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π-Complexes of Copper(I) with But-2-yne-1,4-diol. Synthesis and Crystal Structure of the Anionic π-Complex $(PipH_2)[CuCl_2(HOCH_2C{\equiv}CCH_2OH)]_2 \cdot H_2O$ ($(PipH_2)^{2+}$ is the Piperazinium Cation)

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Abstract—A reaction of but-2-yne-1,4-diol with CuCl in a concentrated aqueous solution of piperazinium dichloride gave the π-complex $(PipH_2)[CuCl_2(HOCH_2C{\equiv}CCH_2OH)]_2 \cdot H_2O$ ($(PipH_2)^{2+}$ is the piperazinium cation). The complex was examined by X-ray diffraction analysis (space group $P\bar{1}$, $a = 7.355(1)$ Å, $b = 10.3572(8)$ Å, $c = 13.632(2)$ Å, $\alpha = 101.055(9)°$, $\beta = 95.350(1)°$, $\gamma = 101.875(9)°$, $Z = 2$). The complex consists of two crystallographically independent anions $[CuCl_2(HOCH_2C{\equiv}CCH_2OH)]^-$ and the biprotonated piperazinium cation. The trigonal environment of the Cu(I) atom in either complex anion includes is made up of two Cl atoms and the C≡C bond. Apart from the hydrogen bonds N–H···O that imparts a directed character to the ionic interaction $Cat^+ \cdots An^-$, the piperazinium cation with molecules of crystallization water with bridging function form the cross-linking hydrogen bonds N–H···OH_2 and OH–H···Cl.

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In concentrated solutions of the Newland system MCl–CuCl–H_2O (M is the alkali metal, ammonium, or organic amine cation), the catalytic transformations of alkynes involve the formation of intermediate copper(I) π-complexes whose composition and structure significantly predetermine the efficiency of alkyne conversion [1–3]. Previously, under the conditions of the Newland system, we have obtained and structurally characterized the crystalline anionic π-complexes $K[CuBr_2(L)]$ [4], $K[CuCl_2(L)]$, $NH_4[CuCl_2(L)]$ [5], $Rb[CuCl_2(L)]$ (modifications A and B) [6], $Cs[CuCl_2(L)] \cdot H_2O$ [7], $Na[CuCl_2(L)] \cdot 2H_2O$ [8], and $ImH[CuCl_2(L)]$ (L is but-2-yne-1,4-diol, ImH^+ is the imidazolium cation) [9]. When studying the structural design of these complexes, we found that the size, type, and shape of the outer-sphere cation M^+ can substantially influence both the formation of the complex structure and the efficiency of the Cu(I)–(C≡C) interaction, although the structure of the coordination π-entity in the complex anions remains virtually unchanged.

Proceeding further in the study of the "architecture" of the anionic π-complexes of CuCl with but-2-yne-1,4-diol, here we replaced the singly charged cation ImH^+ by the larger, doubly charged piperazinium cation ($PipH_2^{2+}$). We obtained the anionic π-complex $(PipH_2)[CuCl_2(L)]_2 \cdot H_2O$ (**I**) in the system $[PipH_2]Cl_2$–CuCl–L–H_2O ($PipH_2^{2+}$ – $C_4N_2H_{12}^{2+}$) and structurally characterized their crystals.

EXPERIMENTAL

Synthesis. Crystals of complex **I** were obtained by a direct reaction of cuprous chloride with but-2-yne-1,4-diol in aqueous piperazinium chloride. The saturated aqueous solution of piperazine (0.4 g, 0.005 mol) was titrated with HCl to pH ~3. Cuprous chloride (1.0 g, 0.01 mol) was dissolved in the resulting solution at ~90°C. Then but-2-yne-1,4-diol (0.9 g, 0.01 mol) was added. Slow cooling to room temperature gave colorless crystals of complex **I**. The density of the crystals was measured by the flotation method in chloroform–bromoform.

X-ray diffraction analysis. A single crystal was studied by the photometric method and reflection intensities were measured on a Kuma KM4CCD single-crystal diffractometer (MoK_α radiation, graphite monochromator) fitted with an Oxford cryogenic camera.

Table 1. Selected crystallographic parameters and a summary of data collection for complex **I**

Parameter	Value
Empirical formula	$(C_4N_2H_{12})_2[CuCl_2(C_4H_6O_2)]_2 \cdot 2H_2O$
M	1094.56
T, K	100(2)
Space group	$P\bar{1}$
Unit cell parameters:	
a, Å	7.355(1)
b, Å	10.357(1)
c, Å	13.632(2)
α, deg	101.055(9)
β, deg	95.350(1)
γ, deg	101.875(9)
V, Å^3	987.8(4)
μ(MoK_α),cm^{-1}	2.8
ρ_{exp}, g/cm^3	1.83(2)
ρ_{calcd}, g/cm^3	1.840
Z	1
Crystal size, mm	$0.2 \times 0.3 \times 0.3$
F(000)	556.0
$2\theta_{max}$, deg	70.00
Number of measured reflections	10614
Number of independent reflections with $\|F \geq 4\sigma(F)\|$	6334
Weighting scheme (w)	$[\sigma(F_o)^2 + 0.001\sigma(F_o)^2]^{-1}$
R	0.0407
R_w	0.0398

Selected crystallographic parameters and a summary of data collection for complex **I** are given in Table 1.

Structure **I** was solved by the direct methods with the CSD program package [10]. All non-hydrogen atoms were located and refined by the least-squares method in the isotropic approximation. An absorption correction was applied using the DIFABS program. Hydrogen atoms were located from the electron-density difference map. Final refinements of structure **I** were performed in the anisotropic (for non-hydrogen atoms) and isotropic approximations (for H atoms).

RESULTS AND DISCUSSION

The projection of structure **I** along the axis [001] is shown in Fig. 1. Like the crystals of the previous anionic π-complexes with but-2-yne-1,4-diol of the formulas M[$CuCl_2$(L)] (M = NH_4^+, K^+ [5], Rb^+ [6], and ImH^+ [9]), Cs[$CuCl_2$(L)] · H_2O [7], and Na[$CuCl_2$(L)] · $2H_2O$ [8], the crystal of complex **I** is built from the discrete complex anions $[CuCl_2(L)]^-$ and the hydrated cations $[PipH_2 \cdot H_2O]^{2+}$. In all the aforementioned complexes, the complex anion $[CuCl_2(L)]^-$ shows a trigonal coordination of the Cu(I) atom to two Cl atoms and the C≡C bond of but-2-yne-1,4-diol, two alcohol OH groups not being involved in the coordination (Fig. 2). Such a way of formation of the coordination π-entity is characteristic of some molecular complexes of cuprous halides, e.g., with 3,3,6,6-tetramethyl-1-thiacycloheptyne-4 ($C_{10}SH_{16}$) and additionally with ammonia ($[CuCl(NH_3)(C_{10}SH_{16})]$), pyridine ($[CuCl(NC_5H_5)(C_{10}SH_{16})]$) [11], and trimethylphosphine ($[CuCl(PC_3H_9)(C_{10}SH_{16})]$) [12], in which the donor S atoms are also not involved in the coordination with Cu(I).

Structure **I** consists of two crystallographically independent coordination π-entities with the central Cu(1) and Cu(2) atoms, respectively; their geometries are similar (Fig. 2). As in the previous complexes, these entities are stacked along the axis [100]. In both coordination π-entities, the Cu–(C≡C) interaction predetermines a change in the geometrical parameters of the ligand compared to free but-2-yne-1,4-diol [13]. For instance, because of π-bonding, the but-2-yne-1,4-diol molecule is bent: the bond angles C–C≡C in two crystallographically independent molecules are 164.9(2)°, 165.7(2)° and 163.1(3)°, 163.8(2)° for the first and second coordination entities, respectively. For comparison, both analogous bond angles in free but-2-yne-1,4-diol are 178.4(2)°. The π-coordinated C≡C bond in two independent molecules of the ligand (1.227(3) Å for Cu(1) and 1.237(3) Å for Cu(2)) is longer than that in free but-2-yne-1,4-diol (1.200(1) Å). The C≡C bond is 1.228(5) Å in the complex K[$CuCl_2$(L)] with potassium as an outer-sphere cation and is 1.208(7) Å in the complex (ImH[$CuCl_2$(L)]) with an organic amine cation.

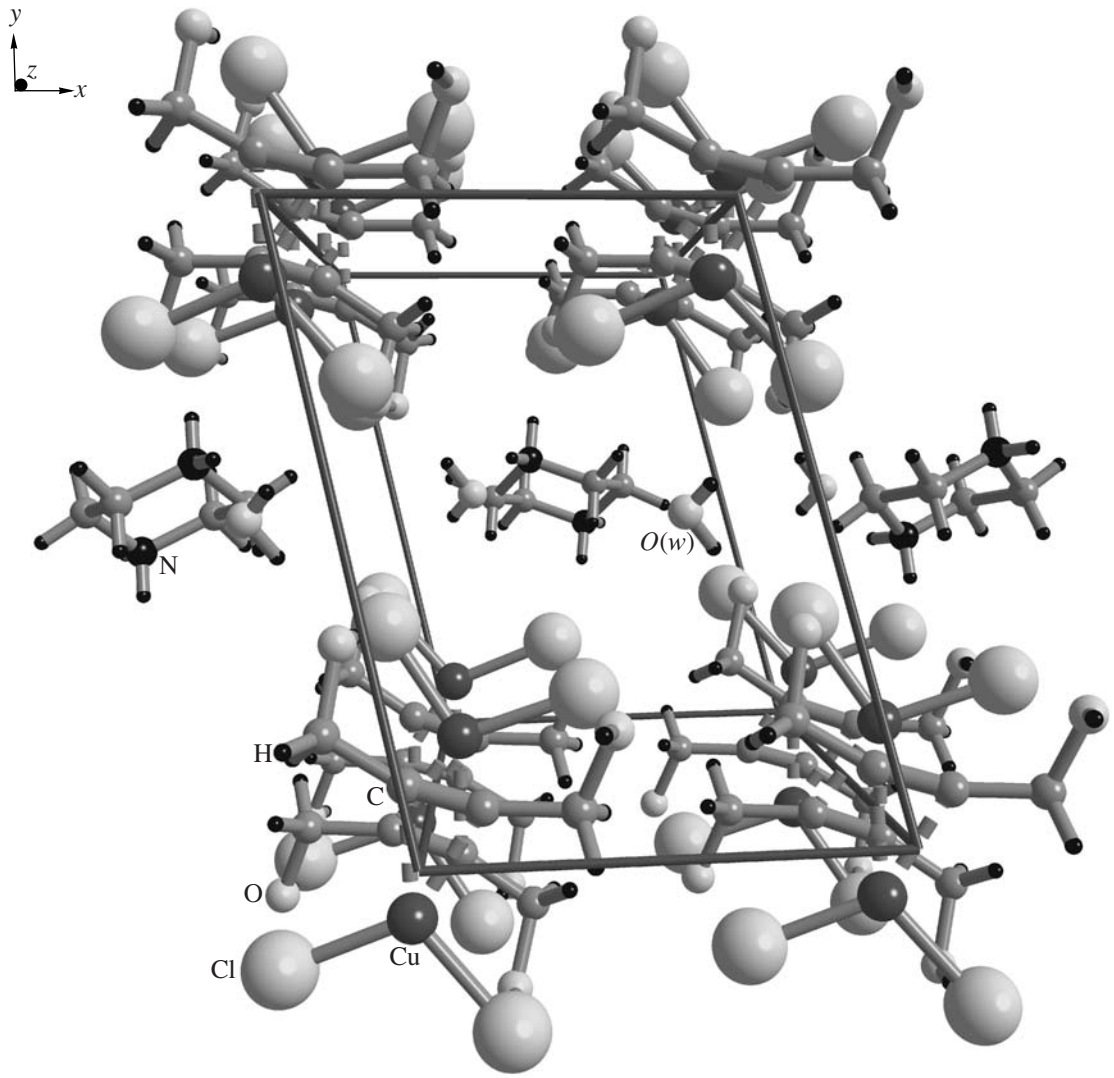

Fig. 1. Projection of structure **I** along the axis [001].

Note that the hydroxymethyl fragments $–CH_2OH$ in two crystallographically independent ligand molecules of complex **I** are in virtually identical positions relative to the C≡C bond. In both the molecules $HOCH_2C{\equiv}CCH_2OH$ and H(1)O(1)C(1)C(2)≡C(3)C(4)O(2)H(2), the hydroxymethyl fragments have a nearly eclipsing conformation (Fig. 2) (the corresponding torsion angles are H(1)O(1)C(1)C(2) –77(2)°; C(3)C(4)O(2)H(2) –79(3)°, H(7)O(3)C(5)C(6) –83(3)°, and C(7)C(8)O(4)H(8) –93(3)°). In free but-2-yne-1,4-diol, the torsion angles H–O–C–C are equal (–77(2)°).

In complex **I**, the bulky piperazinium cations in the chair conformation lie between the anionic stacks (Fig. 1). Such a low packing density favors in the best way possible the penetration of molecules of crystallization water into the cavities of the complex.

The presence of the biprotonated piperazinium cation in structure **I** leads to a wide range of strong hydrogen bonds [14] (Fig. 3), which impart a directed character to the cation–anion interactions. Apart from the hydrogen bonds N–H···O (H(15)···O(3) 2.03(3); H(14)···O(1) 1.95(3)Å) (Table 2) [15], the structure contains cross-linking contacts N–H···O*w* and (O*w*)H···Cl (H(16)···O(5) 2.01(3), H(25)···Cl(1) 2.43(4) Å due to molecules of crystallization water. Unlike the previous complex ImH[$CuCl_2$(L)], structure **I** has no N–H···Cl bonds.

Atomic coordinates and other parameters for complex **I** have been deposited with the Cambridge Crystallographic Data Collection (CCDC No. 692 540); http://www.ccdc.cam.ac.uk/conts/retrieving.html.

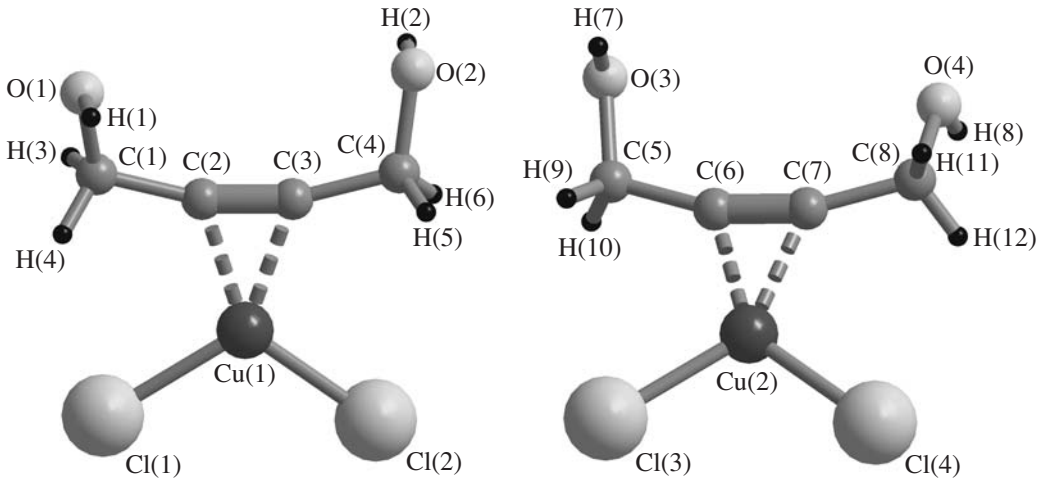

Fig. 2. Crystallographically independent complex anions $[CuCl_2(HOCH_2C{\equiv}CCH_2OH)]^-$ in structure **I**. Selected bond lengths and angles: Cu(1)–m_1^* 1.914(2) Å, Cu(2)–m_2^* 1.903(2) Å, Cu(1)–Cl(1) 2.239(1) Å, Cu(2)–Cl(3) 2.249(1) Å, C(2)≡C(3) 1.227(3) Å, and C(6)≡C(7) 1.237(3) Å (m* is the midpoint of the C≡C bond); Cl(1)Cu(1)Cl(2) 110.62(6)°, Cl(3)Cu(2)Cl(4) 105.86(6)°, Cl(1)Cu(1)m_1 122.62(9)°, Cl(3)Cu(2)m_2 127.20(9)°, C(2)Cu(1)C(3) 35.55(9)°, C(6)Cu(2)C(7) 36.01(9)°, O(1)C(1)C(2) 112.4(2)°, C(1)C(2)C(3) 165.7(2)°, O(3)C(5)C(6) 111.4(2)°, and C(5)C(6)C(7) 163.1(3)°.

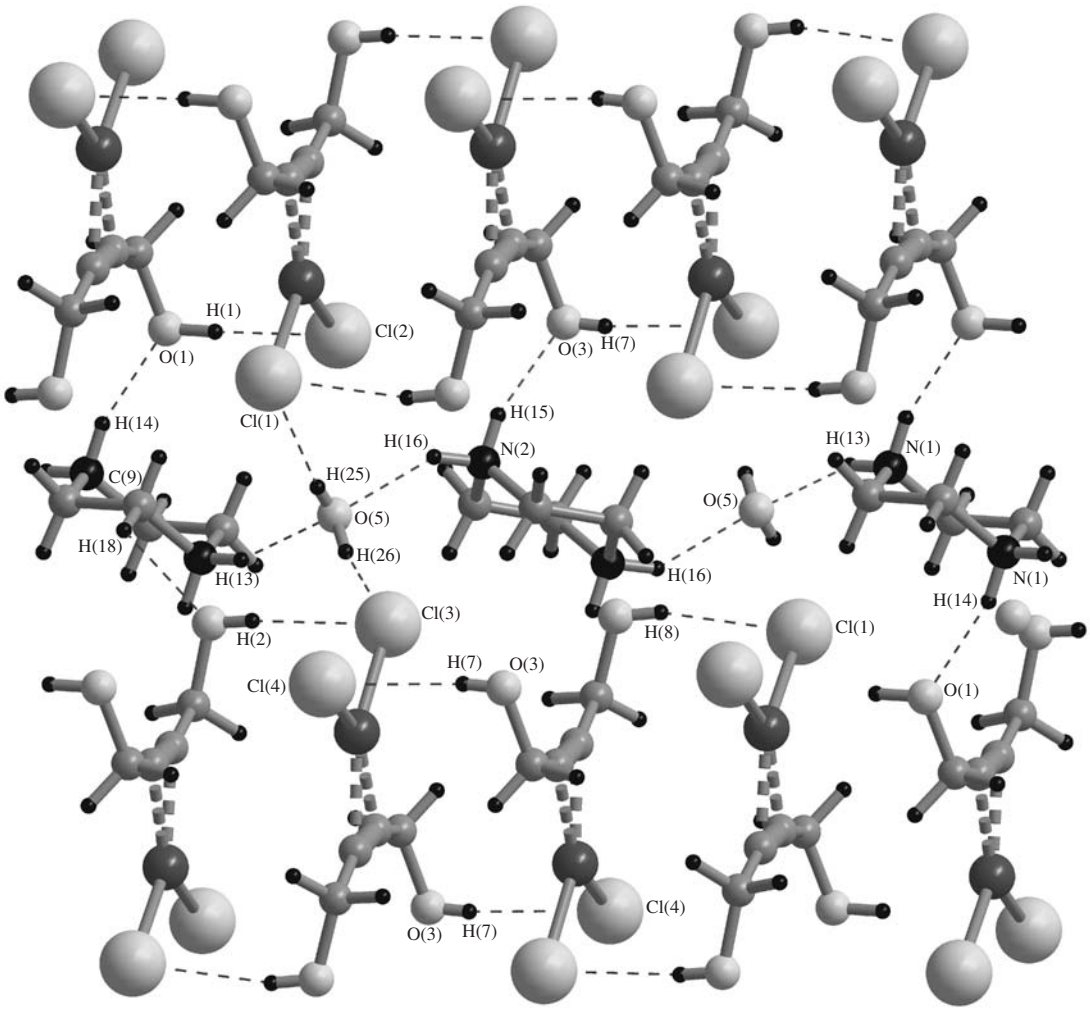

Fig. 3. System of hydrogen bonds in structure **I**.

Table 2. Hydrogen bonding geometry in structure **I**

Contact D–H···A	Distance, Å			D–H···A angle, deg	Coordinates of atom A
	D–H	H···A	D···A		
O(1)–H(1)···Cl(2)	0.89(4)	2.21(4)	3.091(2)	177(4)	–*x*, –*y*, –*z*
O(2)–H(2)···Cl(3)	0.85(3)	2.35(3)	3.158(2)	174(4)	–*x*, –*y*, 1 – *z*
O(3)–H(7)···Cl(4)	0.71(3)	2.39(3)	3.095(2)	171(3)	–*x*, –*y*, 1 – *z*
O(4)–H(8)···Cl(1)	0.76(3)	2.39(3)	3.135(2)	167(3)	–*x*, –*y*, 1 – *z*
N(2)–H(15)···O(3)	0.83(3)	2.03(3)	2.816(3)	157(3)	–*x*, –*y*, 1 – *z*
N(2)–H(16)···O(5)	0.89(3)	2.01(3)	2.783(3)	145(2)	1 – *x*, 1 – *y*, 1 – *z*
N(1)–H(13)···O(5)	0.85(4)	2.02(4)	2.819(3)	156(4)	*x*, *y*, *z*
N(1)–H(14)···O(1)	0.87(3)	1.95(3)	2.792(3)	163(3)	–*x*, –*y*, 1 – *z*
O(5)–H(25)···Cl(1)	0.65(3)	2.43(4)	3.078(2)	174(4)	1 – *x*, 1 – *y*, 1 – *z*
O(5)–H(26)···Cl(3)	0.85(3)	2.35(3)	3.174(2)	165(3)	1 + *x*, *y*, *z*
C(10)–H(19)···O(4)	0.93(4)	2.46(3)	3.201(3)	137(3)	–*x*, –*y*, 1 – *z*
C(11)–H(22)···O(4)	0.96(4)	2.59(4)	3.326(3)	133(3)	1 – *x*, –*y*, 1 – *z*
C(9)–H(18)···O(2)	1.04(4)	2.55(4)	3.279(3)	127(3)	1 – *x*, –*y*, 1 – *z*

REFERENCES

1. Temkin, O.N., Shestakov, G.K., and Treger, Yu.A., *Atsetilen: Khimiya, Mekhanizmy Reaktsii, Tekhnologiya* (Acetylene: Chemistry, Reaction Mechanisms, and Technology), Moscow: Khimiya, 1991.
2. Mykhalichko, B.M., Temkin, O.N., and Mys'kiv, M.G., *Usp. Khim.*, 2000, vol. 69, no. 11, p. 1042.
3. Pavlyuk, A.V., Mykhalichko, B.M., and Mys'kiv, M.G., *Koord. Khim.*, 2004, vol. 30, no. 3, p. 172 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 30, no. 3, p. 159].
4. Mys'kiv, M.G., Osechkin, S.I., Zavalii, P.Yu., and Fundamenskii, V.S., *Koord. Khim.,* 1988, vol. 14, no. 4, p. 524.
5. Mykhalichko, B.M., Slyvka, Yu.I., and Davydov, V.N., *Koord. Khim.*, 2003, vol. 29, no. 10, p. 796 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 29, no. 10, p. 737].
6. Slyvka, Yu.I., Mykhalichko, B.M., and Davydov, V.N., *Zh. Neorg. Khim.,* 2003, vol. 48, no. 9, p. 1500 [*Russ. J. Inorg. Chem.* (Engl. Transl.), vol. 48, no. 9, p. 1364].
7. Slyvka, Yu.I., Mykhalichko, B.M., and Davydov, V.N., *Koord. Khim.*, 2005, vol. 31, no. 12, p. 931 [*Russ. J. Coord. Chem.* (Engl. Transl.), vol. 31, no. 12, p. 884].
8. Slyvka, Yu.I., Mykhalichko, B.M., Goreshnik, E.A., and Davydov, V.N., *Zh. Neorg. Khim.*, 2007, vol. 52, no. 2, p. 205 [*Russ. J. Inorg. Chem.* (Engl. Transl.), vol. 52, no. 2, p. 165].
9. Slyvka, Yu., Kinzhybalo, V., Lis, T., et al., *Z. Anorg. Allg. Chem.*, 2008, vol. 634, no. 4, p. 626.
10. Aksel'rud, L.G., Grin', Yu.N., Zavalii, P.Yu., et al., *Paket programm dlya strukturnogo analiza kristallov - CSD. Obshchie opisanie* (CSD Program Package for Crrystal Structure Analysis. General Description), Lvov: Lvov. Gos. Univ., 1990.
11. Groger, G., Olbrich, F., Schulte, P., and Behrens, U., *J. Organomet. Chem.*, 1998, vol. 557, p. 251.
12. Schulte, P., Groger, G., and Behrens, U., *Z. Anorg. Allg. Chem.*, 2000, vol. 626, p. 679.
13. Steiner, T., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1996, vol. 52, no. 11, p. 2885.
14. Desiraju, G.R., *Ann. Chem. Res.*, 2002, vol. 35, p. 565.
15. Steiner, T., *Angew. Chem., Int. Ed. Engl.*, 2002, vol. 41, no. 1, p. 49.