



# Synthesis, structure and spectroscopic properties of bis(triphenylphosphane)iminium (chlorido)(cyanido)argentates(I)

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## ABSTRACT

Four new compounds containing the (chlorido)<sub>(2-x)</sub>(cyanido)<sub>x</sub>argentate(I) anion ( $x = 2, 1.63, 1$  and  $0.5$ ) are reported. Their solid-state structures with the monocation PPN, bis(triphenylphosphane)iminium, are described; in a few cases the products also contain solvent molecules. The compounds have the formula (PPN)<sub>2</sub>[Ag<sub>2</sub>Cl<sub>3</sub>(CN)], (PPN)[Ag(CN)Cl](CH<sub>2</sub>Cl<sub>2</sub>) and (PPN)[Ag(CN)<sub>1.63</sub>Cl<sub>0.37</sub>](hexane)<sub>0.5</sub> and (PPN)[Ag(CN)<sub>2</sub>](CH<sub>2</sub>Cl<sub>2</sub>). Apart from the molecular structures and the synthetic process, also the solid-state luminescence has been studied.

In the case of (PPN)<sub>2</sub>[Ag<sub>2</sub>Cl<sub>3</sub>(CN)], the silver ions are pseudo-trigonally coordinated, with 2 chloride bridges between the Ag<sup>+</sup> ions. The terminal Cl<sup>-</sup> and terminal CN<sup>-</sup> ligands are disordered over two positions, but only a single <sup>13</sup>C NMR signal is observed for the cyanide ligands of this compound. The compound (PPN)[Ag(CN)<sub>2</sub>] serves as a reference compound and contains the linear [Ag(CN)<sub>2</sub>] unit.

The compound with CN/Cl = 1.0 shows disorder of the [AgCl(CN)] unit, and also in the compounds with other CN/Cl ratios, disorder among the Cl<sup>-</sup> and CN<sup>-</sup> ligands is seen. The Ag<sup>+</sup> ion is linearly coordinated by two ligands in these two cases, and for cyanides normal Ag–C bond lengths are observed in both cases (1.97–1.99 Å). The [Ag(CN)<sub>2</sub>] anion is linear and uneventful. The PPN cation has normal bond lengths in all 4 compounds and no short contacts with other atoms in the lattice are observed. The luminescence properties of the new compounds were explored as solid powders. Only one of the compounds (compound **2**, with  $x = 1$ ) shows luminescence under excitation. The other three compounds do not show emission when irradiated at 320 nm, 350 nm or 380 nm.

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## 1. Introduction

The poor solubility of silver halides has been known for a very long time, and this property is still in common use for the analytical determination of halides in so-called argentometry [1].

These insoluble silver salts can be dissolved in excesses of strong ligands, like ammonia and cyanide. With excess cyanide the [bis(cyanide)argentate(I)] monoanion, [Ag(CN)<sub>2</sub>]<sup>-</sup> is formed in such cases. A large variety of compounds based on this linear anion is known, in which the negative charge is compensated by metal ions, and where the N atom, bridges to the other metal ion. Examples reported in the last decade comprise transition

metals, Cd and lanthanides [2–9]. Remarkably, only very few structures of this linear anion in the free state are known [10–13], i.e. not bridging to another metal ion.

Quite surprisingly, the first steps in this dissolution process have hardly been studied so far, and the mixed anionic species [Ag(CN)<sub>x</sub>Cl<sub>(2-x)</sub>]<sup>-</sup> are poorly known and only one structure has been reported to the best of our knowledge, based on the recent CSD [14]. We therefore undertook a search for the possibility to isolate such species with different Cl/CN ratios, i.e. different values for  $x$  in [Ag(CN)<sub>x</sub>Cl<sub>(2-x)</sub>]<sup>-</sup>, with  $x = 2$  (reference compound), 1.6, 1.0 and 0.5. These species indeed appear to be rare in the literature, and in fact only one species has been structurally characterized, namely (Et<sub>4</sub>N)[Ag<sub>2</sub>(CN)<sub>2</sub>Cl], which has a 3D polymeric structure [15].

For the synthesis and characterization of the compounds in the system, we decided to use non-aqueous solvents, and the very large, innocent cation PPN, bis(triphenylphosphane)iminium was

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selected for charge compensation, and especially, to maximize the chances for obtaining molecular, anionic species. The results of this study are described below, and 3 new compounds are reported together with their 3D structures. To introduce the  $\text{Ag}^+$  ion in a soluble form, we used silver acetylides, available from our previous study [16].

As some Ag compounds are luminescent, like many  $d^{10}$  coinage metal compounds, we have also explored their emission properties in relation to the electronic structure of the compounds [17–22] and these spectra are also reported.

## 2. Experimental part

Starting materials were used as purchased without further purification. The salt bis(triphenylphosphane)iminium chloride, (PPN)Cl, was used as commercially available (Aldrich; Analar grade). Potassium cyanide was also used as commercially available (Koch-Light Labs. Ltd grade). Hexane, methylene chloride, acetone and methanol were used as commercially available (BDH-Analar grade) and kept over molecular sieves. The Ag-acetylide intermediate products were prepared as reported before [16,23]. Synthesis of (PPN)CN: Potassium cyanide, KCN (0.065 g, 1 mmol) was added to a clear solution of bis(triphenylphosphane)iminium chloride, (PPN)Cl (0.574 g, 1 mmol) in acetone (20 mL). After stirring for 20 min a white solid precipitate was formed. The solid was filtered off and collected as KCl, (0.074 g, 98%), m.p. > 3 °C. To the remaining clear solution *n*-hexane (40 mL) was added, upon which a precipitate was formed, which was finally collected as a solid with formula (PPN)CN in high yield (99%, 0.56 g), m.p. 253 °C, FTIR:  $\nu$  max  $\text{cm}^{-1}$  (KBr disk) 1293, 1242 (s, P–N), 1114 (s, P–C), 2214 (vw, C≡N stretch).

### 2.1. Synthesis of (PPN)<sub>2</sub>[Ag<sub>2</sub>Cl<sub>3</sub>(CN)], **1**

3,3-Dimethylbutynylsilver(I) [ $\text{AgC}_2\text{Bu}^t$ ]<sub>n</sub> (0.189 g, 1 mmol) was added to a clear solution of bis(triphenylphosphane)iminium chloride, (PPN)Cl (0.574 g, 1 mmol) in methanol (30 mL). While stirring for 30 min a clear solution was formed, and subsequently potassium cyanide, KCN (0.065 g, 1 mmol), was added and dissolved within 10 min. After 20 min a yellowish solid precipitated. The suspension was evaporated to dryness, and then the residue was extracted with dichloromethane,  $\text{CH}_2\text{Cl}_2$  (25 mL). In a few minutes a yellowish precipitate was formed, which was filtered off and collected as K-C<sub>2</sub>Bu<sup>t</sup> (0.070 g, 93%), m.p. 220 °C. To the remaining clear solution, *n*-hexane (40 mL) was slowly added, resulting in a off-white crystalline material, which was collected by filtration and was isolated in high yield (90%, 0.774 g), m.p. 203 °C. The crystals were found suitable for XRD analysis. Elemental analysis, according to the formula ( $\text{C}_{73}\text{H}_{60}\text{Ag}_2\text{Cl}_3\text{N}_3\text{P}_4$ ): Found (Calc.): C, 61.84 (61.50); H, 4.04 (4.21); N, 3.15 (2.95)%; FTIR:  $\nu$  max  $\text{cm}^{-1}$  (KBr disk) 1283, 1261(s, P–N), 1114 (s, P–C), 2137 (m, C≡N stretch). <sup>13</sup>C NMR (at 25 °C in dmsO, at 400 MHz): single CN signal at 206.28 ppm.

### 2.2. Synthesis of (PPN)[Ag(CN)Cl](CH<sub>2</sub>Cl<sub>2</sub>), **2**

Bis(triphenylphosphane)iminium chloride, (PPN)Cl (0.574 g, 1 mmol) was added to a clear solution of potassium cyanide, KCN (0.065 g, 1 mmol) in methanol (30 mL). While stirring for 60 min a clear solution was obtained, and subsequently, silver phenylacetylide, [ $\text{AgC}_2\text{Ph}$ ]<sub>n</sub> (0.209 g, 1 mmol) was added and dissolved during 15 min. After 30 min a white solid precipitated. The suspension was evaporated to dryness, and then the residue was extracted with dichloromethane,  $\text{CH}_2\text{Cl}_2$  (25 mL), after which an off-white precipitate was formed. This was filtered off and col-

lected as  $\text{KC}_2\text{Ph}$  (0.115 g, 82%), m.p. 250 °C. To the remaining clear solution gradually hexane (35 mL) was added and a crystalline material precipitated, which was filtered and dried for 3 h at 90 °C (95%, 0.713 g), m.p. 180 °C. The elemental analysis indicates a partial loss of lattice methylene chloride according to the formula ( $\text{C}_{37}\text{H}_{30}\text{AgClN}_2\text{P}_2$ )( $\text{CH}_2\text{Cl}_2$ )<sub>0.35</sub>. Found (Calc.): C, 60.74 (60.82); H, 4.04 (4.20); N, 3.93 (3.80)%. FTIR:  $\nu$  max  $\text{cm}^{-1}$  (KBr disk) 1282, 1262 (s, P–N), 1114 (s, P–C), 2135 (m), 2117 (w, C≡N stretch).

### 2.3. Synthesis of (PPN)[Ag(CN)<sub>x</sub>Cl<sub>2-x</sub>](hexane)<sub>0.5</sub>, **3** ( $x = 1.63$ )

Bis(triphenylphosphane)iminium chloride, (PPN)Cl (0.574 g, 1 mmol) was added to a solution of potassium cyanide, KCN (0.065 g, 1 mmol) in methanol (30 mL). While stirring for 60 min a clear solution was obtained, and subsequently, silver phenylacetylide, [ $\text{AgC}_2\text{Bu}^t$ ]<sub>n</sub> (0.189 g, 1 mmol) was added and dissolved during 15 min. After 30 min a white solid precipitated. The suspension was evaporated to dryness, and then the residue was extracted with dichloromethane,  $\text{CH}_2\text{Cl}_2$  (25 mL), after which an off-white precipitate was formed. This was filtered off and collected as  $\text{KC}_2\text{Bu}^t$  (0.097 g, 80%), m.p. 220 °C. To the remaining clear solution gradually hexane (35 mL) was added and a crystalline material precipitated, which was filtered and dried *in vacuo* (95%, 0.713 g), m.p. 190 °C. A suitable crystal for XRD was obtained from the same batch. This synthesis was performed repeatedly, and in different batches slightly different analyses were found. The elemental analyses were performed on a few samples. Found values range (calculated using the formula found from the X-ray refinement,  $\text{C}_{39.13}\text{H}_{33.5}\text{AgCl}_{0.37}\text{N}_{2.63}\text{P}_2$ ): C, 65.23–64.00 (64.97); H, 4.68–4.93 (4.67); N, 3.89–5.83 (5.09); FTIR:  $\nu$  max  $\text{cm}^{-1}$  (KBr disk) 1282, 1262 (s, P–N), 1114 (s, P–C), 2135 (m), 2117 (w, C≡N stretching).

### 2.4. Synthesis of (PPN)[Ag(CN)<sub>2</sub>](CH<sub>2</sub>Cl<sub>2</sub>), **4**

Silver cyanide [ $\text{Ag(CN)}_n$ ] (0.134 g, 1 mmol) was added to a solution of KCN (0.065 g, 1 mmol) in methanol (40 mL) according to Al-Ohaly [24]. After a clear solution had been obtained, (PPN)Cl (0.574 g, 1 mmol) was gradually added to the reaction mixture. Stirring was continued for 15 min. The solution was evaporated to dryness and the white residue was treated with methylene chloride (30 mL). The insoluble KCl (0.065 g) was filtered off. Addition of hexane to the filtrate gave white crystals which were isolated by filtration and dried at 100 °C for 3 h (0.663 g, 95%), m.p.: 188 °C. The elemental analysis indicates a partial loss of lattice methylene chloride according to the formula ( $\text{C}_{38}\text{H}_{30}\text{AgN}_3\text{P}_2$ )( $\text{CH}_2\text{Cl}_2$ )<sub>0.2</sub>. Found (Calc.): C, 65.78 (64.13); H, 4.46 (4.28); N, 5.58 (5.87)%. FTIR: max  $\nu$   $\text{cm}^{-1}$  (KBr disk) 1286, 1266 (s, P–N), 1114 (s, P–C), 2137 (s), C≡N stretching).

Single crystals of compounds **1–4** were collected from the synthetic batches. A suitable crystal for an X-ray structure analysis was selected for each case and measured on a Bruker APEX-II CCD diffractometer. Each crystal was kept at 153.2 K during data collection. Using Olex2 [25] the structures were solved with the Superflip [26–28] structure solution program by Charge Flipping and refined with the SHELXL [29] refinement package, using Least Squares minimization. Structural data are listed in Table 1.

All elemental analyses were performed by using a Perkin Elmer Series II-2400 analyzer and the FT-IR spectra were recorded on a Thermo Scientific Nicolet iS10. NMR spectra (proton and <sup>13</sup>C) were recorded on a JEOL ECP-400 NMR in CDCl<sub>3</sub>.

The excitation and emission spectra were recorded at room temperature using a Shimadzu RF-5301PC spectrofluorophotometer equipped with a solid-state sample holder. The excitation spectrum was recorded by constantly monitoring the emission spectrum at the wavelength of most intense luminescence while

**Table 1**  
Crystal data and structure refinement for compounds 1 – 4.

Sample code	1	2	3	4
CCDC number	1418113	1418114	1418115	1418116
Empirical formula	C <sub>73</sub> H <sub>60</sub> Ag <sub>2</sub> Cl <sub>3</sub> N <sub>3</sub> P <sub>4</sub>	C <sub>38</sub> H <sub>32</sub> AgCl <sub>3</sub> N <sub>2</sub> P <sub>2</sub>	C <sub>39.13</sub> H <sub>33.5</sub> AgCl <sub>0.37</sub> N <sub>2.63</sub> P <sub>2</sub>	C <sub>39</sub> H <sub>32</sub> AgCl <sub>2</sub> N <sub>3</sub> P <sub>2</sub>
Formula weight	1425.21	792.81	723.49	783.38
<i>T</i> (K)	153(1)	153(1)	153(1)	153(1)
Crystal system	orthorhombic	monoclinic	monoclinic	monoclinic
Space group	<i>Pbca</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> (Å)	19.4166(4)	9.1475(4)	9.1083(2)	9.1170(7)
<i>b</i> (Å)	15.9075(3)	23.8402(10)	23.8769(5)	23.9562(18)
<i>c</i> (Å)	20.2452(4)	16.7950(7)	17.0069(4)	16.9256(13)
$\alpha$ (°)	90	90	90	90
$\beta$ (°)	90	101.560(2)	100.8150(10)	100.9935(17)
$\gamma$ (°)	90	90	90	90
<i>V</i> (Å <sup>3</sup> )	6253.1(2)	3588.3(3)	3632.93(14)	3628.9(5)
<i>Z</i>	4	4	4	4
<i>D</i> <sub>calc</sub> (mg/mm <sup>3</sup> )	1.514	1.468	1.323	1.434
Absorption coefficient (mm <sup>−1</sup> )	0.904	0.904	0.700	0.823
<i>F</i> (000)	2896.0	1608.0	1480.0	1592.0
Crystal size (mm <sup>3</sup> )	0.61 × 0.32 × 0.22	0.27 × 0.14 × 0.14	0.40 × 0.28 × 0.20	0.33 × 0.27 × 0.18
Radiation	Mo K $\alpha$ ( $\lambda$ = 0.71073)	Mo K $\alpha$ ( $\lambda$ = 0.71073)	Mo K $\alpha$ ( $\lambda$ = 0.71073)	Mo K $\alpha$ ( $\lambda$ = 0.71073)
2 $\Theta$ range for data collection (°)	5.21–61.088	3.008–61.284	5.69–61.07	4.192–52.772
Index ranges	−27 ≤ <i>h</i> ≤ 27, −22 ≤ <i>k</i> ≤ 22, −28 ≤ <i>l</i> ≤ 28	−12 ≤ <i>h</i> ≤ 12, −32 ≤ <i>k</i> ≤ 34, −23 ≤ <i>l</i> ≤ 24	−13 ≤ <i>h</i> ≤ 13, −34 ≤ <i>k</i> ≤ 34, −24 ≤ <i>l</i> ≤ 24	−11 ≤ <i>h</i> ≤ 11, −29 ≤ <i>k</i> ≤ 29, −21 ≤ <i>l</i> ≤ 21
Reflections collected	109138	42560	64849	25613
Independent reflections	9554 [ <i>R</i> <sub>int</sub> = 0.0363, <i>R</i> <sub>sigma</sub> = 0.0186]	10954 [ <i>R</i> <sub>int</sub> = 0.0266, <i>R</i> <sub>sigma</sub> = 0.0241]	11081 [ <i>R</i> <sub>int</sub> = 0.0375, <i>R</i> <sub>sigma</sub> = 0.0277]	7355 [ <i>R</i> <sub>int</sub> = 0.0288, <i>R</i> <sub>sigma</sub> = 0.0279]
Data/restraints/parameters	9554/0/406	10954/0/451	11081/0/443	7355/0/417
Goodness-of-fit (GOF) on <i>F</i> <sup>2</sup>	1.120	1.023	1.138	1.065
Final <i>R</i> indexes [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0286, <i>wR</i> <sub>2</sub> = 0.0833	<i>R</i> <sub>1</sub> = 0.0400, <i>wR</i> <sub>2</sub> = 0.1104	<i>R</i> <sub>1</sub> = 0.0489, <i>wR</i> <sub>2</sub> = 0.1389	<i>R</i> <sub>1</sub> = 0.0560, <i>wR</i> <sub>2</sub> = 0.1491
Final <i>R</i> indexes (all data)	<i>R</i> <sub>1</sub> = 0.0331, <i>wR</i> <sub>2</sub> = 0.0858	<i>R</i> <sub>1</sub> = 0.0487, <i>wR</i> <sub>2</sub> = 0.1158	<i>R</i> <sub>1</sub> = 0.0544, <i>wR</i> <sub>2</sub> = 0.1425	<i>R</i> <sub>1</sub> = 0.0658, <i>wR</i> <sub>2</sub> = 0.1562
Largest diff. peak/hole [e Å <sup>−3</sup> ]	0.43/−0.37	1.05/−1.28	1.59/−1.05	1.38/−1.50

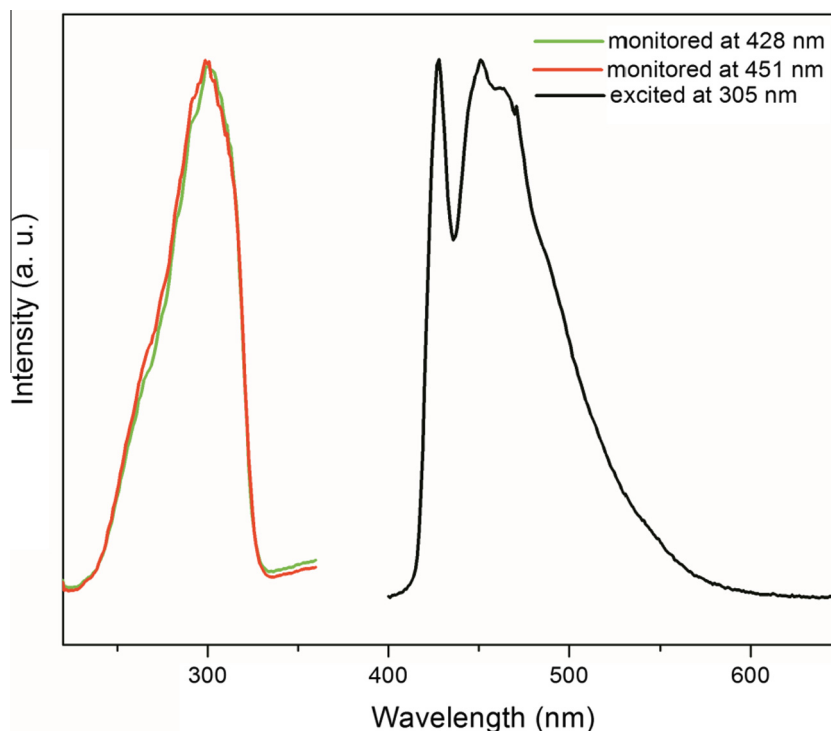


Fig. 1. Room temperature excitation (left) and emission (right) spectra of compound **2**. Details are presented in the inset.

scanning the excitation wavelength from 220 to 400 nm. The excitation spectrum has been corrected for the response of the detector and light source.

### 3. Results and discussion

#### 3.1. Synthesis, characterization and luminescence

Some of the new compounds appeared to crystallize with lattice solvents, filling up the pores in the lattice, i.e. hexane for compound **3**, and methylene chloride for compound **2**. All compounds can be described by the general formula:  $[\text{PPN}][\text{AgCl}_{2-x}(\text{CN})_x]$  (**1**:  $x = 0.5$ , **2**:  $x = 1$ , **3**:  $x = 1.63$ , **4**:  $x = 2$ ). In addition to elemental analyses, see experimental part, the compounds were also investigated by IR spectroscopy. All expected bands for the CN ligand and for PPN bands were observed, and in particular the  $\text{C}\equiv\text{N}$  triple bond, near  $2100\text{ cm}^{-1}$ , is a prominent structural marker. For compound **1** also a  $^{13}\text{C}$  NMR spectrum was recorded to be sure that, given the disordered X-ray structure, only one chemically distinct CN anion was present. The single, sharp resonance peak at 206.9 ppm indeed shows that this is the case.

The emission and excitation spectra of compounds **1–4** (few batches for each) were studied in the solid state and compared with earlier data from our laboratory on related compounds [30–32]. It appears that only a nice, blue intense luminescence is observed for compound **2**, (see Fig. 1) which is comparable to that of related heteronuclear (cyanido)silver compounds [30–32]. Most remarkable, compounds **1**, **3** and **4** do not show any luminescent behavior, under the excitation of 320 nm, 350 nm and 380 nm. For reference purposes, we therefore have also measured the luminescence of the known compound  $[\text{PPN}]\text{Cl}$ , this compound also shows no luminescence. Packing effects, to be discussed below, are therefore the most likely origins for the unique luminescence of compound **2**.

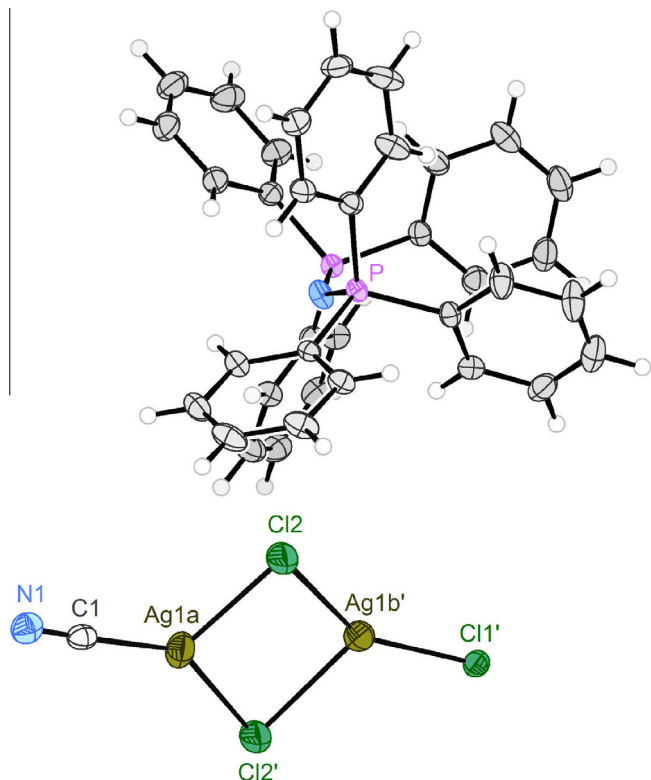
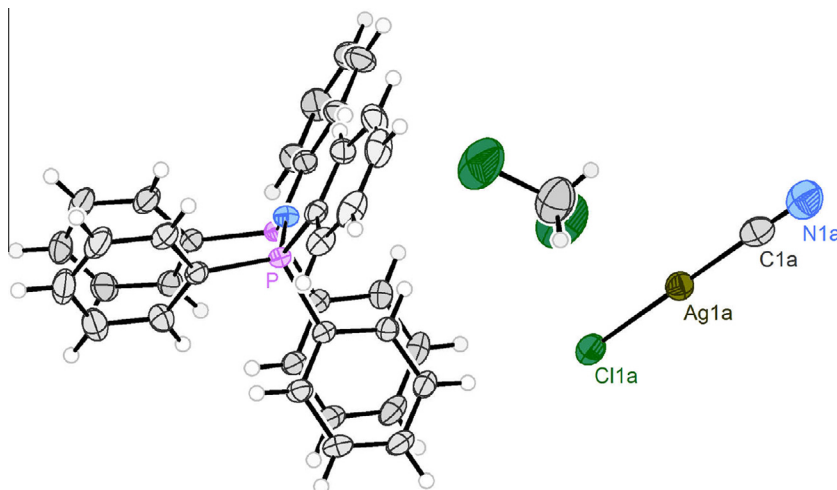


Fig. 2. Projection of cation, anion and lattice solvent molecules in compound **1** with thermal ellipsoid plot at the 50% levels of probability. Only one component (50% occupancy) of the disordered part is depicted. Selected bond lengths [Å] and angles [°] for the metal species are: Ag1a–Cl2 2.625(3), Ag1a–Cl2' 2.509(2), Ag1a–C1 2.033(7), Ag1b'–Cl1' 2.448(3), Ag1b'–Cl2' 2.766(3), Ag1b'–Cl2 2.419(2), C1–N1 1.133(6), Ag1a–Cl2–Ag1b' 85.57(8), Ag1a–Cl2'–Ag1b' 80.94(8), Cl2–Ag1a–Cl2' 97.46(8), Cl2–Ag1b'–Cl2' 95.98(8), Cl2–Ag1b'–Cl1' 150.36(13), Cl2'–Ag1b'–Cl1' 113.66(11).



**Fig. 3.** Projection of cation, anion and lattice solvent molecules in compound **2** with thermal ellipsoid plot at the 50% levels of probability. Only the main component (65% occupancy) of the disordered part is depicted. The large thermal ellipsoid for  $\text{CH}_2\text{Cl}_2$  agree with partial occupancy. Selected bond lengths [Å] and angles [°] for the metal species are: Ag1a–Cl1a 2.3286(19), Ag1a–C1a 2.040(7), C1a–N1a 1.231(14), Cl1a–Ag1a–C1a 178.9(3), Ag1a–C1a–N1a 178.1(11).

### 3.2. Crystal structure descriptions

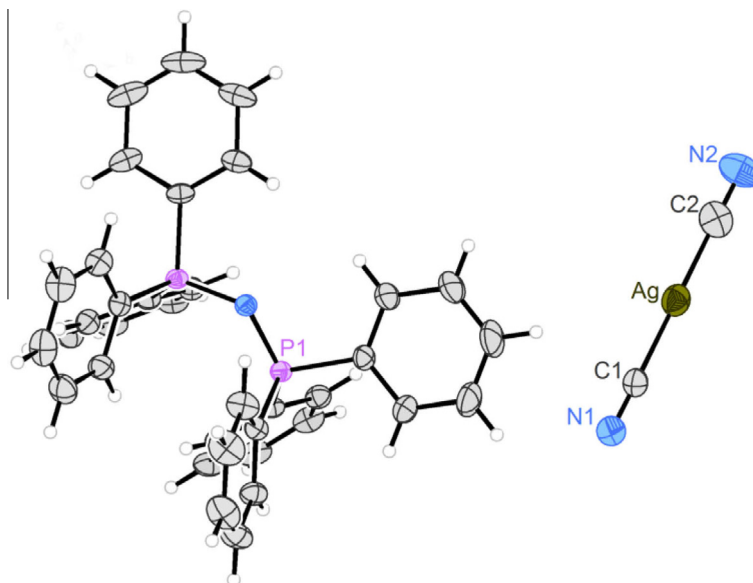
Compound **1**, in which has the value  $x = 0.5$ , contains a dinuclear anion, with trigonally coordinated Ag(I) ions; one of the silver ions is coordinated by 3 chlorides, two of which are bridging, whereas the other silver ion binds to a cyanide as the terminal ligand. In the crystal lattice they are disordered over 2 positions in 50/50 ratio (cf. Fig. S2), but only a single  $^{13}\text{C}$  NMR signal is observed for the cyanide ligand of this compound. The relevant Ag–L distances are given in the figure caption below. There are no close contacts between the cation and the anion in compound **1**. The intramolecular bonds for the PPN cation are uneventful.

A projection of compound **1** is presented in Fig. 2, together with selected geometric details. Other relevant bond lengths and distances are given in the Tables S1 and S2.

Compounds **2** ( $x = 1$ ), **3** ( $x = 1.63$ ) and **4** ( $x = 2$ ) each contain a linear coordinated Ag(I) ion, by cyanide and chloride, albeit over disorder positions for  $x < 2$ . Compounds **2–4** crystallize in the mon-

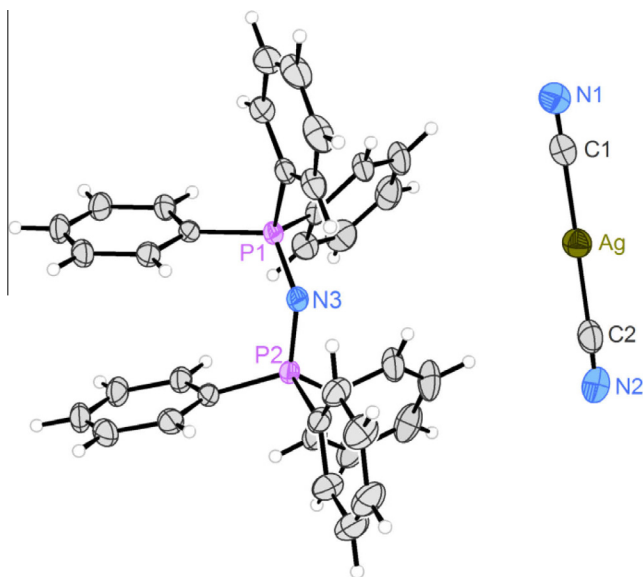
oclinic space group  $P2_1/c$  with very similar lattice constants. The same packing of the  $\text{PPN}^+$  cation and the  $[\text{AgL}_2]^-$  anion is observed with some dichloromethane (**2**, **4**; 0.5 and 0.2 per Ag, resp. from elemental analysis, but refined as 1.0), or 0.5 *n*-hexane (**3**) captured in the crystal lattice (cf. Supporting Information). There are no close contacts between the cation and the anion. A projection of the asymmetric unit displaying the main component of compound **2** is given in Fig. 3, together with selected geometric details. Other relevant bond lengths and distances are given in the SI, Tables S3 and S4. Fig. 4 shows a projection of compound **3**, with relevant details in the caption together with selected geometric details. Other relevant bond lengths and distances are given in Tables S5 and S6.

The structure of the bis(cyanido)argentate compound is presented in Fig. 5. In this case the  $[\text{Ag}(\text{CN})_2]^-$  unit is not disordered and has a linear structure as expected. Selected geometric details are given in the caption. Other relevant bond lengths and distances are given in the Tables S7 and S8.



**Fig. 4.** Projection of cation and anion in compound **3** ( $x = 1.63$ ) with thermal ellipsoid plot at the 50% levels of probability. Only the main component (63% occupancy) of the disordered part is depicted. The partially occupied hexane solvent molecule in the crystal lattice is omitted. Selected bond lengths [Å] and angles [°] for the metal species are: Ag1–C1 2.005(5), Ag1–C2 1.947(7), C1–N1 1.177(5), C2–N2 1.179(8), C1–Ag1–C2 178.6(3).





**Fig. 5.** Projection of cation and anion in compound **4** ( $x = 2$ ) with thermal ellipsoid plot at the 50% levels of probability. The partially occupied disordered dichloromethane solvent molecule in the crystal lattice is omitted. Selected bond lengths [Å] and angles [°] for the metal species are: Ag–C1 2.046(5), Ag–C2 2.059(6), C1–N1 1.133(6), C2–N2 1.063(6), C1–Ag1–C2 179.1(2).

Packing in all compounds appears as uneventful, without significant contacts between cation, anion and solvent. The packing diagrams for the four compounds and the disorder in the anions for compounds **1–4**, are presented in Figs. S1–S7, and the outer coordination spheres with selected contact distances are given in Figs. S8–S11. Careful analyses of the intermolecular contacts cannot explain the fact that only compound **2** shows blue luminescence.

#### 4. Concluding remarks

The results presented above have shown that the chloride ions in AgCl can be gradually replaced by cyanide ligands, thereby generating relatively soluble compounds that can be purified and crystallized. The large bis(triphenylphosphane)iminium counter cation, PPN, remains innocent in the formed compounds and displays no short intermolecular contacts in the solid state. Open spaces in the lattice are filled with  $\text{CH}_2\text{Cl}_2$  or *n*-hexane.

The luminescence differences between the compounds are surprising as only compound **2**, having the Cl/CN ratio 1.0, displays emission, where the other compounds do not, as observed from several samples. Perhaps a quenching in the lattice by the PPN and presence or absence of solvent may play a role, although intermolecular contacts do not show significant packing differences.

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#### Appendix A. Supplementary material

CCDC 1418113–141116 contain the supplementary crystallographic data for compounds **1**, **2**, **3** and **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ica.2015.12.018>.

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