ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2023, Vol. 49, No. 3, pp. 184–188. © Pleiades Publishing, Ltd., 2023.

Synthesis and Structure of the Ionic Complexes $[Ph_3PEt][Au(CN)_2Cl_2]$ and $[Ph_3PCH_2CH_2Br][Au(CN)_2Br_2]$

D. P. Shevchenko[a], * **and A. E. Khabina**[a]

[a] *South Ural State University (National Research University), Chelyabinsk, Russia*

**e-mail: Shepher56@gmail.com*

Received November 13, 2022; revised November 16, 2022; accepted November 18, 2022

Abstract—The reactions of potassium dichloro- and dibromodicyanoaurate with appropriate ethyl and (2-bromoethyl)triphenylphosphonium halides in water gave new dihalodicyanoaurate complexes $[Ph_3PEt][Au(CN)_2Cl_2]$ (**I**) and $[Ph_3PCH_2CH_2Br][Au(CN)_2Br_2]$ (**II**), which were characterized by X-ray diffraction (CCDC nos. 1963511 (**I**) and 2060274 (**II**)). According to X-ray diffraction data, complexes **I** and **II** consist of tetrahedral organyltriphenylphosphonium cations and two types of crystallographically independent square planar dihalodicyanoaurate anions with similar geometric parameters. The phosphorus atoms in the phosphonium cations have a slightly distorted tetrahedral coordination. The centrosymmetric crystallographically independent anions $[Au(CN)_2Cl_2]^-$ in **I** have a nearly undistorted square planar geometry, whereas the geometry of the $[Au(CN)_2Br_2]^-$ anions in **II** is substantially distorted (the CAuBr *cis*-angles vary in the range of 74.5(9)°–105.5(9)°). The spatial organization in the crystals of **I** and **II** is formed by the C–H···N≡C hydrogen bonds and, in the case of complex **II**, also by additional inter-ion C–H···Br–Au contacts.

Keywords: potassium dihalodicyanoaurates, organyltriphenylphosphonium halides, synthesis, structure, X-ray diffraction analysis

DOI: 10.1134/S1070328423700392

INTRODUCTION

Currently, organometallic coordination compounds are of considerable interest for researchers [1–3]. Among the plenitude of building blocks for these compounds, an important place belongs to cyanide complexes, in particular, mono- and trivalent gold derivatives, which possess a broad range of physicochemical properties such as luminescence [4–8], birefringence [9–12], vapochromism [13–16], negative thermal expansion coefficient [17, 18], and magnetism [4, 19–22]. It was noted that the birefringence is higher for dihalocyanoaurate than dicyanoaurate complexes owing to high polarizability of Au–Hal bonds and also to the possibility of halogen–halogen contacts [9].

In the continuation of studies into the structure and properties of dihalodicyanoaurates [23–28], we synthesized the complexes $[Ph_3PEt][Au(CN)_2Cl_2]$ (**I**) and $[Ph_3PCH_2CH_2Br][Au(CN)_2Br_2]$ (**II**) and investigated their structural details by X-ray diffraction.

EXPERIMENTAL

Synthesis of ethyltriphenylphosphonium dichlorodicyanoaurate (I). An aqueous solution of ethyltriphenylphosphonium chloride (92 mg, 0.28 mmol) was added with stirring to a solution of potassium dichlorodicyanoaurate (100 mg, 0.28 mmol) in water (10 mL). The bright yellow precipitate was collected on a filter, washed two times with 5-mL portions of water, dried, and recrystallized from ethanol. The yield of bright yellow crystals of **I** was 151 mg (88%). T_m = 154°C.

IR (ν, cm^{-1}): 3082, 3059, 2990, 2940, 2907, 2878, 2216, 1638, 1616, 1587, 1485, 1454, 1439, 1406, 1385, 1341, 1317, 1265, 1238, 1190, 1115, 1076, 1038, 1015, 997, 932, 768, 752, 735, 721, 691, 665, 615, 530, 501, 488, 457, 419.

(2-Bromoethyl)triphenylphosphonium dibromodicyanoaurate (**II**) was synthesized similarly to **I**. The yield of yellow crystals of **II** was 84%. T_m = 110°C.

IR (ν, cm^{-1}): 3057, 2955, 2922, 2141, 1587, 1485, 1437, 1341, 1315, 1287, 1271, 1204, 1188, 1119, 1107, 1026, 997, 916, 779, 745, 721, 687, 517, 505, 488, 449, 426.

The IR spectra of compounds **I** and **II** were measured on a Shimadzu IRAffinity-1S FTIR spectrometer; the samples were prepared as KBr pellets (4000–400 cm^{-1} absorption range).

X-ray diffraction study of crystals **I** and **II** was carried out on a D8 QUEST Bruker diffractometer (MoK_α radiation, λ = 0.71073 Å, graphite monochromator). Data collection and editing, refinement of unit cell parameters, and applying absorption correc-

Table 1. Crystallographic data and X-ray experiment and structure refinement details for compounds **I** and **II**

Parameter	Value	
	I	**II**
M	611.24	779.06
System	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	10.572(11)	8.341(9)
b, Å	11.384(19)	8.688(13)
c, Å	11.572(12)	17.28(2)
α, deg	114.95(4)	94.01(8)
β, deg	91.90(4)	100.71(5)
γ, deg	115.94(5)	90.02(6)
V, Å^3	1094(2)	1227(3)
Z	2	2
ρ(calcd.), g/cm^3	1.855	2.108
μ, mm^{-1}	7.049	10.955
F(000)	588.0	728.0
Crystal size, mm	0.7 × 0.62 × 0.25	0.65 × 0.31 × 0.19
Data collection range of θ, deg	6.7–79.72	5.102–56.984
Ranges of reflection indices	$-18 \le h \le 18$, $-20 \le k \le 20$, $-20 \le l \le 20$	$-9 \le h \le 9$, $-10 \le k \le 10$, $-20 \le l \le 20$
Number of measured reflections	81720	24858
Number of unique reflections (R_{int})	13161 (0.0566)	4276 (0.0454)
Number of reflections with $I > 2\sigma(I)$	13161	0.0454
Number of refinement parameters	257	230
GOOF	1.032	1.044
R-factors on $F^2 > 2\sigma(F^2)$	$R_1 = 0.0515$, $wR_2 = 0.1030$	$R_1 = 0.1000$, $wR_2 = 0.2783$
R-factors for all reflections	$R_1 = 0.1059$, $wR_2 = 0.1211$	$R_1 = 0.1112$, $wR_2 = 0.2903$
Residual electron density (max/min), e/Å^3	1.42/–2.77	3.18/–2.74

tions were carried out using SMART and SAINT-Plus programs [29]. All calculations for structure solution and refinement were done using the SHELXL/PC [30] and OLEX2 [31] software. The structures were solved by direct methods and refined by the least-squares method in the anisotropic approximation for non-hydrogen atoms. The key crystallographic data and structure refinement details are summarized in Table 1; selected bond lengths and angles are given in Table 2.

The full tables of atom coordinates, bond lengths, and bond angles are deposited with the Cambridge Crystallographic Data Centre (nos. 1963511 (**I**) and 2060274 (**II**), respectively, deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Complexes **I** and **II** were obtained by the reactions of aqueous solutions of potassium dichloro- and dibromodicyanoaurate with the corresponding organyltriphenylphosphonium halides.

Table 2. Bond lengths (*d*) and bond angles (ω) in the structures of **I** and **II**

Bond	*d*, Å	Angle	ω, deg
I			
Au(1)–Cl(1)	2.335(3)	Cl(1a)Au(1)Cl(1)	179.999(1)
Au(1)–Cl(1a)	2.335(3)	C(7)Au(1)Cl(1)	90.4(4)
Au(1)–C(7)	2.198(11)	C(7a)Au(1)Cl(1)	89.6(4)
Au(1)–C(7a)	2.198(11)	Cl(2b)Au(2)Cl(2)	179.999(10)
Au(2)–Cl(2)	2.283(3)	C(8)Au(2)Cl(2)	89.89(13)
Au(2)–Cl(2b)	2.283(3)	C(8b)Au(2)Cl(2)	90.11(13)
Au(2)–C(8)	2.008(5)	C(1)P(1)C(21)	109.28(19)
Au(2)–C(8b)	2.008(5)	C(1)P(1)C(11)	110.39(16)
P(1)–C(1)	1.788(4)	C(1)P(1)C(9)	107.2(2)
P(1)–C(21)	1.790(4)	C(21)P(1)C(11)	108.22(18)
P(1)–C(11)	1.800(4)	C(21)P(1)C(9)	111.4(2)
P(1)–C(9)	1.790(4)	C(9)P(1)C(11)	110.3(2)
Symmetry codes: (a) –*x*, –*y*, –*z*; (b) 2–*x*, 1–*y*, 2–*z*			
II			
Au(1)–Br(1)	2.409(7)	Br(1b)Au(1)Br(1)	180.0
Au(1)–Br(1b)	2.409(7)	C(10a)Au(2)C(10)	180.0
Au(1)–C(9)	1.984(8)	C(9b)Au(1)Br(1)	79.2(7)
Au(1)–C(9b)	1.984(8)	C(9)Au(1)Br(1)	100.8(7)
Au(2)–Br(2)	2.536(5)	C(10a)Au(2)Br(2)	74.5(9)
Au(2)–Br(2a)	2.536(5)	C(10)Au(2)Br(2a)	105.5(9)
Au(2)–C(10)	1.95(3)	C(21)P(1)C(31)	114.7(8)
Au(2)–C(10a)	1.95(3)	C(21)P(1)C(11)	106.0(8)
P(1)–C(11)	1.708(8)	C(1)P(1)C(31)	116.8(9)
P(1)–C(1)	1.890(8)	C(1)P(1)C(21)	94.4(7)
P(1)–C(7)	1.832(9)	C(1)P(1)C(11)	115.3(8)
P(1)–C(21)	1.694(8)	C(11)P(1)C(31)	107.1(8)
C(8)–Br(3)	2.17(2)	C(7)C(8)Br(3)	116.2(15)
Symmetry codes: (a) 2–*x*, 1–*y*, 1–*z*; (b) 1–*x*, 2–*y*, 2–*z*			

$$\mathrm{K[Au(CN)_2Hal_2] + [Ph_3PR]Hal \xrightarrow{H_2O} [Ph_3PR][Au(CN)_2Hal_2] + KHal}$$

$$\mathrm{Hal = Cl,\ R = Et\ (\mathbf{I});}$$

$$\mathrm{Hal = Br,\ R = CH_2CH_2Br\ (\mathbf{II}).}$$

The subsequent recrystallization of the resulting precipitates from ethanol afforded air-stable yellow crystals of **I** and **II**.

The IR spectra of the compounds exhibited weak absorption bands for the C≡N bonds at 2216, 2164 (**I**) and at 2141 (**II**) cm^{-1}. The P–C_{Ph} bonds gave rise to absorption bands in the characteristic ranges of 1450–1435 and 1005–997 cm^{-1} [32]: 1439, 997 (**I**) and 1437, 997 cm^{-1} (**II**).

According to X-ray diffraction data, complex **I** consists of slightly distorted tetrahedral organyltriphenylphosphonium cations and square planar dihalodicyanoaurate anions, whereas the geometry of the cations and anions in complex **II** is significantly distorted, which is untypical of this type of aurate complexes. The general view of compounds **I** and **II** is shown in Figs. 1 and 2 (the thermal ellipsoids are drawn at 50% probability level).

The CPC angles in the cations of **I** and **II** vary in the ranges of 107.2(2)°–111.4(2)° (**I**) and 94.4(7)°–116.8(9)° (**II**), respectively; the P–C bond lengths (1.788(4)–1.800(4) Å (**I**) and 1.694(8)–1.890(8) Å (**II**)) are close to the sum of covalent radii of phosphorus and carbon atoms (1.88 Å [33]).

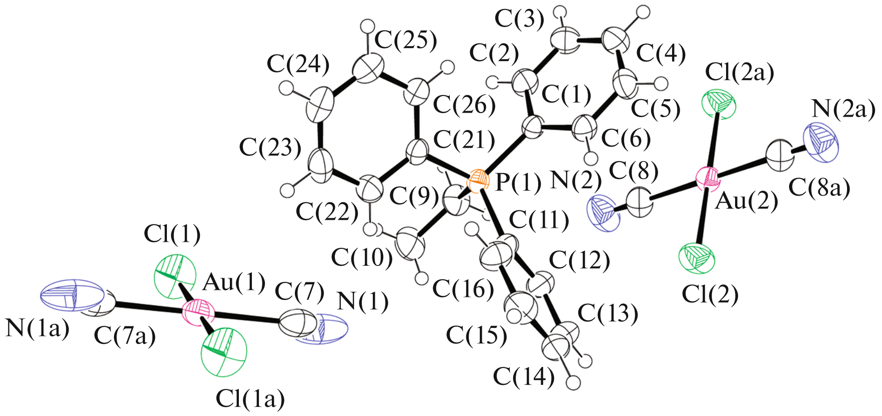

Fig. 1. General view of the complex $[Ph_3PEt][Au(CN)_2Cl_2]$ (**I**).

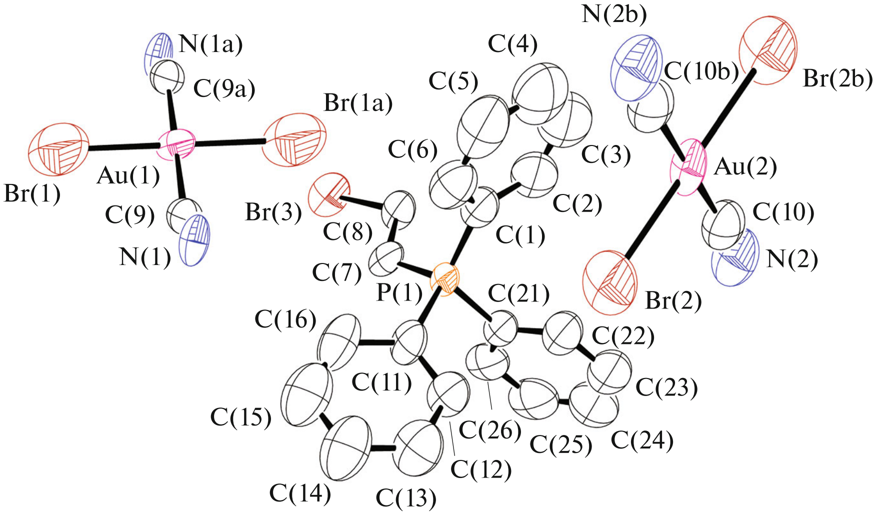

Fig. 2. General view of the complex $[Ph_3PCH_2CH_2Br][Au(CN)_2Br_2]$ (**II**) (hydrogen atoms are omitted).

In the centrosymmetric crystallographically independent $[Au(CN)_2Hal_2]^-$ anions in complexes **I** and **II**, the HalAuHal and CAuC *trans*-angles are 180°; the CAuHal *cis*-angles vary in the ranges of 89.6(4)°–90.4(4)° (**I**) and 74.5(9)°–105.5(9)° (**II**). The Au–C bond lengths (2.198(11), 2.008(5) Å (**I**); 1.95(3), 1.984(8) Å (**II**)) do not differ much from the sum of the covalent radii of gold and carbon atoms (2.05 Å [33]). The Au–Hal distances (2.335(3), 2.283(3) Å (**I**); and 2.536(5), 2.409(7) Å (**II**)) are shorter than the sum of the covalent radii of gold and the corresponding halogen (Au–Cl, 2.38 Å; Au–Br, 2.56 Å [33]).

The spatial structure of compounds **I** and **II** is formed by the C–H···N≡C inter-ion hydrogen bonds (2.63 Å (**I**); 1.86–2.50 Å (**II**)). Also, additional C–H···Br–Au contacts (2.27–2.86 Å) are present in the crystals of **II**, with their length being smaller than the sum of the van der Waals radii of hydrogen and bromine atoms (2.93 Å [34]). No Hal···Hal or Au···Hal contacts were detected in these complexes.

Thus, ethyltriphenylphosphonium dichlorodicyanoaurate (**I**) and (2-bromoethyl)triphenylphosphonium dibromodicyanoaurate (**II**), prepared from potassium dichloro- and dibromodicyanoaurate and ethyl- and (2-bromoethyl)triphenylphosphonium halides in water, have a usual monomeric ionic structure. The geometry of the tetrahedral cations and the square planar anions of complex **II** is markedly distorted, which is unusual for aurate complexes of this type. The spatial structure of the crystals of **I** and **II** is formed by C–H···N≡C inter-ion hydrogen bonds and, in complex **II**, also by the C–H···Br–Au contacts.

ACKNOWLEDGMENTS

The authors are grateful to Professor V.V. Sharutin for performing X-ray diffraction study of the crystals of compounds **I** and **II**.

CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

REFERENCES

1. Batten, S.R. and Champness, N.R., *Phil. Trans. R. Soc., A.*, 2017, vol. 375, no. 2084, p. 20160025. https://doi.org/10.1098/rsta.2016.0032
2. Furukawa, H., Cordova, K.E., O'Keeffe, M., and Yaghi, O.M., *Science*, 2013, vol. 341, no. 6149, p. 1230444. https://doi.org/10.1126/science.1230444
3. Alexandrov, E.V., Virovets, A.V., Blatov, V.A., and Peresypkina, E.V., *Chem. Rev.*, 2015, vol. 115, no. 22, p. 12286. https://doi.org/10.1021/acs.chemrev.5b00320
4. Kumar, K., Stefanczyk, O., Chorazy, S., et al., *Inorg. Chem.*, 2019, vol. 58, no. 9, p. 5677. https://doi.org/10.1021/acs.inorgchem.8b03634
5. Nicholas, A.D., Bullard, R.M., Pike, R.D., and Patterson, H., *Eur. J. Inorg. Chem.*, 2019, vol. 2019, no. 7, p. 956. https://doi.org/10.1002/ejic.201801407
6. Belyaev, A., Eskelinen, T., Dau, T.M., et al., *Chem. Eur. J.*, 2017, vol. 24, no. 6, p. 1404. https://doi.org/10.1002/chem.201704642
7. Katz, M.J., Ramnial, T., Yu, H., and Leznoff, D., *J. Am. Chem. Soc.*, 2008, vol. 130, no. 32, p. 10662. https://doi.org/10.1021/ja801773p
8. Ovens, J.S., Christensen, P.R., and Leznoff, D.B., *Chem. Eur. J.*, 2016, vol. 22, no. 24, p. 8234. https://doi.org/10.1002/chem.201505075
9. Ovens, J.S., Geisheimer, A.R., Bokov, A.A., et al., *Inorg. Chem.*, 2010, vol. 49, no. 20, p. 9609. https://doi.org/10.1021/ic101357y
10. Katz, M.J. and Leznoff, D.B., *J. Am. Chem. Soc.*, 2009, vol. 131, no. 51, p. 18435. https://doi.org/10.1021/ja907519c
11. Thompson, J.R., Goodman-Rendall, K.A.S., and Leznoff, D.B., *Polyhedron*, 2016, vol. 108, p. 93. https://doi.org/10.1016/j.poly.2015.12.026
12. Thompson, J.R., Katz, M.J., Williams, V.E., and Leznoff, D.B., *Inorg. Chem.*, 2015, vol. 54, no. 13, p. 6462. https://doi.org/10.1021/acs.inorgchem.5b00749
13. Lefebvre, J., Batchelor, R.J., and Leznoff, D.B., *J. Am. Chem. Soc.*, 2004, vol. 126, no. 49, p. 16117. https://doi.org/10.1021/ja049069n
14. Lefebvre, J., Korcok, J.L., Katz, M.J., and Leznoff, D.B., *Sensors*, 2012, vol. 12, no. 3, p. 3669. https://doi.org/10.3390/s120303669
15. Varju, B.R., Ovens, J.S., and Leznoff, D.B., *Chem. Commun.*, 2017, vol. 53, no. 48, p. 6500. https://doi.org/10.1039/c7cc03428h
16. Ovens, J.S. and Leznoff, D.B., *Chem. Mater.*, 2015, vol. 27, no. 5, p. 1465. https://doi.org/10.1021/cm502998w
17. Ovens, J.S. and Leznoff, D.B., *Inorg. Chem.*, 2017, vol. 56, no. 13, p. 7332. https://doi.org/10.1021/acs.inorgchem.6b03153
18. Ovens, J.S. and Leznoff, D.B., *CrystEngComm*, 2018, vol. 20, no. 13, p. 1769. https://doi.org/10.1039/c7ce02167d
19. Lefebvre, J., Chartrand, D., and Leznoff, D.B., *Polyhedron.*, 2007, vol. 26, nos. 9–11, p. 2189. https://doi.org/10.1016/j.poly.2006.10.045
20. Geisheimer, A.R., Huang, W., Pacradouni, V., et al., *Dalton Trans.*, 2011, vol. 40, no. 29, p. 7505. https://doi.org/10.1039/c0dt01546f
21. Lefebvre, J., Callaghan, F., Katz, M.J., et al., *Chem. Eur. J.*, 2006, vol. 12, no. 26, p. 6748. https://doi.org/10.1002/chem.200600303
22. Lefebvre, J., Tyagi, P., Pacradouni, V., et al., *Inorg. Chem.*, 2009, vol. 48, no. 1, p. 55. https://doi.org/10.1021/ic801094m
23. Shevchenko, D.P. and Khabina, A.E., *Vestnik Yuzhno-Uralskogo Gosudarstvennogo Universiteta. Seriya Khimiya*, 2021, vol. 13, no. 1, p. 58. https://doi.org/10.14529/chem210106
24. Efremov, A.N., Sharutin, V.V., Sharutina, O.K., et al., *Russ. J. Chem. & Chem. Tech.*, 2020, vol. 63, no. 3, p. 10. https://doi.org/10.6060/ivkkt.20206303.6097
25. Sharutin, V.V., Sharutina, O.K., Tarasova, N.M., et al., *Russ. Chem. Bull.*, 2020, vol. 69, no. 10, p. 1892. https://doi.org/10.1007/s11172-020-2975-4
26. Sharutin, V.V., *Vestnik Yuzhno-Uralskogo Gosudarstvennogo Universiteta. Seriya Khimiya*, 2020, vol. 12, no. 2, p. 74. https://doi.org/10.14529/chem200208
27. Sharutin, V.V., Sharutina, O.K., Tarasova, N.M., and Efremov, A.N., *Russ. J. Inorg. Chem.*, 2020, vol. 65, no. 2, p. 169. https://doi.org/10.1134/S0036023620020151
28. Sharutin, V.V., Sharutina, O.K., Efremov, A.N., and Eltsov, O.S., *Russ. J. Coord. Chem.*, 2020, vol. 46, no. 9, p. 631. https://doi.org/10.1134/S1070328420090031
29. *SMART and SAINT-Plus. Versions 5.0. Data Collection and Processing Software for the SMART System*, Madison: Bruker AXS Inc., 1998.
30. *SHELXTL/PC. Versions 5.10. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data*, Madison: Bruker AXS Inc., 1998.
31. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., et al., *J. Appl. Crystallogr.*, 2009, vol. 42, p. 339. https://doi.org/10.1107/S0021889808042726
32. Pretsch, E., Bühlmann, P., and Affolter, C., *Structure Determination of Organic Compounds*, Berlin: Springer, 2006.
33. Cordero, B., Gómez, V., Platero-Prats, A.E., et al., *Dalton Trans.*, 2008, no. 21, p. 2832. https://doi.org/10.1039/B801115J
34. Mantina, M., Chamberlin, A.C., Valero, R., et al., *J. Phys. Chem. A*, 2009, vol. 113, no. 19, p. 5806. https://doi.org/10.1021/jp8111556

Translated by Z. Svitanko