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Complex $[Ag(PPh_3)_4][2\text{-}B_{10}H_9NH_3 \cdot 2DMF]$: Synthesis and Structure

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Abstract—The formation of complex salt $[Ag(PPh_3)_4][2\text{-}B_{10}H_9NH_3 \cdot 2DMF]$ (**I**) by the reaction of the salts of the $[2\text{-}B_{10}H_9NH_3]^-$ anion with $[Ag(PPh_3)_4]NO_3$ is studied. The anionic moiety of complex **I** is a stable solvate linked by hydrogen bonds of two types. Compound **I** is identified by IR spectroscopy and elemental, X-ray structure, and X-ray diffraction analyses (CIF file CCDC no. 1884451).

Keywords: closo-decaborate anion, ammonio-*closo*-decaborate, dihydrogen bonds

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INTRODUCTION

Cluster boron anions are unique molecular platforms that can act as building blocks for the preparation of new bioinorganic systems [1–3]. Special attention is given to the derivatives of the *closo*-decaborate anion containing *exo*-polyhedral boron–nitrogen, boron–oxygen, and boron–sulfur bonds [4–7]. The coordination chemistry of *closo*-borate anions is also being developed actively at the present time [8, 9]. Numerous approaches to the synthesis of coordination compounds based on *closo*-borate anions were studied. Various coordination modes of the metal to the boron framework are possible. Many examples for the cluster boron anions existing in the external sphere were described [10–12]. However, coordination compounds in which substituted derivatives of the *closo*-borate anions are used as ligands are nearly unknown [13]. At the same time, these compounds contain the metal atom and *exo*-polyhedral group due to which molecular platforms can be produced from them for the further synthesis of complexes with a specified set of properties.

Nowadays there are many methods for the synthesis of the *closo*-decaborate anion derivatives with the *exo*-polyhedral boron–nitrogen bond [14, 15]. Diverse methods based on the electrophilic and nucleophilic substitution are used to obtain similar derivatives. The derivatives containing the nitrilium, nitro, and diazo groups as *exo*-polyhedral substituents are known [16–18]. The derivatives containing ammonium groups, which can be organoelement analogs of organic amines, are of special interest.

In this work, we proposed an approach to the synthesis of the complex salt of the *closo*-decaborate anion $(Ag(PPh_3)_4)[B_{10}H_9NH_3 \cdot 2DMF]$ (**I**) by the reaction of $(Ag(PPh_3)_4)NO_3$ with $(Bu_4N)[2\text{-}B_{10}H_9NH_3]$ in dimethylformamide (DMF) and also studied the physicochemical properties of compound **I**.

EXPERIMENTAL

Solvents and reagents (Khimmed, Sigma-Aldrich) were reagent grade and used as received.

Synthesis of compound I. A solution of $(N^nBu_4)[2\text{-}B_{10}H_9NH_3]$ (0.37 g, 0.98 mmol) obtained according to a known procedure [19] in DMF (10 mL) was added with $[Ag(PPh_3)_4]NO_3$ (1.19 g, 0.98 mmol), and the obtained reaction mixture was stirred at 60°C under argon until all components of the mixture dissolved. Then the solution was cooled to room temperature, and the product was crystallized. The formed crystals were filtered off and washed twice with Et_2O by por-

tions of 5 mL. The yield of compound **I** was 1.10 g (74%).

For $C_{78}H_{86}B_{10}N_3O_2P_4Ag$				
Anal. calcd., %	C, 65.18	H, 6.03	N, 2.92	B, 7.5
Found, %	C, 65.27	H, 6.09	N, 2.99	B, 7.4

IR (KBr), ν, cm^{-1}): 3440, 3246, 3203 ν(NH); 2538, 2516, 2453, 2422 ν(BH).

Elemental analyses to C, H, and N were carried out on a CHNS-3 FA 1108 Elemental Analyser automated gas analyzer (Carlo Erba). Boron was determined by the inductively coupled plasma mass spectrometry (ICP MS) method on an iCAP 6300 Duo atomic emission spectrometer with inductively coupled plasma (Center for Collective Use of the Research Center Kurchatov Institute—IREA).

The IR spectra of the compounds were recorded on an Infralyum FT-08 FT-IR spectrophotometer (NPF AP Lyumeks) in the range 4000–600 cm^{-1} with a resolution of 1 cm^{-1}. The samples were prepared as KBr pellets.

X-ray diffraction analysis (XRD) was carried out on a Bruker D8 Advance X-ray diffractometer (CuK_α radiation, Ni filter, LYNXEYE detector, reflection geometry) in cells of oriented single-crystal silicon in the angle range $2\theta = 5°–70°$ with an increment of 0.01125°. Prior to the detection of the XRD patterns, the studied samples were thoroughly triturated in an agate mortar.

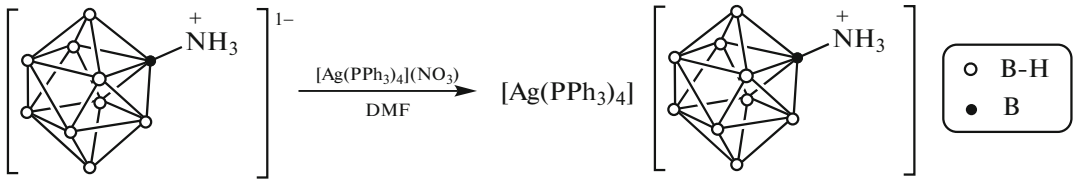
X-ray structure analysis of compound I was carried out on a Bruker KAPPA APEX II automated four-circle diffractometer with a two-dimensional detector (MoK_α radiation) [20] at 100(2) K. The cell parameters were refined over the whole data set [21]. The structure was solved by a direct method [22] and refined by full-matrix least squares [23] for F^2 for all data in the anisotropic approximation for all non-hydrogen atoms (except for disordered atoms if any). The hydrogen atoms of the borohydride moiety were localized from the difference electron density synthesis and refined isotropically without any restraints. The hydrogen atoms of the organic moieties were placed in the geometrically calculated positions and refined with isotropic temperature parameters equal to $1.2U_{eq}$ of the N or C atom for NH, CH, and CH_2 and $1.5U_{eq}$ of the C atom for CH_3. The crystallographic characteristics, X-ray diffraction experimental details, and refinement for the structure of compound **I** are presented in Table 1.

The coordinates of atoms and crystallographic data for compound **I** were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC no. 1884451; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif).

RESULTS AND DISCUSSION

The reaction of the $[2\text{-}B_{10}H_9NH_3]^-$ anion with silver compound **I** was studied to evaluate the reactivity under the complex formation conditions. Numerous silver complexes in which the *closo*-decaborate anion acts as an inner- or outer-sphere ligand are known. For example, the boron cluster was oxidized when attempting to obtain salt $Ag[B_{10}H_9NH_3]$ from aqueous solutions. Evidently, this is related to a decrease in the resistance to oxidation of substituted *closo*-decaborates over the starting $[B_{10}H_{10}]^{2-}$ anion. The gradual oxidation of the boron cluster was also observed when the ammonio-*closo*-decaborate silver salt was obtained in a medium of organic solvents. The introduction of additional amounts of the ligand, for example, triphenylphosphine, into the reaction mixture results in the formation of complex salts with substituted *closo*-decaborate in the external sphere.

This complex was obtained in the pure state by the reaction of $(N^nBu_4)[2\text{-}B_{10}H_9NH_3]$ with $[Ag(PPh_3)_4]NO_3$ in DMF according to the scheme



Complex **I** was isolated by the isothermal crystallization of the reaction product, and its composition and structure were confirmed by the X-ray structure analysis and XRD data.

According to the XRD data, the studied sample is fairly well crystallized: no reflections of the precursor compounds are observed on the XRD pattern. A good coincidence of the curves obtained experimentally (Fig. 1, *1*) and calculated from the X-ray structure analysis data for the single crystals (Fig. 1, *2*) also indicates that the obtained product is pure and homogeneous.

According to the X-ray structure analysis data, the structure of complex **I** is built of $[Ag(PPh_3)_4]^+$ cations and substituted ammonio-*closo*-decaborate anions containing the substituent in the equatorial position

Table 1. Crystallographic data and structure refinement parameters for compound **I**

Parameter	Value
FW	1437.34
Radiation (λ, Å)	MoK_α (λ = 0.71073)
Crystal system; space group	Triclinic; $P\bar{1}$
a, Å	13.7878(4)
b, Å	14.5300(5)
c, Å	19.3842(6)
α, deg	104.892(2)
β, deg	100.220(2)
γ, deg	93.924(2)
V, Å^3	3666.74
Z	2
ρ_{calcd}, g mm^{-3}	1.302
μ, mm^{-1}	0.411
F(000)	1496
Scan range over θ, deg	4.087–29.999
Scan mode	ω
Number of measured reflections	44876
Number of independent reflections (N_1)	21157
R_{int}	0.0583
Number of reflections with $I > 2\sigma(I)$ (N_2)	14548
Number of refined parameters	888
GOOF (F^2)	1.033
R_1 for N_2	0.0521
wR_2 for N_1	0.1118
$\Delta\rho_{max}/\Delta\rho_{min}$, e Å^{-3}	1.706/–0.925

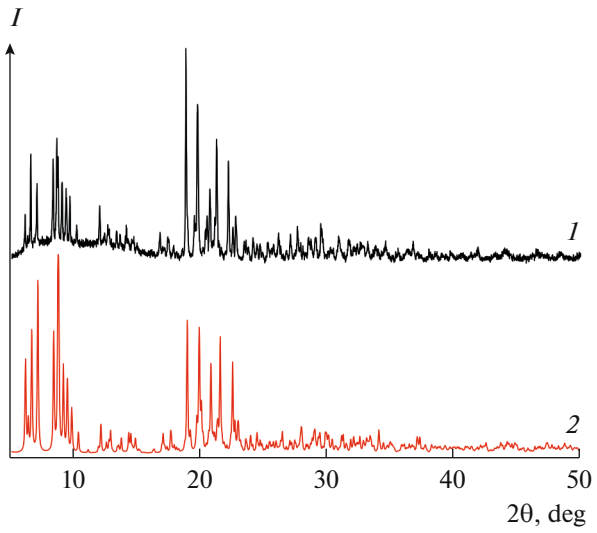


Fig. 1. The (*1*) XRD data and (*2*) theoretically predicted diffraction pattern for compound $[Ag(PPh_3)_4][2\text{-}B_{10}H_9NH_3 \cdot 2DMF]$.

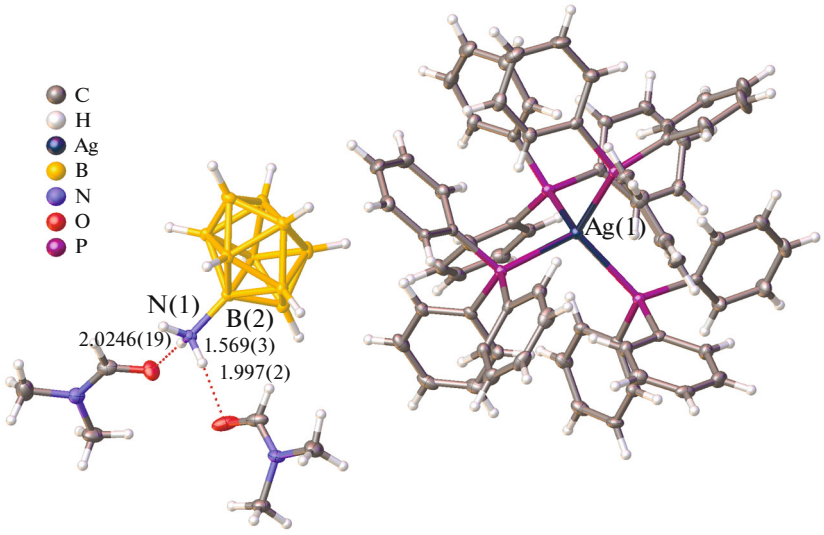


Fig. 2. Structure of the $[Ag(PPh_3)_4][2\text{-}B_{10}H_9NH_3 \cdot 2DMF]$ complex according to the single crystal X-ray structure analysis.

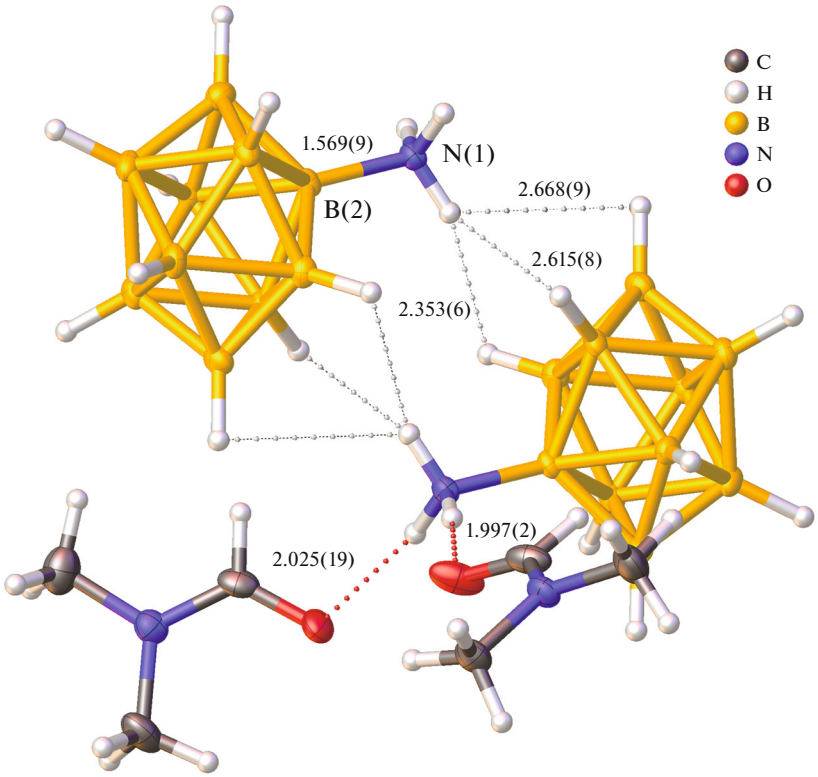


Fig. 3. Supramolecular interactions in the crystals of compound $[Ag(PPh_3)_4][2\text{-}B_{10}H_9NH_3 \cdot 2DMF]$.

(Fig. 2)[1]. The exopolyhedral boron–nitrogen distance is 1.569 Å, which corresponds to the ordinary bond (Table 2). A characteristic feature is the presence of solvate DMF molecules linked by hydrogen bonds between the protons of the ammonium substituent and the oxygen atoms of the solvent molecules (O–O 1.997–2.025 Å). Solvate **I** retains its composition on prolong storage in air or keeping in a desiccator over phosphorus(V) oxide.

[1] Figures 2 and 3 were drawn using the OLEX2 program software [24].

Table 2. Selected bond lengths for compound **I**

Bond	*d*, Å	Bond	*d*, Å
Ag(1)–P(1)	2.6056(8)	B(5)–B(6)	1.827(4)
Ag(1)–P(2)	2.6082(8)	B(5)–B(9)	1.818(4)
Ag(1)–P(3)	2.6337(8)	B(6)–B(7)	1.840(5)
Ag(1)–P(4)	2.5945(6)	B(6)–B(1)	1.690(4)
B(2)–N(1)	1.568(3)	B(6)–B(9)	1.828(3)
B(1)–B(2)	1.675(4)	B(7)–B(8)	1.829(3)
B(1)–B(3)	1.698(5)	B(7)–B(1)	1.694(4)
B(1)–B(4)	1.698(4)	B(8)–B(9)	1.843(5)
B(1)–B(5)	1.703(4)	B(8)–B(1)	1.702(4)
B(2)–B(3)	1.822(4)	B(9)–B(1)	1.696(4)
B(2)–B(5)	1.825(4)	O(1)–C(1)	1.234(3)
B(2)–B(6)	1.803(4)	N(2)–C(1)	1.329(3)
B(2)–B(7)	1.799(4)	N(2)–C(2)	1.455(3)
B(3)–B(4)	1.832(4)	N(2)–C(3)	1.451(4)
B(3)–B(7)	1.822(4)	O(2)–C(4)	1.223(4)
B(3)–B(8)	1.820(4)	N(3)–C(4)	1.332(4)
B(4)–B(5)	1.833(4)	N(3)–C(5)	1.459(4)
B(4)–B(8)	1.823(4)	N(3)–C(6)	1.460(3)
B(4)–B(9)	1.830(4)		

The third proton of the ammonium substituent participates in the intermolecular dihydrogen bond with the adjacent cluster, and the anions form centrosymmetric dimers (Fig. 3). The coordination occurs at one of the apical faces. The O···O distances in the dihydrogen bonds lie in the range 2.353–2.668 Å (Table 3).

The presence of hydrogen bonds is also confirmed by the data of IR absorption spectroscopy. The spectra of the obtained complex **I** (Fig. 4a) exhibit the shift of the absorption bands of the nitrogen–hydrogen bond to lower wavenumbers and a decrease in the intensity of one of the vibration modes. The absorption band in the range of absorption of boron–hydrogen stretching vibrations is also split, indicating that the boron framework is involved in the formation of dihydrogen bonds.

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Analysis to boron was carried out at the Center for Collective Use of the Research Center Kurchatov Institute—IREA. The XRD and X-ray structure analyses were con-

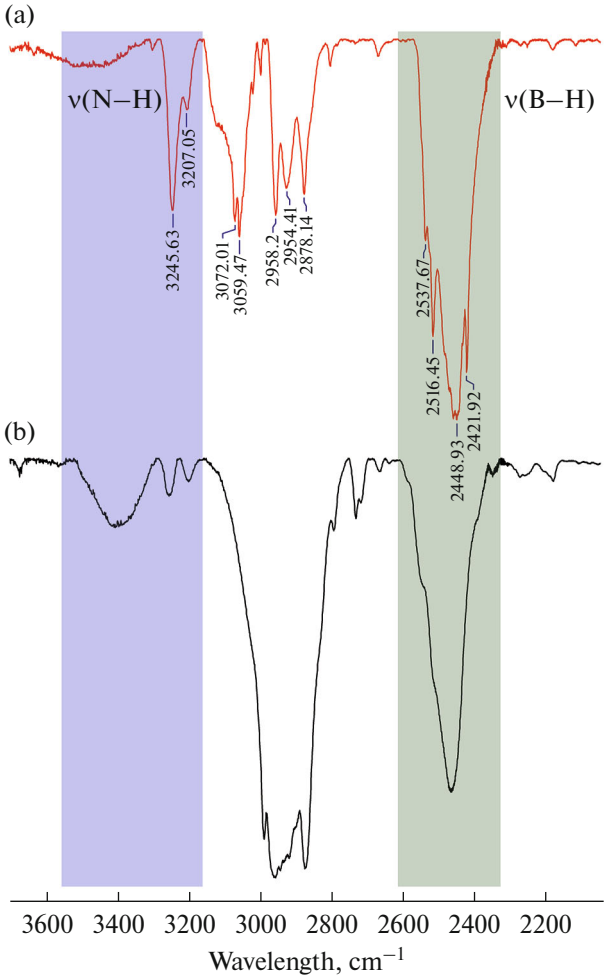

Fig. 4. Fragments of the IR absorption spectra of (a) complex **I** and (b) starting salt $(N^nBu_4)[2\text{-}B_{10}H_9NH_3]$.

Table 3. Selected geometric parameters of hydrogen bonds for compound **I**

D–H···A	Distance, Å			Angle DHA, deg
	D–H	H···A	D···A	
N(1)–H(1*C*)···O(1)	0.910	2.025	2.910	164
N(1)–H(1*B*)···O(2)	0.910	1.997	2.906	176
B(6)–H(6)···H(1*D*)	1.120	2.354	2.720	97
B(7)–H(7)···H(1*D*)	1.119	2.615	2.851	90
B(10)–H(10)···H(1*D*)	1.120	2.668	2.798	85

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