A new class of polymeric complexes having Pt–Ag interactions: Crystal structure of |{[(PPh₃)(C₆F₅)Pt(μ-Cl)]₂Ag}(μ-Cl)₂Ag(MeOH)|ₙ

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ABSTRACT

The reaction of $(NBu_4)[trans\text{-}PtCl_2(C_6F_5)L]$ (L = PPh₃, AsPh₃) with AgClO₄ (1:1) molar ratio in a CH₂Cl₂/MeOH mixture leads to the polymeric complexes $[PtAgCl_2(C_6F_5)L]_n$ (L = PPh₃ **1**, AsPh₃ **2**). The structure of complex $|\{[(PPh_3)(C_6F_5)Pt(\mu\text{-}Cl)]_2Ag\}(\mu\text{-}Cl)_2Ag(MeOH)|_n$ (**1**·MeOH) has been determined by single-crystal X-ray diffraction, showing a chain polymer in which the silver atoms are in two different environments with or without Pt–Ag bond.

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1. Introduction

Polymeric complexes have interested chemists for a long time, not only because of their structural features but also because of the possibility of having novel solid-state properties [1]. Our group has been involved in the synthesis of heteronuclear Pt–Ag complexes, with or without donor–acceptor Pt → Ag bonds, which in some cases have a polymeric nature [2–14]. Our synthetic approach consists on the reaction between an anionic perhalophenylplatinate(II) complex and a silver salt or complex. The nature of the resulting products is dependent on the basicity of the platinum complexes, on the presence and type of potentially bridging ligands, on the formation of metal–metal interactions and on the presence of ortho-X contacts between the silver center and the halogen atoms in ortho position of the pentahalophenyl ligands. It seems that a delicate balance among all these factors, most of them consisting on very weak donor–acceptor interactions, is responsible for the wide variety of stoichiometries and structures found. One of the features that has attracted our attention is the difference found in the products of the reaction of pentachloro- and pentafluoroplatinate(II) derivatives of the same stoichiometry. An interesting example is the case of the complexes $\{(NBu_4)[PtAgCl_2(C_6X_5)]\}_n$, obtained by reacting $(NBu_4)_2[trans\text{-}$

$PtCl_2(C_6X_5)_2]$ with AgClO₄. When X = F, n = 2 and the complex contains Pt–Pt and Ag–Ag bonds along with Pt(μ-Cl)Ag bridges and o-F···Ag contacts (Scheme 1a) [3]; whereas for X = Cl, the resulting neutral complex is a polymer (n = ∞), without Pt–Ag bonds, but with Pt(μ-Cl)Ag bridges and o-Cl···Ag contacts (Scheme 1b) [4]. Several years ago we investigated the reactions of $(NBu_4)[trans\text{-}PtCl_2(C_6Cl_5)L]$ (L = neutral ligand) with AgClO₄, which resulted in the formation of neutral polymers of stoichiometry $\{[PtAgCl_2(C_6Cl_5)L]\}_n$ [11] (see Scheme 2a) and our interest was to compare the structure of these complexes with that of complexes with similar stoichiometry but with pentafluorophenyl ligands. However, the difficulty on synthesizing the adequate starting materials $(NBu_4)[trans\text{-}PtCl_2(C_6F_5)L]$ and latter the difficulty on obtaining suitable crystals of the resulting complexes for an X-ray study prevented to compare the results. Here we report now the synthesis of a new type of polymeric complexes of stoichiometry $\{[PtAg Cl_2(C_6F_5)L]\}_n$ and the structure of $|\{[(PPh_3)(C_6F_5)Pt(\mu\text{-}Cl)]_2Ag\}(\mu\text{-}Cl)_2Ag(MeOH)|_n$ (**1**·MeOH).

2. Results and discussion

2.1. Synthesis and reactivity of [PtAgCl₂(C₆F₅)L] (L = PPh₃ **1**, AsPh₃ **2**)

The reaction between $(NBu_4)[trans\text{-}PtCl_2(C_6F_5)L]$ (L = PPh₃, AsPh₃) [15] and AgClO₄ in CH₂Cl₂ (1:1 molar ratio) proceeds with the formation of a pale yellow solid, which is isolated by filtration. Due to the low solubility of the AgClO₄ in CH₂Cl₂, the reaction needs at least 30 min to completion. This time can be shortened to 10 min when a few ml of MeOH, in which AgClO₄ is more soluble,
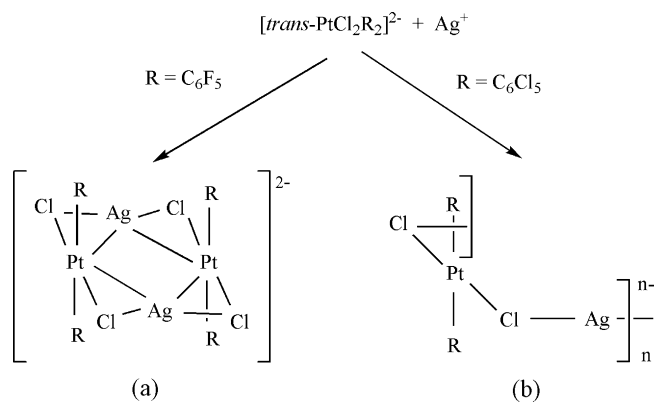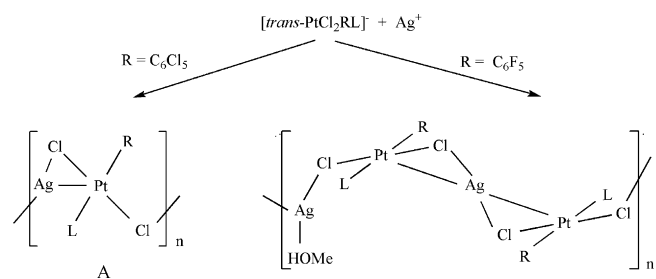
Scheme 1.

Scheme 2.

are added. In any case, the resulting products which are shown in Eq. (1), whose elemental analyses are in agreement with the stoichiometry [PtAgCl$_2$(C$_6$F$_5$)L], are obtained with high purity and good yields. Their insolubility in common organic solvents and therefore NMR spectra or conductivity measurements are not possible. This insolubility made getting suitable crystals for X-ray

diffraction measurements difficult. After many attempts, crystals of complex **1**, which crystallized with a MeOH molecule, were obtained and the determination of the crystal structure showed it to be a polymer, |{[(PPh$_3$)(C$_6$F$_5$)Pt(μ-Cl)]$_2$Ag}(μ-Cl)$_2$Ag(MeOH)|$_n$ (**1**·MeOH). The presence of the methanol molecule, that is absent in the bulk solid, seems to be a determinant factor in obtaining the crystals, as it is bound to the silver atom in the solid state structure.

$$n(NBu_4)[trans\text{-}PtCl_2(C_6F_5)L] + nAgClO_4$$
$$\rightarrow [PtAgCl_2(C_6F_5)L]_n + nNBu_4ClO_4 \qquad (1)$$
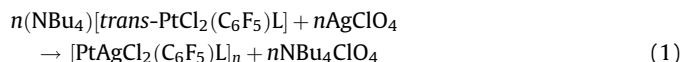
L = PPh$_3$ **1**, AsPh$_3$ **2**.

In spite of its low solubility, **1** reacts with neutral ligands as PPh$_3$ to give soluble species. The cleavage reaction probably proceeds, as for the [PtAgCl$_2$(C$_6$Cl$_5$)L]$_n$ analogous complexes [11], by breaking Ag–Cl bridges and coordination of the PPh$_3$ ligand to give [L(C$_6$F$_5$)ClPt(μ-Cl)Ag(PPh$_3$)]. However, after many attempts we have not been able to obtain a pure product due to further decomposition of the complexes formed to [cis-PtCl(C$_6$F$_5$)(PPh$_3$)L] and AgCl. Even working at low temperature and shortening the reaction times to the strictly needed the decomposition reaction could not be prevented. Another synthetic strategy to obtain complexes [L(C$_6$F$_5$)ClPt(μ-Cl)Ag(PPh$_3$)], consisting on the reaction of (NBu$_4$)[trans-PtCl$_2$(C$_6$F$_5$)(PPh$_3$)] with O$_3$ClOAgL, that gives good results in the case of pentachlorophenyl derivatives [12], also did not result in the desired complex, which shows that the pentafluorophenyl derivatives are often more difficult to prepare and isolate than the pentachlorophenyl analogues.

2.2. Crystal structure of |{[(PPh$_3$)(C$_6$F$_5$)Pt(μ-Cl)]$_2$Ag}(μ-Cl)$_2$Ag(MeOH)|$_n$ (**1**·MeOH)

Fig. 1 shows the structure of the repeating unit of the polymer and Table 1 collects the main distances and angles in the molecule. For clarity we can consider the polymer as formed by trinuclear units containing two platinum and one silver atoms conforming a geometry consisting on two fused square pyramids sharing the apex. These [Pt$_2$Ag] units are bonded though silver atoms forming a
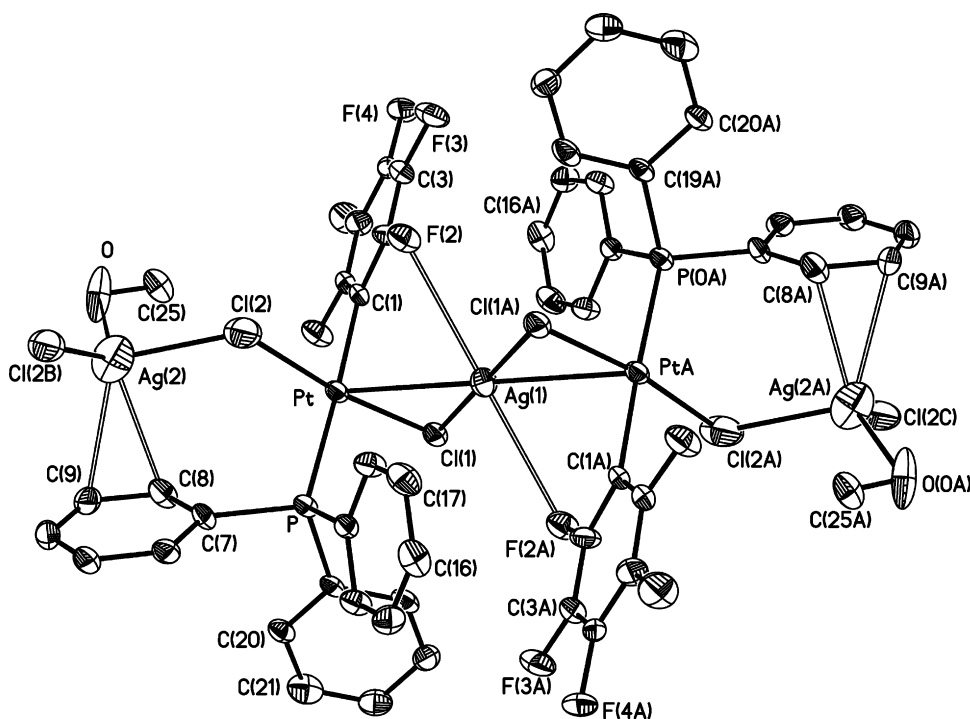

Fig. 1. Structure of the repeating unit of complex **1**·MeOH showing the numbering scheme. Symmetry codes: (A) −x, −y, −z; (B) −x, −y − 1, −z; (C) x, y + 1, z.

Table 1
Selected bond lengths (A) and angles (deg) for |{[(PPh₃)(C₆F₅)Pt (μ-Cl)]₂Ag}(μ-Cl)₂Ag(MeOH)|ₙ (**1**·MeOH).

Pt–C(1)	2.050(10)
Pt–Cl(2)	2.295(4)
Pt–Cl(1)	2.308(3)
Pt–P	2.336(3)
Pt–Ag(1)	2.8770(9)
Ag(1)–Cl(1A)	2.551(3)
Ag(2)–Cl(2)	2.400(6)
Ag(2)–Cl(2B)	2.225(5)
Ag(2)–O	2.422(17)
Ag(2)–C(8)	2.708(13)
Ag(2)–C(9)	2.725(13)
C(1)–Pt–Cl(2)	86.8(3)
C(1)–Pt–Cl(1)	87.3(3)
Cl(2)–Pt–Cl(1)	172.54(12)
C(1)–Pt–P	177.8(3)
Cl(2)–Pt–P	91.60(13)
Cl(1)–Pt–P	94.36(10)
C(1)–Pt–Ag(1)	85.4(3)
Pt(A)–Ag(1)–Pt	180.00(2)
Cl(2A)–Ag(2)–Cl(2)	106.71(17)
Cl(2B)–Ag(2)–C(8)	118.2(3)
Cl(2)–Ag(2)–C(8)	84.7(3)
O–Ag(2)–C(8)	106.0(6)

Symmetry transformations used to generate equivalent atoms: (A) −x, −y, −z; (B) −x, −y − 1, −z.

chain polymer (Fig. 2). All the platinum atoms have the same environment, but there are two types of silver centers: Ag(1), that is bonded to two platinum and two chlorine atoms, and Ag(2), that seems to be not involved in metal–metal bonds. The platinum atom is located at the center of the base of a distorted square pyramid formed by C(1), Cl(1), Cl(2) and P. The distances between Pt and the atoms located in the square plane are within the expected ranges (Table 1) [16]. Ag(1) occupies the apical position of the pyramid, with the Pt–Ag(1) line forming an angle of 10.3° with the perpendicular to the basal plane, showing the distortion in the environment. The Pt–Ag(1) distance of 2.877(1) Å indicates metal–metal interaction. This distance compares well with that found in complex {[PtAgCl₂(C₆Cl₅)L]}ₙ [11] (2.859 Å) and lies in the range of Pt–Ag metal–metal bond distances (2.637 [13] to 3.063 Å [3]). This bond is supported by a bridging chlorine, but the Ag(1)–Cl(1) distance (2.551(3) Å) is long enough to conclude that the metal–metal interaction is an important part of the bond between both metals. Cl(2) is bonded to Ag(2), so Ag(2) links two platinum moieties through bridging chlorine. It is remarkable that the distances Ag(2)–Cl(2) and Ag(2)–Cl(2A) are very different: 2.400(6) and 2.225(5) Å. Ag(2) also coordinates a molecule of methanol, which has been used in the crystallization process. The Ag(2)–O distance of 2.46(2) Å indicates a strong interaction between both atoms [17]. In addition to that, both silver atoms establish weak interactions with other donors in order to satisfy their requirements of electron density. Thus, the pentafluorophenyl ring orientates in a way to allow the o-F atom F(2) interact weakly with Ag(1). Many examples of this situation are known [2]. The angle of the coordination plane of the platinum and that of the C₆F₅ group is 71.8°. Ag(2) does not interact with F atoms, since they are very far away, but interacts with one of the phenyl rings of the PPh₃

ligand. This interaction takes place through a double bond of the phenyl ring, being the Ag(2)–C(8) and Ag(2)–C(9) distances of 2.708(13) and 2.725(13) Å, respectively. Although this interaction is significant, the C(8)–C(9) distance of 1.373(16) Å does not seem to be affected. The presence of all these interactions shows that the total balance of electron density for each atom is reached through a delicate equilibrium between donors and acceptors in which many atoms are involved.

2.3. Comparison of the structure of |{[(PPh₃)(C₆F₅)Pt(μ-Cl)]₂Ag}(μ-Cl)₂Ag(MeOH)|ₙ (**1**·MeOH) with that of [PtAgCl₂(C₆Cl₅)PPh₃]ₙ (**A**)

In spite of both complexes having a rather similar stoichiometry (except for the MeOH molecule), their structures show some important differences. The first difference is that in complex **A** there is only one type of silver center, whereas in complex **1** there are two types of silver center: one is bonded to a platinum atom and the other one is not. The repeat units in **A** are formed by the square-planar [trans-PtCl₂(C₆Cl₅)PPh₃]⁻ fragment and a silver center, and the polymeric chain is the result of the propagation of this fragment by the a glide plane, with the silver atoms connecting each two of these units though chloride bridges, one of them additional to a Pt–Ag interaction. The silver atom receives electron density from the platinum center, from the two bridging chlorides and from one of the Cl atoms in ortho position of the C₆Cl₅ group. In complex **1**, the repeat units consist on [PPh₃(C₆F₅) ClPt(μ-Cl)Ag(μ-Cl)PtClC(C₆F₅)PPh₃]⁻ fragments in which the bridging chlorines are supporting Pt–Ag(1) bonds. These fragments are linked by another Ag atom –Ag(2)– through Ag–Cl bonds. Ag(1) is bonded to two platinum atoms by two Pt–Ag bonds supported by bridging Cl and also to two o-F atoms, each from a C₆F₅ group. By contrast, Ag(2) is bonded to two chlorine atoms and a MeOH molecule, and also receives electron density from a phenyl ring of the PPh₃ ligand. The silver atom in **A** is located in a distorted tetrahedral environment and in **1** is located in a octahedral environment with two additional interactions consisting on a Pt–Ag bond and a o-F···Ag contact. Since in both molecules the Pt–Ag distance is similar (2.859 and 2.877 Å), and so are the distances Pt–Cl and Ag–Cl in the fragments, the most significant difference in the environment of Ag(1) is the strength of the o-X···Ag interaction: in **A** is strong, while in **1** is weak, with values of ρ = 1.22 and 1.44, respectively (ρ = distance/sum of covalent radii). The other silver atom in complex **1**, Ag(2), has a tetrahedral environment and is significant the short Ag(2)–Cl(2) distance of 2.225(5) Å as compared with the other Ag–Cl distances.

Finally, the presence of MeOH coordinated to one of the silver centers seems also to play an important structural role in the structure of the complex.

3. Experimental

The C, H and N analyses were carried out with a Perkin-Elmer 240-B microanalyzer. IR spectra were recorded on a Perkin-Elmer 833 spectrophotometer (4000–200 cm⁻¹) using Nujol mulls between polyethylene sheets. The complexes (NBu₄)[trans-PtCl₂(C₆F₅)L] [15] (L = PPh₃, AsPh₃) and O₃ClOAgL (L = PPh₃ [13],
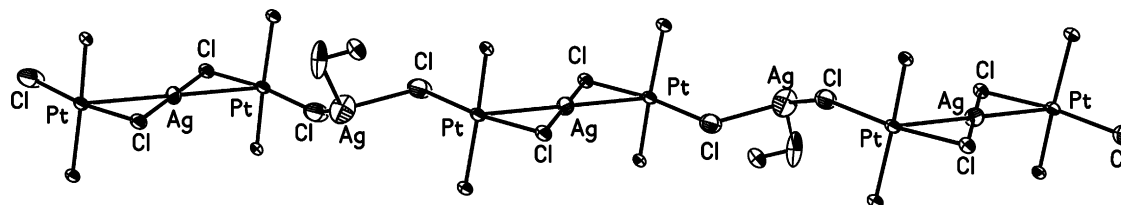

Fig. 2. Schematic view of the polymer.

Table 2
Crystal data and structure refinement parameters for $|\{[(PPh_3)(C_6F_5)Pt(\mu\text{-}Cl)]_2Ag\}(\mu\text{-}Cl)_2Ag(MeOH)|_n$ (**1**·MeOH).

Empirical formula	$C_{24.5}H_{17}AgCl_2F_5OPPt$	
Formula weight	819.21	
Temperature	200(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	$a = 9.020(3)$ Å	$\alpha = 112.08(2)°$
	$b = 12.163(3)$ Å	$\beta = 93.06(3)°$
	$c = 12.439(4)$ Å	$\gamma = 91.78(2)°$
Volume	1260.9(7) Å^3	
Z	2	
Density (calculated)	2.158 mg/m^3	
Absorption coefficient	6.645 mm^{-1}	
$F(0\,0\,0)$	774	
Crystal size	0.20 mm × 0.15 mm × 0.08 mm	
Theta range for data collection	2.26–25.01°	
Index ranges	$-10 \leq h \leq 10$, $-14 \leq k \leq 13$, $-11 \leq l \leq 14$	
Reflections collected	7274	
Independent reflections	4436 [$R(\text{int}) = 0.0526$]	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	4436/6/331	
Goodness-of-fit on F^2	1.011	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0499$, $wR2 = 0.1135$	
R indices (all data)	$R1 = 0.0795$, $wR2 = 0.1223$	
Largest diff. peak and hole	1.429 and -1.636 e Å^{-3}	

$R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR2 = \left[\Sigma w(F_o^2 - F_c^2)/\Sigma wF_o^2\right]^{1/2}$; goodness-of-fit $= \left[\Sigma w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})\right]$; $w = [\sigma^2(F_o) + (g_1P)^2 + g_2P]^{-1}$; $P = \left[\max(F_o^2; 0 + 2F_c^2)\right]/3$.

SC$_4$H$_8$ [18]) were prepared as described elsewhere. Other reagents and solvents were commercial and used without further treatment. All reactions were carried out at room temperature with exclusion of light.

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with great caution only in small quantities.

3.1. Preparation of polynuclear complexes [PtAgCl$_2$(C$_6$F$_5$)L]$_n$ (L = PPh$_3$ **1**, AsPh$_3$ **2**)

To a solution of (NBu$_4$)[*trans*-PtCl$_2$(C$_6$F$_5$)PPh$_3$] (0.137 g, 0.14 mmol) in 20 mL of CH$_2$Cl$_2$ was added an equimolecular amount of AgClO$_4$ (0.03 g, 0.14 mmol). Immediately, a pale yellow solid formed. After 30 min of reaction (if AgClO$_4$ is dissolved in 10 ml of MeOH the reaction time can be shortened to 10 min) the solid was filtered off, washed with CH$_2$Cl$_2$, ^{i}PrOH and *n*-hexane and air dried. Yield: 72%. Anal. Calc. for C$_{24}$H$_{15}$AgCl$_2$F$_5$PPt: C, 35.88; H, 1.87. Found: C, 35.31; H, 1.59. IR (cm^{-1}): ν(C$_6$F$_5$)$_{X\text{-sensitive}}$ 789 (m) [19], ν(Pt–Cl) 336 (m).

Complex **2** was prepared similarly. Reagents: 0.10 g (0.10 mmol) of (NBu$_4$)[*trans*-PtCl$_2$(C$_6$F$_5$)AsPh$_3$] and 0.021 g (0.10 mmol) of AgClO$_4$. Yield: 73%. Anal. Calc. for C$_{24}$H$_{15}$AgAsCl$_2$F$_5$Pt: C, 34.03; H, 1.77. Found: C, 33.77; H, 1.86. IR (cm^{-1}): ν(C$_6$F$_5$)$_{X\text{-sensitive}}$ 793 (m) [19], ν(Pt–Cl) 326 (m, sh).

3.2. Preparation of crystals of $|\{[(PPh_3)(C_6F_5)Pt(\mu\text{-}Cl)]_2Ag\}(\mu\text{-}Cl)_2Ag(MeOH)|_n$ (**1**·MeOH)

Crystals of **1**·MeOH were obtained by slow diffusion of a methanol solution of AgClO$_4$ into a CH$_2$Cl$_2$ solution of (NBu$_4$)[*trans*-PtCl$_2$(C$_6$F$_5$)PPh$_3$] in equimolecular quantity at -18 °C.

3.3. X-ray structure analysis of $|\{[(PPh_3)(C_6F_5)Pt(\mu\text{-}Cl)]_2Ag\}(\mu\text{-}Cl)_2Ag(MeOH)|_n$ (**1**·MeOH)

A pale yellow plate-shaped crystal was fixed with epoxy on top of a glass fiber and transferred to the cold stream of the low temperature device of an automated four circle diffractometer Siemens STOE/AED2 (Table 2). Data were collected at 200 K by the omega/2 theta method. Cell constants were calculated from 46 well centered reflections with 2θ angles over 20°. Three check reflections measured every 360 min showed no loss of intensity at the end of data collection. An empirical absorption correction based on psi scans (13 reflections) was applied (maximum and minimum transmission factors = 1.000, 0.608). The structure was solved by the Patterson method. All non-hydrogen atoms were located in succeeding difference Fourier syntheses and refined with anisotropic thermal parameters. Hydrogen atoms were added at calculated positions and assigned isotropic displacement parameters equal to 1.2 times the U_{iso} value of their respective parent carbon atoms. There are two sites occupied by silver atoms, each refined at half occupancy, one of them is a center of symmetry –Ag(1)– and the other is a general position –Ag(2)–. By symmetry, Ag(2) generates another silver atom Ag(2A) very close to the former, so it is clear that in the crystal both atoms will occupy alternate positions at full occupancy. The maximum peak in the final map is 1.58 e Å^{-3}, located close to the heavy atoms and without any chemical meaning. All calculations were carried out using the program SHELXL-97 [20].

Supporting information

Crystallographic data (excluding structure factors) for the structure of **1**·MeOH have been deposited with the Cambridge Crystallographic Data Center, CCDC number 768259. Copies of this information may be obtained on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

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