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Organyltriphenylphosphonium Dichlorodicyanoaurates $[Ph_3PR][Au(CN)_2Cl_2]$ (R = *n*-Pr, *i*-Bu, and *n*-Hp): Synthesis and Structures

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Abstract—The reactions of potassium dichlorodicyanoaurate with *n*-propyl-, *iso*-butyl-, and *n*-heptyltriphenylphosphonium bromides in water followed by recrystallization from acetonitrile give dichlorodicyanoaurate complexes $[Ph_3P(n\text{-Pr})][Au(CN)_2Cl_2]$ (**I**), $[Ph_3P(i\text{-Bu})][Au(CN)_2Cl_2]$ (**II**), and $[Ph_3P(n\text{-Hp})][Au(CN)_2Cl_2]$ (**III**). Compounds **I**–**III** are identified by elemental analysis and IR spectroscopy. The structure of compound **III** is also proved by X-ray diffraction (XRD) (CIF file CCDC no. 2094701). According to the XRD data, complex **III** consists of *n*-heptyltriphenylphosphonium cations and crystallographically independent planar square dichlorodicyanoaurate anions of two types with similar geometric parameters. The steric organization of the crystal of complex **III** is formed by hydrogen bonds C–H···N≡C (2.55–2.63 Å) and C–H···Cl–Au (2.87 Å). In addition, the structure contains C–H···π(Ph) contacts with the distances from the hydrogen atom to the benzene ring plane equal to 2.80 Å.

Keywords: potassium dichlorodicyanoaurate, organyltriphenylphosphonium bromides, complex, gold, synthesis, structure, XRD

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INTRODUCTION

Cyanide complexes of transition metals attract attention of scientists for a long time due to their physical and chemical properties. An important property of the cyanide complexes is their ability to form coordination polymers prone to modification by a strategical selection of additional coordination sites and auxiliary ligands. For instance, the gold-containing cyanide and cyanohalide coordination polymers can manifest such properties as luminescence [1–5], birefringence [6–9], vapochromism [10–13], negative thermal expansion [14, 15], magnetism [1, 16–19], etc. Thus, the gold complexes can be applied as sensors of volatile organic compounds, building blocks in supramolecular architecture, OLED materials, and others.

Continuing the study of the structures and properties of dihalodicyanoaurates [20–25], we synthesized complexes $[Ph_3P(n\text{-Pr})][Au(CN)_2Cl_2]$ (**I**), $[Ph_3P(i\text{-Bu})][Au(CN)_2Cl_2]$ (**II**), and $[Ph_3P(n\text{-Hp})][Au(CN)_2Cl_2]$ (**III**). The structure of compound **III** was characterized by XRD.

EXPERIMENTAL

Potassium dihalodicyanoaurates prepared by the oxidative addition of the corresponding halogen to potassium dicyanoaurate (analytical grade, DTsM-Analitika) and commercially available organyltriphenylphosphonium bromides $[Ph_3P(n\text{-Pr})]Br$ (99%, Alfa Aesar), $[Ph_3P(i\text{-Bu})]Br$ (98+%, Alfa Aesar), and $[Ph_3P(n\text{-Hp})]Br$ (98+%, Alfa Aesar) were used.

Synthesis of *n*-propyltriphenylphosphonium dichlorodicyanoaurate (I). A solution of *n*-propyltriphenylphosphonium bromide (108 mg, 0.28 mmol) in water (10 mL) was added with stirring to a solution of potassium dichlorodicyanoaurate (100 mg, 0.28 mmol) in water (10 mL). A light yellow precipitate was filtered off, washed with water, and dried. Recrystallization from acetonitrile gave light yellow crystals of complex **I** with T_m = 125°C. The yield was 176 mg (91%).

IR (ν, cm^{-1}): 3095, 3063, 3028, 2972, 2932, 2903, 2876, 2214, 2170, 1587, 1574, 1487, 1462, 1454, 1437, 1391, 1346, 1335, 1323, 1314, 1246, 1217, 1190, 1167, 1111, 1080, 1045, 1026, 995, 1026, 984, 934, 905, 851, 833, 779, 756, 745, 735, 719, 689, 615, 529, 507, 492, 447, 428.

iso-Butyl-(**II**) and *n*-heptyltriphenylphosphonium (**III**) dichlorodicyanoaurates were synthesized using a similar procedure.

Complex **II**: light yellow crystals, T_m = 141°C, 89% yield.

Table 1. Crystallographic data and experimental and structure refinement parameters for complex **III**

Parameter	Value
FW	681.37
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	9.252(11)
b, Å	10.164(13)
c, Å	17.354(19)
α, deg	99.67(4)
β, deg	92.54(4)
γ, deg	114.13(7)
V, Å^3	1457(3)
Z	2
ρ_{calc}, g/cm^3	1.554
μ, mm^{-1}	5.305
F(000)	668.0
Crystal size, mm	0.58 × 0.37 × 0.2
Range of data collection over θ, deg	5.7–72.44
Ranges of reflection indices	$-15 \le h \le 15$, $-16 \le k \le 16$, $-28 \le l \le 28$
Measured reflections	83496
Independent reflections (R_{int})	13482 (0.0840)
Refinement variables	302
GOOF	1.054
R factors for $F^2 > 2\sigma(F^2)$	$R_1 = 0.1053$, $wR_2 = 0.3126$
R factors for all reflections	$R_1 = 0.1916$, $wR_2 = 0.3646$
Residual electron density (max/min), e/Å^3	6.00/–4.47

IR (ν, cm^{-1}): 3059, 3028, 2980, 2963, 2934, 2903, 2868, 2218, 2176, 1589, 1558, 1541, 1508, 1485, 1464, 1437, 1418, 1389, 1373, 1339, 1319, 1252, 1192, 1163, 1113, 1067, 1026, 997, 843, 810, 777, 748, 739, 718, 687, 532, 505, 496, 451, 430.

Complex **III**: light yellow crystals, T_m = 102°C, 93% yield.

IR (ν, cm^{-1}): 3084, 3063, 3028, 2951, 2930, 2868, 2849, 2216, 2172, 1587, 1558, 1541, 1483, 1460, 1439, 1375, 1339, 1317, 1223, 1192, 1169, 1113, 1074, 1028, 1015, 995, 930, 891, 849, 812, 802, 789, 770, 750, 737, 721, 691, 532, 511, 503, 494, 482, 451, 430.

The IR spectra of compounds **I**–**III** were recorded on a Shimadzu IRAffinity-1S FT-IR spectrometer in an absorption range of 4000–400 cm^{-1} for samples prepared by pelleting with KBr.

XRD of the crystal of complex **III** was carried out on a Bruker D8 QUEST automated four-circle diffractometer (MoK_α radiation, λ = 0.71073 Å, graphite monochromator) at *T* = 273 K. Data were collected and edited, unit cell parameters were refined, and an absorption correction was applied using the SMART and SAINT-Plus programs [26]. All calculations on structure determination and refinement were performed using the SHELXL/PC [27] and OLEX2 [28] programs. The structures were solved by a direct method and refined by least squares in the anisotropic approximation for non-hydrogen atoms. The crystallographic data and structure refinement results are given in Table 1. The bond lengths and bond angles are listed in Table 2.

The full tables of atomic coordinates, bond lengths, and bond angles for the structure of compound **III** were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 2094701; deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Complexes **I**–**III** were synthesized by the reactions of aqueous solutions of potassium dichlorodicyanoaurate with *n*-propyl-, *iso*-butyl-, and *n*-heptyltriphenylphosphonium bromides. The subsequent recrystalli-

Table 2. Selected geometric parameters of complex **III***

Bond	*d*, Å	Angle	ω, deg
Au(1)–Cl(1)	2.406(3)	Cl(1a)Au(1)Cl(1)	179.999(1)
Au(1)–Cl(1a)	2.406(3)	C(7)Au(1)Cl(1)	90.7(4)
Au(1)–C(7)	2.021(14)	C(7a)Au(1)Cl(1)	89.3(4)
Au(1)–C(7a)	2.021(14)	Cl(2b)Au(2)Cl(2)	180.00(8)
Au(2)–Cl(2)	2.388(3)	C(8)Au(2)Cl(2)	90.5(4)
Au(2)–Cl(2b)	2.388(3)	C(8b)Au(2)Cl(2)	90.5(4)
Au(2)–C(8)	2.037(13)	C(11)P(1)C(1)	109.4(5)
Au(2)–C(8b)	2.037(13)	C(21)P(1)C(11)	109.6(4)
P(1)–C(11)	1.811(10)	C(21)P(1)C(31)	110.5(5)
P(1)–C(21)	1.801(10)	C(21)P(1)C(1)	108.3(5)
P(1)–C(31)	1.809(10)	C(21)P(1)C(1)	109.3(5)
P(1)–C(1)	1.831(10)	C(9)P(1)C(11)	109.7(5)

* Symmetry transforms: (a) $-1-x, 1-y, 2-z$; (b) $2-x, 1-y, 1-z$.

zation from acetonitrile gave stable in air light yellow crystals of dichlorodicyanoaurate complexes **I**–**III**.

$$K[Au(CN)_2Cl_2] + [Ph_3PR]Br \rightarrow [Ph_3PR][Au(CN)_2Cl_2] + KBr$$

R = *n*-Pr (**I**), *i*-Bu (**II**), *n*-Hp (**III**).

The IR spectra of the synthesized compounds exhibit weakly intense absorption bands of C≡N bonds at 2214, 2170 (**I**), 2218, 2176 (**II**), and 2216, 2172 (**III**) cm^{-1} characteristic of similar complexes. The absorption bands at 1437 (**I**), 1437 (**II**), and 1439 cm^{-1} (**III**) correspond to the $P-C_{Ph}$ bond vibrations.

According to the XRD data, complex **III** consists of the *n*-heptyltriphenylphosphonium cation and crystallographically independent planar square dichlorodicyanoaurate anions of two types with similar geometric parameters. The structure of compound **III** is shown in Fig. 1 (thermal ellipsoids are given with 50% probability; hydrogen atoms are omitted).

The phosphorus atom in the cation has a weakly distorted tetrahedral coordination with the CPC angles ranging from 108.3(5)° to 110.5(5)°. The P–C distances range from 1.801(10) to 1.832(10) Å, which does not exceed the sums of covalent radii of the phosphorus atom and sp^3-hybridized carbon atom (1.88 Å [29]).

The planar square coordination of the gold atoms in the centrosymmetric anions $[Au(CN)_2Cl_2]^-$ almost is not distorted: the *trans*-CAuC and *trans*-ClAuCl angles are 180°, and the *cis*-CAuCl angles vary in a narrow range of 89.3(5)–90.7(4)°. The Au–Cl bond lengths in the anions are close to the sums of the covalent radii of gold and chlorine atoms (Au–Cl 2.38 Å [29]) and amount to 2.406(3) and 2.388(3) Å. The Au–C distances do not exceed the sum of covalent

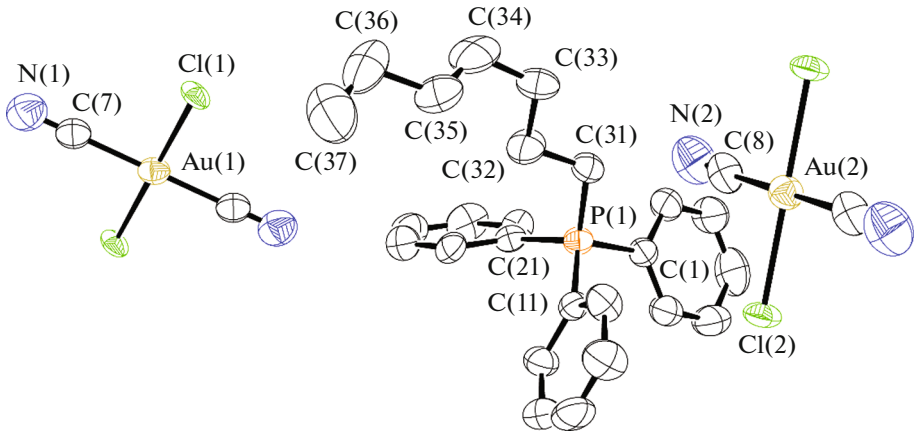

Fig. 1. Structure of complex $[Ph_3P(n\text{-Hp})][Au(CN)_2Cl_2]$ (**III**).

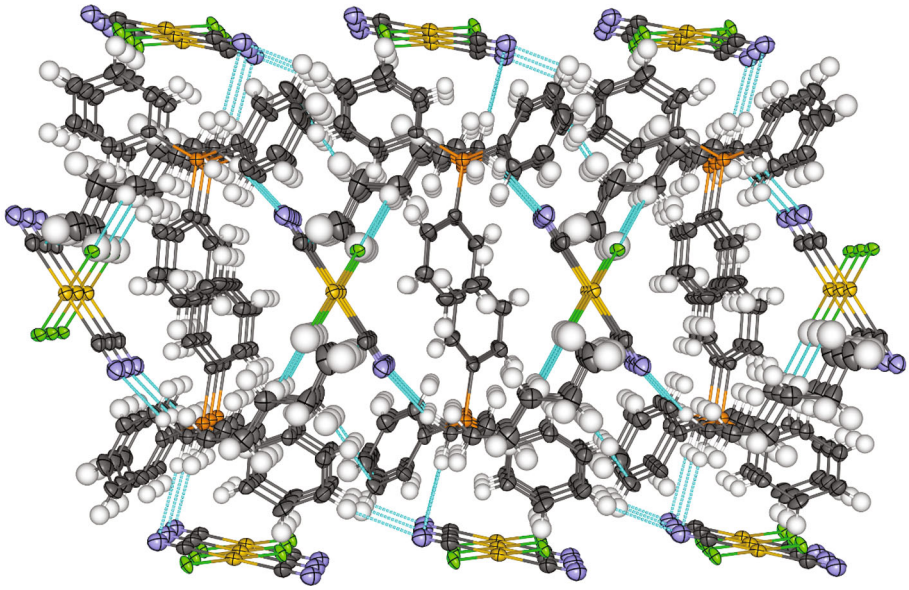

Fig. 2. Packing of the crystal of complex **III** (view along the crystallographic axis *b*).

radii of gold and carbon atoms (2.05 Å [29]) and are equal to 2.021(14) and 2.037(13) Å.

The steric organization in the crystals of complex **III** is due to hydrogen bonds C–H···N≡C (2.55–2.63 Å) and C–H···Cl–Au (2.87 Å), whose lengths are close to the sums of the van der Waals radii of the corresponding atoms (H···N 2.65 Å, H···Cl 2.85 Å [30]). In addition, the structure contains contacts C(36)–H···π(Ph) with the distances from the hydrogen atom to the benzene ring plane equal to 2.80 Å [31]. The steric structure and interionic contacts in the crystal of complex **III** are shown in Fig. 2.

Thus, the reactions of potassium dichlorodicyanoaurate with *n*-propyl-, *iso*-butyl-, and *n*-heptyltriphenylphosphonium bromides afforded the dichlorodicyanoaurate complexes of *n*-propyl-, *iso*-butyl-, and *n*-heptyltriphenylphosphonium, respectively. According to the XRD data, complex **III** has the ionic structure and consists of nearly undistorted organyltriphenylphosphonium cations of dichlorodicyanoaurate anions. The steric structure in the crystals of complex **III** is formed by the C–H···N≡C and C–H···Cl–Au hydrogen bonds and C–H···π(Ph) contacts.

CONFLICT OF INTEREST

The authors of this work declare that they have no conflicts of interest.

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