General and Inorganic Chemistry

Synthesis of dialkoxy- and alkoxy-amino-disubstituted derivatives of $B_{12}H_{12}^{2-}$

*B. Brellochs[a] and A. Semioshkin[b]**

[a]*Institute of Inorganic Chemistry of Munich University, 1 Meiserstrasse, 80333 Munich, Germany**
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 117813 Moscow, Russian Federation. Fax: +7 (095) 135 5085*

Dichloromethoxymethane reacts with the sodium salt of *closo*-dodecahydrododecaborate $Na_2B_{12}H_{12}$ to give disubstituted cluster, which readily decomposes when treated with various reagents. This cluster reacts with water, forming the previously described 1,7-$B_{12}H_{10}(OH)_2^{2-}$, reaction with alcohols results in a novel 1,7-dialkoxy derivative, whereas interaction with morpholine in acetone solution affords the novel anion, 1-O-I-Pr^i-7-O(CH_2CH_2)N-$B_{12}H_{10}^{2-}$. All of these derivatives were isolated as cesium salts and characterized by one- and two-dimensional NMR techniques.

Key words: *closo*-dodecahydrododecaborate, dichloromethoxymethane, 1,7-dialkoxy derivatives, 1-isopropoxy-7-morpholino-*closo*-decahydrododecaborate, NMR-spectra.

The sodium salt of $B_{12}H_{12}^{2-}$ can be easily acylated with aliphatic and aromatic acyl chlorides in acetone, and the mono-hydroxy substituted cluster is always formed as a by-product.[1,2]

$$B_{12}H_{12}^{2-} + RCOCl \xrightarrow[2.\ H_2O]{1.\ (Me_2)CO} B_{12}H_{11}COR^{2-} + B_{12}H_{11}OH^{2-}$$

Since dichloromethoxymethane is a stronger electrophilic agent than acyl chlorides,[3] it was interesting to investigate its behavior toward the $B_{12}H_{12}^{2-}$ dianion.

We found that dichloromethoxymethane reacts with the sodium salt of *closo*-dodecahydrododecaborate in acetone to give the unstable product **A** of unknown nature.

The reaction is accompanied by the formation of two equivalents (with respect to $Na_2B_{12}H_{12}$) of sodium chloride. The same feature was observed in the reaction of $Na_2B_{12}H_{12}$ with acyl chlorides, however in that case the formation of only one equivalent of NaCl was observed.[1,2] In the ^{11}B NMR spectrum of **A** there were 5 signals with the intensity ratio 2:2:4:2:2. This pattern is typical of a disubstituted cluster with two equivalent substituents. The signal of the substituted boron atoms was observed at 1.7. In the ^1H NMR spectrum of **A** the signals at 8.08 and 3.61 were shifted downfield (about 0.5 ppm) compared to Cl_2CHOMe. In the ^{13}C NMR the two main signals were at 55.4 and 162.4.

Compound **A** is not stable and readily decomposes when treated with various reagents (water, alcohols,

* Institut für Anorganische Chemie der Universität Munchen, Meiserstr. 1, 80333-München, Deutschland.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 421—424, March, 1995.

1066-5285/95/4403-0406 $12.50

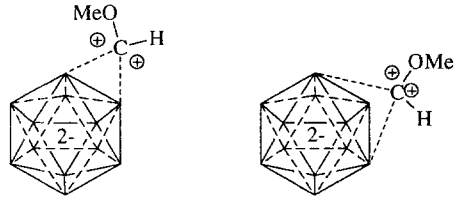
amines). It reacts with water to form the previously described[4] 1,7-$B_{12}H_{10}(OH)_2^{2-}$ anion. In the ^{13}C NMR spectrum of the hydrolysate there was a signal at 49.2 ppm, which is typical of dimethyl ether.[5]

We have already proved, that in acylation of $B_{12}H_{12}^{2-}$ acylium cations are formed.[2] For similar reasons we suggest that in the reaction with Cl_2CHOMe a dication is also formed. This dication reacts then with a cluster resulting in **A**:

$$Cl_2CHOMe + Na_2B_{12}H_{12} \xrightarrow[-2NaCl]{} MeOCH^{2+} + B_{12}H_{12}^{2-} \longrightarrow$$

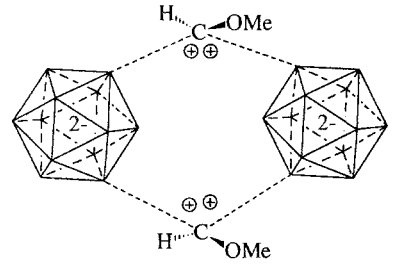
$$\longrightarrow \boxed{A} \xrightarrow{H_2O} 1,7\text{-}B_{12}H_{10}(OH)_2^{2-} + Me_2O$$

There are two ways in which the dication formed can coordinate with one molecule of cluster (**a** and **b**). However path **a** is not possible because in this case after hydrolysis of such an intermediate, the 1,2- and not the 1,7-dihydroxy isomer would be formed. Path **b** is not likely due to steric reasons.

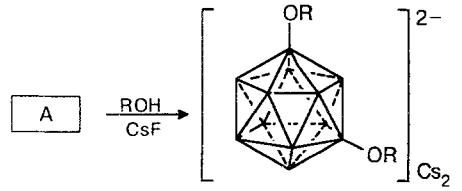


a **b**

Thus the most probable structure of **A** seems to be the one in which two molecules of the cluster coordinate with two dications:

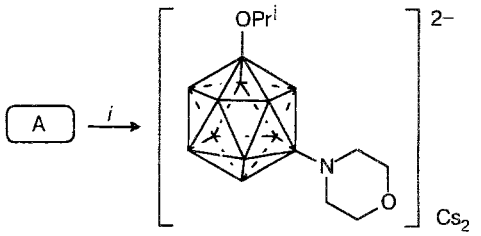


Compound **A** reacts with alcohols leading to the novel 1,7-$B_{12}H_{10}(OR)_2^{2-}$ disubstituted systems **1**, **2**:



1: R = Me
2: R = Et

Treatment of an acetone solution of **A** with morpholine results in the formation of 1-isopropoxy-2-morpholino-*closo*-decahydrododecaborate **3**, which is the first disubstituted B_{12}-cluster containing a B—N bond.



3

i. 1. morpholine/acetone; 2. CsF/MeOH.

In this case not only does nucleophilic attack by morpholine take place, but also the addition of B—H protons to the CO bond of acetone.

The products **1—3** were isolated as cesium salts and characterized by ^1H, ^{11}B, and ^{13}C NMR spectra.

The ^{11}B NMR spectra of the 1,7-dialkoxy derivatives **1**, **2** 1,7-$B_{12}H_{10}(OR)_2^{2-}$ are typical of B_{12}-clusters with two identical substituents. There are 5 signals with the intensity ratio 2:2:4:2:2. The signals of the B atoms in the substituted positions at δ 3.5 (dimethoxy) and 3.9 (diethoxy) are shifted downfield compared to 1,7-$B_{12}H_{10}(OH)_2^{2-}$ (2.2 ppm for [1,7-$B_{12}H_{10}(OH)_2$][NBu_4]$_2$ in CD_3OD).[4] The chemical shift of the B atom in the substituted position of the corresponding cesium salt in D_2O is the same (2.2 ppm).

The meta (1,7)-substitution of clusters **1**, **2** was confirmed by ^{11}B—^{11}B-COSY spectra (Fig. 1, *a*). In the COSY spectrum of the dimethoxy derivative **1** the signal of the B atom in the substituted position has three crosspeaks: two signals (relative intensity 2) at −15.6 and −23.8 ppm and one signal (relative intensity 4) at −17.5 ppm. If **1** were an ortho(1,2)-isomer, the signal of the B atom in substituted position would have only two crosspeaks. The signal at −15.6 ppm (relative intensity 2) has two crosspeaks: one to the substituted position (B(1,7)) and one to the signal with relative intensity 4 (B(4,6,8,11)). Therefore, this signal can result only from B(2,3). The signal at −20.4 ppm has no crosspeaks to the substituted position and results from B(9,10). Finally, the signal at −23.9 ppm belongs to B(5,12). For the diethoxy derivative **2** the signals were assigned in a similar manner (Table 1).

In the ^{11}B NMR spectra of the morpholino-isopropoxy derivative **3** (1-OPr^i-7-$O(CH_2CH_2)_2N$-$B_{12}H_{10}^{2-}$) there are 7 signals with an intensity ratio 1:1:2:4:2:1:1. Two signals with relative intensity 1 belong to the substituted B atoms at 4.3 and 3.1 ppm. We deliberately assigned the signal at 4.3 ppm to B—OPr^i because the O-substituted atom should be shifted more downfield than the N-substituted B-atom.

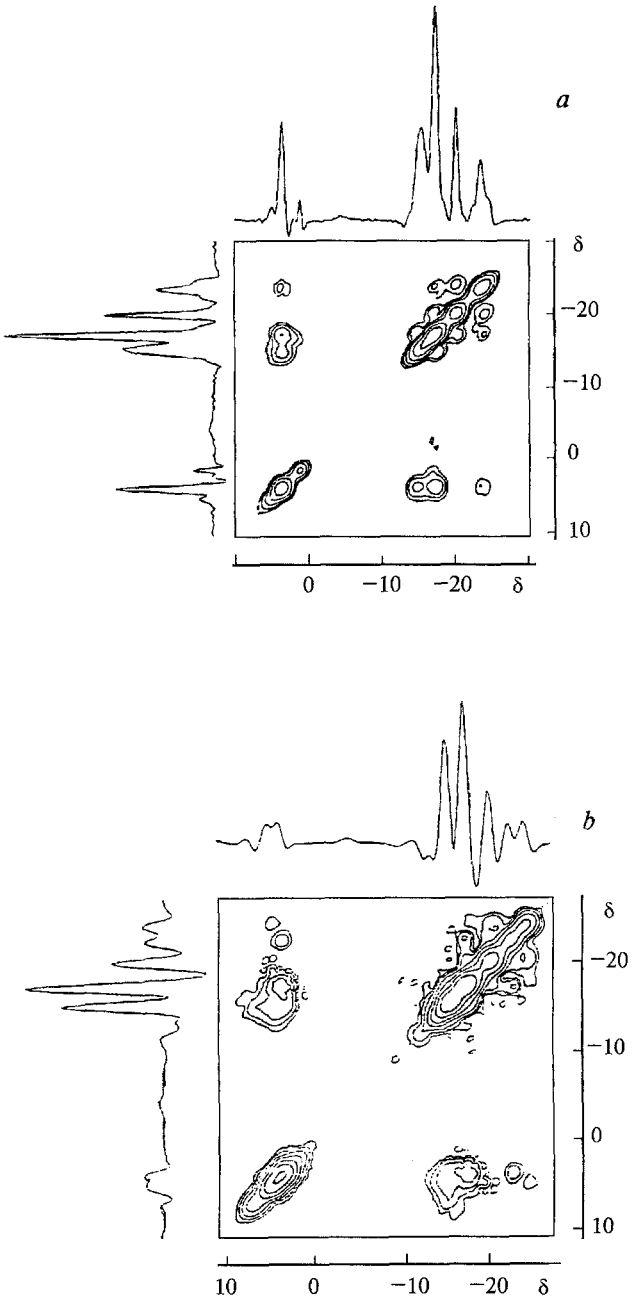


Fig. 1. $^{11}B—^{11}B$-COSY spectra (δ, ppm, in D_2O) of **1**(*a*), **3**(*b*).

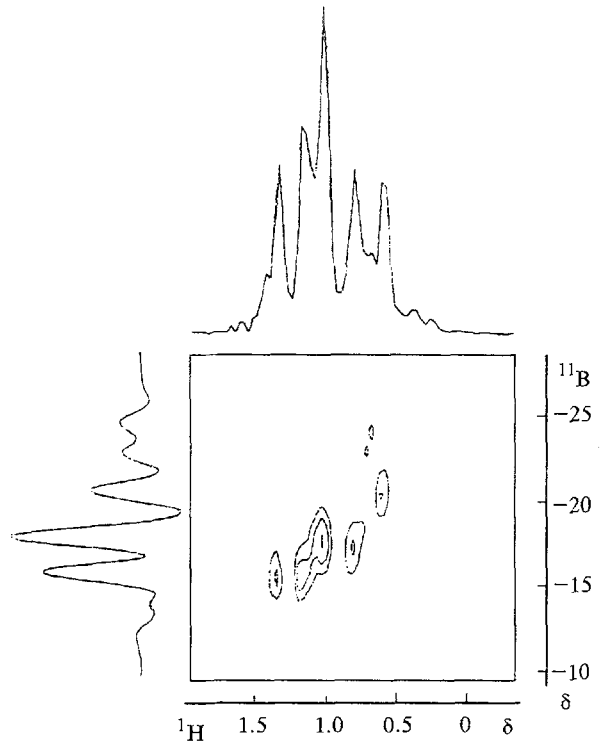


Fig. 2. $^1H—^{11}B$-2D NMR spectra (ppm, in D_2O) of **3**.

Table 1. The ^{11}B NMR spectra parameters (ppm, in D_2O) of $1,7\text{-}B_{12}H_{11}(OR)_2$ (**1**, **2**)

Compound	R	Boron atoms in positions				
		1, 7	2, 3	4, 6, 8, 11	9, 10	5, 12
1	Me	3.5	−15.6	−17.5	−20.4	−23.9
2	Et	3.9	−14.9	−17.2	−20.0	−23.6

Table 2. The ^1H NMR of the B—H protons of **1—3** (ppm)

Compound	H-atoms in positions			
	2, 3	4, 6, 8 ,11	9, 10	5 и 12
1	1.37	1.06	0.67	0.67
2	1.41	1.09	0.69	0.69
3	1.42	1.11	0.70	0.88

The signal of the O-substituted B atom (B(1)) in $^{11}B—^{11}B$-COSY-spectrum (Fig.1, *b*) of **3** has three crosspeaks and no crosspeaks to the N substituted B atom, as expected for the 1,7-isomer. The N-substituted atom (B(7)) also has three crosspeaks with unsubstituted B atoms.

Atom B(1) has a crosspeak to the signal with relative intensity 1 (−24.8 ppm), therefore the latter can be assigned to B(5). Accordingly, the signal at −23.0 ppm with relative intensity 1 belongs to B(12). Both signals of the substituted boron atoms have no crosspeaks to the signal at −20.8 ppm. The latter can be assigned to B(9,10) atoms. The signal at −16.1 ppm has no crosspeaks to the unsubstituted B-atoms with relative intensity 1, *i.e* it should belong to the B(2,3) atoms. Consequently, the signal at −18.0 ppm results from B(6,8,10,11).

In the ^1H NMR spectrum of $1,7\text{-}B_{12}H_{11}(OMe)_2^{2-}$ (**1**) there was only a singlet at 3.21 ppm. In the ^{13}C NMR spectrum the methyl groups were represented by a resonance at 53.2 ppm.

In the ^1H NMR spectrum of the diethoxy derivative **2** there was a triplet at 0.98 ppm and a quartet at

3.50 ppm with a ratio of 3:2. In the ^{13}C NMR spectrum the signals were also typical for the OEt group (18.4 and 59.0 ppm).

The ^{1}H NMR spectrum of **3** showed a doublet at 0.98 ppm, a heptet at 3.45 ppm (O—Pr^i group), and two triplets at 2.87 and 3.63 ppm (morpholino group). In the ^{13}C NMR spectrum there were signals at 25.24, 72.48 ppm (O—Pr^i) and 48.51, 67.08 (morpholine).

The signals of the protons of the B—H groups were detected by recording ^{1}H—{^{11}B}-decoupled NMR spectra and suppressing the signals of all other protons. The signals were assigned (Table 2) using ^{1}H—^{11}B-two-dimensional spectra (Fig. 2).

Experimental

Materials and equipment. Materials were reagent grade and were used as received from standard commercial vendors (Bayer AG, Aldrich). Acetone was distilled from P_2O_5 immediately prior to use. The ^{1}H, ^{11}B and ^{13}C NMR spectra were recorded at 200.13, 64.21 and 50.32 MHz, respectively, on a Bruker ACP-200 spectrometer. Chemical shifts are given in the δ scale relative to internal standards (TMS, DMSO-d_6, $BF_3 \cdot Et_2O$).

Reactions of $Na_2B_{12}H_{12}$ with Cl_2CHOMe. Cl_2CHOMe (0.5 ml, 5.6 mmol) was added to a solution of 0.95 g (5 mmol) of $Na_2[B_{12}H_{12}]$ in 25 ml of dry acetone and the mixture was stirred for 12—14 h. The precipitate (NaCl, 0.55 g, 9.4 mmol) was filtered off. A large excess (approximately 3 mL) of a reagent (MeOH, EtOH, morpholine) was added to the filtrate. After stirring for about 0.5 h, relatively pure products **1—3** were precipitated by the addition of 1.52 g (10 mmol) of CsF dissolved in 40 ml of MeOH. The precipitate obtained was filtered off, washed with 2x10 mL of MeOH, and air-dried.

Dicesium-1,7-dimethoxy-*closo*-decahydrododecaborate (1). Yield 1.34 g of **1** (2.8 mmol, 57%), m.p. > 360°C. Found (%): C, 4.68; H, 3.38. $C_2H_{16}B_{12}Cs_2O_2$. Calculated (%): C, 5.14; H, 3,45. ^{11}B NMR (D_2O, δ, ppm): 3.6 (s, 2 B, B(1,7)); −15.6 (d, 2 B, B(2,3), J_{B-H} = not resolved); −17.5 (d, 4 B, B(4,6,8,11), J_{B-H} = 28.1 Hz); −20.4 (d, 2 B, B(9,10), J_{B-H}= not resolved); −23.9 (d, 2 B, B(5,12); J_{B-H} = 127.6). ^{1}H NMR (D_2O, δ, ppm): 3.2 (s, 6 H, O—CH_3); B—H: 1.37 (s, 2 H, H(2,3)); 1.06 (s, 4 H, H(4,6,8,11); 0.67 (s, 4 H, H(9,10 and 5,12)). ^{13}C NMR (D_2O/DMSO-d_6, 10:1, δ, ppm): 52.13 (O—CH_3)

Dicesium-1,7-diethoxy-*closo*-decahydrododecaborate (2). Yield 1.64 g of **2** (3.215 mmol, 64.3 %), m.p. > 360°C. Found (%): C, 9.29: H, 4.09. $C_4H_{20}B_{12}Cs_2O_2$. Calculated (%): C, 9.71; H, 4.07. ^{11}B NMR (D_2O, δ, ppm): 3.9 (s, 2 B, B(1,7)); −15.6 (d, 2 B, B(2,3), J_{B-H} = 128.2 Hz); −17.4 (d, 4 B, B (4,6,8,11); J_{B-H} = 140.1 Hz); −20.3 (d, 2 B, B(7-9,10); J_{B-H} = not resolved), −23.6 (d, 2 B, B(5,12), J_{B-H} = 128.5 Hz). ^{1}H NMR (D_2O, δ, ppm): 3.5 (q, 4 H, O-CH_2(−)); 1.0 (t, 6 H, CH_3); B—H: 1.58 (s, 2 H, H(2,3)); 1.03 (s, 4 H, H(4,6,8,11)); 0.70 (s, 4 H, H(39, 10 and 5, 12)). ^{13}C NMR (D_2O/DMSO-d_6, δ, ppm): 62.01 (O—CH_2); 18.4 (—CH_3).

Dicesium-1-isopropoxy-7-morpholino-*closo*-decahydrododecacaborate (3). Yield 2.21 g of **3** (4.1 mmol, 82%), m.p. >350°C. $C_7H_{25}B_{12}Cs_2NO_2$. Found (%): C, 15.02; H, 4.61; N, 6.24. Calculated (%): C, 15.26: H, 4.57; N, 2.54. ^{11}B NMR (D_2O, δ, ppm): 4.3 (s, 1 B, B(1)); 3.14 (d, 1B, B(7)); −16.1 (d, 2 B, B(2,3)); −18.0 (d, 2B, B (4, 6, 8, 11)); −20.8 (d, 2 B, B(9, 10)); −23.0 (d, 1 B, B (12)); −24.9 (s, 1 B, B(5); J_{B-H} = not resolved). ^{1}H NMR (D_2O, δ, ppm): 3.56 (t, 4 H, O—CH_2); 3.49 (m, 1 H, O—CH); 2.87 (t, 4 H, N—CH_2); 0.93 (d, 6 H, CH_3); B—H: 1.42 (s, 2 H, H(2,3)); 1.11 (s, 4 H, H(4,6,8,11)); 0.88 (s, 2 H, H(5, 12)); 0.70 (s, 2 H, H(9, 10)). ^{13}C NMR (D_2O/DMSO-d_6, 10:1, δ, ppm): 72.45 (CH); 67.09 (O—CH_2); 45.51 (N—CH_2); 25.24 (CH_3).

Acknowledgements. Many thanks to Prof. H. Noeth (University of Munich) for making his laboratory available for this work.

References

1. B. Brellochs and A. Semioshkin, *J. Chem. Soc. Dalton. Trans.*, 1995, *in press.*
2. A. Semioshkin, *Ph. D. Thesis* (*Chem*), München, BRD, 1994, 51p.
3. J. March, *Advanced Organic Chemistry*, 3rd edition, John Wiley & Sons, New York, 1985.
4. B. Brellochs and A. Semioshkin *J. Chem. Soc. Dalton. Trans.*, 1995, in press
5. H. O. Kalinowski, S. Berger, and S. Brown, *^{13}C NMR-Spectroscopy.*, Georg Thieme Verlag, Stuttgart — New York, 1984, 288.

Received September 28, 1994.