



Supramolecular coordination polymers of silver(I) with 2-isocyanopyridine or 1,2-phenylenediisocyanide

Camino Bartolomé^a, Pablo Espinet^{a,*}, Jose M. Martín-Alvarez^a, Katerina Soulantica^b, Jonathan P.H. Charmant^c

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

^b Université de Toulouse; INSA, UPS; LPCNO, 135 avenue de Rangueil, F-31077 Toulouse, France; CNRS; LPCNO, F-31077 Toulouse, France

^c School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1T, United Kingdom

ARTICLE INFO

Article history:

Received 20 November 2009

Received in revised form 28 January 2010

Accepted 8 February 2010

Available online 12 February 2010

Keywords:

Silver

Helical coordination polymers

Diisocyanides

2-Isocyanopyridines

ABSTRACT

The silver(I) complexes $[\text{Ag}\{\text{C}_5\text{H}_4\text{N}(\text{NC})\}]_n(\text{BF}_4)_n$ (**1**), $[\text{Ag}\{\text{C}_5\text{H}_4\text{N}(\text{NC})\}_2]_n(\text{BF}_4)_n$ (**2**), $[\text{Ag}\{\text{C}_6\text{H}_4(\text{NC})_2\}]_n(\text{BF}_4)_n$ (**3**), and $[\text{Ag}\{\text{C}_6\text{H}_4(\text{NC})_2\}_2]_n(\text{BF}_4)_n$ (**4**) have been synthesized using different Ag:L ratios of 2-isocyanopyridine (or 2-pyridylisocyanide, CNPy-2) or 1,2-phenylenediisocyanide ligands. The polymeric complex **2** has been characterized by X-ray diffraction revealing a polymeric chain structure. Breaking the polymeric structure of $[\text{Ag}\{\text{C}_6\text{H}_4(\text{NC})_2\}]_n(\text{BF}_4)_n$ (**3**) with acetonitrile, the dimeric complex $[\text{Ag}\{(\text{CN})_2\text{C}_6\text{H}_4\}(\text{NC-Me})_2]_2(\text{BF}_4)_2$ (**5**) is formed, which has been also characterized by X-ray diffraction.

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1. Introduction

Supramolecular polymer chemistry is an area of current interest, focusing on the formation of polymers by the connection of molecular monomers [1,2]. The engineering of this kind of polymers is based on the concepts of supramolecular interactions and supramolecular synthons [3]. Thus, a supramolecular polymer is generated by self-assembly of complementary monomeric compounds through reversible intermolecular interactions (e.g. labile coordination bonds and hydrogen bonds). The reversible bonds connecting the building blocks allow for the polymer to rearrange and adopt the supramolecular self-assembled structure. Reversible formation of bonds of moderate energy often allows for solubilization of the polymers in coordinating solvents and then crystallization of the resulting polymers for single-crystal X-ray diffraction structure investigation. In other cases, complexes derived from fragmentation of the original polymer are obtained [4].

A very fruitful area of coordination polymers is based on silver(I) metal centers connected in simple geometric dispositions to bridging ligands with nitrogen donors [5]. The most common N-donor fragments are the pyridyl ligand, with bond energy of about 47.0 kJ mol^{-1} to silver(I) [6], and the much weaker bonding cyano group. Very recently polymers or oligomers derived from bis-bidentate imino-pyridine ligands and their reduced N-methyl

derivatives have been reported [7]. By contrast, isocyanides, which are known to bind more strongly to many transition metals, have been little used. Silver polymers based on 1,8-diisocyanopmenthane [8], similar to those produced with the weakly bonding but structurally similar bis or tris(nitrile) ligands, have been reported [9]. Mixed donors 1,3- and 1,4-cyanoisocyanoarenes have been used to obtain Pd/Cu mixed complexes [10] and Ag polymers [11]. However, 2-isocyanopyridine or 1,2-phenylenediisocyanide (Fig. 1) has not been used.

Both ligands, defining identical bonding directions at 60° but with different structural constraints, show some other differences. The 2-isocyanopyridine ligand has two coordinating functions with different bond strengths, and can be expected to act either as bidentate or as monodentate with only the isocyanide group coordinated to the metal. This selective behavior cannot be expected from 1,2-phenylenediisocyanide. On the other hand, the 1,2-phenylenediisocyanide is a symmetric ligand, whereas the 2-isocyanopyridine is less symmetric, imposing two different M-ring

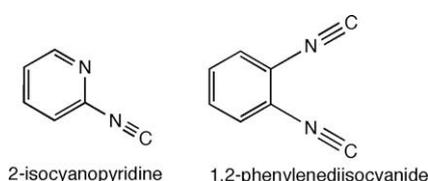


Fig. 1. Ligands used as building blocks in the synthesis of the silver complexes.

* Corresponding author.

E-mail address: espinet@qi.uva.es (P. Espinet).

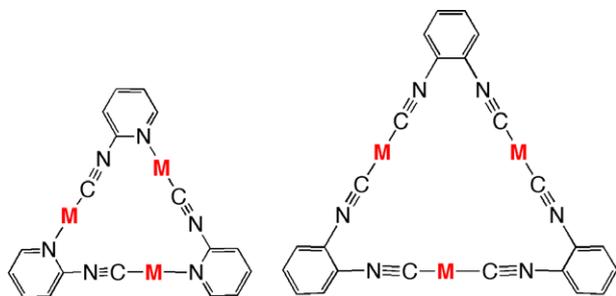


Fig. 2. Possible trimeric structures for linear coordination geometry of the metal center. The structure at the right has been found for $M = \text{trans-Pt}(\text{C}_6\text{F}_5)_2$.

lengths. Possible structural consequences of this are illustrated in (Fig. 2) for the event of the formation of metallatriangles from metal centers imposing linear coordination, as reported for $[\text{Pt}(\text{C}_6\text{F}_5)_2\{\mu\text{-C}_6\text{H}_4(\text{NC})_2\}]_3$ [12], where two *trans* positions of the square-planar Pt(II) have been blocked with C_6F_5 before the diisocyanide is coordinated.

The coordination sphere of Ag(I) is far more flexible than that of Pt(II) and can adopt coordination numbers between two and six and various coordination modes from linear through trigonal to tetrahedral, trigonal pyramidal or even octahedral. This structural flexibility could give rise to other structural outcomes, including coordination polymers. The aim of this work is to study the behavior of the structurally related 2-isocyanopyridine (CNPy-2) and 1,2-phenylenediisocyanide ligands in the construction of silver-based polymers.

2. Results and discussion

The 1:1 reaction of 2-isocyanopyridine and AgBF_4 in acetone leads to the formation of $[\text{Ag}\{\text{C}_5\text{H}_4\text{N}(\text{NC})\}]_n(\text{BF}_4)_n$ (**1**), whereas the treatment of AgBF_4 with 2-isocyanopyridine (1:2 molar ratio) in acetone affords $[\text{Ag}\{\text{C}_5\text{H}_4\text{N}(\text{NC})_2\}]_n(\text{BF}_4)_n$ (**2**). Similar results are obtained with 1,2-phenylene diisocyanide and AgBF_4 affording $[\text{Ag}\{\text{C}_6\text{H}_4(\text{NC})_2\}]_n(\text{BF}_4)_n$ (**3**) and $[\text{Ag}\{\text{C}_6\text{H}_4(\text{NC})_2\}]_n(\text{BF}_4)_n$ (**4**), respectively (Scheme 1).

In the four complexes the C, H, and N analyses are consistent with the proposed empirical formula. These, as well as relevant IR data for all the complexes, are given in the experimental part. All the complexes show typical IR absorptions of coordinated isocyanide at higher wavenumbers (ca. 100 cm^{-1}) than the free ligands [13].

All the complexes are poorly soluble in most organic solvents, which can be a consequence of the plausible polymeric structure of the complexes. Attempts to obtain crystals suitable for X-ray diffraction the polymers, **1–4**, from extremely diluted solutions of the complexes in acetone, were unsuccessful, except for $[\text{Ag}\{\text{C}_5\text{H}_4\text{N}(\text{NC})_2\}]_n(\text{BF}_4)_n$ (**2**). Views of the asymmetric unit of **2** and its extended polymeric structure are given in Fig. 3.

The polymeric structure of the cation of helical $[\text{Ag}\{\text{C}_5\text{H}_4\text{N}(\text{NC})_2\}]_n$ chains. Each ligand is bridging two silver atoms,

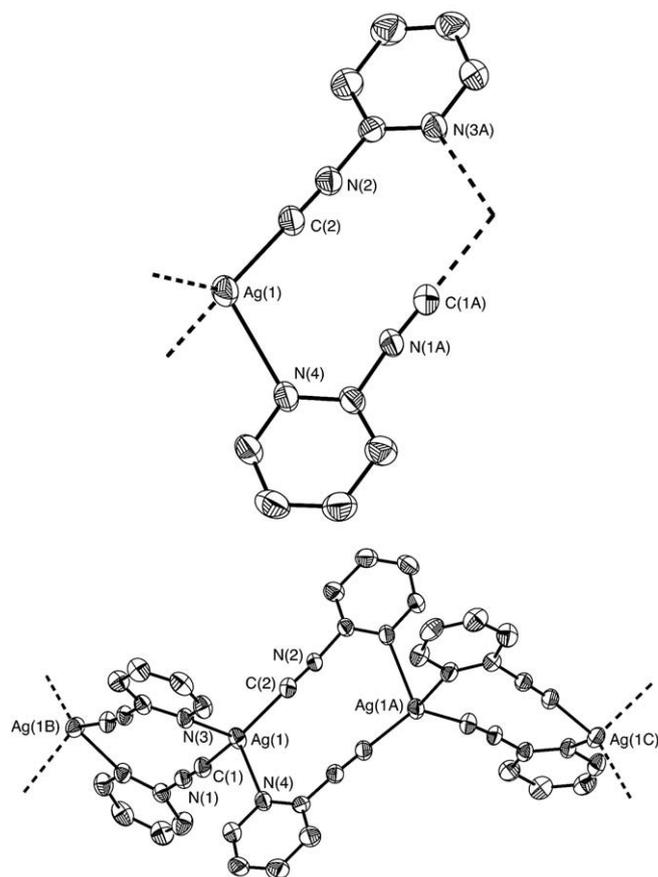
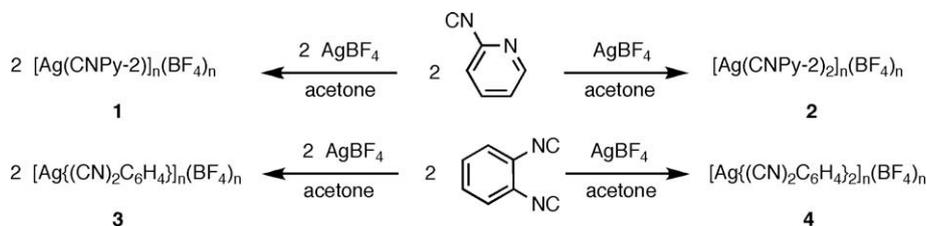


Fig. 3. Above: molecular structure of $[\text{Ag}\{\text{C}_5\text{H}_4\text{N}(\text{NC})_2\}]_n(\text{BF}_4)_n$ (**2**) showing 30% thermal ellipsoids. Below: cationic infinite chain of **2** (anions omitted for clarity). Bond lengths (Å): Ag(1)–C(2), 2.125(6); Ag(1)–C(1), 2.137(6); Ag(1)–N(4), 2.465(4); Ag(1)–N(3), 2.482(4). Bond angles ($^\circ$): N(4)–Ag(1)–N(3), 87.68(14); C(2)–Ag(1)–C(1), 129.4(2); C(2)–Ag(1)–N(4), 110.82(18); C(1)–Ag(1)–N(4), 106.0(2); C(2)–Ag(1)–N(3), 106.56(19); C(1)–Ag(1)–N(3), 108.40(18). Symmetry transformations used to generate equivalent atoms: (A) $-y + 1, x, z + 1/4$; (B) $y, -x + 1, z - 1/4$.

and each silver atom coordinates with two pyridyl nitrogen atoms and two isocyanide carbon atoms, giving rise to a four-coordinate silver(I) complex with distorted tetrahedral coordination. The average plane described by each pair of 2-isocyanopyridine ligands making a double-bridge is tilted by 86.7° with respect to the previous or the next double-bridge plane in the polymeric chain.

The Ag–C distances found in **2** do not differ significantly from those found in other silver isocyanide complexes in the Cambridge Data Base. The Ag–N distances are longer than those found for the silver coordination polymers $[\text{Ag}_2(\mu\text{-2-cyanopyridine})_2(\text{NO}_3)_2]_n$ and $[\text{Ag}(\mu\text{-2-cyanopyridine})_2(\text{BF}_4)_2]_n$ [14,15], in which the silver atoms occupy a distorted trigonal-planar environment and the anions support the polymer chain.

Fig. 4 shows the space-fill representation of a fragment of the infinite chain, and a view of the chain along the helix axis. All



Scheme 1. Synthesis of Ag(I) polymers based on 2-isocyanopyridine or 1,2-phenylene diisocyanide.

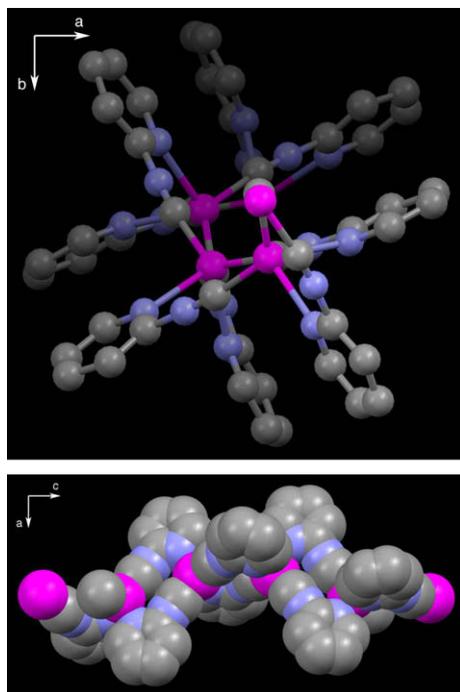


Fig. 4. Above: View of $[\text{Ag}\{\text{C}_5\text{H}_4\text{N}(\text{CN})\}_2](\text{BF}_4)_n$ (**2**) running along the helical axis (in the c direction). Below: Space-filling representation of the helix in $[\text{Ag}\{\text{C}_5\text{H}_4\text{N}(\text{CN})\}_2](\text{BF}_4)_n$ (**2**) with the tetrafluoroborate anion omitted for clarity.

the chains in the crystal structure have the same helicity, so the compound crystallizes as a racemic conglomerate of enantiomerically pure crystals [16]. The structure of **2** is one of the various examples of metallohelicities where a 1D silver coordination polymer spontaneously assumes a helical conformation [17].

Although the four silver polymeric complexes **1–4** are poorly soluble in most organic solvents, all of them are soluble in acetonitrile. This gain in solubility in a coordinating solvent suggests that the polymeric structures of the silver complexes are being broken due to the coordination of NCMe to the metal center. Unfortunately, all the attempts to obtain suitable crystals from solutions of the rest of the complexes in MeCN were unsuccessful. Due to lack of experimental data, the polymeric structures of **1** and **3** can only be speculative. However, the stoichiometry seems only

compatible with linear coordination for silver, which should lead to a zig-zag polymeric structure for both complexes [18]. This hypothesis is consistent with the result found in the X-ray diffraction study of $[\text{Ag}\{(\text{CN})_2\text{C}_6\text{H}_4\}(\text{NCMe})_2]_2(\text{BF}_4)_2$ (**5**), the crystals of which were obtained by the addition of a mixture of toluene and n -hexane to a solution of **3** in acetonitrile and cooling for several days. The molecular structure shows a rearrangement of the coordination mode of the diisocyanide (see below) that necessarily involves the splitting by acetonitrile of the initial silver polymer (Scheme 2). This is supported by the observation, in the infrared spectrum of an acetonitrile solution of **3**, of a $\nu(\text{C}\equiv\text{N})$ at a frequency corresponding to the uncoordinated isocyanide (2128 cm^{-1}), which would correspond to intermediates on the way from **3** to **5**.

The structure of the dication of **5** determined by X-ray diffraction shows a dimer with each silver(I) center in a distorted tetrahedral environment involving two bridging 1,2-phenylene diisocyanide ligands and two acetonitriles (Fig. 5). The Ag–C distances are similar to those found for silver bis(isocyanide) complexes in the Cambridge Crystallographic Data Base and in complex (**2**). The main angular distortions from tetrahedral, associated to the C–Ag–C angles, are close to 130° .

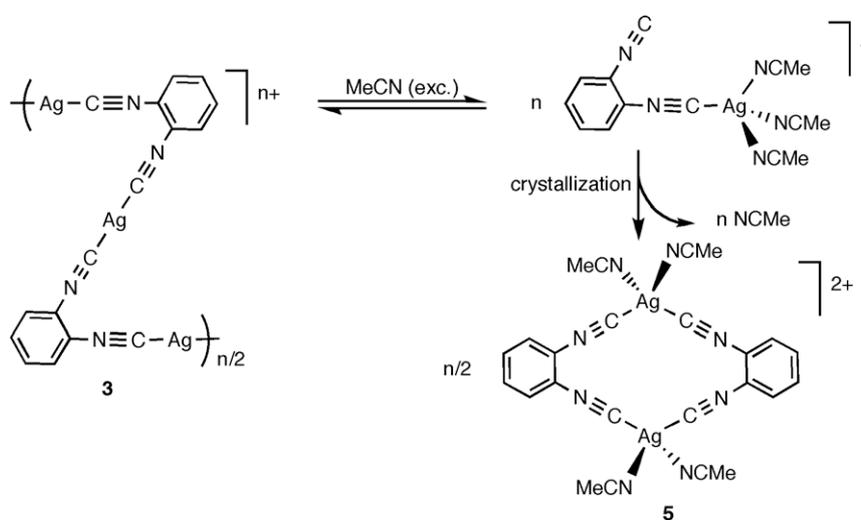
Although dimer **5** derives from polymer **3** (both have an Ag:diisocyanide = 1:1 ratio), the structure found is a good model for **4** (Ag:diisocyanide = 1:2 ratio), which can be generated by replacing the four acetonitrile ligands by two bridging diisocyanides. This would produce a polymeric structure entirely similar to that found for **2**.

In conclusion, the two bidentate ligands behave rather similarly toward silver(I) and give either single-bridged or double-bridged polymers, depending on the Ag:ligand ratio. These structures can be split in coordinating solvents.

3. Experimental

3.1. General remarks

The reactions of AgBF_4 with 1,2-phenylenediisocyanide or 2-isocyanopyridine were carried out under nitrogen, using standard Schlenk-type flasks and without exposure to light. Workup procedures were done in air. All solvents were dried and purified according to standard methods. The ligand 2-isocyanopyridine was obtained according to the reported procedure [19]. 1,2-Phenylene-



Scheme 2. Synthesis of **5** upon crystallization of a solution of **3** in acetonitrile.

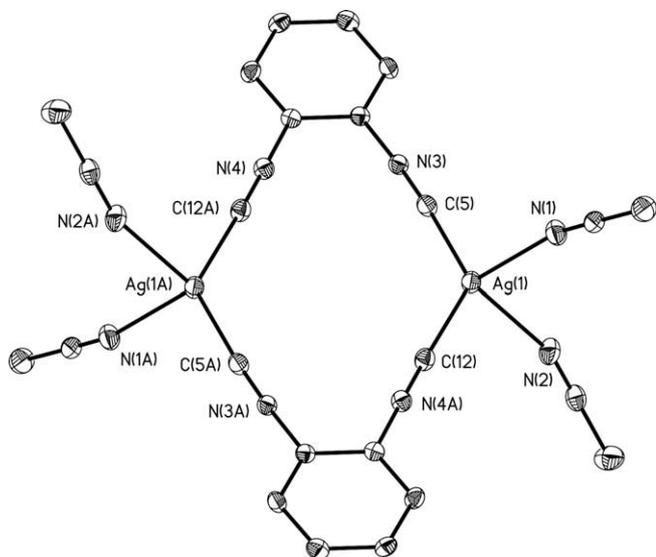


Fig. 5. Molecular structure $[Ag\{(CN)_2C_6H_4\}(NCMe)_2]_2(BF_4)_2$ (**5**) (BF_4^- anions omitted for clarity) showing 30% thermal ellipsoids. Bond lengths (Å): Ag(1)–C(5), 2.133(3); Ag(1)–C(12), 2.148(3); Ag(1)–N(1), 2.365(3); Ag(1)–N(2), 2.399(3). Bond angles (°): N(1)–Ag(1)–N(2), 91.81(9); C(5)–Ag(1)–C(12), 129.57(10); C(5)–Ag(1)–N(1), 107.28(10); C(12)–Ag(1)–N(1), 109.00(10); C(5)–Ag(1)–N(2), 115.42(10); C(12)–Ag(1)–N(2), 97.24(10); C(1)–N(1)–Ag(1), 163.4(3); C(3)–N(2)–Ag(1), 159.0(3).

diisocyanide was obtained by dehydrating the corresponding diformamide [20] with triphosgene [21]. Infrared spectra were recorded in a Perkin–Elmer 883 apparatus as Nujol mulls between polyethylene films. NMR spectra were recorded on a Bruker AC-300 or ARX-300 instrument. NMR spectra are referred to TMS. Elemental analyses were performed on a Perkin–Elmer 2400B microanalyzer.

3.2. Synthesis

The silver polymers prepared are sensitive to light under long exposure, but can be stored indefinitely in the dark at low temperature (253 K, in the freezer).

3.2.1. $[Ag\{C_5H_4N(CN)\}]_n(BF_4)_n$ (**1**)

2-CNPY (13.6 mL, 1.9 mmol, 0.144 M solution in acetone) was added to a solution of $AgBF_4$ (0.371 g, 1.9 mmol) in acetone (30 mL). After stirring for 30 min at room temperature the volatiles were pumped off and the pale brown residue was washed with *n*-hexane (3×5 mL) and vacuum dried yielding 0.153 g (78%). IR: 2220, 2196 $\nu(C\equiv N)$. 1H NMR (300 MHz, Me_2CO-d_6 , 298 K): δ 8.70 (dm, 1H, CNC_5H_4N), 8.25 (m, 1H, CNC_5H_4N), 7.98 (d, $J = 8$ Hz, 1H, CNC_5H_4N), 7.82 (m, 1H, CNC_5H_4N). Anal. Calc. for $C_6H_4N_2AgBF_4$: C, 24.10; H, 1.35; N, 9.37. Found: C, 23.74; H, 1.67; N, 8.98%.

3.2.2. $[Ag\{C_5H_4N(CN)\}_2]_n(BF_4)_n$ (**2**)

A solution of 2-CNPY (0.9 mL, 0.13 mmol, 0.144 M in acetone) in 20 mL of acetone was added to a solution of $AgBF_4$ (0.0126 g, 0.065 mmol) in acetone (20 mL). The orange solution was cooled to $-20^\circ C$. The orange crystals thus formed were decanted, washed with cold acetone, and dried, yielding 0.012 g (46%). Suitable crystals of $[Ag\{C_5H_4N(CN)\}_2]_n(BF_4)_n$ were grown by slow diffusion of a diluted acetone solution of the complex into *n*-hexane at $-20^\circ C$. IR acetone: 2188 $\nu(C\equiv N)$. 1H NMR (300 MHz, Me_2CO-d_6 , 298 K): δ 8.66 (d, $J = 4$ Hz, 1H, CNC_5H_4N), 8.18 (m, 1H, CNC_5H_4N), 7.89 (d, $J = 8.5$ Hz, 1H, CNC_5H_4N), 7.76 (dd, $J = 4$ and 8, 1H, CNC_5H_4N). Anal.

Calc. for $C_{12}H_8N_4AgBF_4$: C, 35.77; H, 2.00; N, 13.91. Found: C, 36.11; H, 2.05; N, 13.50%.

3.2.3. $[Ag\{C_6H_4(NC)_2\}]_n(BF_4)_n$ (**3**)

A solution of *o*-(CN) $_2$ C $_6$ H $_4$ (0.0623 g, 0.49 mmol) in acetone (10 mL) was added to a solution of $AgBF_4$ (0.0946 g, 0.49 mmol) in acetone (10 mL) at room temperature and a pale orange solid was formed. The volatiles were pumped off and the pale brown residue was washed with *n*-hexane (3×5 mL) yielding 0.126 g (80%). IR: 2204, 2175 $\nu(C\equiv N)$. 1H NMR (300 MHz, Me_2CO-d_6 , 298 K): δ 8.12 (m, 2H, C_6H_4), 7.93 (m, 2H, C_6H_4). Anal. Calc. for $C_8H_4N_2AgBF_4$: C, 29.77; H, 1.25; N, 8.68. Found: C, 29.38; H, 1.24; N, 8.35%. Suitable crystals of $[Ag\{(CN)_2C_6H_4\}(NCMe)_2]_2(BF_4)_2$ (**5**) were grown by slow diffusion of a concentrated acetonitrile solution of the complex into *n*-hexane and toluene at $-20^\circ C$.

3.2.4. $[Ag\{C_6H_4(NC)_2\}_2]_n(BF_4)_n$ (**4**)

A solution of *o*-(CN) $_2$ C $_6$ H $_4$ (0.1240 g, 0.97 mmol) in acetone (10 mL) was added to a solution of $AgBF_4$ (0.0942 g, 0.484 mmol) in acetone (10 mL) at room temperature and a brown solid was formed. The volatiles were pumped off and the pale brown residue was washed with *n*-hexane (3×5 mL) yielding 0.176 g (81%). IR: 2174 $\nu(C\equiv N)$. 1H NMR (300 MHz, Me_2CO-d_6 , 298 K): δ 7.85 (m, 2H, C_6H_4), 7.75 (m, 2H, C_6H_4). Anal. Calc. for $C_{16}H_8N_4AgBF_4$: C, 42.62; H, 1.79; N, 12.42. Found: C, 42.81; H, 1.83; N, 11.94%.

4. X-ray crystallography

Suitable single crystals of **2** were obtained from an acetone/*n*-hexane solution. Crystals of **5** were obtained by adding a mixture of toluene and *n*-hexane to a solution of **3** in acetonitrile. Crystals were mounted on glass fibers, and diffraction measurements were made using a Bruker SMART CCD area-detector diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å) [22]. Intensities were integrated from several series of exposures, each exposure covering 0.3° in ω , the total data set being almost a sphere for compound **5** and almost a hemisphere for compound **2** [23]. Absorption corrections were applied based on multiple and symmetry-equivalent measurements [24]. The structures were solved by direct methods

Table 1
Crystal Data and Structure Refinement for **2** and **5**.

	2	5
Empirical formula	$C_{12}H_8AgBF_4N_4$	$C_{24}H_{20}Ag_2B_2F_8N_8$
Formula weight	402.90	809.8
Temperature (K)	298(2)	293(2)
Wavelength (λ) (Å)	0.71073	0.71073
Crystal system	tetragonal	monoclinic
Space group	$P4(1)$	$P21/c$
<i>a</i> (Å)	8.3597(12)	5.918(1)
<i>b</i> (Å)	8.3597(12)	18.401(3)
<i>c</i> (Å)	21.041(4)	14.052(3)
β (°)	90.00	91.97(2)
<i>V</i> (Å 3)	1470.4(4)	1529.2(5)
<i>Z</i>	4	2
<i>D</i> _{calc} (g cm $^{-3}$)	1.820	1.759
Absorption coefficient (mm $^{-1}$)	1.413	1.359
<i>F</i> (0 0 0)	784	792
Crystal size (mm)	0.22 \times 0.08 \times 0.07	0.3 \times 0.2 \times 0.1
Theta range for data collection (°)	2.44–25.36	1.82–27.49
Reflections collected	8211	9692
Independent reflections (<i>R</i> _{int})	2700 (0.0262)	3505 (0.0236)
Absorption correction	SADABS	SADABS
Data/restraints/parameters	2700/1/200	3505/0/229
Flack parameter	–0.05(4)	–
Goodness-of-fit (GOF) on <i>F</i> 2	1.064	1.088
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0334	0.0313
<i>wR</i> ₂ (all data)	0.0928	0.0678

and refined by least squares on weighted $|F|^2$ values for all reflections (see Table 1) [25]. All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints. All the hydrogen atoms were calculated with a riding model. Complex neutral-atom scattering factors were used [26].

Acknowledgments

This work was supported by the Spanish Comisión Interministerial de Ciencia y Tecnología [Projects CTQ2008-03954/BQU, and INTECAT Consolider Ingenio 2010 (CSD2006-0003)], and the Junta de Castilla y León (Project VA012A08 and GR169).

Appendix A. Supplementary material

CCDC 713334 and 713335 contain the supplementary crystallographic data for this paper. 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.2010.02.007.

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