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# Synthesis and Reactivity of a New Class of Neutral Polymeric Complexes $[PtAgX_2(C_6Cl_5)L]_x$. Crystal Structure of $[PtAgCl_2(C_6Cl_5)PPh_3]_x \cdot 1.5xCH_2Cl_2$

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Reacting $(NBu_4)[$*trans*-$PtX_2(C_6Cl_5)L]$ (X = Cl, L = $PPh_3$, $SC_4H_8$, *p*-$MeC_6H_4NH_2$, $NC_5H_5$; X = Br, L = $PPh_3$) with $AgClO_4$ in 1:1 molar ratio leads to the polymeric complexes $[PtAgX_2(C_6Cl_5)L]_x$ (X = Cl, L = $PPh_3$ (**1**), $SC_4H_8$ (**2**), *p*-$MeC_6H_4NH_2$ (**3**), $NC_5H_5$ (**4**); X = Br, L = $PPh_3$ (**5**)). The structure of complex **1** has been solved by single-crystal X-ray diffraction. The compound crystallizes in the orthorhombic system, space group *Pna*$2_1$ with $a = 10.327(3)$ Å, $b = 18.094(6)$ Å, $c = 18.451(5)$ Å, $V = 3447.69$ Å$^3$, and $Z = 4$. The structure was refined to residuals of $R = 0.0414$ and $R_w = 0.0492$. Each repeat unit is formed by the interaction of the square planar fragment $[$*trans*-$PtCl_2(C_6Cl_5)PPh_3]^-$ with $Ag^+$ via a Pt–Ag bond (Pt–Ag = 2.855(2) Å) which is supported by a $\overline{\mathrm{Pt}(\mu\text{-Cl}(2))\mathrm{Ag}}$ bridge. These units are connected by a Pt($\mu$-Cl(1))Ag bridging system, resulting in the formation of the polymer. The silver atom also makes a short contact with one *o*-Cl atom of the $C_6Cl_5$ group (*o*-Cl···Ag = 2.838(6) Å). Complex **1** reacts with $PPh_3$ (1:1) to give $[PPh_3(C_6Cl_5)ClPt(\mu\text{-}Cl)AgPPh_3]$, but the reaction with $SC_4H_8$ results in the elimination of AgCl and formation of $[PtCl(C_6Cl_5)PPh_3(SC_4H_8)]$.

## Introduction

A well-documented procedure for the syntheses of polynuclear complexes often displaying donor–acceptor Pt→Ag bonds consists of the reaction between an anionic (perhalophenyl)platinate(II) complex and a silver salt ($AgClO_4$, $AgNO_3$) or complex ($O_3ClOAgL$, L = $PPh_3$, $SC_4H_8$).[1] The formation and the strength of the Pt→Ag bonds are strongly dependent on the basic character of the platinate substrata and on the presence or absence of other potentially bridging ligands (X) in the coordination sphere of the platinum center, since the formation of a Pt($\mu$-X)Ag bridging system can weaken, or even prevent, the formation of the Pt→Ag bonds. Moreover, other apparently secondary factors seem to be of decisive importance for the stability and the final structure of the isolable complex. For instance, reacting the platinate complexes $(NBu_4)_2[$*trans*-$PtCl_2(C_6X_5)_2]$ (X = F, Cl) with $AgClO_4$ or $AgNO_3$ leads to heteronuclear complexes of the overall stoichiometry $\{(NBu_4)[PtAgCl_2(C_6X_5)_2]\}_n$. When X = $C_6F_5$, then $n = 2$ and the resulting tetranuclear complex $(NBu_4)_2[Pt_2Ag_2Cl_4(C_6X_5)_4]$ contains Pt–Ag, Pt($\mu$-Cl)Ag, and Ag–Ag bonds, along with four *o*-F···Ag short contacts (two to each Ag atom),[2] while for X = Cl the polymeric $\{(NBu_4)[Pt(C_6Cl_5)_2(\mu\text{-}Cl)_2Ag]\}_x$ (A) displays no metal–metal bond but Pt($\mu$-Cl)Ag bridges and four additional *o*-Cl···Ag contacts.[3] Therefore, the presence, number, and nature of these *o*-X···Ag contacts seem to determine the outcome of the reaction. These and other results in this field were recently reviewed.[1]

Here we present the results of the reactions between $(NBu_4)[$*trans*-$PtX_2(C_6Cl_5)L]$ (X = Cl, L = $PPh_3$, $SC_4H_8$, *p*-$MeC_6H_4NH_2$, $NC_5H_5$; X = Br, L = $PPh_3$) and $AgClO_4$ (or $AgNO_3$) which afford a new type of polymeric complex characterized by the presence of $\overline{\mathrm{Pt}(\mu\text{-Cl}(2))\mathrm{Ag}}$ units interconnected by Pt($\mu$-Cl(1))Ag bridges. The reactivity of the polynuclear complexes with different neutral ligands ($PPh_3$, $SC_4H_8$, or *p*-$MeC_6H_4NH_2$) has also been studied, and the results are reported.

## Experimental Section

The C, H, N, and S analyses were carried out with Perkin-Elmer 240-B and 2400 microanalyzers. Chlorine analyses were performed as described by White,[4] a few milligrams of sucrose being added to facilitate combustion.[5] IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer (4000–200 cm$^{-1}$) using Nujol mulls between polyethylene sheets. The complexes $(NBu_4)[$*trans*-$PtX_2(C_6Cl_5)L]$ (X = Cl, L = $PPh_3$, $SC_4H_8$, *p*-$MeC_6H_4NH_2$, $NC_5H_5$; X = Br, L = $PPh_3$) were prepared by literature methods.[6] $O_3ClOAg(SC_4H_8)$ was prepared as described elsewhere.[7] All reactions were carried out at room temperature with exclusion of light.

**Safety Note.** Perchlorate salts are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

**(a) Preparation of the Polynuclear Complexes $[PtAgX_2(C_6Cl_5)L]_x$ (X = Cl, L = $PPh_3$ (1), $SC_4H_8$ (2), *p*-$MeC_6H_4NH_2$ (3), $NC_5H_5$ (4); X = Br, L = $PPh_3$(5)). (i) $[PtAgCl_2(C_6Cl_5)PPh_3]_x$ (1).** To a solution of $(NBu_4)[$*trans*-$PtCl_2(C_6Cl_5)PPh_3]$ (0.100 g, 0.098 mmol) in 10 mL of MeOH was added an equimolecular amount of $AgClO_4$ (0.020 g, 0.098 mmol). Immediately a pale yellow solid formed. After 15 min of reaction, the solid was filtered off, washed with MeOH, $^i$PrOH, and *n*-hexane, and air-dried. Yield: 81%. Anal. Calc for $PtAgCl_7PC_{24}H_{15}$: C, 32.55; H, 1.69; Cl, 28.03. Found: C, 32.21; H, 1.57; Cl, 27.51. The use of $AgNO_3$ instead of $AgClO_4$ gave analogous results.

Complexes **2–5** were similarly prepared.

**(ii) $[PtAgCl_2(C_6Cl_5)(SC_4H_8)]_x$ (2).** Reactants: 0.200 g (0.236 mmol) of $(NBu_4)[$*trans*-$PtCl_2(C_6Cl_5)(SC_4H_8)]$; 0.049 g (0.236 mmol) of $AgClO_4$. Yield: 90%. Anal. Calc for $PtAgCl_7SC_{10}H_8$: C, 16.88; H, 1.12; Cl, 34.89. Found: C, 16.56; H, 1.04; Cl, 35.38.

**(iii) $[PtAgCl_2(C_6Cl_5)(p\text{-}MeC_6H_4NH_2)]_x$ (3).** Reactants: 0.200 g (0.231 mmol) of $(NBu_4)[$*trans*-$PtCl_2(C_6Cl_5)($*p*-$MeC_6H_4NH_2)]$; 0.048 g (0.231 mmol) of $AgClO_4$. Yield: 89%. Anal. Calc for $PtAgCl_7NC_{13}H_9$: C, 21.38; H, 1.23; N, 1.92; Cl, 33.98. Found: C, 21.31; H, 1.22; N, 1.90; Cl, 34.42.

**(iv) $[PtAgCl_2(C_6Cl_5)(NC_5H_5)]_x$ (4).** Reactants: 0.10 g (0.119 mmol) of $(NBu_4)[$*trans*-$PtCl_2(C_6Cl_5)(NC_5H_5)]$; 0.025 g (0.119 mmol) of $AgClO_4$. Yield: 88%. Anal. Calc for $PtAgCl_7NC_{11}H_5$: C, 18.81; H, 0.71; N, 1.99; Cl, 35.34. Found: C, 19.11; H, 0.67; N, 2.05; Cl, 34.84.

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**Table 1.** Crystallographic Data for $[PtAgCl_2(C_6Cl_5)PPh_3]_x \cdot 1.5xCH_2Cl_2$ (**1**)

| | | | |
|---|---|---|---|
| chem formula | $PtAgCl_7PC_{24}H_{15} \cdot 1.5CH_2Cl_2$ | $Z$ | 4 |
| fw | 1012.81 | $d_{calc}$, g cm$^{-3}$ | 1.948 |
| space group | $Pna2_1$ (No. 33) | $\mu$(Mo K$\alpha$), mm$^{-1}$ | 5.46 |
| $a$, Å | 10.327(3) | $T$, °C | $-73 \pm 1$ |
| $b$, Å | 18.094(6) | $R^a$ | 0.0414 |
| $c$, Å | 18.451(5) | $R_w{}^b$ | 0.0492 |
| $V$, Å$^3$ | 3447.69 | | |

$^a$ $R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b$ $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. $^c$ $w^{-1} = [\sigma^2(|F_o|) + 0.0014|F_o|^2]$.

**(v) $[PtAgBr_2(C_6Cl_5)PPh_3]_x$ (5).** Reactants: 0.100 g (0.09 mmol) of $(NBu_4)[$*trans*-$PtBr_2(C_6Cl_5)PPh_3]$; 0.019 g (0.09 mmol) of $AgClO_4$. Yield: 80%. Anal. Calc for $PtAgBr_2Cl_5PC_{24}H_{15}$: C, 29.63; H, 1.54. Found: C, 29.38; H, 1.60.

**(b) Reaction of $[PtAgX_2(C_6Cl_5)PPh_3]_x$ (X = Cl (1), Br (5)) with $PPh_3$. (i) X = Cl.** To a suspension of $[PtAgCl_2(C_6Cl_5)PPh_3]_x$ (**1**) (0.036 g, 0.041 mmol) in 10 mL of $CH_2Cl_2$ was added 0.011 g (0.041 mmol) of $PPh_3$. The solid was immediately dissolved, and after 30 min of stirring, the solution was evaporated to dryness. The residue was treated with $^iPrOH$ to give a pale yellow solid identified as $[PPh_3(C_6Cl_5)ClPt(\mu\text{-}Cl)AgPPh_3]$ (**6**).[8] Yield: 77%.

**(ii) X = Br.** Similarly, 0.041 g (0.0421 mmol) of $[PtAgBr_2(C_6Cl_5)PPh_3]_x$ (**5**) was reacted with 0.011 g (0.0421 mmol) of $PPh_3$ to give $[PPh_3(C_6Cl_5)BrPt(\mu\text{-}Br)AgPPh_3]$ (**7**)[9] in 86% yield.

**(c) Reaction of $[PtAgCl_2(C_6Cl_5)PPh_3]_x$ (1) with $SC_4H_8$ (1:1).** To a suspension of $[PtAgCl_2(C_6Cl_5)PPh_3]_x$ (**1**) (0.080 g, 0.09 mmol) in $CH_2Cl_2$ (10 mL) was added an equimolecular quantity of $SC_4H_8$ (8 μL, 0.090 mmol). The complete disappearance of the solid to form a clear solution was immediately followed by the precipitation of a white solid, which was filtered off and dissolved again in acetone to separate a small insoluble fraction (AgCl). The solution was evaporated to dryness and the residue treated with $^iPrOH$ to render the neutral complex $[Pt(C_6Cl_5)ClPPh_3(SC_4H_8)]$ (**8**). Yield: 63%. Anal. Calc for $PtCl_6SPC_{28}H_{23}$: C, 40.50; H, 2.77; S, 3.85. Found: C, 40.15; H, 2.92; S, 3.64.

**(d) Reaction of $(NBu_4)[$*trans*-$PtCl_2(C_6Cl_5)PPh_3]$ (1) with $O_3ClOAg(SC_4H_8)$.** A 0.100-g (0.098-mmol) sample of $(NBu_4)[$*trans*-$PtCl_2(C_6Cl_5)PPh_3]$ was reacted with 0.029 g (0.098 mmol) of $O_3ClOAg(SC_4H_8)$ in 10 mL of $CH_2Cl_2$. After 30 min, the yellow solid that formed was filtered off, washed with $CH_2Cl_2$, and air-dried. The solid was identified as $[PPh_3(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(SC_4H_8)]$ (**9**). Yield: 62%. Anal. Calc for $PtAgCl_7SPC_{28}H_{23}$: C, 34.52; H, 2.36; S, 3.28. Found: C, 34.20; H, 2.27; S, 2.96.

**(e) X-ray Structure Analysis of $[PtAgCl_2(C_6Cl_5)PPh_3]_x \cdot 1.5xCH_2Cl_2$ (1).** Crystals of the title complex were obtained by slow diffusion (ca. 2 weeks at −30 °C) of a MeOH solution of $AgClO_4$ into a $CH_2Cl_2$ solution of $(NBu_4)[$*trans*-$PtCl_2(C_6Cl_5)PPh_3]$ in a molar ratio of 1:1.

A yellow crystal (approximate dimensions 0.30 × 0.27 × 0.38 mm$^3$) was mounted on a Siemens/STOE AED2 four-circle diffractometer. Graphite-monochromated Mo K$\alpha$ ($\lambda$ = 0.710 73 Å) radiation was used. The extremely rapid loss of solvent of the crystal at room temperature was reduced by protecting it with cold lithium grease and operating at low temperature (200 K). However, the crystal probably had already lost a part of the interstitial solvent during the mounting procedure, leading to the high background observed in the reflections. Accurate lattice parameters were determined by measuring the center of 29 typical reflections with $20° < 2\theta < 30°$, including Friedel pairs. The crystal data are summarized in Table 1. The intensity data ($+h,+k,+l$) were collected by the $\omega$–$\theta$ scan technique. Three check reflections were measured every 90 min, and an average 7% loss of intensity was observed during the data collection time. Interpolative decay corrections were applied. Data reduction included an absorption correction ($\Psi$-scan method, 10 reflections). Maximum and minimum transmission factors were 0.893 and 0.750, respectively. No extinction correction was applied.

The positions of the platinum and silver atoms were determined from the Patterson map. The remaining atoms were located in successive Fourier syntheses. In spite of the poor quality of the data, all non-hydrogen atoms but two C atoms—C(7) and C(21)—were refined with anisotropic temperature factors. H atoms were fixed at calculated positions through the use of a riding model in which the C–H distance was fixed at 0.96 Å with the common isotropic factor refining at 0.050(17) Å$^2$.

Two sites in the crystallographic asymmetric unit were found to be occupied by disordered $CH_2Cl_2$ moieties. There is a molecule of $CH_2Cl_2$ at one of the sites with one of the Cl atoms disordered over two atomic sites—Cl(9) and Cl(9′)—with occupancies of 0.75 and 0.25, respectively, while the other atoms—C(25) and Cl(8)—have full occupancies. At the second site, there are two $CH_2Cl_2$ molecules—C(26), Cl(10), Cl(11) and C(27), Cl(12) Cl(13)—each one with an occupancy of 0.25. A common displacement parameter was given for the atoms of the molecule formed by C(27), Cl(12), and Cl(13). Since there was no convergence of the refinement due to the $CH_2Cl_2$ solvent in the second site, the variables corresponding to the two molecules of $CH_2Cl_2$—C(26), Cl(10), Cl(11) and C(27), Cl(12) Cl(13)—were not allowed to refine in the final cycles and then the convergence was satisfactory. Loose geometrical restraints were applied to the C–Cl and Cl···Cl distances, and no hydrogen atoms of the solvent molecules were located. The highest peak on the final difference Fourier map corresponds to 1.14 e/Å$^3$, and it is located in the solvent area, very close to one of the disordered $CH_2Cl_2$ molecules.

The final $R$ factors for the correct enantiomorph are $R$ = 0.0414 and $R_w$ = 0.0492 (vs $R$ = 0.0518 and $R_w$ = 0.0632 for the other enantiomorph). A total of 2201 data with $F > 5\sigma(F_o)$ were used to refine 314 parameters.

The calculations were performed on a Local Area VAX cluster (VAX/VMS V5.5) with the Siemens SHELXTL PLUS software package.[10]

## Results and Discussion

**(a) Reaction of $(NBu_4)[$*trans*-$PtX_2(C_6Cl_5)L]$ with $AgClO_4$ (1:1).** The 1:1 reaction between $(NBu_4)[$*trans*-$PtX_2(C_6Cl_5)L]$ and $AgClO_4$ in MeOH proceeds with the rapid formation of a pale yellow solid, which is isolated by filtration. When $AgNO_3$ is used, instead of $AgClO_4$, the same complexes and similar yields are obtained. The process is shown in eq 1.

$$x(NBu_4)[\textit{trans}\text{-}PtX_2(C_6Cl_5)L] + xAgClO_4 \rightarrow [PtAgX_2(C_6Cl_5)L]_x + x(NBu_4)ClO_4 \quad (1)$$

$$X = Cl,\ L = PPh_3\ (\mathbf{1}),\ SC_4H_8\ (\mathbf{2}),$$
$$p\text{-}MeC_6H_4NH_2\ (\mathbf{3}),\ NC_5H_5\ (\mathbf{4})$$

$$X = Br,\ L = PPh_3\ (\mathbf{5})$$

The complexes, obtained in very good yield (>80%), have been characterized on the basis of their microelemental analyses (C, H, N, and Cl) and IR spectra. In the case of $[PtAgCl_2(C_6Cl_5)PPh_3]_x$ (**1**), a single-crystal X-ray diffraction study reveals its polymeric structure. Because of the similarity of all the complexes, we assume that all of them display similar structures. The insolubility of these complexes has precluded any conductivity or molecular weight measurements. Significant IR absorptions are collected in Table 2. All of them show a single absorption due to the X-sensitive mode of the $C_6Cl_5$ ligand and one absorption assignable to $\nu$(M–C), as expected for complexes of this type with only one $C_6Cl_5$ group.[11] In spite of the presence of two different types of bridging chloride ligands (see structure of **1**), the complexes show only one absorption in the $\nu$(M–Cl) region. The complexes also display characteristic absorptions due to the ligand L present in each one.[12]

**(b) Crystal Structure of $[PtAgCl_2(C_6Cl_5)PPh_3]_x \cdot 1.5xCH_2Cl_2$ (1).** Fractional atomic coordinates and selected bond distances and angles for $[PtAgCl_2(C_6Cl_5)PPh_3]_x \cdot 1.5xCH_2Cl_2$ (**1**) are given in Tables 3 and 4, respectively. The polymeric scheme of the structure is shown in Figure 1.

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**Table 2.** Significant IR Absorptions ($cm^{-1}$) for Complexes **1–5**, **8**, and **9**

| | $C_6Cl_5$[12] | | | | |
|---|---|---|---|---|---|
| | X-sensitive[11] | $\nu$(Pt–C) | other | $\nu$(Pt–Cl) | L |
| $[PtAgCl_2(C_6Cl_5)(PPh_3)]_x$ (**1**) | 838 (m) | 618 (m) | 1327 (s), 1315 (s), 1289 (s), 1225 (m), 670 (s) | 324 (s) | 1099 (vs), 745 (vs), 694 (vs), 533 (s), 512 (s), 495 (s) |
| $[PtAgCl_2(C_6Cl_5)(SC_4H_8)]_x$ (**2**) | 847 (w) | 636 (s) | 1332 (s), 1320 (s), 1292 (s, sh) | 298 (m) | |
| $[PtAgCl_2(C_6Cl_5)(p\text{-}MeC_6H_4NH_2)]_x$ (**3**) | 850 (m) | 633 (s) | 1340 (s), 1322 (s), 1297 (s, sh), 1230 (m), 670 (s) | 320 (s) | 3295 (s), 3240 (s), 1602 (vs), 1571 (s), 1510 (s), 1115 (s), 818 (s), 682 (s), 540 (m) |
| $[PtAgCl_2(C_6Cl_5)(NC_5H_5)]_x$ (**4**) | 846 (m) | 631 (m) | 1338 (s), 1319 (s), 1307 (s), 1295 (s), 1223 (s), 674 (s) | 328 (s) | 1609 (s), 1092 (vs), 1068 (s), 753 (s), 691 (s), 648 (s) |
| $[PtAgBr_2(C_6Cl_5)(PPh_3)]_x$ (**5**) | 838 (m) | 618 (m) | 1330 (s), 1318 (s), 1290 (s), 1225 (m), 670 (s) | | 1098 (s), 742 (s, sh), 694 (s, sh), 530 (s), 511 (s), 493 (s) |
| $[PtCl(C_6Cl_5)PPh_3(SC_4H_8)]$ (**8**) | 838 (m) | 619 (m) | 1331 (s), 1320 (s), 1295 (s), 1225 (m), 670 (s) | 323 (s) | 1096 (s), 752 (s), 744 (s), 705 (s), 695 (s), 534 (s), 516 (s), 498 (s) |
| $[(PPh_3)(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(SC_4H_8)]$ (**9**) | 838 (w) | 618 (w) | 1331 (s), 1319 (s), 1294 (s), 1229 (m), 669 (s) | 342 (m), 315 (m) | 1100 (s), 755 (s), 705 (s), 695 (s), 536 (s), 512 (s), 498 (m) |

**Table 3.** Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for $[PtAgCl_2(C_6Cl_5)PPh_3]_x \cdot 1.5xCH_2Cl_2$

| | *x* | *y* | *z* | *U*(eq)[a] |
|---|---|---|---|---|
| Pt(1) | 544(1) | 1409(1) | 0 | 29(1) |
| Ag(1) | 2679(2) | 2398(1) | −159(1) | 52(1) |
| Cl(1) | −1296(4) | 1701(3) | 657(3) | 35(2) |
| Cl(2) | 2299(5) | 1129(3) | −729(3) | 40(2) |
| Cl(3) | 626(5) | 3058(3) | −950(3) | 44(2) |
| Cl(4) | −703(6) | 3297(3) | −2428(3) | 55(2) |
| Cl(5) | −2376(7) | 2060(4) | −3121(3) | 64(2) |
| Cl(6) | −2858(6) | 592(3) | −2281(3) | 47(2) |
| Cl(7) | −1512(6) | 323(3) | −805(3) | 50(2) |
| P(1) | 1549(5) | 1031(3) | 1061(3) | 31(2) |
| C(1) | −414(17) | 1687(12) | −955(10) | 33(6) |
| C(2) | −311(18) | 2337(10) | −1321(10) | 32(6) |
| C(3) | −907(19) | 2481(12) | −2001(12) | 42(7) |
| C(4) | −1650(21) | 1937(11) | −2287(10) | 37(7) |
| C(5) | −1839(18) | 1252(11) | −1923(10) | 32(6) |
| C(6) | −1245(20) | 1150(10) | −1253(11) | 35(7) |
| C(7) | 1902(17) | 1772(10) | 1693(10) | 28(4) |
| C(8) | 1270(25) | 2419(11) | 1678(12) | 48(8) |
| C(9) | 1585(24) | 2986(12) | 2154(17) | 64(10) |
| C(10) | 2489(26) | 2869(16) | 2688(16) | 68(11) |
| C(11) | 3068(29) | 2216(17) | 2752(15) | 81(12) |
| C(12) | 2798(28) | 1656(13) | 2257(17) | 72(11) |
| C(13) | 477(21) | 382(10) | 1532(12) | 40(7) |
| C(14) | −33(22) | −181(12) | 1131(15) | 50(8) |
| C(15) | −834(22) | −719(13) | 1490(15) | 57(9) |
| C(16) | −1078(26) | −571(18) | 2254(18) | 77(12) |
| C(17) | −603(29) | 9(16) | 2631(14) | 69(10) |
| C(18) | 160(20) | 494(10) | 2261(12) | 35(7) |
| C(19) | 3123(18) | 556(10) | 960(12) | 37(7) |
| C(20) | 4182(16) | 993(11) | 828(14) | 46(8) |
| C(21) | 5414(22) | 689(12) | 757(12) | 46(5) |
| C(22) | 5519(24) | −42(15) | 776(13) | 62(9) |
| C(23) | 4476(27) | −501(15) | 923(14) | 62(10) |
| C(24) | 3281(24) | −203(11) | 972(13) | 50(8) |
| C(25) | −5391(36) | −271(21) | −1099(22) | 98(13) |
| Cl(8) | −5906(9) | −251(5) | −1965(5) | 96(3) |
| Cl(9) | −4408(14) | −1023(8) | −904(8) | 112(4) |
| Cl(9′) | −5498(47) | −1251(26) | −812(27) | 127(14) |
| C(26) | −1408(43) | −1597(41) | −401(52) | 67(31) |
| Cl(10) | −1702(44) | −2374(26) | 160(30) | 154(20) |
| Cl(11) | 239(44) | −1559(25) | −668(25) | 120(15) |
| C(27) | −855(89) | −1583(79) | −980(45) | 135(11) |
| Cl(12) | −1733(39) | −1971(28) | −122(30) | 135(11) |
| Cl(13) | 800(42) | −1353(29) | −543(29) | 135(11) |

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

**Table 4.** Selected Bond Lengths (Å) and Angles (deg) for $[PtAgCl_2(C_6Cl_5)PPh_3]_x \cdot 1.5xCH_2Cl_2$

| | | | |
|---|---|---|---|
| Pt(1)–Ag(1) | 2.855(2) | Pt(1)–Cl(1) | 2.315(5) |
| Pt(1)–Cl(2) | 2.313(5) | Pt(1)–P(1) | 2.319(5) |
| Pt(1)–C(1) | 2.083(19) | Ag(1)–Cl(2) | 2.556(6) |
| Ag(1)–Cl(3) | 2.838(6) | Cl(1)–Ag(1A)[a] | 2.458(5) |
| P(1)–C(7) | 1.814(19) | P(1)–C(13) | 1.833(21) |
| P(1)–C(19) | 1.848(19) | | |
| | | | |
| Ag(1)–Pt(1)–Cl(1) | 123.0(1) | Ag(1)–Pt(1)–Cl(2) | 58.2(1) |
| Cl(1)–Pt(1)–Cl(2) | 176.0(2) | Ag(1)–Pt(1)–P(1) | 85.7(1) |
| Cl(1)–Pt(1)–P(1) | 89.6(2) | Cl(2)–Pt(1)–P(1) | 94.3(2) |
| Ag(1)–Pt(1)–C(1) | 97.4(5) | Cl(1)–Pt(1)–C(1) | 89.9(5) |
| Cl(2)–Pt(1)–C(1) | 86.1(5) | P(1)–Pt(1)–C(1) | 176.6(6) |
| Pt(1)–Ag(1)–Cl(2) | 50.3(1) | Pt(1)–Ag(1)–Cl(1B)[b] | 133.3(1) |
| Cl(2)–Ag(1)–Cl(1B) | 156.1(2) | Pt(1)–Cl(1)–Ag(1A) | 100.7(2) |
| Pt(1)–Cl(2)–Ag(1) | 71.6(2) | | |

[a] Symmetry operation for generating Ag(1A): −0.5 + *x*, 0.5 − *y*, *z*.
[b] Symmetry operation for generating Cl(1B): 0.5 + *x*, 0.5 − *y*, *z*.

Each of the repeated units of the polymer is formed by the interaction of the square planar $[trans\text{-}PtCl_2(C_6Cl_5)PPh_3]^-$ fragment and the silver cation through a Pt–Ag bond which is supported by a bridging chloride ($\overline{\mathrm{Pt}(\mu\text{-}\mathrm{Cl}(2))\mathrm{Ag}}$). These units are connected by a Pt($\mu$-Cl(1))Ag bridging system, resulting in the formation of the polymeric structure (Figure 1). The Pt(1) atom is located in the center of a nearly square plane formed by the Cl(1), Cl(2), C(1), and P(1) atoms, with the Ag(1) atom occupying the apical position of a strongly distorted square pyramidal environment.

The angles between cis ligands in the square planar configuration range from 86.1(5) to 94.3(2)°, while the angles between trans ligands are identical within experimental error (176.6(6) and 176.0(2)°). The distances Pt(1)–C(1) (2.083(19) Å) and Pt(1)–P(1) (2.319(5) Å) are similar to the corresponding distances found in other (pentahalophenyl)platinum–silver complexes such as $[PPh_3(C_6Cl_5)ClPt(\mu\text{-}Cl)AgPPh_3]$ (**6**),[8] $(NBu_4)[PtAgCl_2(C_6Cl_5)_2PPh_3]$,[3] or $\{(NBu_4)[PtAgCl_2(C_6Cl_5)_2]\}_x$ (**A**).[3] Pt–Cl distances are as follows: Pt(1)–Cl(1) = 2.315(5) Å; Pt(1)–Cl(2) = 2.313(5) Å.

The Ag(1) atom is located 2.855(2) Å from the platinum center, Pt(1), which indicates a bonding interaction between the two metals,[13] although shorter Pt–Ag bonds have been found in other (pentachlorophenyl)platinum–silver complexes such as $(NBu_4)[PtAgCl_2(C_6Cl_5)_2PPh_3]$[3] (2.782(3) Å). In addition, the platinum–silver bond is supported by a bridging chloride (Ag–Cl(2) = 2.556(6) Å), and the small Pt(1)-Cl(2)-Ag(1) angle of 71.6(2)° is also an indication of the presence of the Pt–Ag bond. This Pt–Ag bond forms an angle of 33.1(1)° with the perpendicular to the best least-squares plane which contains the platinum center.

The other chlorine atom bonded to the platinum center, Cl(1), acts as a bridge between the platinum and the silver atom, Ag(1A) of a neighboring unit, thus resulting in the formation of the polymer (see Figure 1). The Cl(1)–Ag(1A) distance is 2.458(5) Å, shorter than the Ag(1)–Cl(2) distance (2.556(6) Å). However, the Ag(1A)($\mu$-Cl(1))Pt(1) angle is 100.7(2)° and the resulting Ag(1A)–Pt(1) distance is 3.679(2) Å, excluding any bonding interaction between the two metals.

Finally, the $C_6Cl_5$ ring is nearly perpendicular (97.1(4)°) to the basal coordination plane of the platinum center. This

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[13] For a discussion about Pt–Ag distances and *o*-X···Ag contacts see ref 1, pp 171 and 173, respectively.

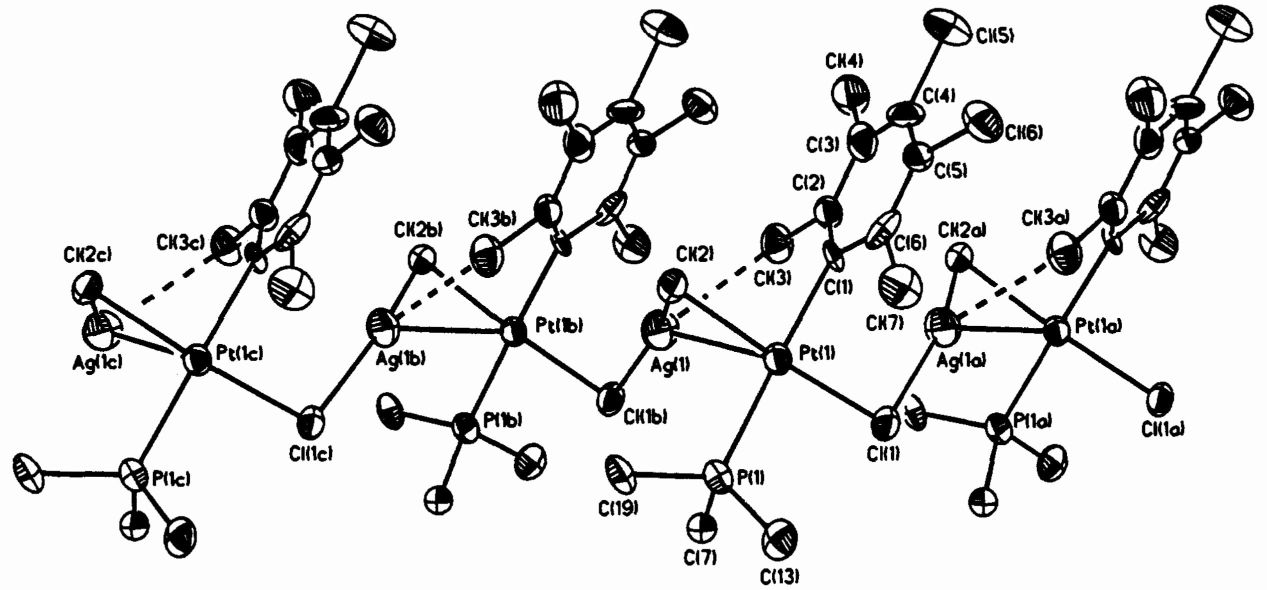
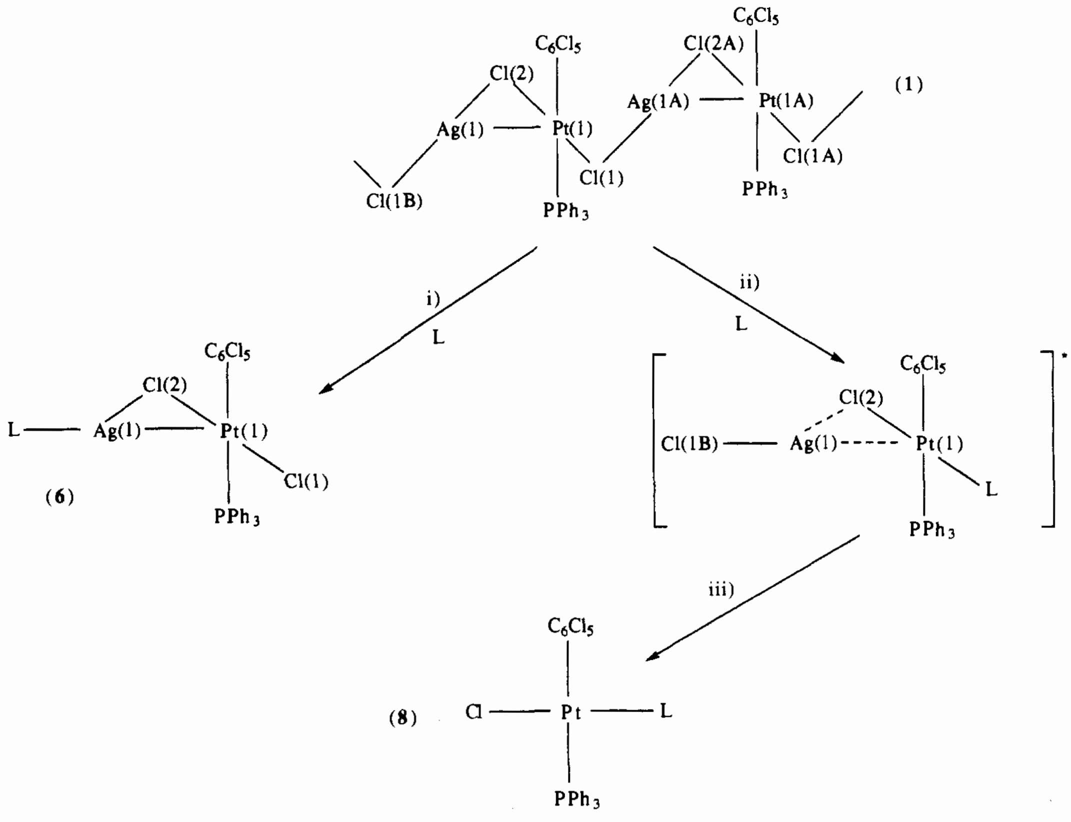


**Figure 1.** Diagram of the polymeric structure of complex $[PtAgCl_2(C_6Cl_5)PPh_3]_x$ (**1**). Carbon atoms of the phenyl rings, except the ipso ones, have been omitted for clarity.

**Scheme 1**[a]



[a] (i) L = $PPh_3$. The ligand cleaves the Cl(1)–Ag(1) bonds to give a binuclear complex (**6**). (ii) L = $SC_4H_8$. The ligand cleaves the Cl(1)–Pt(1) bonds to give a nonisolable binuclear complex. (iii) Under elimination of AgCl, a mononuclear complex (**8**) is formed.

orientation enables contacts between the silver atom and one of the ortho chlorine atoms of the ring. The *o*-Cl(3)···Ag(1) distance (2.838(6) Å) is in the lower end of the range of distances found for similar *o*-Cl···Ag contacts in other (pentachlorophenyl)platinum–silver complexes and contributes to the stability of this heterometallic compound.[13] Considering this contact, the two Ag–Cl bonds, and the Pt–Ag interaction, the silver atom is located in the center of a distorted tetrahedron (Figure 1).

The polymeric chain is the result of the propagation of the fundamental unit [*trans*-$PtCl_2(C_6Cl_5)PPh_3$] by the *a* glide plane. The silver atoms connect each two of these units through chloride bridges, one of them additional to the Pt–Ag interaction. Finally, the basal planes of two consecutive platinum centers form a dihedral angle of 43.9(1)°.

**(c) Reactivity of $[PtAgX_2(C_6Cl_5)PPh_3]_x$ with $PPh_3$, $SC_4H_8$, or *p*-$MeC_6H_4NH_2$.** The polymeric nature of complexes **1–5** with two different types of bridging halides Pt(μ-Cl)Ag or Pt(μ-Cl)-Ag offers the possibility of a selective splitting of one of the bridges using neutral monodentate ligands L in the appropriate (Pt-Ag:L = 1:1) molar ratio. If a reaction takes place at all, the cleavage of only one bridge and the formation of binuclear Pt–Ag complexes should be expected. The selected L ligands were $PPh_3$, $SC_4H_8$, and *p*-$MeC_6H_4NH_2$, and each of them behaves in a

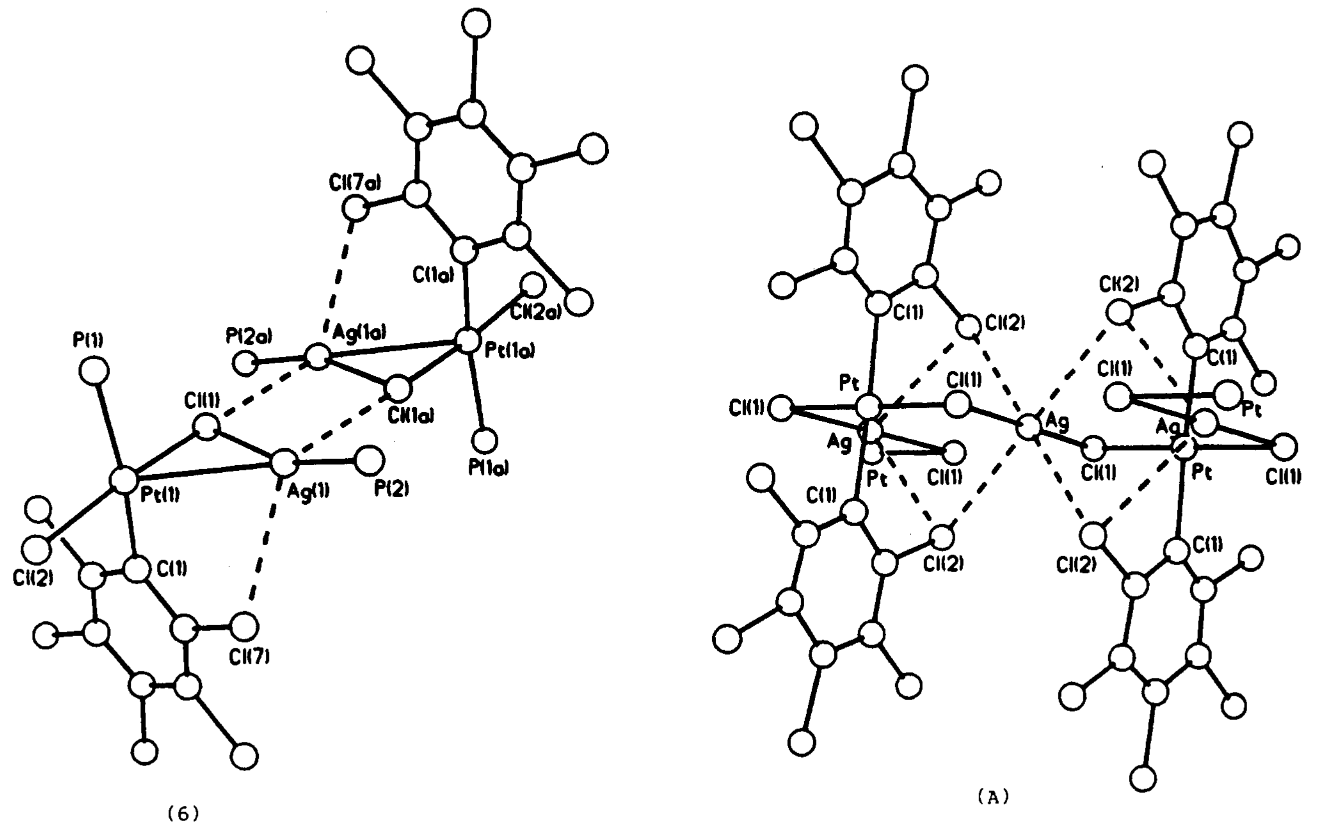


Figure 2. Schematic representation of the structures of $[PPh_3(C_6Cl_5)ClPt(\mu\text{-}Cl)AgPPh_3]_2$ (6) and $\{[PtAgCl_2(C_6Cl_5)_2]^-\}_x$ (A).

Table 5. Comparison of Distances (Å) and Angles (deg) for Polynuclear Pentachlorophenyl Pt–Ag Compounds

| | Pt–Ag | Cl–Ag | Ag–P | Pt–Cl–Ag | *o*-Cl···Ag | Ag···Cl(A) |
|---|---|---|---|---|---|---|
| $\{(NBu_4)[PtAgCl_2(C_6Cl_5)_2]\}_x$ (A) | 3.203(1) | 2.477(5) | | 83.6(2) | 3.010(8)<br>3.092(8) | |
| $[PPh_3(C_6Cl_5)ClPt(\mu\text{-}Cl)AgPPh_3]_2$ (6) | 2.945(1) | 2.514(2) | 2.382(3) | 71.6(1) | 3.041(4) | 3.023(2) |
| $[PtAg(C_6Cl_5)Cl_2PPh_3]_x$ (1) | 2.859(2) | 2.550(6)<br>2.475(6) | | 71.7(2)<br>100.5(2) | 2.839(6) | |

different way. $PPh_3$ gives, at room temperature, dinuclear complexes, with the entering $PPh_3$ attached to the silver center. With $SC_4H_8$, AgCl is precipitated and only the mononuclear platinum complex can be isolated. Finally, *p*-$MeC_6H_4NH_2$ does not react with **1** under similar conditions. Scheme 1 collects the observations and the interpretations of the two different processes.

The attack of $PPh_3$ on the Ag center causes the cleavage of the Cl(1)–Ag(1) bond, and the neutral dinuclear complex $[Ph_3P(C_6Cl_5)ClPt(\mu\text{-}Cl)AgPPh_3]$ (**6**) (or, starting from the polymeric bromide derivative (**5**), the binuclear bromide complex (**7**)) is obtained. Complexes **6** and **7** have previously been synthesized by reaction between $(NBu_4)[\textit{trans}\text{-}PtX_2(C_6Cl_5)PPh_3]$ (X = Cl, Br) and $O_3ClOAgPPh_3$, and their structures (schematized in Figure 2) have been established by a single-crystal X-ray study.[8,9] If tetrahydrothiophene behaved similarly toward **1**, the corresponding dinuclear complexes $[Ph_3P(C_6Cl_5)ClPt(\mu\text{-}Cl)AgL]$ whould be expected; however, AgCl precipitates in this case.

$$(NBu_4)[\textit{trans}\text{-}PtCl_2(C_6Cl_5)PPh_3] + O_3ClOAg(SC_4H_8) \rightarrow \underset{\mathbf{9}}{[PPh_3(C_6Cl_5)ClPt(\mu\text{-}Cl)Ag(SC_4H_8)]} + (NBu_4)ClO_4 \quad (2)$$

Since the reaction between $(NBu_4)[\textit{trans}\text{-}PtCl_2(C_6Cl_5)PPh_3]$ and $O_3ClOAg(SC_4H_8)$ (eq 2) gives the dinuclear complex **9**, which can be isolated (see Experimental Section) in the form of a stable yellow solid, we assume that, in the present case, the ligand tetrahydrothiophene acts on the Pt(1) center and the cleavage of the Cl(1)–Pt(1) bond in the polymer leads to the unstable binuclear complex (see Scheme 1(ii), bracketed complex). The exchange of an anionic ligand (Cl) for a neutral one ($SC_4H_8$) deprives the platinum center of the excess of electron density which is necessary for it to act as a Lewis base toward the $Ag^+$ center. Therefore, AgCl is precipitated and the final stable and isolable product is a mononuclear Pt(II) complex with four different ligands in its coordination sphere: $[PtCl(C_6Cl_5)PPh_3(SC_4H_8)]$ (**8**).

Finally, *p*-$MeC_6H_4NH_2$ does not react with **1** at room temperature, but in refluxing $CH_2Cl_2$, a reaction takes place leading to the precipitation of AgCl. Since complexes **6** and **7**, if refluxed in $CH_2Cl_2$, also decompose under precipitation of AgCl, the participation of *p*-$MeC_6H_4NH_2$ in the reaction path is doubtful.

**(d) Comparison of the Structure of $[PtAgCl_2(C_6Cl_5)PPh_3]_x \cdot 1.5xCH_2Cl_2$ (1) with Other Related Pt–Ag Complexes.** Despite the fact that the reactions of $(NBu_4)[\textit{trans}\text{-}PtCl_2(C_6Cl_5)PPh_3]$ and $(NBu_4)_2[\textit{trans}\text{-}PtCl_2(C_6Cl_5)_2]$ with $AgClO_4$ (or $AgNO_3$) lead to polymeric Pt–Ag complexes (**1** and $\{(NBu_4)_2[PtAgCl_2(C_6Cl_5)_2]\}_x$[3] (**A**), respectively), both structures show important differences. The structure of **A** (Figure 2) is a highly symmetrical one, with all the metals on a plane and the $C_6Cl_5$ groups nearly perpendicular to this plane and so positioned that each silver atom in the polymeric chain displays four *o*-Cl···Ag contacts along with two Ag–Cl bonds; i.e., each silver atom is located in the center of a rhombically distorted octahedron of chlorine atoms which are donating electron density to the acidic silver center, thereby making unnecessary or impossible the existence of Pt→Ag bonds (Pt–Ag distance = 3.203(1) Å). In complex **1**, with only one $C_6Cl_5$ group on each platinum atom, the symmetry is decreased; and while all the platinum atoms are in the *xy* plane, the chain of silver atoms is situated 0.292(2) Å below this plane.

Each silver atom accepts electron density from the two chloride ligands and from one *o*-Cl atom. Possibly, more electron density is required to compensate for the acidity of the silver center, so that a Pt→Ag bond is formed. For a comparison of distances and angles, see Table 5.

On the other hand, **1** reacts with $PPh_3$, yielding $[PPh_3(C_6Cl_5)ClPt(\mu\text{-}Cl)AgPPh_3]$ (**6**), which has also been obtained by reacting $(NBu_4)[\textit{trans}\text{-}PtCl_2(C_6Cl_5)PPh_3]$ with $O_3ClOAgPPh_3$. The structure of **6**, which has been reported previously[8] and is presented in Figure 2, can easily be explained as the result of the splitting of the Pt($\mu$-Cl)Ag bridging bonds with coordination of the $PPh_3$ to the silver center. It is interesting to notice that, in this case (see Table 5), the Pt–Ag interaction is weaker than that in **1**, and the silver center fulfills its requirements for electron density through two strong interactions with $PPh_3$ and with the bridging chloride ligand (the Ag–Cl distance being equal, within experimental error, to that in the polymeric compound **1**). In addition, two weaker interactions complete the coordination sphere of the silver center in **6**—an *o*-Cl···Ag contact, which has a strength similar to that observed in **A**, although weaker than that observed in **1**, and a weak Cl(1)···Ag(1A) interaction, which produces the polymerization of the compound (see Figure 2).

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**Supplementary Material Available:** A detailed description of the development and refinement of the structural model, a diagram of the solvent molecules, and tables of crystallographic data, bond lengths, bond angles, anisotropic displacement parameters, and H atom coordinates (10 pages). Ordering information is given on any current masthead page.