По реакции дицианоаргентата калия с бромидами органилтрифенилфосфония в воде синтезированы комплексы \([\text{Ph}_3\text{P(CH}_3)_2\text{PPh}_3]^{2+} [\text{Ag} (\text{CN})_2]^- [\text{Br}]^-\) (1), [\(\text{Ph}_2\text{PR}^- [\text{Ag} (\text{CN})_2]^-\), \(\text{R} = \text{CH}_3\text{CH}_2\text{OH}, \text{CH}_2\text{C}_6\text{H}_4\text{F}-4\)

SYNTHESIS AND STRUCTURE
OF ORGANYLTRIPHENYLPHOSPHONIUM DICYANOARGENTATES:
\([\text{Ph}_3\text{P(CH}_3)_2\text{PPh}_3]^{2+} [\text{Ag} (\text{CN})_2]^- [\text{Br}]^-\) AND \([\text{Ph}_2\text{PR}^- [\text{Ag} (\text{CN})_2]^-\), \(\text{R} = \text{CH}_3\text{CH}_2\text{OH}, \text{CH}_2\text{C}_6\text{H}_4\text{F}-4\)

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spectra of compounds 1, 2, 3 are apparent in the range 1437-1439 cm\(^{-1}\). The XRD data have been obtained at 293 K on a Bruker D8 QUEST automatic four-circle diffractometer: crystals 1 (\(\text{C}_{29}\text{H}_{35}\text{AgBrN}_{3}\text{P}_{3}\)), M 806.44, triclinic syngony, crystal size 0.72 × 0.37 × 0.3 mm, 2 (\(\text{C}_{29}\text{H}_{36}\text{Ag}_{2}\text{N}_{3}\text{O}_{2}\)), M 467.24, triclinic syngony, crystal size 0.8 × 0.52 × 0.35 mm, 3 (\(\text{C}_{29}\text{H}_{36}\text{AgF}_{2}\text{N}_{3}\text{P}\)), M 531.30, monoclinic syngony, crystal size 0.28 × 0.23 × 0.22 mm). According to the XRD data, crystals 1, 2, 3 contain organyltriphenylphosphonium cations and linear dicyanoargentate anions. Besides, bromide anions are observed in crystal 1. A characteristic feature of complexes with the \([\text{Ag}(\text{CN})_{2}]^{+}\) anions is their perspective utility for development of new nano- and liquid crystal systems. The organyltriphenylphosphonium cations have a distorted tetrahedral configuration: the \(\text{Ag} \cdots \text{Ag}\) distances equal 171.75(10)° – 178.37(8)°.

**Key words:** potassium dicyanoargentate, organyltriphenylphosphonium bromide, X-ray diffraction analysis, alkyltriphenylphosphonium dicyanoargentates

**INTRODUCTION**

At the present time complexes of metal dicyanides attract researchers' interest in the context of their use for production of semiconductors and optically active materials, which take on various properties [1–6]. Thus, the peculiar structure of dicyanoargentate anions favoring oligomer formation leads to appearance of magnetic activity [7]. Complexes with the \([\text{Ag}(\text{CN})_{2}]^{+}\) anions show great promise for development of new nano- and liquid crystal systems [8, 9].

From the standpoint of a search for structures with valuable physicochemical properties, variation of a cation part of the dicyanoargentate complexes looks promising [10], as the dicyanoargentate anions in crystals, depending on the cation structure, can appear as monomers [2, 11, 12], branched polymers [13, 14], perform the bridging function for cations and anions [15], form "dimers" with short \(\text{Ag} \cdots \text{Ag}\) distances [16]. It is pertinent to note that the \([\text{Ag}(\text{CN})_{2}]^{+}\) complexes with organic and organoelement cations are practically unstudied. In the literature the examples of such systems are few in number: with imidazolium cations [11, 17, 18], \(\text{bis}(\text{triphenylphosphine})\text{jiminium}\) [19] and triphenyltellurium [20].

**EXPERIMENTAL PART**

In the present study organyltriphenylphosphonium dicyanoargentate complexes were synthesized and their structures were characterized, namely: \([\text{Ph}_{3}\text{P}(\text{CH}_{2})_{2}\text{PPh}_{3}]^{2+}[\text{Ag}(\text{CN})_{2}]^{-}[\text{Br}]^{-}\) (1) and \([\text{Ph}_{3}\text{PR}]^{+}[\text{Ag}(\text{CN})_{2}]^{-}\), \(\text{R} = \text{CH}_{2}\text{CH}_{2}\text{OH}\) (2), \(\text{CH}_{2}\text{C}_{6}\text{H}_{4}\text{F}-4\) (3). Complexes 1–3 were synthesized from potassium dicyanoargentate and organyltriphenylphosphonium bromides in aqueous solutions: \([\text{Ph}_{3}\text{P}(\text{CH}_{2})_{2}\text{PPh}_{3}]^{2+}[\text{Br}]^{-} + \text{K}[\text{Ag}(\text{CN})_{2}] \rightarrow \rightarrow [\text{Ph}_{3}\text{P}(\text{CH}_{2})_{2}\text{PPh}_{3}]^{2+}[\text{Ag}(\text{CN})_{2}]^{-}[\text{Br}]^{-} + \text{KBr} (1)\)

\(\text{K}[\text{Ag}(\text{CN})_{2}] + [\text{Ph}_{3}\text{PR}]^{+}[\text{Ag}(\text{CN})_{2}]^{-} + \text{KBr} \rightarrow \rightarrow [\text{Ph}_{3}\text{PR}]^{+}[\text{Ag}(\text{CN})_{2}]^{-} + \text{KBr},\)

\(\text{R} = \text{CH}_{2}\text{CH}_{2}\text{OH} (2), \text{CH}_{2}\text{C}_{6}\text{H}_{4}\text{F}-4 (3)\)

After evaporation of water, drying of the solid precipitate and its recrystallization from acetonitrile, thecolorless crystals, stable in air, were obtained. It is known that in IR spectra of organic and inorganic compounds the range of the cyano groups absorption is in the fairly narrow range of 2200–2000 cm\(^{-1}\), which means that the surroundings do not influence the vibrations of these bonds significantly [21]. Consequently, cyanides are easily identified on the strength of their absorption in the stated range. Thus, in the spectra of compounds 1, 2, 3 the intensive bands have been observed at 2133,2135, 2131 cm\(^{-1}\), respectively.

The absorption bands existing in the spectra of compounds 1, 2, 3 that characterize the P–Ph bonds [21] are observed in the range 1437-1439 cm\(^{-1}\). Besides, spectrum 2 contains the absorption band at 3283 cm\(^{-1}\) that characterizes the hydroxyl group vibrations [21].

According to the XRD data, crystals 1, 2, 3 consist of organyltriphenylphosphonium cations and monomer dicyanoargentate anions, and in crystal 1 bromide anions are also observed (Fig. 1-3).
Tetrahedral coordination of the phosphorus atoms in cations is somewhat distorted: the CPC angles deviate from the theoretical value and amount to $106.70(8)^\circ$-$113.37(9)^\circ$ (1), $106.75(10)^\circ$-$112.67(10)^\circ$ (2), $106.88(7)^\circ$-$111.09(7)^\circ$ (3); the lengths of the P–CPh bonds (1.7875(19)-1.8049(18), 1.7925(19)-1.7983(19) Å (1),1.7926(19)-1.798(2) Å (2), 1.7977(16)-1.8009(17) Å (3)) are close to each other, but they are shorter than the P–Calk distances (1.7987(17), 1.8112(18) Å (1), 1.807(2) Å (2), 1.8123(16) Å (3)).

The [Ag(CN)$_2$]$^-$ anions deviate from the linear configuration, the CAgC angles equal $176.10(11)^\circ$ (1), $171.75(10)^\circ$ (2), $178.37(8)^\circ$ (3). The Ag–C distances in anions 1–3 are significantly different: 2.063(3) and 2.089(3) Å in 1, 2.054(3) and 2.186(3) Å in 2, 2.069(2) and 2.062(2) Å in 3. The C≡N triple bonds in the cyanide ligands of these anions equal 1.035(3), 1.091(4) Å (1); 0.841(4), 1.134(4) Å (2), 1.114(3), 1.130(3) Å (3). Structural organization of the crystals is caused by weak hydrogen bonds N…H–C between cations and anions (2.74–2.58 Å (1), 2.54–2.68 Å (2), 2.48–2.73 Å (3)), as well as C…H–C (2.77 Å (1),(2.81–2.90 Å (2)). In crystals 1 and 2 close contacts H…Br (2.69–2.99 Å) and N…H–O (1.98 Å) are present, respectively.

Thus, the silver complexes, obtained from organyltriphenylphosphonium bromides and potassium dicyanoargentates in water, have ionic structure with monomer dicyanoargentate anions.

RESULTS AND DISCUSSION

The IR spectra of complexes 1–3 were recorded on a Fourier transform infrared spectrophotometer Shimadzu IR Affinity-1S in a KBr pellet.

The XRD analysis of crystals 1–3 was performed on a Bruker D8 QUEST automatic four-circle diffractometer (two-coordinate CCD detector, Mo Kα emission, λ = 0.71073 Å, graphite monochromator) at 293 K. The data were collected and analyzed, the unit cell parameters were refined, and the absorption correction was applied using the SMART and SAINT-Plus programs [22]. All calculations for structure determination and refinement were performed using the SHELXL/PC [23] and OLEX2 [24] programs. The structures were determined by the direct method and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. The main crystallographic data and refinement results for structures 1–3 are listed in Table.

The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC 1897387 (1), 1897370 (2),1897369 (3); deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).
Table 1. Crystallographical data and refinement results for structures 1–3

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**Crystallographical data and refinement results for structures 1–3**

Synthesis of trimethylene-bis(triphenylphosphonium) dicyanoargentate bromide [Ph$_2$PCH$_2$CH$_2$PPh$_2$][Ag(CN)$_2$][Br$^-$] (1). To the solution of 181 mg (0.25 mmol) trimethylene-bis(triphenylphosphonium) dibromide in 10 mL of water the solution of 50 mg (0.25 mmol) potassium dicyanoargentate in 4 mL of water was added. The mixture was kept at 20 $^\circ$C for 14 h. Water was removed, the residue was extracted into acetonitrile (4 mL twice). During slow evaporation of the solvent formation of colorless crystals was observed. The yield was 185 mg (92%) of complex 1, m.p. 139.6 $^\circ$C.


Found, %: C 59.75, H 4.53.
ForC$_{42}$H$_{36}$AgBrN$_2$P$_2$ calculated, %: C 61.01, H 4.46.
Compounds 2, 3 were synthesized along similar lines.

(2) (91%), m.p. 153.0 $^\circ$C. The IR spectrum ($\nu$, cm$^{-1}$): 3282, 3086, 3059, 3028, 2947, 2899, 2881, 2850, 2750, 2216, 2135, 1975, 1905, 1826, 1782, 1670, 1610, 1587, 1483, 1436, 1394, 1340, 1315, 1296, 1213, 1192, 1163, 1112, 1078, 1026, 1008, 997, 948, 854, 812, 754, 748, 731, 717, 694, 686, 661, 543, 499, 491, 462, 439.

Found, %: C 56.39, H 4.35.
ForC$_{32}$H$_{20}$AgN$_2$OP calculated, %: C 56.53, H 4.28.

(3) (93%), m.p. 214.0 $^\circ$C. The IR spectrum ($\nu$, cm$^{-1}$): 3441, 3167, 3095, 3072, 3024, 2993, 2972, 2935, 2895, 2848, 2804, 2686, 2586, 2208, 2131,
Thus, the interaction of potassium dicyanoargentate with organytriphenylphosphonium bromides in water was used to synthesize new complexes of organytriphenylphosphonium dicyanoargentates [Ph₃P(CH₂)₃PPh₃]⁺ [Ag(CN)₂]⁻ [Br⁻] and [Ph₃PR]⁺ [Ag(CN)₂]⁻, R = CH₂CH₂OH, CH₂C₆H₄F-4, whose structure was characterized by X-ray diffraction and IR spectroscopy.

CONCLUSION

Thus, the interaction of potassium dicyanoargentate with organytriphenylphosphonium bromides in water was used to synthesize new complexes of organytriphenylphosphonium dicyanoargentates [Ph₃P(CH₂)₃PPh₃]⁺ [Ag(CN)₂]⁻ [Br⁻] and [Ph₃PR]⁺ [Ag(CN)₂]⁻, R = CH₂CH₂OH, CH₂C₆H₄F-4, whose structure was characterized by X-ray diffraction and IR spectroscopy.

REFERENCES


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