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17-Crown-5 ether condensed with 11-vertex *nido*-carborane*

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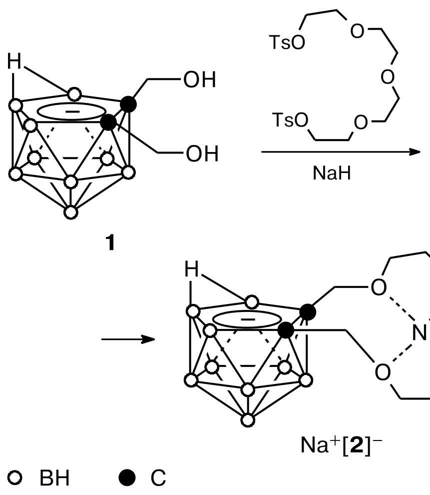
The reaction of easily accessible *nido*-carborane [*nido*-7,8-$(HOCH_2)_2$-7,8-$C_2B_9H_{10}]^-$ with tetraethylene glycol tosylate produces *nido*-carborane sodium salt condensed with 17-crown-5 ether, Na[*nido*-7,8-$O(CH_2CH_2OCH_2CH_2OCH_2)_2$-7,8-$C_2B_9H_{10}$]. The structures of solvate complexes of this crown ether with acetone, ethanol, and water were studied by X-ray diffraction analysis.

Key words: carboranes, crown ethers, sodium.

Anionic polyhedral boron compounds attract attention of researchers due to their unique ability to extract highly toxic radioactive metal cations (primarily, $^{137}Cs^+$ and $^{90}Sr^{2+}$) from solutions of spent nuclear fuel.[1,2] To enhance efficiency and selectivity of extraction, polyhedral anions are often bound to molecules of other complexing agents, such as podands, crown ethers, and calixarenes. As a rule, these substituents are introduced by nucleophilic opening of dioxane derivatives[3] of cobaltacarboranes.[4—7] In addition, alkylation of amino-[8] and thio-substituted[9—11] polyhedral anions is used sometimes. In this work, we propose an alternative approach to the synthesis of carborane crown ethers based on the condensation of easily accessible 1,2-bis(hydroxymethyl)-*ortho*-carborane.

The cleavage of 1,2-bis(hydroxymethyl)-*ortho*-carborane by an ethanolic solution of KOH gives an 11-vertex monoanion [*nido*-7,8-$(HOCH_2)_2$-7,8-$C_2B_9H_{10}]^-$ (**1**), which was isolated as a salt with the Me_3NH^+ cation in 82% yield. The subsequent interaction of **1** with tetraethylene glycol tosylate in the presence of NaH affords sodium salt of *nido*-carborane anion $[\mathbf{2}]^-$ containing the 17-crown-5 ether fragment in 64% yield (Scheme 1). The high yield of the cyclic product is related, most likely, to the template effect of sodium ion.

Scheme 1



Salts $Me_3NH^+[\mathbf{1}]^-$ and $Na^+[\mathbf{2}]^-$ were characterized by the ^1H and ^{11}B NMR spectra and elemental analysis. The ^1H NMR spectrum of salt $Na^+[\mathbf{2}]^-$ remains almost unchanged in the presence of twofold excess of dibenzo-18-crown-6, indicating stronger binding of crown ether $[\mathbf{2}]^-$ with sodium ion.** Unfortunately, it is difficult to exactly determine the binding constant of $[\mathbf{2}]^-$ with Na^+ by NMR titration because of a complicated structure of the spectrum.

Slow evaporation of solutions of $Na^+[\mathbf{2}]^-$ in acetone, ethanol, and water produces crystals of three solvate forms, whose structures were studied by X-ray diffraction analysis (Figs 1—3, Table 1). All the three solvates have the nearly identical structure of the carborane cage resembling that of the initial anion $[\mathbf{1}]^-$ (see Ref. 13). Remarkably, the distance from the sodium atom to the oxygen atoms of crown ether (2.388—2.566 Å, average 2.478 Å) is notably longer than a similar distance to the oxygen atoms of the solvate molecules (2.272—2.343 Å, average 2.316 Å).

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* Dedicated to Academician of the Russian Academy of Sciences Yu. N. Bubnov on the occasion of his 80 birthday and the 60th anniversary of the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences.

** The binding constant of dibenzo-18-crown-6 for the Na^+ ion is pK = 6.7 (see Ref. 12).

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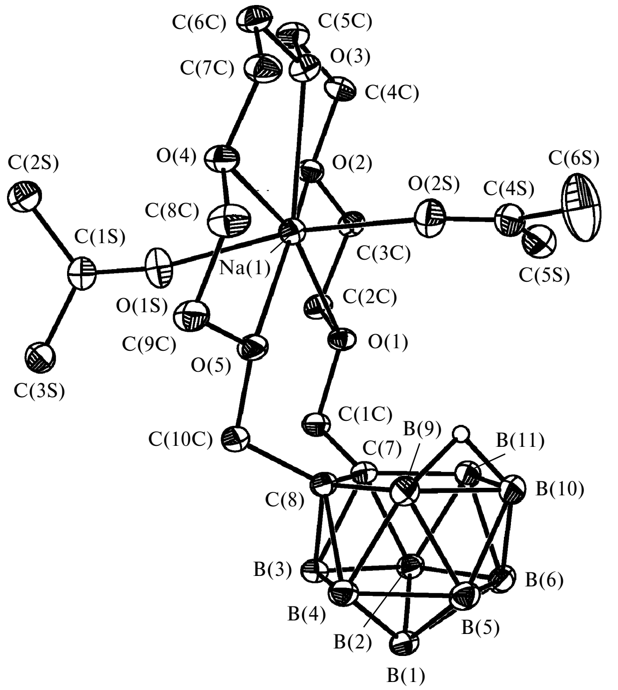

Fig. 1. Structure of solvate $Na^+[\mathbf{2}]^- \cdot 2(Me)_2CO$ in the representation of atoms by thermal ellipsoids ($p = 50\%$). The disordered part of the acetone molecule and hydrogen atoms, except for the bridging B(9)—H—B(10) fragments, are omitted.

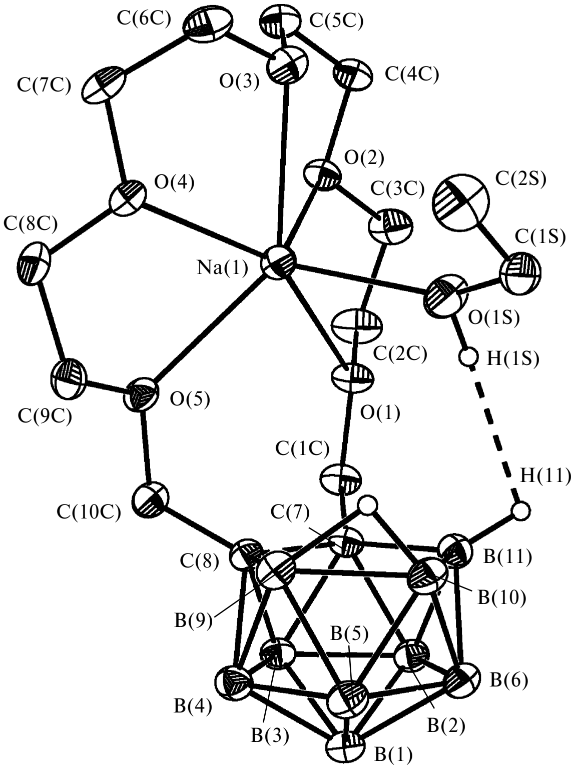

Fig. 2. Structure of solvate $Na^+[\mathbf{2}]^- \cdot EtOH$ in the representation of atoms by thermal ellipsoids ($p = 50\%$). Hydrogen atoms, except for the bridging B(9)—H—B(10) fragments, are omitted.

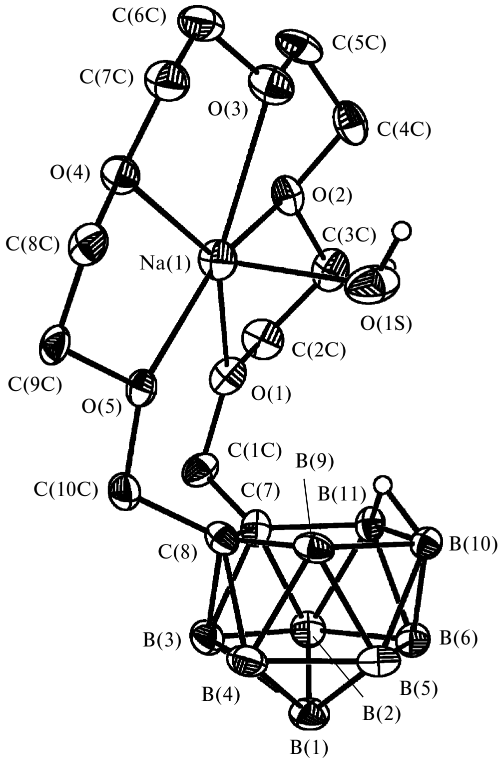

Fig. 3. Structure of solvate $Na^+[\mathbf{2}]^- \cdot H_2O$ in the representation of atoms by thermal ellipsoids ($p = 50\%$). Only one of two independent molecules is shown. Hydrogen atoms, except for the bridging B(10)—H—B(11) fragments, are omitted.

This difference indicates that the 17-crown-5 fragment cannot coordinate sodium ion with optimum Na—O distances, probably, due to conformational restrictions. A similar pattern is observed for the $[Na(15\text{-crown-}5)(H_2O)]^+$ cation.[14] Interestingly, the solvate ethanol molecule in crystal $Na^+[\mathbf{2}]^- \cdot EtOH$ forms the intramolecular dihydrogen bond[15,16] O(1)S—H(1)S···H(11)—B(11) with the distance H(1)S···H(11) 2.11 Å and angle O(1)S—H(1)S···H(11) 163°. It is most likely that the

Table 1. Selected distances (d) in the solvates

Distance	d/Å		
	$Na^+[\mathbf{2}]^- \cdot \cdot 2(Me)_2CO$	$Na^+[\mathbf{2}]^- \cdot \cdot EtOH$	$Na^+[\mathbf{2}]^- \cdot \cdot H_2O$
Na(1)—O(1)	2.5389(12)	2.5417(12)	2.412(3)
Na(1)—O(2)	2.4726(10)	2.3926(12)	2.431(3)
Na(1)—O(3)	2.4904(11)	2.5393(13)	2.501(3)
Na(1)—O(4)	2.4847(11)	2.3880(12)	2.434(3)
Na(1)—O(5)	2.4413(10)	2.4591(12)	2.456(3)
Na(1)—O(1S)	2.3367(11)	2.2716(14)	2.310(3)
Na(1)—O(2S)	2.3432(11)	—	—
C(7)—C(8)	1.5778(15)	1.5793(19)	1.581(4)
H(1S)—H(11)	—	2.11(1)	—

strength of this bond is not high, since the structure with the solvate water molecule does not have a similar contact.

Thus, we proposed the simple approach to the synthesis of carborane crown ethers. The obtained anion [**2**]$^-$ can be used further for the synthesis of transition metal complexes.

Experimental

All reactions were carried out in argon, and procedures associated with isolation of substances were carried out in air. ^{1}H and ^{11}B NMR spectra were recorded on a Bruker Avance-400 instrument. Chemical shifts are presented in δ scale relative to signals of residual protons of the solvent used as an internal standard.

Synthesis of trimethylammonium 7,8-bis(hydroxymethyl)-7,8-dicarba-*nido*-undecaborate ([Me$_3$NH][1]). A solution of 1,2-bis(hydroxymethyl)-*ortho*-carborane[17] (2.04 g, 10 mmol) and KOH (2.80 g, 50 mmol) in ethanol (30 mL) was refluxed for 6 h. The solvent was evaporated *in vacuo*, and the residue was dissolved in water (10 mL) and filtered off. The obtained solution was neutralized using HCl, and $Me_3NH^+Cl^-$ (1.90 g, 20 mmol) was added. A white precipitate was formed, filtered off, washed with water, and dried *in vacuo*. The yield of the product was 2.08 g (82%). ^{1}H NMR (acetone-d$_6$), δ: –2.50 (br.s, H, BHB bridge); 3.16 (s, 9 H, Me_3NH^+); 3.58 (d, 2 H, CH$_2$OH, J = 12 Hz); 3.83 (d, 2 H, CH$_2$OH, J = 12 Hz). ^{11}B NMR (acetone-d$_6$), δ: –37.8 (1 B), –34.2 (1 B), –19.4 (2 B), –17.0 (2 B), –12.7 (1 B), –9.4 (2 B). Found (%): C, 33.22; H, 10.71; B, 38.04. $C_7H_{26}B_9NO_2$. Calculated (%): C, 33.15; H, 10.33; B 38.37. Other salts of this *nido*-carborane were obtained earlier; however, they were not characterized in detail.[18]

Synthesis of sodium 7,8-(2,5,8,11,14-pentaoxapentadecane-1,15-diyl)-7,8-dicarba-*nido*-undecarborate (Na$^+$[2]$^-$). A solution of [Me$_3$NH]$^+$[**1**]$^-$ (633 mg, 2.5 mmol) and tetraethylene glycol tosylate[19] (1.25 g, 2.5 mmol) in THF (50 mL) was added dropwise for 2 h to a boiling suspension of NaH (0.6 g, 15 mmol) in THF (50 mL). The obtained mixture was additionally refluxed for 3 h and then diluted with water (50 mL). A white precipitate was formed. The solution was neutralized with HCl, the most THF was evaporated *in vacuo*, and the resulting mixture was filtered off. The product was washed with water, dried, dissolved in acetone, and passed through an Al_2O_3 layer (3 cm). The obtained solution was evaporated, and the precipitate was reprecipitated from acetone by the addition of Et$_2$O. The yield of the product was 0.6 g (64%). ^{1}H NMR (acetone-d$_6$), δ: –2.75 (br.s, H, BHB bridge); 3.31 (d, 2 H, J = 11 Hz); 3.57—3.75 (m, 16 H); 3.99 (d, 2 H, J = 11 Hz). ^{11}B NMR (acetone-d$_6$), δ: –37.8 (1 B), –34.2 (1 B), –19.4 (2 B), –17.0 (2 B), –12.7 (1 B), –9.4 (2 B). Found (%): C, 36.65; H, 8.39; B, 24.52. $C_{12}H_{30}B_9NaO_5 \cdot H_2O$. Calculated (%): C, 36.70; H, 8.21; B, 24.78. A similar procedure was used previously for the synthesis of organic crown ethers.[20,21]

X-ray diffraction analysis. Colorless crystals of compounds Na$^+$[**2**]$^-\cdot$2(CH$_3$)$_2$CO, Na$^+$[**2**]$^-\cdot$EtOH and Na$^+$[**2**]$^-\cdot$H$_2$O were grown by the slow evaporation of solutions of Na$^+$[**2**]$^-$. X-ray diffraction studies were carried out on a SMART 1000 CCD diffractometer (MoKα radiation, graphite monochromator, ω scan mode). The structures were solved by a direct method and

Table 2. Main crystallographic data and refinement parameters

Parameter	Na$^+$[**2**]$^-\cdot$2(CH$_3$)$_2$CO	Na$^+$[**2**]$^-\cdot$EtOH	Na$^+$[**2**]$^-\cdot$H$_2$O
Empirical formula	$C_{18}H_{42}B_9NaO_7$	$C_{14}H_{36}B_9NaO_6$	$C_{12}H_{32}B_9NaO_6$
Molecular weight	490.80	420.71	392.66
T/K	100	100	100
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1$
$Z(Z')$	4	4	4 (2)
a/Å	9.0550(18)	10.0877(10)	9.256(3)
b/Å	16.938(3)	25.078(2)	20.784(6)
c/Å	18.664(4)	9.4027(9)	11.482(4)
β/deg	96.57(3)	99.638(2)	104.687(12)
V/Å^3	2843.7(10)	2345.1(4)	2136.6(12)
d_{calc}/g cm^{-3}	1.146	1.192	1.221
μ/cm^{-1}	0.89	0.94	0.99
F(000)	1048	896	832
2θ$_{max}$/deg	60	58	56
Number of reflections			
(R_{int})	(0.0304)	(0.0280)	(0.0345)
with $I > 2\sigma(I)$	6200	4568	8398
measured	27069	14216	15967
independent	8214	6186	9998
Number of refined parameters	360	315	571
R_1	0.0384	0.0474	0.0693
wR_2	0.1097	0.1286	0.1691
Goodness-of-fit	0.974	1.016	1.055
Residual electron density /e Å^{-3}(d_{max}/d_{min})	0.325/–0.203	0.373/–0.207	0.523/–0.339

refined by the least-squares method in the anisotropic full-matrix approximation for $F^2{}_{hkl}$. The hydrogen atoms for the BH groups and solvate molecules were localized from the difference electron density Fourier syntheses and refined in the isotropic approximation, and other hydrogen atoms were placed in the calculated positions and refined by the riding model. All calculations were performed using the SHELXTL PLUS program package. The main crystallographic data and refinement parameters are given in Table 2. The full data on the geometric parameters were deposited with the Cambridge Crystallographic Data Centre (CCDC 1004843 (Na^+[**2**]$^-$•2$(CH_3)_2CO$), CCDC 1004844 (Na^+[**2**]$^-$•EtOH), and CCDC 1004845 (Na^+[**2**]$^-$•H_2O).

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