Silver(I) and Copper(I) Complexation with Decachloro-Closo-Decaborate Anion

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Abstract: A series of complexation reactions of silver(I) and copper(I) in the presence of a polyhedral weakly coordinating \([B_{10}Cl_{10}]^{2-}\) anion has been carried out. The effect of the solvent and the presence of \(Ph_3P\) on the composition and structure of the reaction product were studied. Eight novel complexes were obtained and characterized by \(^{11}B\) Nuclear magnetic resonance, Infra-Red, and Raman spectroscopies as well as powder and single-crystal X-ray diffraction techniques. The \([B_{10}Cl_{10}]^{2-}\) anion demonstrated weaker coordinating ability towards coinage metals than \([B_{10}H_{10}]^{2-}\) at similar reaction conditions. The \([B_{10}Cl_{10}]^{2-}\) anion remains unreacted in the copper(I) complexation reaction, while in the absence of competing ligands, we obtained the first complexes containing decachloro-closo-decaborate anion directly coordinated by the metal atom. The bonding between metal atoms and the boron cluster anions was studied using the atomic Hirshfeld surfaces. Besides edge and face coordination of the polyhedral anion, this method allowed us to reveal the Ag–Ag bond in crystal of \([Ag_2(DMF)]_2[B_{10}Cl_{10}]\)\(_n\), the presence of which was additionally supported by the Raman spectroscopy data.

Keywords: atomic Hirshfeld surface; boron cluster; copper(I); decachloro-closo-decaborate anion; decahydro-closo-decaborate anion; silver(I)

1. Introduction

Boron cluster anions and their analogs, carboranes and metallacarboranes [1–4], are fascinating objects in modern inorganic and organoboron chemistry because of their geometric and electronic structures and promising properties. Possessing 3D aromaticity and a tendency to participate in reactions of electrophilic and nucleophilic substitution, boron clusters form numerous derivatives with exo-polyhedral substituents [5–7]. In addition, boron cluster anions form complexes and salts with different composition and structure [8–10]. Boron clusters are used to design compounds that can be applied in boron neutron capture therapy, for radionuclide diagnostics and therapy, in catalysis, for preparation of safety coatings and thermally stable polymers, extraction of radionuclides, etc. [11–15].

Boron clusters and their derivatives are considered as soft Lewis bases because of their large size and relatively low charge; quite logically, they form a great variety of inner-sphere complexes with metals that are soft Lewis acids, such as silver(I), copper(I), lead(II), etc. Different positions of metal atoms around a bulky boron cage results in the preparation of positional isomers of mononuclear and binuclear copper(I) and silver(I) complexes, which are discussed in detail in references [16–18].
In crystallography, polyhedral boranes and carboranes and their halogen derivatives are considered weakly coordinating anions [19–22], and X-ray diffraction data allow metal atoms and various polyhedral boranes to be ranked in accord with their ability to form salts or complexes. For partially substituted halogen derivatives of boron cages, competition between halogen atoms and unsubstituted BH groups to form M...Hal−B or three-centered two-electron MHB bonds can give an insight about the relative coordination ability of a boron cage and its (per)halogenated analog. For example, in the structure of two silver mononuclear complexes [Ag(Ph3P)2][Ag(Ph3P)2][An], where [An] are the [B10H10]2− and [B10H10Cl]2− anions cocrystallized [17] (positional isomers with an equatorial and an apical edges coordinated), it has been found that the monosubstituted anion [B10H8Cl]2− in both isomers is coordinated by the metal atom through the appropriate edge opposite to the chlorine atom introduced into the boron cage. Thus, one can propose that decahydro-closo-decaborate has stronger coordinating ability toward a silver(I) atom than its perchlorinated derivative. Indeed, the decachloro-closo-decaborate anion acts as a counterion in X-rayed complexes of copper(II) [23], cobalt(II) [24], and manganese(II) [25] complexes with phen (1,10-phenanthroline) and bipy (2,2-bipyridyl), and of silver complex of the [Ag(NH3)2]2[B10Cl10] composition [26]. For the latter complex, weak non-bonding Ag...Cl interactions as long as 3.25–3.41 Å manifest themselves in 35Cl NQR spectra; thus, X-ray diffraction and associated methods of analysis of chemical bonding remain the best choice to reveal any M...Hal−B bonding.

In contrast with [B10Cl10]2− complexes, chloro-, bromo- and iododerivatives of carboranes and a dodecaborane are better represented in the Cambridge Structural Database [27] (see, for example, references [28–35]). Thus, in this study we investigate the coordination ability of the [B10Cl10]2− anion towards silver(I) and copper(I) atoms in the absence of N-donor ligands. Complexation reactions in the presence of Ph3P and without it were carried out; and various solvents were attested that allowed the first complexes of coordinated [B10Cl10]2− to be obtained, and Ag...Cl−B bonds in these complexes can be compared with those in silver(I) complexes with chlorocarboranes and dodecacloro-closo-dodecaborane.

2. Experimental

2.1. Synthesis

Commercially available organic solvents (HPLC acetonitrile and DMF) and anhydrous Ph3P were purchased from Aldrich (St. Louis, MO, USA). All the reactions were carried out in air. [HNEt3]2[B10H10] was synthesized from decaborane-14 according to the known procedure [36]. The reaction between [HNEt3]2[B10H10] and KOH afforded K2[B10H10] with release of Et3N. Chlorination of aqueous K2[B10H10] by chlorine was carried out in accordance with the procedure reported [37] to form K2[B10Cl10]. [HNEt3]2[B10Cl10] precipitated from aqueous solutions of K2[B10Cl10] and the corresponding alkylammonium chloride as reported in Reference [26]. [Ag(Ph3P)3NO3] was synthesized according to the method reported in Reference [38]. [Cu(Ph3P)3Cl] was synthesized according to the known procedure [39].

[Ag(Ph3P)2(DMF)2][B10Cl10] (1) A solution of Ph3P (4 mmol) in DMF (10 mL) was added to a DMF solution (10 mL) containing AgNO3 (2 mmol) and (Et3NH)2[B10Cl10] (1 mmol). The resulting colorless solution was allowed to stand at room temperature in air. Slow evaporation of the reaction solution (about a week) gave compound 1 as colorless crystals 1 · 2 DMF (yield, 74%). The resulting crystals were filtered off and dried in air. Single crystal 1 · 2 DMF used for X-ray diffraction was chosen directly from the reaction mixture. 11B NMR (64.297 MHz, [D7]DMF, 25 °C): δ = 4.65 (2B, s, Bap); −2.71 (8B, s, Bos); IR (NaCl, Nujol mull, cm−1): 1665s, 1309, 1182, 1158s, 1093s, 1002s, 846, 745s, 695s; elemental analysis calcd (%) for Ag2C98H100B10Cl10N2O6P4 = 2166.08: Ag 9.96, C 49.90, H 4.75, N 3.88; B 4.65; found: Ag 10.02, C 49.81, H 4.65, N 3.78, B 5.03.

[Ag(Ph3P)3(Ph2O)]2[B10Cl10] (2) A solution of [Ag(Ph3P)3NO3] (6 mmol) in DMF (10 mL) was added to a DMF solution (10 mL) containing (Et3NH)2[B10Cl10] (3 mmol). Slow evaporation of the
reaction solution in air (about 72 h) gave compound 2 as colorless crystals 2 · 4 DMF (76%). The resulting crystals were filtered off and dried in air. Single crystal 2 · 4 DMF used for X-ray diffraction was chosen directly from the reaction mixture. IR (NaCl, Nujol mull): 3524, 3461w, 1665s, 1157s, 1093s, 1004s; 1093, 846, 745s, 695s; elemental analysis calcd (%) for Ag$_2$C$_{12}$H$_{12}$B$_{10}$Cl$_{10}$N$_4$O$_6$P$_6$ (2580.49): Ag 8.36, C 55.85, H 4.77, B 4.19; found: Ag 8.24, C 55.79, H 4.69, B 4.13.

[Cu(Ph$_3$P)$_3$Cl] · 2DMF (3 · 2DMF) and [Cu(Ph$_3$P)$_4$(µ-Cl)$_2$] (4) A solution of [Cu(Ph$_3$P)$_3$Cl] (6 mmol) in DMF (10 mL) was added to a DMF solution (10 mL) containing (Et$_3$NH)$_2$[B$_{10}$Cl$_{10}$] (3 mmol). Slow evaporation of the reaction solution in air (about 36 h) gave a mixture of compounds 3 · 2DMF and 4 as colorless crystals. The resulting crystals were filtered off and dried in air. Single crystals 3 · 2DMF and 4 suitable for X-ray diffraction studies were chosen directly from the reaction mixture.

[Ag(Ph$_3$P)$_4$][Ag(Ph$_3$P)$_2$B$_{10}$H$_{10}$] (5) A solution of [Ag(Ph$_3$P)$_3$NO$_3$] (6 mmol) in DMF (10 mL) was added to a DMF solution (10 mL) containing (Et$_3$NH)$_2$[B$_{10}$H$_{10}$] (3 mmol). Slow evaporation of the reaction solution in air (about 72 h) gave compound 5 as colorless crystals (yield, 79%). The resulting crystals were filtered off and dried in air. Single crystal 5 · 0.1H$_2$O was used for X-ray diffraction. $^{11}$B NMR (64.297 MHz, [D$_7$]DMF, 25 °C): δ = 1.19 (2B, d, B$_{eq}$); −2.85 (8B, s, B$_{ap}$); −29.27 (8B, d, B$_{eq}$); IR (NaCl, Nujol mull, cm$^{-1}$): 2451br, 2299br, 1673w, 1310, 1159, 1093s, 1027, 998, 745s, 695s; elemental analysis calcd (%) for Ag$_2$C$_{10}$H$_{10}$B$_{10}$Cl$_{10}$ (1907.63): Ag 11.31, C 68.00, H 5.28, B 5.67; found: Ag 11.24, C 59.96, H 5.19, B 5.63.

[Ag[B$_{10}$Cl$_{10}$]$_{2n}$ (6) A solution of AgNO$_3$ (6 mmol) in water (10 mL) was added to a water solution (10 mL) containing K$_2$[B$_{10}$Cl$_{10}$] (3 mmol). The resulting colorless solution was allowed to stand in air at room temperature gradually acquiring grey color. Grey crystals 6 and white powder KNO$_3$ precipitated after 72 h, when water was almost completely evaporated (yield, 95%). For physicochemical studies, grey crystals were chosen mechanically from the mixture. $^{11}$B NMR (64.297 MHz, [D$_7$]DMF, 25 °C): δ = 4.34 (2B, s, B$_{ap}$); −2.85 (8B, s, B$_{eq}$); IR (NaCl, Nujol mull, cm$^{-1}$): 1159, 1007, 850, 744; Raman (cm$^{-1}$): 2936, 2310, 2284, 1369, 1151, 937, 734, 564, 385, 309s, 281, 111; elemental analysis calcd (%) for Ag$_2$B$_{10}$Cl$_{10}$ (678.38): Ag 31.80 B 15.94; found: Ag 31.65, B 15.79.

[Ag$_2$(DMF)$_2$][B$_{10}$Cl$_{10}$]$_{2n}$ (7) A solution of AgNO$_3$ (6 mmol) in DMF (10 mL) was added to a DMF solution (10 mL) containing (Et$_3$NH)$_2$[B$_{10}$Cl$_{10}$] (3 mmol). The resulting colorless solution was allowed to stand in air at room temperature gradually acquiring black color because of partial reduction of silver. Slow evaporation of the reaction solution in air (about 72 h) gave compound 7 as grey crystals (65%). The resulting crystals were filtered off and dried in air. Single crystal 6 chosen directly from the reaction solution was used for X-ray diffraction studies. IR (NaCl, Nujol mull, cm$^{-1}$): 1665, 1159, 1007, 849, 745; Raman (cm$^{-1}$): 1600, 1386, 1127, 1069s, 845, 308s, 185; elemental analysis calcd (%) for Ag$_2$C$_{10}$H$_{10}$N$_2$O$_2$B$_{10}$Cl$_{10}$ (824.56): Ag 26.16, C 8.74, H 1.71, B 13.11; found: Ag 26.07, C 8.62, H 1.63, B 13.13.}

$^{2.2.}$ Methods

Elemental analysis for carbon and hydrogen was carried out on a Carlo Erba CHNS-3 FA 1108 automated elemental analyzer (Carlo Erba Instruments, Milan, Italy). Determination of boron and metals was performed on an iCAP 6300 Duo ICP emission spectrometer (Thermo Scientific, Waltham, MA, USA) with inductively coupled plasma. For elemental analysis, samples were dried in vacuum to
constant weight. IR spectra of compounds were recorded on a Lumex Infralum FT-02 Fourier-transform spectrophotometer in the range of 4000–6000 cm\(^{-1}\) at a resolution of 1 cm\(^{-1}\). Samples were prepared as Nujol mulls (Aldrich, St. Louis, MO, USA); NaCl pellets were used. Raman spectra of solid samples of compounds 6–8 were measured using a VERTEX 70 spectrometer (Bruker Optics, Ettlingen, Germany) equipped with a RAM II FT-Raman module. IR spectra of complexes 1–8 and Raman spectra of 6–8 are shown in Figures S1–S7 (see Electronic Supporting Information, ESI). \(^{11}\)B NMR spectra of compounds 1, 5, and 6 in [D\(_7\)]DMF were recorded on a Bruker AC 200 spectrometer (Bruker AXC, Inc., Karlsruhe, Germany) at a frequency of 64.297 MHz using BF\(_3\)·Et\(_2\)O as an external standard.

### 2.3. X-ray Diffraction

For single-crystal X-ray diffraction, the intensities of reflections were collected with a Bruker Apex II CCD diffractometer with MoK\(_\alpha\) radiation (\(\lambda = 0.71073\) Å, graphite monochromator). Single crystals of 1–8 were obtained from reaction mixtures. Intensities of the reflections were measured with a Bruker Apex II CCD diffractometer (Bruker AXS, Inc., Madison, WI, USA) using graphite monochromated MoK\(_\alpha\) radiation (\(\lambda = 0.71073\) Å). The structures were solved by direct method and refined by full-matrix least squares against F\(^2\). Non-hydrogen atoms were refined anisotropically, except for some disordered fragments. The boron cage in 5 is equally disordered over two sites, and boron atoms of the cage were refined isotropically. Positions of hydrogen atoms were calculated, and all hydrogen atoms were included in the refinement by the riding model with U\(_{iso}(H) = 1.5U_{eq}(X)\) for methyl groups and water molecules, and \(U_{eq}(X) = 1.2U_{eq}(X)\) for the other atoms. All calculations were made using the SHELXL2014 [40] and OLEX2 [41] program packages. Experimental details and crystal parameters are listed in Table 1.

The crystallographic data for 1–8 have been deposited with the Cambridge Crystallographic Data Centre (CCDC no. 1937727–1937734). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/structures/.

The X-ray powder diffraction patterns for 1·2DMF, 6, and 7 were obtained on a Bruker D8 Advance Vario diffractometer equipped with a Ge(111) monochromator and a LynxEye position-sensitive detector (CuK\(_\alpha\) radiation, \(\lambda = 1.540596\) Å, (Bruker AXS, Inc., Madison, WI, USA) at the Shared Equipment Center of the Kurnakov Institute (IGIC RAS). The X-ray powder diffraction data agrees with the calculated X-ray single crystal data, indicating that each sample predominately represents a single phase (Figures S9–S11, see ESI).
Table 1. X-ray crystallographic data for complexes 1–8.

| Parameter | 1 - 2DMF | 2 - 4DMF | 3 - 2DMF | 4 | 5 - 0.1H2O | 6 | 7 | 8 |
|-----------|---------|---------|---------|---|------------|---|---|---|
| Formula   | C90H102Ag2B10Cl10N6O6P4 | C120H120Ag2B10Cl10N6O6P4 | C90H102Ag2B10Cl10N6O6P4 | C84H102Ag2B10Cl10N6O6P4 | C90H102Ag2B10Cl10N6O6P4 | C90H102Ag2B10Cl10N6O6P4 | C90H102Ag2B10Cl10N6O6P4 | C90H102Ag2B10Cl10N6O6P4 |
| Fw        | 2165.99 | 2580.37 | 1031.99 | 984.76 | 1909.34 | 678.34 | 824.52 | 842.56 |
| Crystal system, space group | Monoclinic, C2/c | Monoclinic, C2/c | Triclinic, P21/c | Monoclinic, P21/c | Hexagonal, P622 | Monoclinic, C2/c | Tetragonal, P41212 |
| T (K)     | 120.0(2) | 120.0(2) | 120.0(2) | 120.0(2) | 120.0(2) | 120.0(2) | 120.0(2) | 120.0(2) |
| a (Å)     | 36.319(2) | 37.202(3) | 37.202(3) | 37.202(3) | 37.202(3) | 37.202(3) | 37.202(3) | 37.202(3) |
| b (Å)     | 12.284(7) | 13.151(9) | 13.151(9) | 13.151(9) | 13.151(9) | 13.151(9) | 13.151(9) | 13.151(9) |
| c (Å)     | 23.321(14) | 27.6119(19) | 20.3604(7) | 20.3604(7) | 20.3604(7) | 20.3604(7) | 20.3604(7) | 20.3604(7) |
| α (°)     | 90 | 90 | 108.352(1) | 90 | 90 | 90 | 90 |
| β (°)     | 107.761(1) | 114.188(2) | 138.248(3) | 138.248(3) | 138.248(3) | 138.248(3) | 138.248(3) | 138.248(3) |
| γ (°)     | 90 | 90 | 90.535(1) | 90 | 90 | 90 | 90 |
| V (Å³)    | 9908.8(10) | 12,323.7(18) | 2615.85(17) | 4584.710(15) | 4719.1(4) | 1423.5(3) | 2564.9(11) | 2838.9(2) |
| Z         | 4 | 4 | 2 | 4 | 2 | 3 | 2 | 4 |
| µ (cm⁻¹)  | 0.784 | 0.667 | 0.608 | 1.166 | 0.566 | 3.449 | 2.580 | 2.331 |
| No. of meas., indep. and obs. refl. | 72,769, 16,960, 12,277 | 57,468, 14,880, 11,554 | 48,895, 12,935, 6575 | 41,719, 18,266, 13,442 | 20,906, 1595, 1387 | 18,259, 4748, 3764 | 28,810, 4927, 3373 |
| R(Fo)     | 0.0712 | 0.0595 | 0.0343 | 0.1904 | 0.0434 | 0.1126 | 0.0594 | 0.0702 |
| R(Fc)     | 0.0422, 0.0944, 1.004 | 0.0425, 0.1151, 0.999 | 0.0481, 1.1203, 1.006 | 0.0655, 0.0921, 1.007 | 0.0411, 0.0944, 0.987 | 0.0345, 0.0694, 1.058 | 0.0395, 0.1018, 0.996 | 0.0403, 0.0855, 0.998 |
| ∆ρ(max), ∆ρ(min) (e Å⁻³) | 0.91, −0.33 | 2.45, −1.09 | 1.01, −0.52 | 0.98, −0.88 | 1.28, −0.57 | 0.79, −0.80 | 2.15, −1.51 | 0.75, −0.49 |
3. Results

3.1. Complexes with Non-Coordinated [B_{10}Cl_{10}]^{2-} Anion

A great number of mononuclear and binuclear silver complexes have been prepared where the unsubstituted [B_{10}H_{10}]^{2-} anion was allowed to react with [Ag(Ph_3P)_3NO_3] and a mixture of AgNO_3 + Ph_3P in organic media [16,17]. Taking this fact into consideration, the coordination ability of the perchlorinated anion was studied in the same conditions in the presence of Ph_3P.

First, the reaction between the [B_{10}Cl_{10}]^{2-} anion, AgNO_3, and a two-fold excess of Ph_3P was studied. The reaction was found to proceed according to Scheme 1.

\[
2\text{AgNO}_3 + 4\text{Ph}_3\text{P} + (\text{Et}_3\text{NH})_2 \rightarrow \text{[Ag(Ph}_3\text{P)}_3\text{Cl]} \cdot 2\text{DMF} \cdot \text{[B}_{10}\text{Cl}_{10}] \cdot 2\text{DMF}
\]

Scheme 1. Synthesis of complex 1.

The reaction proceeded in DMF which slowly evaporates at room temperature, and crystals [Ag(PPh_3)_2(DMF)_2][B_{10}Cl_{10}] \cdot 2\text{DMF} (1 \cdot 2\text{DMF}) precipitated directly from the reaction solution after a week of keeping the solution in air.

In this compound, the coordination sphere of silver is formed by Ph_3P and DMF molecules (Figure 1). This cation has not been found in compounds containing the boron cluster anions before.

When previously prepared silver complex [Ag(Ph_3P)_3NO_3] was used as the initial reagent, the reaction proceeded according to Scheme 2 and crystals [Ag(Ph_3P)_3(H_2O)]_2[B_{10}Cl_{10}] \cdot 4\text{DMF} (2 \cdot 4\text{DMF}) precipitated from the reaction mixture.
In this case, the metathesis reaction proceeded in the coordination sphere of silver atom when the nitrate anion was replaced by H$_2$O molecule while the number of coordinated Ph$_3$P ligands remained unchanged (Figure 1). It seems that the source of water molecules is air, because we use HPLC solvents; however, the reaction mixture was allowed to stand in air for a continuous time and some water vapor could dissolve in the reaction mixture.

It is known that the boron cluster anions form copper(I) complexes with Ph$_3$P with a general formula [(Ph$_3$P)$_4$Cu$_2$[B$_n$H$_n$]] (n = 6, 10, 12) [42–46]. Therefore, we attempted to obtain analogous compounds with copper(I) according to similar reactions using [Cu(Ph$_3$P)$_3$Cl] and salts of the [B$_{10}$Cl$_{10}$]$^{2–}$ anion. However, when [Cu(Ph$_3$P)$_3$Cl] was added to the reaction mixture containing [B$_{10}$Cl$_{10}$]$^{2–}$, copper(I) complexes with Ph$_3$P and chloride anions 3 · 2DMF and 4 precipitated (Scheme 3), with the [B$_{10}$Cl$_{10}$]$^{2–}$ salts being in the reaction solution.

Both crystals 3 · 2DMF and 4 are colorless, precipitated together, and contain no boron cluster (Figure 2). Both compounds were characterized only by the X-ray single crystal diffraction; the elemental analysis could not be carried out because it is hardly possible to separate both types of crystals from the mixture in required amounts. Crystal structures of pure 3 and 4 as well as some of their solvates have previously been published [39,47–49]; none of these previous publications mentioned the cocrystallization of the monomer 3 and dimer 4. The structure of 3 · 2DMF is novel, and this crystal is isostructural with previously reported acetone solvate [39]. Crystal parameters of 4 do not coincide with those for the [CTPPCu] Refcode family in the Cambridge Structural Database (see, for example, [CTPPCU03] [47]) due to different space group settings, however theoretical powder XRD patterns indicate that these phases are identical (Figure S8, Supplementary Materials). The initial closo-decaborate salt remains in the solution and precipitates after about two weeks of standing in air.

The cation [Ag(Ph$_3$P)$_3$(H$_2$O)]$^+$ found in 2 · 4DMF was earlier obtained in silver complexation reactions with the [B$_{20}$H$_{18}$]$^{2–}$ anion when using [Ag(Ph$_3$P)$_3$NO$_3$] as the initial reagent to form [Ag(Ph$_3$P)$_4$][Ag(Ph$_3$P)$_3$(H$_2$O)][B$_{20}$H$_{18}$] [17,18]. At the same time, for the paternal [B$_{10}$H$_{10}$]$^{2–}$ anion, the reaction between [B$_{10}$H$_{10}$]$^{2–}$ and [Ag(Ph$_3$P)$_3$NO$_3$] has been studied only in CH$_3$CN when a binuclear complex [Ag$_2$(Ph$_3$P)$_4$][B$_{10}$H$_{10}$] with the [B$_{10}$H$_{10}$]$^{2–}$ coordinated was obtained [16]. Thus, in order to study the silver complexation with [B$_{10}$H$_{10}$]$^{2–}$ and [B$_{10}$Cl$_{10}$]$^{2–}$ in similar conditions (in the same solvent), the silver complexation with the [B$_{10}$H$_{10}$]$^{2–}$ was performed in DMF instead of CH$_3$CN. It was found that the reaction results in [Ag(Ph$_3$P)$_4$][Ag(Ph$_3$P)$_2$(B$_{10}$H$_{10}$)] (5) according to Scheme 4. This compound is isostructural with previously reported [Ag(Ph$_4$P)$_4$][Ag(Ph$_3$P)$_2$(An)], where [An] are the [B$_{10}$H$_{10}$]$^{2–}$ and [B$_{11}$H$_{12}$Cl]$^{2–}$ anions cocrystallized in the 50:50 ratio [17].
In the IR spectra of compounds 1 · 2DMF and 2 · 4DMF, bands ν(BCI) (near 1155 cm⁻¹ and 1000 cm⁻¹) from the boron cluster and ν(CO) (near 1660 cm⁻¹) from DMF molecules are observed, as well as a set of bands in the region 1100–600 cm⁻¹ corresponded to Ph₃P coordinated by metal atom. In the IR spectrum of crystals 5 · 0.1H₂O, bands ν(BH) and ν(BH)MHB corresponded to the BH groups free and coordinated by the metal atom, respectively, are observed in the region 2500–2200 cm⁻¹. A weak band with a maximum near 1673 cm⁻¹ is assigned to ν(CO) of solvent DMF molecules contained in freshly prepared crystals. Water molecule is not seen in the IR spectrum of crystals. In addition, a set of bands in the region 1100–600 cm⁻¹ corresponded to Ph₃P coordinated by metal atom is observed. As in the case of 2 · 4DMF, the source of water molecules seems to be air because of continuous standing of the reaction mixture in air.

Complexes 1–5 obtained from DMF at presence of Ph₃P contain no coordinated [B₁₀Cl₁₀]²⁻ anion. In complexes 1, 2, and 5 silver(I) is tetracoordinated (Figures 1 and 3). Coordination polyhedra Ag²P₂O₂ (1 · 2DMF), Ag₅P₅O (2 · 4DMF), and Ag₅P₄ or Ag₅P₃H₂ (5 · 0.1H₂O) possess tetrahedral geometry. Bond lengths Ag–P increase from bis to tetrakis Ph₃P-substituted complexes due to steric hindrances (Table 2). The Ag–O bonds in 1 · 2DMF strongly deviate from each other (Table 2), although both correspond to interactions between a metal atom and a DMF molecule. Crystals of 1 · 2DMF and 2 · 4DMF contain also solvent DMF molecules, while 2 · 4DMF and 5 · 0.1H₂O contain a coordinated and an uncoordinated water molecules, respectively. The [B₁₀Cl₁₀]²⁻ anion in 1 · 2DMF and 2 · 4DMF acts as a counterion involved in numerous C–H...Cl intermolecular interactions with hydrogen atoms of Ph and Me groups. The [B₁₀H₁₀]²⁻ anion in 5 · 0.1H₂O is coordinated by silver(I) atom via one of equatorial edges. The same coordination accompanied with the anion disorder was observed in its’ monochlorosubstituted isostructural analog [17]. Two disordered anions are coordinated via 2–6 or 2–9 edges of the boron polyhedral anion. One of two copper(I) atoms in 4 and that in 3 also exhibit tetrahedral geometry. Bond distances reflect the fact that copper(I) atom has smaller radius.

**Figure 2.** Molecular view of (a) 3 and (b) 4 in representation of atoms with thermal ellipsoids (p = 50%). Solvent molecules are omitted.
than silver(I). For both bis (1, 4) and tris (2, 3) PPh$_3$-containing complexes, the M–P bond distances are shorter in copper(I) complexes. The Cu(2) atom in 4 has the trigonal-planar coordination. Molecular geometries of 3 and 4 are very similar with previously published analogs [39,47–49]. Both the M–P and M–Cl distances are the shortest among compounds under discussion for this atom.

The obtained data allow us to compare the coordination ability of the three boron clusters in silver(I) complexation at presence of Ph$_3$P as the following: [B$_{10}$H$_{10}$]$^{2-}$ > [B$_{20}$H$_{18}$]$^{2-}$ > [B$_{10}$Cl$_{10}$]$^{2-}$. This conclusion is made based on the fact that no silver(I) complexes with uncoordinated [B$_{10}$H$_{10}$]$^{2-}$ can be found among numerous silver(I) complexes with Ph$_3$P known to date (polymeric, isomers of mononuclear silver complexes, isomers of dinuclear silver complexes); for [B$_{20}$H$_{18}$]$^{2-}$, complexes with coordinated and non-coordinated eicosaborate anion can be formed depending on the reagent ratio; as for the perchlorinated anion, only compounds with outer-sphere boron cluster have been isolated. The obtained data indicate also that it is more favorable for copper(I) to form neutral mononuclear or binuclear complex with Ph$_3$P and Cl rather than a cationic copper(I) complex with the [B$_{10}$Cl$_{10}$]$^{2-}$ anion as counterion. It seems that the Cu–Cl bonds are not favorable to be formed with the perchlorinated closo-decaborate anion, at least in the conditions studied here, thus further studies were carried out only for silver(I) atoms.

### 3.2. Silver Complexes with Coordinated [B$_{10}$Cl$_{10}$]$^{2-}$ Anion

It is known that the secondary Ag ... Hal bonds are found in a number of halogenated carboranes [28–35]; thus, to synthesize silver(I) complexes with the coordinated [B$_{10}$Cl$_{10}$]$^{2-}$ anion, a series of complexation reactions was carried out in the absence of organic ligands. AgNO$_3$ and salts of [B$_{10}$Cl$_{10}$]$^{2-}$ were used as the reagents.

#### 3.2.1. Synthesis in Water

First, the complexation reaction between (Et$_3$NH)$_2$[B$_{10}$Cl$_{10}$] and AgNO$_3$ was performed in water. By the same approach [Ag$_2$[B$_{10}$H$_{10}$]]$_n$ was previously obtained [50,51] in a quantitative yield immediately after fusing aqueous solutions of (Et$_3$NH)$_2$[B$_{10}$H$_{10}$] and AgNO$_3$ taken in the 1:2 molar

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**Figure 3.** Molecular view of complex 5 · 0.1H$_2$O in representation of atoms with thermal ellipsoids ($p = 50\%$). Only one of two positions of the disordered cage anion is depicted.

**Table 2.** Selected geometrical parameters (Å) of coordination polyhedra of 1–5.

| Bond       | 1 · 2DMF | 2 · 4DMF | 3 · 2DMF | 4         | 5 · 0.1H$_2$O |
|------------|----------|----------|----------|-----------|---------------|
| M–Ag$^{I}$ |          |          |          | Cu$^{I}$  |               |
| M–O        | 2.374(2) | 2.476(2) |          | 2.177(1)  | 2.4921(8)–2.6516(8) |
| M–P        | 2.4174(5)–2.4262(5) | 2.4873(7)–2.4967(7) | 2.3125(5)–2.3197(4) | 2.177(1)–2.236(1) | 2.4921(8)–2.6516(8) |
| M … B      | 2.374(2)–2.536(2) | 2.476(2) |          |           | 2.646(6)–2.758(6) |
| M–Cl       | 2.3358(4) |          |          | 2.245(1)–2.452(1) | 2.245(1)–2.452(1) |
ratio. [Ag2[B10H10]n precipitates as white powder and its 3D framework structure was succeeded to be determined by in situ synchrotron radiation powder X-ray diffraction [52]. However, when aqueous solutions of (Et3NH)2[B10Cl10] and AgNO3 (in the 1:2 molar ratio) were poured in one beaker, no precipitate was observed. After continuous standing of the reaction mixture in air at room temperature, when water is almost evaporated, single crystals of [Ag2[B10Cl10]n (6) formed (Scheme 5).

![Scheme 5. Synthesis of complex 6.](image)

Note that the reaction mixture becomes black because of partial reduction of silver to form Ag+; in the above experiments. The presence of Ph3P stabilized Ag+ in the reaction mixture (complexes 1 · 2DMF and 2 · 4DMF were prepared in air at daylight conditions, the reaction mixtures remained colorless and transparent and no black or grey color was observed).

Molecular structure of complex 6 and the environment of both ions are depicted in Figure 4a. The cation coordinates three anions in a chelate mode through five-membered Cl–B–B–Cl–Ag rings to form an AgCl6 octahedron with bond distances varying from 2.706(1) to 2.893(1) Å (Table 3). Each anion interacts with six cations. Four of them coordinate one apical and one equatorial chlorine atom, and two silver atoms interact with two equatorial chlorine atoms (Figure 4b). The resulting 3D network contains isolated pores (see Figure S12), but no residual electron density was found in these regions. Note that in [Ag2[B12Cl12]]n [34], similar octahedral coordination of cations was found, and each anion bridges six cations, but total connectivity of 3D networks is different. Simplification of 3D frameworks of [Ag2[B10Cl10]n and [Ag2[B12Cl12]]n results to 3,6-connected underlying nets (3-connected silver atoms and 6-connected anions) with topology of hexagonal anatase and pyrite.

![Figure 4. (a) Asymmetric unit of 6 and (b) closest environment of ions in representation of atoms with thermal ellipsoids (p = 50%).](image)
Table 3. Selected parameters (Å) of silver(I) coordination polyhedra in complexes with some chlorinated boron cages.

| Complex | M–Cl        | M–N        | M–O        | Reference |
|---------|-------------|------------|------------|-----------|
| 6       | 2.706(1)–2.893(1) | 2.391(2)   | This work |
| 7       | 2.636(9)–3.4908(8) | 2.391(2)   | This work |
| 8       | 3.000(1)–3.619(1) | 2.158(6)–2.159(6) | This work |
| [Ag₂[Cl₂]₄]ₙ | 2.825(2)–2.851(2) | 2.188(3)–2.227(3) | [28]   |
| [Ag(CH₃CN)][(Me₃N)B₁₂Cl₁₁]ₙ | 2.652(1)–3.016(1) | 2.523(4) | [32]   |
| [Ag₂(SO₃)][(Me₃N)B₁₂Cl₁₁]₂·SO₂₅ | 2.652(1)–2.899(1) | 2.523(4) | [32]   |
| [[Ag][Me₃(N)Cl₁₂]₁]·0.5CH₂Cl₂ₙ | 2.668(2)–2.957(1) | 2.523(4) | [32]   |

The preparation of solvent-free crystals containing [B₁₀Cl₁₀]²⁻ anion is a rare case, because this anion tends to form numerous secondary interactions with solvent molecules containing in the structures. This is the only structure besides [Ag(NH₃)₂][B₁₀Cl₁₀] [26] that contains no solvent molecules. It seems that the coordination capacity of the boron cluster in 6 is spent to form numerous Ag–Cl bonds, which resulted in isolation of solvent-free crystals.

3.2.2. Synthesis in DMF

When AgNO₃ was allowed to react with (Et₂NH)₂[B₁₀Cl₁₀] in DMF, the reaction mixture became black because of partial silver reduction to Ag⁰. Grey crystals of target complex [Ag₂(DMF)₂[B₁₀Cl₁₀]]ₙ (7) precipitated from the reaction solution (Scheme 6).

Scheme 6. Synthesis of complex 7.

Asymmetric unit of 7 contains a silver(I) ion, a DMF molecule, and half an anion (Figure 5a). DMF acts as a bridge ligand, and the anion is bridge-chelate octadentate. While Ag–O_DMF distances in 1 are comparable with the shortest Ag–O_DMF distance in 7, the Ag–Cl bonds vary in a wide range from 2.6364(9) to 3.4908(8) Å (Table 3). Besides, the Ag–Ag bond seems to be present in the complex as short as 3.2023(8) Å. Eight chlorine atoms of the 10-vertex anion participate in coordination with four silver(I) atoms. Two cations interact with the anion through the cage edges including one apical and two equatorial atoms, and two others form six-membered Ag₁–Ag₁–Cl₁–B₃–B₃–Cl₃ rings. The presence of bridge DMF molecules and anions results in formation of infinite chains of complex 7 parallel with the crystallographic axis c (Figure 5b).

Note that when studying the analogous silver(I) complexation reaction in the presence of the [B₁₀H₁₀]²⁻ anion, polymeric complex [Ag₂(DMF)[B₁₀H₁₀]]ₙ [53] was obtained having a 3D framework structure (containing no Ag–Ag bonds); eight BH groups form the AgHB bonds with the complexing agent.
were formed after 24 h on the surface of the reaction mixture, but the cell parameters coincided with those reported for the Ag–N coordination bonds in crystals. Silver atom also coordinates two solvent molecules and two anions to form an additional structure (containing no Ag–Ag bonds); eight BH groups form the AgHB bonds with the complexing agent.

Finally, the silver(I) complexation were performed in acetonitrile. Knowing that KNO\(_3\) remains unsolved in acetonitrile, we use potassium salt K\(_2\)[B\(_{10}\)Cl\(_{10}\)] to avoid the presence of foreign ions in the reaction solution. Indeed, when a solution of AgNO\(_3\) was added to a solution of K\(_2\)[B\(_{10}\)Cl\(_{10}\)] in the same solvent, KNO\(_3\) precipitated almost quantitatively which was filtered off. White precipitate [Ag\(_2\)(MeCN)\(_2\)][B\(_{10}\)Cl\(_{10}\)]\(_n\) (8) was formed in the mother solution after 24 h (Scheme 7).

### 3.2.3. Synthesis in Acetonitrile

Finally, the silver(I) complexation were performed in acetonitrile. Knowing that KNO\(_3\) remains unsolved in acetonitrile, we use potassium salt K\(_2\)[B\(_{10}\)Cl\(_{10}\)] to avoid the presence of foreign ions in the reaction solution. Indeed, when a solution of AgNO\(_3\) was added to a solution of K\(_2\)[B\(_{10}\)Cl\(_{10}\)] in the same solvent, KNO\(_3\) precipitated almost quantitatively which was filtered off. White precipitate [Ag\(_2\)(MeCN)\(_2\)][B\(_{10}\)Cl\(_{10}\)]\(_n\) (8) was formed in the mother solution after 24 h (Scheme 7).

![Scheme 7. Synthesis of complex 8.](image)

The effect of a complexing agent on the coordination ability of the perchlorinated boron cage can additionally be demonstrated on the example of [Ag\(_2\)(MeCN)\(_2\)][B\(_{10}\)Cl\(_{10}\)]\(_n\) (8). Its asymmetric unit is depicted on Figure 6a. Silver atom also coordinates two solvent molecules and two anions to form an Ag\(_2\)Cl\(_4\) coordination polyhedron, but acetonitrile is a stronger donor of the electron density; thus, the Ag–N coordination bonds in 8 are shorter than the Ag–O bonds in 7, while the Ag–Cl bonds are...
elongated despite less steric hindrances from acetonitrile. Each anion is involved in bonding with four metal atoms; as a result, a 3D network occurs as depicted on Figure 6b.

![Figure 6](image_url)

**Figure 6.** (a) Asymmetric unit of 8 in representation of atoms with thermal ellipsoids (p = 50%) and (b) fragment of crystal packing of 8.

In the IR spectra of compound 6, only bands ν(BCl) are present. The bands are observed at the same regions as in salts K₂[B₁₀Cl₁₀] and (Et₃NH)₂[B₁₀Cl₁₀]. Therefore, we are unable to discuss the structure of compound 6 based on IR spectra only. In the IR spectrum of compound 8, ν(C≡N) corresponding to acetonitrile molecules and ν(BCl) bands are observed. In the Raman spectrum of 7 there are bands at 308 and 281 cm⁻¹ which could be assigned to ν(BCl) and ν(AgCl), respectively, analogously with the spectrum of compound 4. Besides ν(BCl) bands, the spectra of 7 contain the ν(CO) band corresponding to DMF molecules. In the Raman spectrum of 6 (see Figure S4), a strong band at 309 cm⁻¹ is observed, which corresponds to ν(BCl) as it was assigned in ref. [55] for [B₁₀Cl₁₀]²⁻ anion; a band at 281 cm⁻¹ can be attributed to ν(AgCl) based on data indicated for AgCl [56]. In the Raman spectrum of 8, ν(BCl) and ν(AgCl) bands are observed similarly to the Raman spectra of compounds 4 and 5.

Summarizing the results obtained for silver complexation, we can confirm that both [B₁₀H₁₀]²⁻ anion and its perchlorated analog form coordination bonds with silver atom, but [B₁₀Cl₁₀]²⁻ needs strict conditions to form inner-sphere complexes. First, no competing ligands and cations should be present; second, the tendency of the [B₁₀Cl₁₀]²⁻ anion to form numerous Cl…X and Cl…H–X interactions (X = C, N, O) with organic cations, ligands, and solvent molecules should be taken into account. This type of interactions can be assumed based on the X-ray diffraction data and are confirmed by ³⁵Cl NQR spectroscopic studies for a number of salts and complexes [23,26,54,57]. These interactions can result in a solvent shell appeared around the [B₁₀Cl₁₀]²⁻ anion in solution, which prevent it from forming direct contacts with metals and can be a reason for high solubility of its compounds. All three complexes are the first representatives of the coordinated [B₁₀Cl₁₀]²⁻ anion that demonstrate inclination of the anion to form five-membered Cl–B–B–Cl–Ag rings via various coordination modes. High distortion of coordination polyhedra and prominent variation of Ag…Cl bond distances makes it difficult to propose a coordination mode of the anion and coordination environment of the silver(I) atom. In this case, other approaches besides interatomic distances such as the atomic Hirshfeld surface can be very helpful.
3.3. The Hirshfeld Analysis of Ag ... Cl–B Bonding

The atomic Hirshfeld surfaces (sAHS) proved themselves to be an easy and valuable tool for analysis of chemical bonding including multicentered one between metal atoms and boron cages [18,58,59]. Besides, the AHS can be used to compare chemical bonding for a series of similar compounds [60,61]. The curvedness plotted on the AHS allows visualization of the degree of covalency for a given bond. Red regions (flat surface) are associated with covalent bonding position, and green-blue denotes ionic bonding [62–64]. CrystalExplorer 17.5 [65] was used to obtain AHS of copper(I) atoms in 4, silver(I) atoms for 5–8 and some chlorinated dodeca(car)boranes.

Visual difference between Ag–H–B and Ag ... Cl–B is demonstrated on Figure 7. The former bonds are more sphere-like, and boron atoms take part in this bonding that manifests itself through corresponding green regions on the atomic Hirshfeld surface mapped with curvedness (ranged from −1.4 to −0.3). The latter bonds are all flat that is typical for covalent bonds. Even Ag–O and Ag–N bonds between silver(I) atoms and solvent molecules demonstrate more prominent curvedness. The majority of coordination polyhedra of silver(I) atoms are much distorted, and Ag–Cl bonds vary in a large range from 2.652(1) to 3.619(1) Å, thus the AHS become a convenient method to distinguish various coordination isomers of boron cages. Using this approach, it is easy to conclude that [B10Cl10]2– and [B12Cl12]2– anions in respectively [Ag2[B10Cl10]n] (6) or [Ag2(MeCN)2[B10Cl10]]n (8) and [Ag2[B12Cl12]]n [34] are both coordinated through their edges, while in crystals of (7), [Ag(CH3CN)(Me3N)B12Cl11]n [28], ([Ag2(SO2)2(Me3N)B12Cl11] · SO2)2n [32] and ([Ag(Me3N)B12Cl11] · 0.5CH3Cl2)n [32] the coordination through boron faces and vertices was found. Although Ag–Cl bonds for these four complexes are in the same range, and dodecaboron cages are larger than decaboron one, the faces of an AHS corresponding to all three Ag–Cl bonds with a face of a chlorinated dodecaboron anion are similar, and those corresponding to the bonds with the [B10Cl10]2– anion in 7 are not equivalent. This fact may be indicative of lower coordination ability of [B10Cl10]2– than [RB12Cl11]− or of non-equivalence of apical and equatorial atoms in the former anion. Non-equivalence of AHS faces of silver atoms and the lengths of Ag–Cl bonds in [Ag2[B10Cl10]n] (6) as compared with [Ag2[B12Cl12]]n support the second assumption. It is known that the apical vertices of the [B10H10]2– anion are more negatively charged and are more inclined to take part in MHB bonding. The same is observed for compounds 6–8, where all apical chlorine atoms are involved in Ag–Cl bonding (Figure 8). The [B10Cl10]2– anion takes part in bonding with up to six silver(I) atoms that is unusual for the smaller [B10H10]2– analog. All three anions have different coordination.

In (7), the AHS indicates presence of an Ag–Ag bond (Figure 7d). The AHSs of two metal atoms share a face that is associated with the concentration of charge density. The spectroscopic evidence of the presence of the Ag–Ag bond can be provided from the Raman spectrum of complex 7 (Figure S5): a peak with a maximum at 185 cm−1 can be attributed to the Ag–Ag bond analogously with the data presented in [66] for Ag4+. Note that in the Raman spectra of [Ag2[B10Cl10]n] (6) this band in absent. For comparison, metal atoms in the copper-containing dimer 4 do not share any AHS face (Figure 7a), although the distance between these atoms is shorter than between silver(I) atoms in 7 (2.900(1) Å as compared with 3.2022(9) Å). This Cu ... Cu distance is similar with the distance observed in complex 4 crystallized from other polar solvents [47] while crystallization from non-polar media results in elongation of Cu ... Cu bonds. Previously reported DFT calculations of 4 demonstrated stabilization of this dimer due to delocalization of electron density along the four-membered ring [47].

Thus, the atomic Hirshfeld surfaces of metal atoms in silver(I) complexes with coordinated decachloro-closo-decaborate anions indicate covalent character of Ag–Cl bonding. This approach allows revealing metal-metal bonding and the coordination mode of cage anions. The anions are prone to form numerous Ag–Cl bonds through the cage edges and faces; and apical chlorine atoms more readily form Ag–Cl bonds.
The majority of coordination polyhedra of silver(I) atoms are much distorted, and Ag–Cl bonds vary in curvature. The spectroscopic evidence for the presence of the Ag–Ag bond can be provided from the Raman spectrum of complex crystals. The coordination modes. High distortion of coordination polyhedra and prominent variation of Ag…Cl bond distances makes it difficult to propose a coordination mode of the anion and coordination environment of the silver(I) atom. In this case, other approaches besides interatomic distances such as the atomic Hirshfeld surface can be very helpful.

The atomic Hirshfeld surfaces (sAHS) proved themselves to be an easy and valuable tool for analysis of chemical bonding including multicentered one between metal atoms and boron cages. Besides, the AHS can be used to compare chemical bonding for a series of similar compounds. The curvedness plotted on the AHS allows visualization of the degree of covalency for a given bond. Red regions (flat surface) are associated with covalent bonding position, which prevent it from forming direct contacts with metals and can be a reason for high solubility of its compounds. All three complexes are the first representatives of the coordinated \([\text{B}10\text{Cl}10]^-\) anion which share a face that is associated with the concentration of charge density.

These interactions can result in a solvent shell appeared around the \([\text{B}10\text{Cl}10]^-\) anion in solution, unusual for the smaller \([\text{B}10\text{H}10]^-\) anion as the atomic Hirshfeld surface can be very helpful.

Figure 7. Curvedness plotted on atomic Hirshfeld surface and mapped from −1.4 (flat; red) to −0.3 (sphere-like; blue) for the silver atoms in (a) 4, (b) 5, (c) 6, (d) 7, (e) 8, (f) \([\text{Ag}_2[\text{B}12\text{Cl}12]]_n\), (g) \([\text{Ag}(\text{CH}_3\text{CN})](\text{Me}_3\text{N})\text{B}_{12}\text{Cl}_{11}]_n\) (only one of four symmetrically independent atoms is depicted), (b) \([\text{Ag}_2(\text{SO}_2)](\text{Me}_3\text{N})\text{B}_{12}\text{Cl}_{11}]_2\cdot \text{SO}_2)_n\) (one of two symmetrically independent atoms is depicted), (i) \([\text{Ag}[(\text{Me}_3\text{N})\text{B}_{12}\text{Cl}_{11}]\cdot 0.5\text{CH}_2\text{Cl}_2)_n\) (one of two symmetrically independent atoms is depicted).

Figure 8. Coordination mode of \([\text{B}_{10}\text{Cl}_{10}]^{2-}\) in (a) 6, (b) 7, and (c) 8.
4. Conclusions

Silver(I) complexation with the [B_{10}Cl_{10}]^{2-} anion was studied in the presence of Ph_3P and without it. It was found that depending on the started Ag'/Ph_3P ratio, compounds [Ag(PPPh_3)_{2}(DMF)]_{2}[B_{10}Cl_{10}] or [Ag(Ph_3P)_n(2H_2O)]_{2}[B_{10}Cl_{10}] can be selectively isolated, both containing the uncoordinated boron cage. For comparison, the analogous reaction performed when using [B_{10}H_{10}]^{2-} resulted in compound [Ag(Ph_3P)_4][Ag(Ph_3P)_2[B_{10}H_{10}]], which contains silver mononuclear complexes: anionic [Ag(Ph_3P)_2[B_{10}H_{10}]]^{2-} and cationic [Ag(Ph_3P)_4]^+. The data obtained indicate lower coordination ability of the perchlorinated anion in silver(I) complexation in the presence of Ph_3P as compared to the [B_{10}H_{10}]^{2-} anion. However, [B_{10}Cl_{10}]^{2-} can participate in coordination when the reaction is carried out at the absence of bulky cations and ligands in the reaction mixture. Three complexes with 3D frameworks were synthesized: [Ag_2[B_{10}Cl_{10}]]_n, [Ag_2(DMF)_2[B_{10}Cl_{10}]]_n, and [Ag_2(CH_3CN)_2[B_{10}Cl_{10}]]_n from water, DMF, and acetonitrile, respectively. The boron cages are coordinated by silver; the Ag–Ag bonds can be assumed in [Ag_2(DMF)_2[B_{10}Cl_{10}]]_n based on the X-ray diffraction and Raman spectroscopy data. Note that copper(I) reactions in the presence of Ph_3P result in preparation of mononuclear [Cu(Ph_3P)_3Cl]·2DMF and binuclear [Cu_2(Ph_3P)_3(µ-Cl)_2] copper(I) complexes rather than boron-containing complexes; the perchlorinated closo-decarbaborane anion remains unreacted.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4352/10/5/389/s1, Figures S1–S7: IR spectra of complexes 1–8 and Raman spectra of complexes 6–8, Figures S8–S11: X-ray powder diffraction data for 1–2DMF, 4, 6, and 7, Figure S12: Calculated voids in solid 6.

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