H⁸), 7.63 (t, $J_{\rm HH}$ = 7.6 Hz, 2H, H⁷), 7.73 (d, $J_{\rm HH}$ = 5.7 Hz, 2H, H⁴), 7.82 (t, $J_{\rm HH}$ = 7.7 Hz, 2H, H⁶), 7.87 (d, $J_{\rm HH}$ = 8.2 Hz, 2H, H⁵), 8.59 (d, $J_{\rm HH}$ = 5.7 Hz, 2H, H³). ¹H NMR $(-55 \circ C, CDCl_3)$: $\delta 6.75-7.45$ (m, 34H, Ph + H⁸ + H⁷), 7.69 (t, $J_{\rm HH}$ = 7.6 Hz, 2H, H⁶), 7.81 (d, $J_{\rm HH}$ = 7.7 Hz, 2H, H⁵), 7.85 (d, $J_{\rm HH}$ = 5.7 Hz, 2H, H⁴), 8.61 (d, $J_{\rm HH}$ = 5.7 Hz, 2H, H³). ¹⁹F NMR (CDCl₃): δ -78.1 (s). ³¹P{¹H} NMR (CDCl₃): δ 14.9 (d, ¹J_{Ag-P} = 687.7 Hz). ³¹P{¹H} NMR (-55 °C, CDCl₃): δ 12.1 (d, ¹J_{109Ag-P} = 760.1 Hz, ${}^{1}J_{107Ag-P}$ = 669.8 Hz). IR (KBr): 1288, 1241, 636 (CF₃SO₃) cm⁻¹. Yield of 4: 81 mg, 69%. Anal. Calc. for C, 47.2; H, 3.27; N, 2.39. Found: C, 46.88; H, 3.24; N, 2.25%. ¹H NMR (CDCl₃): δ 1.75 (d, J_{HP} = 6.6 Hz, 6H, Me), 7.13–7.46 (m, 20H, Ph), 7.51 (d, $J_{\rm HH}$ = 8.3 Hz, 2H, H⁸), 7.59 (t, $J_{\rm HH}$ = 8.7 Hz, 2H, H⁷), 7.75 (t, $J_{\rm HH}$ = 7.8 Hz, 2H, H⁶), 7.82 (d, $J_{\rm HH} = 6.2$ Hz, 2H, H⁴), 7.85 (d, $J_{\rm HH} = 8.3$ Hz, 2H, H⁵), 8.85 (d, $J_{\rm HH} = 6.2$ Hz, 2H, H³). ¹H NMR (-55 °C, CDCl₃): δ 1.57 (brs, 6H, Me), 6.91–7.45 (m, 22H, Ph + H⁸), 7.61 (t, J_{HH} = 7.5 Hz, 2H, H⁷), 7.71 (d, $J_{\rm HH} = 6.1$ Hz, 2H, H⁴), 7.82 (m, 4H, H⁵ + H⁶), 8.85 (d, $I_{\rm HH} = 6.1$ Hz, 2H, H³). ¹⁹F NMR (CDCl₃): δ -78.0 (s). ³¹P{¹H} NMR (CDCl₃): δ -3.5 (br). ³¹P{¹H} NMR (-55 °C, CDCl₃): δ -4.6 (d, ${}^{1}J_{109Ag-P}$ = 786.2 Hz, ${}^{1}J_{107Ag-P}$ = 681.8 Hz). IR (KBr): 1280, 1246, 638 (CF₃SO₃) cm⁻¹. Yield of **5**: 86 mg, 80%. *Anal.* Calc. for C, 49.33; H, 3.58; N, 2.61. Found: C, 48.95; H, 3.46; N, 2.60%. ¹H NMR (CDCl₃): δ 1.79 (d, J_{HP} = 7 Hz, 6H, Me), 7.08–7.46 (m, 20H, Ph), 7.55 (d, $J_{\rm HH}$ = 7.8 Hz, 2H, H⁸), 7.60 (t, $J_{\rm HH}$ = 7.8 Hz, 2H, H⁷), 7.76 (t, $J_{\rm HH}$ = 7.8 Hz, 2H, H⁶), 7.85 (d, $J_{\rm HH}$ = 6.2 Hz, 2H, H⁴), 7.86 (d, $J_{\rm HH}$ = 8.7 Hz, 2H, H⁵), 8.85 (d, $J_{\rm HH}$ = 6.2 Hz, 2H, H³). ¹H NMR (-55 °C, CDCl₃): δ 1.72 (brs, 6H, Me), 6.92-7.44 (m, 20H, Ph), 7.53 (d, $J_{\rm HH}$ = 7.9 Hz, 2H, H⁸), 7.61 (t, $J_{\rm HH}$ = 8 Hz, 2H, H⁷), 7.77 (t, $J_{\rm HH}$ = 8 Hz, 2H, H⁶), 7.85 (br, 2H, H⁵ + H⁴), 8.80 (br, 2H, H³). ¹⁹F NMR (CDCl₃): δ -78.3 (s). ³¹P{¹H} NMR (CDCl₃): δ -3.0 (d, ¹J_{Ag-} $_{P}$ = 717.8 Hz). $^{31}P{^1H}$ NMR (-55 °C, CDCl₃): δ -2.9 (d, $^{1}J_{109Ag-}$ $_{P}$ = 789.9 Hz, $^{1}J_{107Ag-P}$ = 691.3 Hz). IR (KBr): 1098, 621 (ClO₄) cm⁻¹.

2.3. Synthesis of $[(\mu-biisoq)_2{AgX(PRR'_2)}_2]$, $X = CIO_4$; R = R' = Ph (**8**), R = Me, R' = Ph (**9**). $X = CF_3SO_3$, R = Me, R' = Ph (**10**)

To a dichloromethane solution (20 mL) of $[AgX(PRR'_2)](0.1 \text{ mmol};$ $X = ClO_4$, R = R' = Ph 47 mg, R = Me, $R' = Ph 41 mg X = CF_3SO_3$, R = Me, R' = Ph 46 mg,) was added biisoquinoline (0.1 mmol, 26 mg). The mixture was stirred for 1 h protected from the light. The solution was concentrated to ca. 5 mL. The addition of diethyl ether afforded compounds as white off (8) or light yellow (9–10) solids. A second fraction was obtained by concentration and addition of hexane. Yield of 8: 47 mg, 65%. Anal. Calc. for C, 59.56; H, 3.75; N, 3.86. Found: C, 59.81; H, 3.83; N, 3.92%. ¹H NMR (CDCl₃): δ 7.05–7.44 (m, 30H, Ph), 7.47 (t, $J_{\rm HH}$ = 7.6 Hz, 4H, H⁷), 7.58 (d, $J_{\rm HH}$ = 7.6 Hz, 4H, H⁸), 7.75 (t, $J_{\rm HH}$ = 7.9 Hz, 4H, H⁶), 7.88 (d, $J_{\rm HH}$ = 6.2 Hz, 4H, H⁴), 7.97 (d, $J_{\rm HH}$ = 8.3 Hz, 4H, H⁵), 8.55 (d, $J_{\rm HH}$ = 6.2 Hz, 4H, H³). ¹H NMR (-55 °C, CDCl₃): δ 6.84-7.75 (brm, 50H, Ph + H⁴⁻⁸), 8.25 (brs, 4H, H³). ¹⁹F NMR (CDCl₃): δ –78.1 (s). ³¹P{¹H} NMR (CDCl₃): δ 15.1 (d, ${}^{1}J_{Ag-P}$ = 692 Hz). ${}^{31}P{}^{1}H$ NMR (-55 °C, CDCl₃): δ 14.8 (d, ${}^{1}J_{109Ag-}$ $_{\rm P}$ = 717 Hz, $^{1}J_{107Ag-P}$ = 621.8 Hz). IR (KBr): 1096, 622 (ClO₄) cm⁻ Yield of **9**: 41 mg, 61%. *Anal*. Calc. for C, 56.09; H, 3.80; N, 4.22. Found: C, 55.98; H, 3.95; N, 4.35%. ¹H NMR (CDCl₃): δ 1.86 (d, J_{HP} = 6.6 Hz, 6H, Me), 7.22–7.41 (m, 20H, Ph), 7.49 (t, *J*_{HH} = 7.6 Hz, 4H, H⁷), 7.55 (d, $J_{\rm HH}$ = 7.9 Hz, 4H, H⁸), 7.75 (t, $J_{\rm HH}$ = 7.6 Hz, 4H, H⁶), 7.88 (d, $J_{\rm HH} = 5.7$ Hz, 4H, H⁴), 7.95 (d, $J_{\rm HH} = 8.3$ Hz, 4H, H⁵), 8.64 (d, $J_{\rm HH}$ = 5.7 Hz, 4H, H³). ¹H NMR (-55 °C, CDCl₃): δ 1.74 (brs, 6H, Me), 7.0–8.01 (brm, 40H, Ph + H^{4–8}), 8.39 (brs, 4H, H³). ¹⁹F NMR (CDCl₃): $\delta - 78.2$ (s). ³¹P{¹H} NMR (CDCl₃): $\delta - 3.6$ (br). ³¹P{¹H} NMR (-55 °C,

CDCl₃): δ –4.1 (d, ¹J_{109Ag-P} = 729 Hz, ¹J_{107Ag-P} = 628.4 Hz). IR (KBr): 1077, 622 (ClO₄) cm⁻¹. Yield of **10**: 50 mg, 70%. *Anal.* Calc. for C, 53.87; H, 3.53; N, 3.93. Found: C, 53.58; H, 3.55; N, 3.90%. ¹H NMR (CDCl₃): δ 1.77 (d, *J*_{HP} = 7 Hz, 6H, Me), 7.11–7.44 (m, 20H, Ph), 7.52 (t, *J*_{HH} = 7.5 Hz, 4H, H⁷), 7.57 (d, *J*_{HH} = 7.9 Hz, 4H, H⁸), 7.75 (t, *J*_{HH} = 7.6 Hz, 4H, H⁶), 7.86 (d, *J*_{HH} = 5.7 Hz, 4H, H⁴), 7.93 (d, *J*_{HH} = 8.3 Hz, 4H, H⁵), 8.70 (d, *J*_{HH} = 5.7 Hz, 4H, H³). ¹H NMR (-55 °C, CDCl₃): δ 1.59 (brs, 6H, Me), 6.92–7.97 (brm, 40H, Ph + H⁴⁻⁸), 8.54 (brs, 4H, H³). ¹⁹F NMR (CDCl₃): δ –78.2 (s). ³¹P{¹H} NMR (CDCl₃): δ –3.5 (br). ³¹P{¹H} NMR (-55 °C, CDCl₃): δ –4.4 (d, ¹*J*_{109Ag-P} = 758.2 Hz, ¹*J*_{107Ag-P} = 650.1 Hz). IR (KBr): 1280, 1256, 637 (CF₃SO₃) cm⁻¹.

2.4. Crystal structure determination of compounds **3a**, **6a**, **6b**, **6c**, **8a**, **9** and **10**

The crystal was mounted on a glass fiber and transferred to the Bruker SMART CCD or SuperNova Oxford Diffraction diffractometers. Crystal data and details of data collection and structure refinement are given in Tables 1 and 2. Cell parameters were retrieved using SMART [11] software and refined with SAINT [12] 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) [13]. For the SuperNova diffractometer was used the CrysAlis system software [14]. The structure was refined anisotropically on F^2 [15]. 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 chloroform molecule of monocrystal 3a is 'incipiently' disordered. Triflate anion of dimer 6a was disordered: two CF₃ were used and refined to be 65% and 35%, respectively; the majority was used in Fig. 6. There is some disorder in the coordinated acetone molecule and in the triflate

Table 1

Details of crystal data and	structure refinement for	complexes 3a, 6a-c.
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anion of dimer **6b**. Polymer **6c**: silver centres occupy special positions with 0.5 occupancies. Coordinated water in **3a** and **6c**: H of water were localized in Fourier maps, then the water molecule was refined as a rigid unit. The diffraction intensity of crystal **8a** was low, but it was the best we could get. In compound **10** the dichloromethane crystallization molecule was fixed because of disorder.

3. Results and discussion

3.1. Synthesis and structural characterization

The reaction of different silver(I) compounds with 1,1'-biisoquinoline in different ratios gave rise to the structural types gathered in Scheme 1.

The silver salts $Ag(CF_3SO_3)$ and $Ag(BF_4)$ react with 1,1'-biisoguinoline in 1:2 M ratio yielding $[Ag(biisoq)_2]_n X_n$ (1: X = CF₃SO₃; 2: X = BF₄). Compounds 1 and 2 are air-stable white solids at room temperature, and were characterized by elemental analysis, IR and NMR spectroscopy. In their ¹H NMR spectra, the aromatic biisoquinoline protons H³ and H⁸ are slightly high-field shifted compared to the free ligand, whilst H⁴⁻⁷ are slightly high- or low-field shifted depending on the compound (see Section 2). The largest shifts are 0.32-0.58 ppm for H³ and 0.24–0.39 ppm for H⁸. The ¹H NMR spectra show only one kind of isoquinoline unit even at low temperature (-55 °C), which points out to symmetric coordination for the 1.1'biisoquinoline ligand. The ¹⁹F NMR spectra show a singlet at -78.3 or -153 ppm, due to the triflate or tetrafluoroborate anion. The compounds are poorly soluble in acetone, chloroform or dichloromethane, and insoluble in hexane or diethyl ether. Crystals of compounds 1-2 suitable for X-ray diffraction could not be obtained. Related derivatives with planar 2,2'-bipyridine type ligands and several anions are mononuclear [16]. The higher flexibility of

Compound	3a ·CHCl ₃	6a	6b	6c
Empirical formula	$C_{57}H_{45}Ag_2Cl_3F_6N_2O_7P_2S_2$	$C_{50}H_{48}Ag_2F_6N_4O_{10}S_2$	$C_{44}H_{36}Ag_2F_6N_4O_8S_2$	C ₁₉ H ₁₄ AgF ₃ N ₂ O ₄ S
fw	1432.10	1258.78	1142.63	531.25
Т (К)	298(2)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	monoclinic	orthorhombic	monoclinic
Space group	ΡĪ	C2/c	Pbcn	C2/c
Unit cell dimension				
a (Å)	14.2337(5)	14.8433(5)	13.0336(3)	19.8010(6)
b (Å)	14.2910(6)	19.8286(4)	17.9025(3)	9.7134(3)
c (Å)	15.8288(5)	19.9058(7)	20.0081(4)	21.1092(6)
α (°)	68.190(4)	90	90	90
β(°)	81.252(3)	110.999(4)	90	107.643(3)
χ (°)	85.340(3)	90	90	90
V (Å ³)	2953.49(19)	5469.6(3)	4668.59(16)	3869.0(2)
Ζ	2	4	4	8
D_{calc} (Mg/m ³)	1.610	1.529	1.626	1.824
Absorption coefficient (mm ⁻¹)	0.995	0.870	1.008	1.208
F(000)	1436	2544	2288	2112
Crystal habit	prism	prism	plate	prism
Crystal size (mm)	$\textbf{0.38} \times \textbf{0.14} \times \textbf{0.11}$	$0.37 \times 0.30 \times 0.20$	$0.36 \times 0.20 \times 0.09$	$0.39 \times 0.19 \times 0.18$
Θ range for data collection	2.82-28.78	2.94-28.82	2.81-28.83	2.89-28.81
Index ranges	$-19 \le h \le 19$	$-19 \le h \le 18$	$-17 \le h \le 17$	$-17 \le h \le 26$
	$-19 \le k \le 19$	$-26 \le k \le 25$	$-24 \le k \le 24$	$-10 \le k \le 12$
	$-21 \le l \le 21$	$-18 \le l \le 26$	$-27 \le l \le 27$	$-26 \le l \le 27$
Reflections collected	19965	10632	11843	7555
Independent reflections	$12223 [R_{int} = 0.0210]$	5713 [<i>R</i> _{int} = 0.0216]	4979 $[R_{int} = 0.0214]$	$4063 [R_{int} = 0.0226]$
Maximum and minimum transition	0.966 and 0.916	0.864 and 0.597	0.992 and 0.980	1.00000 and 0.76569
Data/restraints/parameters	12223/0/729	5713/0/375	4979/0/298	4063/0/272
Goodness-of-fit (GOF) on F^2	0.971	0.994	0.932	1.034
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0471, wR_2 = 0.1228$	$R_1 = 0.0455, wR_2 = 0.1275$	$R_1 = 0.0388, wR_2 = 0.1108$	$R_1 = 0.0338, wR_2 = 0.0858$
R indices (all data)	$R_1 = 0.0780, wR_2 = 0.1339$	$R_1 = 0.0718, wR_2 = 0.1370$	$R_1 = 0.0675, wR_2 = 0.1178$	$R_1 = 0.0464, \ wR_2 = 0.0897$
Largest difference in peak hole (e Å ⁻³)	0.922 and –0.972	0.750 and -0.655	0.590 and -0.422	0.592 and -0.502

Table 2

Details of crystal data and structure refinement for complexes 8a, 9 and 10.

Compound	8a	9 [•] (CH ₂ Cl ₂) ₂	10 [•] (CH ₂ Cl ₂) ₂
Empirical formula	$C_{81}H_{72}Ag_2Cl_2N_4O_{11}P_2$	$C_{64}H_{54}Ag_2Cl_6N_4O_8P_2$	$C_{66}H_{54}Ag_2Cl_4F_6N_4O_6P_2S_2$
fw	1626.01	1142.63	1596.73
T (K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic
Space group	PĪ	PĪ	P 2 ₁ /c
Unit cell dimension			
a (Å)	14.4358(12)	12.4994(7)	13.5878(8)
b (Å)	14.6764(10)	12.6733(8)	21.7748(14)
c (Å)	20.5851(19)	12.7547(6)	12.5713(7)
α (°)	104.042(7)	73.762(5)	90
β (°)	105.431(8)	61.149(6)	110.516(7)
χ (°)	105.840(7)	65.462(6)	90
V (Å ³)	3803.5(5)	1601.86(16)	3483.6(4)
Ζ	2	1	2
D_{calc} (Mg/m ³)	1.420	1.552	1.522
Absorption coefficient (mm ⁻¹)	0.689	0.969	0.889
F(000)	1664	756	1608
Crystal habit	prism	prism	prism
Crystal size (mm)	$0.35 \times 0.19 \times 0.11$	$0.32 \times 0.15 \times 0.12$	$0.35\times0.26\times0.15$
Θ range for data collection	2.90-28.69	3.06–28.80°.	2.89-28.64
Index ranges	$-15 \le h \le 18$	$-16 \le h \le 16$	$-17 \le h \le 12$
	$-18 \le k \le 11$	$-17 \le k \le 17$	$-18 \le k \le 28$
	$-26 \le l \le 25$	$-17 \le l \le 17$	$-14 \le l \le 16$
Reflections collected	16580	10747	13966
Independent reflections	13157 [R _{int} = 0.0201]	6648 $[R_{int} = 0.0350]$	7306 $[R_{int} = 0.0346]$
Maximum and minimum transition	0.963 and 0.884	0.899 and 0.797	0.914 and 0.847
Data/restraints/parameters	13157/0/925	6648/0/389	7306/3/416
Goodness-of-fit (GOF) on F ²	1.017	0.950	1.045
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0495, wR_2 = 0.1256$	$R_1 = 0.0576, wR_2 = 0.1475$	$R_1 = 0.0609, wR_2 = 0.1762$
R indices (all data)	$R_1 = 0.0876$, $wR_2 = 0.1395$	$R_1 = 0.1029$, $wR_2 = 0.1645$	$R_1 = 0.0888, wR_2 = 0.1860$
Largest difference in peak hole (e Å ⁻³)	0.750 and -0.482	1.346 and -0.780	1.074 and -0.665



Scheme 1. Structural types of Ag(I) complexes with 1,1'-biisoquinoline.

1,1'-biisoquinoline might produce the same kind of structure data (structure **A** in Fig. 1), or alternatively give rise to oligomeric or polymeric species (structure **B** in Fig. 1), compatible with the previous data. In fact, the values of molar conductivity at different concentrations do not correspond to a 1:1 electrolyte, but support oligomerization in solution. Thus, the slope of the plot of Λ_e (equivalent

conductivity) vs. \sqrt{c} (*c* = equivalent concentration) in MeNO₂ for **1** is -2200, supporting a 4:1 or higher electrolyte; for **2** the slope is -600, suggesting values of oligomerization between 2:1 and 3:1 [17]. For the structure in the solid state there is only indirect support, but a polymeric structure, as found in solution would also explain better the low solubility of the compounds. Moreover, as seen below, all the structures found here contain bridging biisoquinoline, not chelating biisoquinoline. Overall, all that indirect evidence seems to be compatible with an oligomeric structure for **1**-**2** also in the solid state.

Treatment of complexes [AgXL] with 1,1'-biisoquinoline in 2:1 M ratio leads to dinuclear compounds **3–5** with a bridging biisoquinoline ligand [(μ -biisoq){AgX(PRR'₂)}₂] (**3**: X = OSO₂CF₃, L = PPh₃; **4**: X = OSO₂CF₃, L = PMePh₂; **5**: X = OCIO₃, L = PMePh₂). Compounds **3–5** are air-stable white solids at room temperature, and were characterized by elemental analysis, IR, and NMR spectroscopy. Their main features are: (a) the aromatic biisoquinoline protons are slightly low-field (H⁶ and H⁷ for **3–5**, H³ and H⁴ for **4–5**) or highfield (H⁵ and H⁸ for **3–5**, H³ and H⁴ for **3**) shifted, the largest shifts values being 0.15–0.20 ppm for H⁸; (b) the ¹H NMR spectra at –55 °C show only one kind of isoquinoline half; (c) the integrations confirm a 1:2 M ratio of the two kinds of ligand; (d) a singlet in the ¹⁹F NMR spectra in **3** and **4** corresponds to the triflate anion; (e) a broad resonance for the coordinated phosphine, due to unresolved



Fig. 1. Alternative bonding modes of 1,1'-biisoquinoline in 1-2.

coupling to the two silver isotopes, was observed in the ³¹P{¹H} NMR spectra; the two Ag–P couplings are resolved at low temperature (-55 °C), where two doublets are observed centred at 12.1 ppm (${}^{1}J_{109Ag-P}$ = 760.1 Hz, ${}^{1}J_{107Ag-P}$ = 669.8 Hz) for complex **3**, -4.6 (${}^{1}J_{109Ag-P}$ = 786.2 Hz, ${}^{1}J_{107Ag-P}$ = 681.8 Hz) for **4**, and -2.9 ppm (d, ${}^{1}J_{109Ag-P}$ = 789.9 Hz, ${}^{1}J_{107Ag-P}$ = 691.3 Hz) for **5**.

The solid-state structure of a derivative of 3 was solved by single-crystal X-ray diffraction studies. The crystal studied was obtained by slow diffusion of hexane into a solution of 3 in chloroform at -18 °C. The compound crystallized in the $P\bar{1}$ space group, and the asymmetric unit contained one molecule. Unexpectedly, the molecule was non-symmetric and corresponded to the formula $[(\mu-biisoq){Ag(OSO_2CF_3)(PPh_3)}{Ag(OH_2)(PPh_3)}](CF_{3-}$ SO_3), labeled as **3a**. The molecular structure of the cation is shown in Fig. 2, with selected bond lengths and angles in Table 3, and displays the expected dinuclear structure with a bridging biisoquinoline. There are two different silver centres: both are tricoordinated by the bridging biisoquinoline, the phosphine, and an oxygen atom from one triflate anion or a water molecule, respectively. Each silver atom displays a highly distorted trigonal geometry, with large P-Au-N angles of 141.93(7)° and 153.50(8)°, and small N-Ag-O angles of 87.27(7)° and 93.35(13)°. The Ag-N distances are 2.292(3) and 2.208(3) Å, while the Ag-O distances are 2.3963 (for the water) and 2.533(3) Å (for triflate). The biisoquinoline ligand displays a torsional angle NCCN of 113.1°, which produces a long intramolecular silver-silver distance (5.157 Å) precluding any Ag...Ag interaction. The shortest nonbonding intermolecular Ag-Ag distance is 7.660 Å. We have not found related X-ray structures for 2,2'-bypiridine-type ligands. Apparently the compound studied was formed by reaction of 3 with adventitious water during crystallization. It is not unreasonable to think that the structure of complex 3 might be related to that of 3a, but with a second coordinated triflate in the place of water, as water is not observed in the IR spectrum

The most interesting structures were produced in the reactions using Ag:biisoquinoline = 1:1 ratio. Depending on the ancillary ligands and other conditions, three structural types were found. As discussed below, the three types display bridging coordination of the 1,1'-biisoquinoline ligand.

The reaction of biisoquinoline with [AgXL] (X = CIO₄, CF₃SO₃; L = phosphine) complexes in a 1:1 M ratio, led to the corresponding phosphine/biisoquinoline compounds [(μ -biisoq)₂{AgXL}₂] **8–10** (Scheme 1; **8**: X = OCIO₃, L = PPh₃; **9**: X = OCIO₃, L = PMePh₂; **10**: X = OSO₂CF₃, L = PMePh₂). Compounds **8–10** are air-stable pale yellow solids at room temperature, and were characterized by elemental analysis, IR, and NMR spectroscopy. The ¹H NMR spectra



Fig. 2. Structure of the cation [(µ-biisoq){Ag(OSO₂CF₃)(PPh₃)}{Ag(OH₂)(PPh₃)}]⁺
 (3a), derived from 3. Displacement ellipsoids are at 20% probability level (H atoms omitted for clarity).

Table 3

Selected bond lengths [Å] and angles [°] for complex 3a.

	3a
Ag(1)–N(1)	2.292(3)
Ag(1) - P(1)	2.3746(9)
Ag(1)–O(1) water	2.3963
N(1)-C(1)	1.330(4)
N(1)-C(9)	1.361(5)
Ag(2)–N(2)	2.208(3)
Ag(2)–P(2)	2.3597(12)
Ag(2)–O(2) triflate	2.533(3)
N(2)-C(10)	1.321(4)
N(2)-C(18)	1.376(5)
N(1)-Ag(1)-P(1)	141.93(7)
N(1)-Ag(1)-O(1)	87.27(7)
P(1)-Ag(1)-O(1)	130.71(4)
C(1)-N(1)-C(9)	118.1(3)
C(1)-N(1)-Ag(1)	119.8(2)
C(9)-N(1)-Ag(1)	121.9(2)
N(2)-Ag(2)-P(2)	153.50(8)
N(2)-Ag(2)-O(2)	93.35(13)
P(2)-Ag(2)-O(2)	111.45(11)
C(10)-N(2)-C(18)	117.8(3)
C(10)-N(2)-Ag(2)	120.5(2)
C(18)-N(2)-Ag(2)	121.6(2)

confirm the 1:1 biisoquinoline:phosphine molar ratio. The biisoquinoline protons H³ and H⁸ are slightly high-field shifted, whilst H⁴ is low-field shifted. A singlet around -78 ppm is observed in the ¹⁹F NMR spectra due to the triflate anion. Finally, the ³¹P{¹H} NMR spectra show a broad resonance at *ca*. 15 or -3.5 ppm, respectively, for the coordinated PPh₃ or PPh₂Me coupled to the two silver isotopes. The two doublets due to Ag-P coupling are seen at low temperature (-55 °C) at 14.8 ($^{1}J_{109Ag-P}$ = 717 Hz, $^{1}J_{107Ag-P}$ = 621.8 Hz) for **8**, -4.1 ($^{1}J_{109Ag-P}$ = 729 Hz, $^{1}J_{107Ag-P}$ = 628.4 Hz) for **9**, and -4.4 ($^{1}J_{109Ag-P}$ = 758.2 Hz, $^{1}J_{107Ag-P}$ = 650.1 Hz) ppm for **10**.

The dinuclear structures of 8-10 were solved by single-crystal X-ray diffraction studies and confirmed the bridging coordination of the ligand bijsoquinoline. The molecules are shown in Figs. 3–5, with selected bond lengths and angles in Table 4. Compounds 8 and 9 crystallize in the triclinic $P\bar{1}$ space group, and compound **10** in the monoclinic $P2_1/c$ space group. The crystal obtained by slow diffusion of hexane into an acetone solution of **8** at -18 °C, displayed two independent molecules with slightly different distances and angles, and showed that acetone had displaced perchlorate as ligand during crystallization producing a ionic derivative of **8**, with formula $[(\mu - biisoq)_2 \{ Ag(acetone)(PPh_3) \}_2] (ClO_4)_2$, labeled as **8a**. This is not the case of the crystals of **9** and **10**, crystallized by slow diffusion of hexane into an acetone/dichloromethane solution of 9 or by slow diffusion of diethyl ether/tetrahydrofurane into a dichloromethane solution of 10, both at -18 °C, which show neutral dinuclear molecules with perchlorate or triflate coordinated to silver.

The three structures have many features in common. Each silver atom is tetracoordinated, and is bonded to two different biisoquinoline bridging ligands, to the corresponding phosphine (PPh₃ for **8a**, PPh₂Me for **9** and **10**), and to an oxygen donor atom from acetone (**8a**), perchlorate (**9**) or triflate (**10**). This coordination gives rise to a 10-membered metallacycle containing four N and two Ag atoms. The small differences in the metallic fragment lead to torsional NCCN angles in the biisoquinoline of 100.3 (94.5° for the second molecule) for **8a**, 79.7° for **9**, 98.9° for **10**, and therefore, to different intramolecular Ag–Ag distances: 4.070 Å (4.434 Å for the second molecule) for **8a**), 3.684 Å for **9**), and 4.392 Å for **10**). These Ag–Ag distances are clearly longer than accepted for argentophilic interactions (2.88–3.44 Å). The silver atoms display a highly distorted tetrahedral geometry, with larger N–Ag–P angles (in the range 125.23(10)°–138.41(11)°) and smaller N–Ag–O (in the range



Fig. 3. Structure of the cation of compound 8a. Ellipsoids are at 20% probability level (H atoms omitted for clarity).



Fig. 4. Structure of compound 9. Ellipsoids are at 20% probability level (H atoms omitted for clarity).

82.82(19)°–92.55 (16)°) and N–Ag–N angles (in the range 90.46(14)°–97.93(14)°), as observed in structure of **3a**. All the Ag–N distances are very similar, in the range 2.304(4)–2.353(4) Å, and are longer than those found in **3a** for tricoordinated silver (2.208(3) and 2.292(3) Å). The Ag–P distances, in the range 2.3705(14)–2.3849(13) Å, are similar to or slightly longer than those found for **3a** (2.3597(12) and 2.3746(9) Å). The Ag–O distances of 2.746(4) and 2.819(4) Å for compound **8a** (acetone), 2.736(5) Å for compound **9** (perchlorate) and 2.758(4) Å for compound **10** (triflate), are much longer than observed in compound **3a** (2.3963 and 2.553 Å). The biisoquinoline ligand displays the expected distances and angles. In addition there is π – π stacking between the C2–C7 biisoquinoline ring and a phenyl phosphine ring: several C–C distances in the range 3.53–3.71, 3.52–3.76 and 3.43–3.73 Å are found, respectively, for compounds **8a**, **9** and **10**.

Related silver compounds with 2,2'-bypiridine-type ligands and phosphines in AgX:phosphine:*N*,*N*-ligand 1:1:1 ratio are well-studied and characterized. In all the cases they yield mononuclear compounds with a chelate *N*,*N*-ligand, and the coordination sphere is completed with the phosphine, and sometimes with the anion [18]. In contrast, the 1,1'-biisoquinoline ligand shows high preference to act as a bridging ligand in a dimer.



Fig. 5. Structure of compound 10. Ellipsoids are at 20% probability level (H atoms omitted for clarity).



Fig. 6. Structure of the dimeric molecule of compound **6a**. Ellipsoids are at 20% probability level (H atoms and acetone of crystallization omitted for clarity).

Table 4

Selected bond lengths [Å] and angles [°] for complexes 8a (two inequivalent molecules), 9 and 10.

	8a	8a (2nd mol)	9	10
Ag–N	2.333(3)	2.304(4)	2.326(4)	2.314(4)
	2.347(4)	2.346(3)	2.353(4)	2.350(4)
Ag–P	2.3772(12)	2.3796(12)	2.3849(13)	2.3705(14)
Ag–O	2.746(4)	2.819(4)	2.736(5)	2.758(4)
	(acetone)	(acetone)	(perchlor.)	(triflate)
N-C	1.360(6)	1.318(5)	1.315(6)	1.382(7)
	1.325(6)	1.372(6)	1.372(6)	1.315(6)
N–Ag–N	90.46(14)	93.42(13)	97.73(14)	91.68(16)
N–Ag–P	138.41(11)	134.34(10)	136.63(10)125.23(10)	135.84(12)
	130.96(10)	131.60(10)		132.45(11)
N-Ag-O	91.71(12)	89.36(14)	82.82(19)	87.75(15)
	85.80(14)	84.72(13)	92.55(16)	89.20(15)
P-Ag-O	88.48(9)	88.03(10)	99.22(16)	93.67(12)
C-N-C	118.8(4)	117.7(4)	117.7(4)	117.2(5)
	117.8(4)	117.7(4)	117.5(4)	117.5(5)

Finally, the reactions of the silver salts $Ag(CF_3SO_3)$ and $Ag(BF_4)$ with 1,1'-biisoquinoline in 1:1 M ratio yield apparently simple compounds of stoichiometry [AgX(biisoq)] (6: X = CF₃SO₃; 7: $X = BF_4$). Compounds **6** and **7** are air-stable white solids at room temperature, and were characterized by elemental analysis, IR and NMR spectroscopy. They are poorly soluble in acetone, chloroform or dichloromethane, and insoluble in hexane or diethyl ether. In their ¹H NMR spectra, the aromatic biisoquinoline protons H³ and H⁸ are slightly high-field shifted by comparison to the free ligand, whilst H⁴⁻⁷ are slightly high or low-field shifted depending on the compound (see Section 2). The biggest shifts are 0.32-0.58 ppm for H³ and 0.24–0.39 ppm for H⁸. Even the ¹H NMR spectra at low temperature $(-55 \circ C)$ show only one kind of isoquinoline unit, which points out to symmetric coordination for the 1.1'-biisoquinoline ligand. The ¹⁹F NMR spectra show a singlet at -78.3 or -153 ppm due to the triflate or tetrafluoroborate anion.

Crystals of **6**, obtained by slow diffusion of diethyl ether in a solution of acetone at -18 °C, showed two different polymorphs of the same molecular structure. One, denoted **6a**, is [(μ -biisoq)₂{Ag(OSO₂CF₃)(ace-

Table 5				
Selected bond lengths	[Å] and an	gles [°] for o	complexes	6a-c

	6a	6b	6c
Ag(1)-N(1)	2.277(3)	2.285(3)	2.231(2)
Ag(1)-N(2)/N(1A)	2.264(3)	2.248(3)	2.231(2)
Ag(1)-O(1) trif.	2.553(7)	2.399(3)	-
Ag(1)-O(4) acet.	2.542(3)	2.511(4)	-
Ag(1)-O(1) water	-	-	2.5347
Ag(1)-Ag(1)#1	3.0737(6)	3.1358(6)	-
Ag(2)-N(2)	-	-	2.159(2)
Ag(2)-N(2B)	-	-	2.159(2)
N(1)-C(1)	1.322(4)	1.309(4)	1.333(3)
N(1)-C(9)	1.378(5)	1.364(4)	1.370(3)
N(2)-C(10)	1.320(5)	1.316(4)	1.323(3)
N(2)-C(18)	1.369(5)	1.372(4)	1.376(4)
N(2)-Ag(1)-N(1)	140.28(11)	141.85(11)	-
N(1A)-Ag(1)-N(1)	-	-	147.90(11)
N(2)-Ag(2)-N(2B)	-	-	180.00
N(2)-Ag(1)-O(4)	105.69(11)	112.65(15)	-
N(1A)-Ag(1)-O(1A)	-	-	99.00(5)
N(1)-Ag(1)-O(4)	92.38(12)	90.28(15)	-
N(1)-Ag(1)-O(1A)	-	-	103.02(5)
N(2)-Ag(1)-O(1)	127.43(15)	110.31(11)	-
N(1A)-Ag(1)-O(1)	-	-	103.03(5)
N(1)-Ag(1)-O(1)	88.02(17)	94.77(11)	99.00(5)
O(4) - Ag(1) - O(1)	86.3(2)	98.82(17)	-
O(1)-Ag(1)-O(1A)	-	-	92.7
C(1)-N(1)-C(9)	118.2(3)	118.6(3)	118.5(2)
C(1)-N(1)-Ag(1)	121.8(2)	121.4(2)	122.71(17)
C(9)-N(1)-Ag(1)	119.7(2)	119.8(2)	118.78(17)
C(10)-N(2)-C(18)	-	-	118.0(2)
C(10)-N(2)-Ag(2)	-	-	123.78(18)
C(18)-N(2)-Ag(2)	-	-	117.51(17)

tone) $_2$]·2acetone and crystallizes in the monoclinic C2/c system; the other, denoted **6b**, is [(μ -biisoq) $_2$ {Ag(OSO $_2$ CF $_3$)(acetone) $_2$] and crystallizes in the orthorhombic *Pbcn* system. Their main difference is that the monoclinic polymorph is solvated with two molecules of acetone per dimer; this crystallization acetone is lost easily, often cracking the crystals. The structures were established by X-ray diffraction. In both cases, the asymmetric unit is half of the molecule. The molecule is shown in Fig. 6, with selected bond lengths and angles in Table 5.

Compounds **6a** and **6b** are dimers, with two tetracoordinated silver(I) centres in a highly distorted tetrahedral arrangement and a double biisoquinoline bridge between them. Each silver centre is bonded to two N-donor atoms of the biisoquinoline ligands, and to two oxygens: one of the triflate anion, and the second of an acetone molecule. Besides, the dimer displays a short intramolecular Ag. Ag distance of 3.0737(6) or, respectively, 3.1358(6)Å for **6a** or **6b**. The shortest intermolecular Ag-Ag distance is of 8.513 or, respectively, 9.573 Å, for **6a** or **6b**. Polynuclear molecular compounds containing monovalent coinage metals show a remarkable tendency to aggregation despite their formally closed-shell d¹⁰ electronic configuration [19]. This behavior has been particularly well documented for gold, but experimental and theoretical evidence has also been reported for the analogous argentophilic interaction [3]. Typically, Ag-Ag distances in the range 2.88 (metallic distance) to 3.44 Å (sum of van der Waals radii) are indicative of these interactions.

Another structure related to 6, denoted as 6c, was crystallized by slow diffusion of hexane in a solution of dichloromethane at -18 °C. Again, the compound crystallizes in the monoclinic C2/c space group. The molecular X-ray diffraction structure is shown in Fig. 7, with selected bond lengths and angles in Table 5. Compound 6c displays an asymmetric unit of formula [(µ-biisoq)A $g(OH_2)_2(\mu$ -biisoq)Ag]_n(CF₃SO₃)_{2n}. The asymmetric unit contains a dinuclear fragment, with the silver atoms in 0.5 occupancies. In this structure the biisoquinoline ligands act as a single-bridge (instead of double-bridge) between silver atoms, which leads to a 1D polymer instead of a dimer. One silver centre is tetracoordinated with two N atoms of two different biisoquinoline ligands and two water molecules. The second independent silver centre is only linearly dicoordinated to two biisoquinoline ligands. There is no Ag-Ag interaction. The 2.159(2) Å Ag-N distance in the 2-coordinate silver centre, is clearly shorter than 2.231(2) Å in the 4-coordinate silver centre; the later is in turn slightly shorter than observed for 4-coordinate silver centres in the dimeric compounds **6a-b** (2.248(3)-2.285(3)Å) or in compounds **8a-10** (2.304(4) to 2.353(4) Å). The Ag–O distances are quite similar, in the range 2.511(4)-2.553(7) Å, independently of the nature of the ligand (acetone, triflate or water); only one Ag-O (triflate) distance of 2.399(3) Å for the unsolvated dimer is shorter. These distances are similar to those found in 3a (2.3963 and 2.553 Å) and much





Fig. 8. Solid state excitation and emission spectra of compounds 6 (regular line) and 10 (bold line): (a) at 298 K; (b) at 77 K.

shorter than those observed for **8a–10** (from 2.736(5) to 2.819(4) Å). The tetracoordinated silver centre shows the largest N–Ag–N angle (140.28(11)–147.90(11)°), and the biisoquinoline ligand displays similar distances and angles in the three crystal structures, although the torsional angles (NCCN) are different. This angle is being larger for the polymer than for the dimers, as expected from the geometry: 66.0° and 67.8° for **6a**, 68.2 and 79.9° for **6b**, and 111.8° for **6c**.

It is interesting to compare these results with those obtained for silver complexes with 2,2'-bipyridine and related ligands. Mononuclear derivatives have been reported with these *N*,*N*-ligands acting as chelate and the coordinating sphere of silver bonded to the anion and/or a coordinating solvent, for instance [Ag(CF₃CO₂)(bipy)], [Ag(ClO₄)(bq)] (bq: 2,2'-biquinolyl) and [Ag(NO₃)(Me-bipy)] (Me-bipy: 4,4'-dimethyl-2,2'-bipyridine [20,16c]. Also one-dimensional polymers, with bridging *N*,*N*-ligand as in [Ag(ClO₄)(bipy)], or bridging anion as in [Ag(NO₃)(bipy)], have been reported [20]. As found for compound **6c**, the coordination polymers derived from silver ions and bipyridine-type ligands show a preference for two-coordinate linear geometry silver centres, although they can adopt higher coordination numbers [3d,4c,4f,20,21].

As for compound **7**, we failed to obtain monocrystals for X-ray diffraction study from different solvents. The IR spectrum of the original preparation of **7** shows splitting of the v(B-F) band around 1050 cm⁻¹, indicating the existence of some kind of interaction or coordination involving the anion, which that decreases the *Td* symmetry of the free anion [22]. In case of coordination, the solid state structure would correspond to a neutral compound. However, with only these data a specific structure cannot be proposed.

3.2. Photophysical studies

The absorption spectra of the compounds, as isolated in the experimental part, were measured in dichloromethane in the range 200–600 nm. The detailed results are given as Supplementary material (Table S1). The main features for the spectra of the gold derivatives are, monotonically, the following: (1) an intense absorption at 230–234 nm, due to phenyl rings [23]; (2) absorptions around 266–278 nm, also related with the aromatic rings of the biisoquinoline or phosphine ligands; (3) a broad peak with intensity maxima in the range 331–338 nm, related to π - π * transitions in the biisoquinoline ligand, but red-shifted after coordination to silver(I), which can also be related to metal–ligand charge transfer transitions.

The emission and excitation spectra of the free ligand and the silver complexes were recorded in the solid-state and in CH_2Cl_2 solution, at 298 and 77 K. All the derivatives, including the free 1,1'-biisoquinoline ligand, emit at 77 and 298 K in the solid state and in solution. The detailed results are given in the Supplementary material (Tables S2 and S3). The spectra of compounds **6** and **10** in the solid state are shown in Fig. 8. All the derivatives, including the free 1,1'-biisoquinoline ligand, emit at 77 and 298 K in the solid state and in solution.

In the solid state, the emission maxima range goes from 397 to 519 nm at 298 K. Actually, compounds 1-7 (and the ligand) emit in the short range 397-414 nm, whilst compounds 8-10 emit at 494-519 nm. At 77 K there are again two groups of emissive compounds: the ligand and derivatives 1-7 show emission maxima from 366 to 399 nm (up to 435 nm by considering lower intensity emission spectra), and derivatives 8-10 emit at 468-523 nm. Moreover, the emission spectra are more complex, and in some cases a second (even a third for 8) less intense spectra can be observed. The low temperature emission and excitation maxima peaks are slightly blue shifted, except the emission for compound 10, which is slightly red shifted. The biisoquinoline ligand is luminescent, as expected from the presence of naphthalene-type units. It is reasonable to assign the emission as ligand centred slightly modified by the silver fragment for compounds 1-7. Dinuclear derivatives 8-10 display a clearly different emission, red-shifted around 100 nm, but the presence of vibronic progressions (1165-1207 cm⁻¹, close to those found in the IR spectra for skeletal vibrations in the biisoquinoline) suggests that biisoquinoline is participating in the transition. This emission could be tentatively assigned as a metal to ligand charge-transfer transition [5d,5e].

All the compounds show emission maxima in CH₂Cl₂ solution at 298 K in the range 376–490 nm (495 nm taking into account lower intensity emission spectra). Actually, there is an emission centred at *ca*. 380 nm, and a second centred at 460 nm with a vibronic peak at 490 nm (as observed for compounds **8** and **10** in the solid state at 77 K). At low temperature, the emission range is shorter than observed at room temperature and strongly blue-shifted: 376–402 nm. The 77 K emission spectra are simpler: the peaks centred at *ca*. 460 and 490 nm have disappeared, and all the derivatives show spectra similar to the biisoquinoline spectrum. Therefore, the higher energy emission can be tentatively assigned as ligand centred slightly modified by the silver fragment, whilst the lower energy emission could be related to a metal to ligand charge-transfer transition.

4. Conclusions

1,1'-Biisoquinoline is an extraordinarily flexible and versatile ligand. In the complexes reported here it always acts as bridging ligand that can modify the Ag–Ag distance in dinuclear bridged compounds by changing the torsion angle between the two isoquinoline subunits. We have found torsion angles in the range 66.0–79.9°, with intramolecular Ag–Ag short distances from 3.0737(6) to 3.68 Å, for compounds **6a**, **6b** and **9**; but also torsional angles from 94.5° to 113.1° with intramolecular Ag–Ag large distances in the range 4.070–5.157 Å, for compounds **3a**, **8a** and **10**. The ligand can also form polymers as **6c** with a torsional angle of 111.8°. This flexibility induces a ligand response to the number and steric requirements of the auxiliary ligands, the number of bridging biisoquinoline ligands available per silver atom (one or two), and other forces involved such as argentophilic interactions or coordination of weak ligands (anions, solvent, water).

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Appendix A. Supplementary material

Supplementary material CCDC 856923–856929 contains the supplementary crystallographic data for the complexes **3a**, **6a**, **6b**, **6c**, **8a**, **9** and **10**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2012.01.059.

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