Synthesis and properties of multinuclear cobalt(III) complexes containing dicarbollide(2−) and dicarbacanastide(4−) anions

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A series of chain multinuclear cobaltacarboranes of the general formula $[(C_2B_9H_{11})_2Co_n(C_2B_8H_{10})_{n-1}]^{n-}$, where n = 4 to 7, were synthesized. These compounds, containing derivatives of *ortho*-carborane(12) as ligands and dicarbollide $C_2B_9H_{11}^{2-}$ and bidentate dicarbacanastide $C_2B_8H_{10}^{4-}$ ligands, were studied by IR, UV, and ^{1}H and ^{11}B NMR spectroscopy. The nonequivalence of the dicarbacanastide ligands that occupy different positions in the chain with respect to the terminal dicarbollide ligands was discovered.

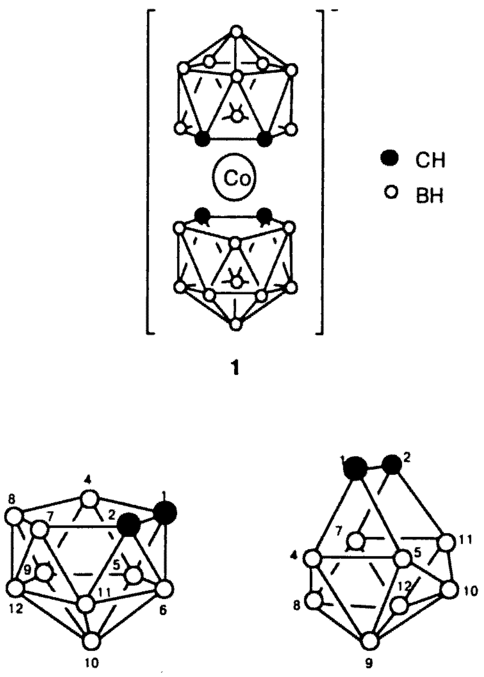
Key words: cobaltacarboranes, multinuclear complexes, NMR spectroscopy, dicarbollide ligand, dicarbacanastide ligand.

The search for new materials with valuable optical, magnetic, and electrophysical properties is one of the most important tasks of modern chemistry. In this connection, special attention is devoted to the synthesis of polymeric systems containing "multideck" sandwich organometallic and metalloborane fragments. Approaches to the synthesis of polymers incorporating bidentate diborolenyl and thiaborolenyl ligands[1] and multinuclear systems containing metallocarborane fragments ($C_2B_3R_5ML$) have been developed.[2]

Along with this, the chemistry of dicarbollide metal complexes is being developed extensively. The dicarbollide ion 1,2-$C_2B_9H_{11}^{2-}$ (**1a**) (from here on, the notation of the carbon atoms is omitted, because only this type of isomers is considered) is a derivative of *ortho*-carborane(12) and is a truncated icosahedron with an open pentagonal surface with a η^5-bonding to the metal ion similar to that in metallocenes (Fig. 1). It has been found[3] that cleavage of one of the two dicarbollide ligands in the complex $[(C_2B_9H_{11})_2Co]^-$ (**1**) leads to the formation of the bidentate dicarbacanastide ligand $C_2B_8H_{10}^{4-}$ (**1b**) (see Fig. 1).

Chain cobaltacarboranes containing two (**2**), three[3] (**3**), and four[4] (**4**) cobalt atoms have been synthesized in this way (Figs. 2, 3). These compounds are cluster analogs of sandwich metallocene-like polymeric systems; the most interesting property of these clusters is delocalization of their charge.[5]

The purpose of the present work is to study the possibility and the characteristic features of the synthesis of chain multinuclear cobaltacarboranes containing more than four cobalt ions in the chain, as well as to study the physicochemical properties of compounds of this class.



1

1a **1b**

Fig. 1. Schemes of the structures: **1a** is the dicarbollide ligand $C_2B_9H_{11}^{2-}$; **1b** is the dicarbacanastide ligand $C_2B_8H_{10}^{4-}$; **1** is the cobalt(III) bis-dicarbollide complex $[(C_2B_9H_{11})_2Co]^-$.

Results and Discussion

The syntheses of bi- and trinuclear complexes **2** and **3** were carried out in 40% aqueous alkali at 90 °C for

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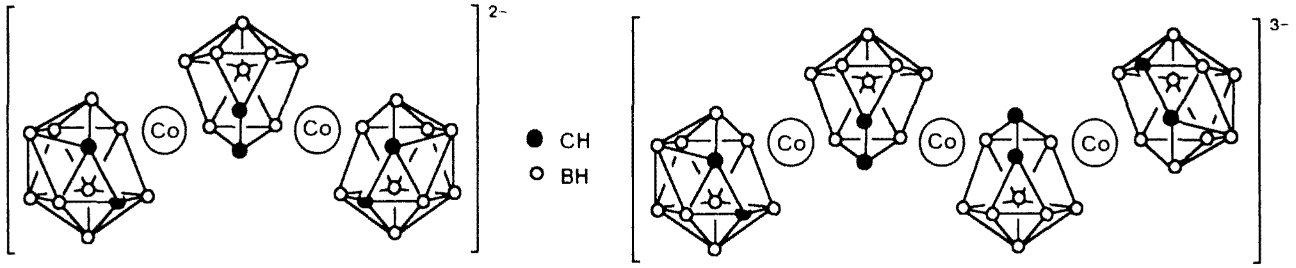
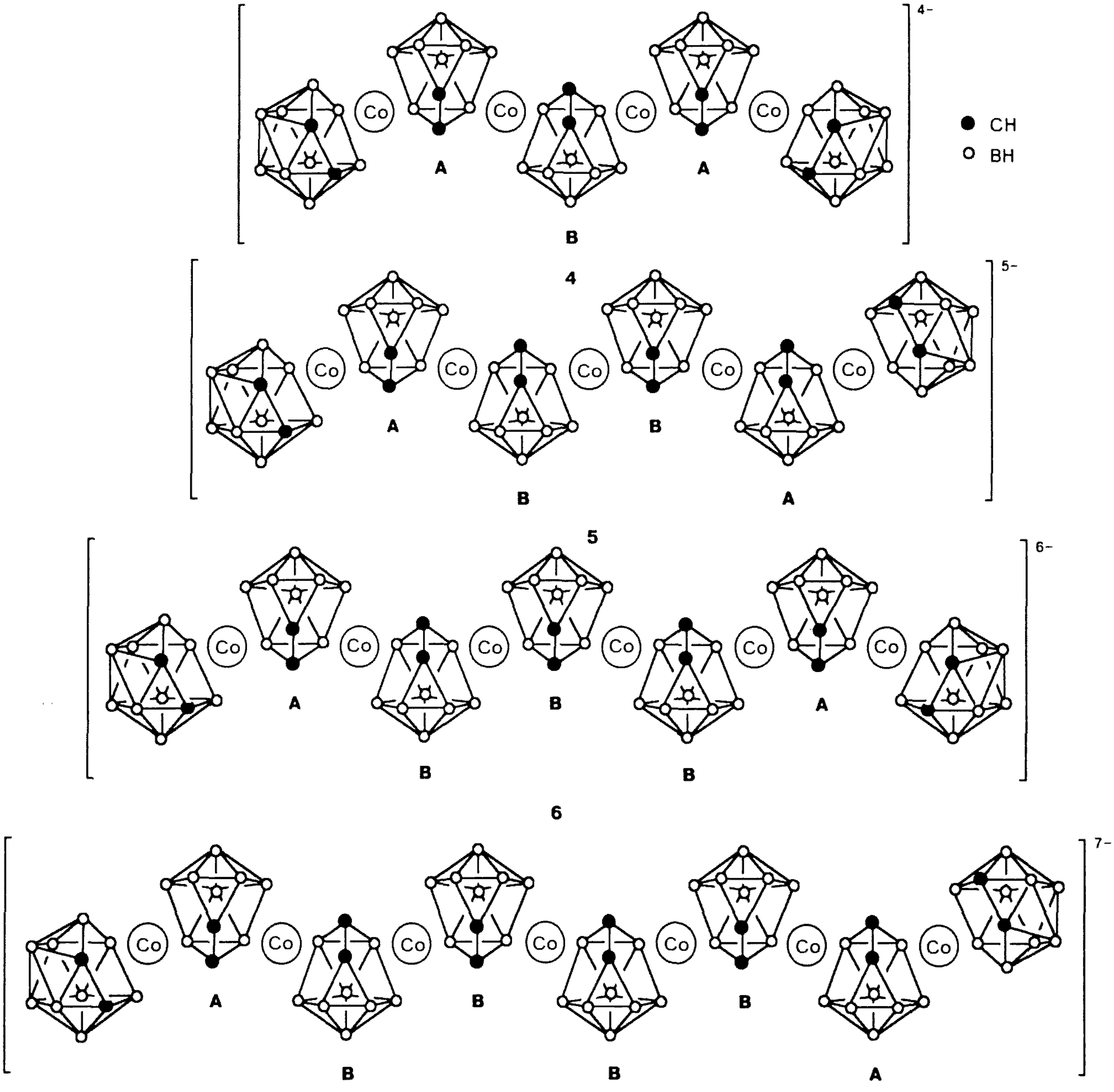


2

3

Fig. 2. Structures of cobaltacarboranes:[7,8] 2 is $[(C_2B_9H_{11})_2Co_2(C_2B_8H_{10})]^{2-}$; 3 is $[(C_2B_9H_{11})_2Co_3(C_2B_8H_{10})_2]^{3-}$.



4

5

6

7

Fig. 3. Scheme of the tentative structures: **4** is $[(C_2B_9H_{11})_2Co_4(C_2B_8H_{10})_3]^{4-}$; **5** is $[(C_2B_9H_{11})_2Co_5(C_2B_8H_{10})_4]^{5-}$; **6** is $[(C_2B_9H_{11})_2Co_6(C_2B_8H_{10})_5]^{6-}$; 7 is $[(C_2B_9H_{11})_2Co_7(C_2B_8H_{10})_6]^{7-}$. Two types of dicarbacanastide ligands **A** and **B** are shown in the schemes.

2 h, starting from both complex **1** and the anion $C_2B_9H_{12}^-$, which is rapidly converted[3] into **1** under the reaction conditions. Complexes **2** and **3** were obtained in 15 and 6 % yield, respectively. We found that an increase in the temperature, in the concentration of the alkali, or in the reaction time results in an increase in the yields of the products and also in the appearance of tetra- (**4**), penta- (**5**), hexa- (**6**), and heptanuclear (**7**) complexes among the reaction products (see Fig. 3). In addition, the reaction mixture contained compounds with longer chains and traces of compounds indicating the possibility of the occurrence of some side processes, in particular, the "polyhedron compression" reaction.[6] However, these compounds are difficult to isolate in a pure state, since their amounts are too small.

The formation of the multinuclear cobaltacarboranes under consideration can be described by the following scheme:

$$[(C_2B_9H_{11})_2Co_n(C_2B_8H_{10})_{n-1}]^{n-} + OH^- + Co^{2+} + C_2B_9H_{11}^{2-} \rightarrow$$

$$\rightarrow [(C_2B_9H_{11})_2Co_{n+1}(C_2B_8H_{10})_n]^{(n+1)-}.$$

During the reaction, the degradation of the framework of one of the terminal dicarbollide ligand occurs. The $[B(6)H]^{2+}$ fragment linked to two C atoms is removed from it through the action of alkali, and the second open pentagonal surface is thus formed. The resulting intermediate complex reacts with a cobalt ion and with one more dicarbollide ligand, which is formed upon deprotonation of the $C_2B_9H_{12}^-$ anion. Note that the high negative charges of the dicarbollide and dicarbacanastide ligands (2− and 4−, respectively) stabilize the unusually high formal oxidation state of cobalt Co^{III}, which is achieved in the disproportionation.

$$3Co^{II} \longrightarrow 2Co^{III} + Co^0$$

Compounds **2**—**7** are dark-brown powders, stable in air in the solid state and in solutions. The UV spectra of the complexes exhibit a fairly intense band in the region of 290 nm, the extinction coefficient of which increases as the chain in the cobaltacarboranes becomes longer (Table 1). To interpret the UV spectra, further studies are needed.

The structures of the binuclear and trinuclear complexes were determined[7,8] by X-ray diffraction analysis. Our attempts to prepare single crystals of the higher representatives of this series of compounds have so far been unsuccessful. Nevertheless, the use of NMR spectroscopy makes it possible to obtain important information concerning the structures of the metallocarborane complexes in question.

The considerable difference between the chemical shifts of the signals of the C—H protons in the dicarbollide and dicarbacanastide ligands ($\Delta\delta \approx 1$) allows the lengths of the chains in these complexes to be found from the ratio of the intensities of these signals in the ^1H NMR spectrum (Table 2). In the spectrum of **2**, this ratio is equal to two, which is consistent with the structure established for this compound: it incorporates two terminal dicarbollide ligands and one bidentate dicarbacanastide ligand. In the case of complex **3**, these signals have equal intensities, which reflects the presence of two terminal ligands and two bidentate ligands. The spectrum of the tetranuclear complex **4**, apart from the signals corresponding to the dicarbollide C—H protons, exhibits two signals with 4:2 intensity ratio in the region of the C—H protons of the dicarbacanastide ligands, which can be explained by the nonequivalence of the dicarbacanastide ligands that occupy different positions with respect to the terminal dicarbollide ligands (see Fig. 3). Two ligands (we designate them as type **A**) are bound directly to the terminal $CoC_2B_9H_{11}$ fragments, whereas one ligand (type **B**) is bound to two $CoC_2B_8H_{10}Co$ fragments. The appearance of the two types of dicarbacanastide ligands in the complex is accompanied by an upfield shift of the signals of the C—H protons of the ligand that is remote from the terminal fragments. The intensities of the signals of the type **B**

Table 1. Electronic absorption spectra of cobaltacarborane complexes **1**—**7**

Compound	λ/nm(ε)
1*	205 (35000), 290 (58000), 350 sh (38000), 430 sh (11000)
2*	210 (7000), 292 (30000), 454 sh (410)
3*	209 (26000), 290 (44000), 324 (31000)
4**	288 (75000), 345 sh (50000), 423 sh (20000)
5**	288 (85000), 346 sh (60000), 421 sh (26000)
6**	289 (100000), 347 sh (73000), 421 sh (36000)
7**	289 (115000), 347 sh (86000), 420 sh (47000)

* See Ref. 3. ** The cesium salts of the complex anions were studied.

Table 2. Data of the ^1H NMR spectra of the cobaltacarborane complexes **1**—**7**

Compound	δ (intensity of the signal)		
	I	II	III
1*	3.81		
2**	3.29 (4 H)	4.28 (2 H)	
3**	3.12 (4 H)	4.13 (4 H)	
4	3.25 (4 H)	4.15 (4 H)	3.91 (2 H)
5	3.33 (4 H)	4.25 (4 H)	4.07 (4 H)
6	3.34 (4 H)	4.28 (4 H)	4.12 (6 H)
7	3.34 (4 H)	4.31 (4 H)	4.15 (8 H)

Note. The signals of the C—H protons in the $C_2B_9H_{11}^{2-}$ ligands (I), the $C_2B_8H_{10}^{4-}$ (type **A**) ligands (II), and the $C_2B_8H_{10}^{4-}$ ligands (type **B**) (III) of cobaltacarboranes are presented.

* Recorded in deuterioacetone. ** See Ref. 3.

Table 3. Data of the ^{11}B NMR spectra of the cobaltacarborane complexes **1**—**7**

Compound	δ (intensity of the signal; J_{B-H}/Hz)							
	I			II				
	B(8, 10)	B(4, 5, 7, 11)	B(9, 12)	B(8)	B(10)	B(4, 7, 9, 12)	B(5, 11)	B(6)
2	22.3 (2 B, *J* = 120)	0.9 (4 B, *J* = 135)	−6.4 (2 B, *J* = 120)	5.2 (2 B, *J* = 128)	−2.7 (2 B, *J* = 143)	−7.1 (8 B, *J* = 120)	−18.5 (4 B, *J* = 144)	−23.1 (2 B, *J* = 170)
3	21.1 (2 B, *J* = 104); 17.3 (2 B, *J* = 118)	−1.9 (8 B)	−9.1*	3.2 (2 B, *J* = 113)	−5.1 (2 B, *J* = 135)	−9.1 (12 B, *J* = 127)*	−20.3 (4 B, *J* = 113)	−24.8 (2 B, *J* = 110)
4	21.1 (2 B, *J* = 100); 17.4 (2 B, *J* = 130); 16.3 (2 B, *J* = 140)	−2.9 (12 B)	−9.6*	2.8 (2 B, *J* = 100)	−5.7 (2 B, *J* = 125)	−9.6 (14 B, *J* = 107)*	−20.6 (4 B, *J* = 113)	−24.9 (2 B, *J* = 100)
5	21.3 (2 B, *J* = 110); 17.3 (2 B, *J* = 119); 16.5 (4 B, *J* = 113)	−3.7 (16 B)	−9.7 (8 B, *J* = 117)	3.0 (2 B, *J* = 120)	−5.4 (2 B, *J* = 115)	−10.4 (8 B, *J* = 100)	−20.5 (4 B, *J* = 100)	−24.7 (2 B, *J* = 110)
6	21.4 (2 B, *J* = 105); 17.5 (2 B, *J* = 120); 16.5 (6 B, *J* = 100)	−4.0 (20 B)	−9.7 (10 B, *J* = 120)	3.1 (2 B, *J* = 130)	−5.5 (2 B, *J* = 125)	−10.6 (8 B, *J* = 125)	−20.5 (4 B, *J* = 115)	−24.4 (2 B, *J* = 115)
7	21.3 (2 B, *J* = 115); 16.5 (10 B)	−4.1* (26 B)	−9.7 (12 B, *J* = 125)	3.0 (2 B, *J* = 120)	−5.3*	−10.8 (8 B, *J* = 130)	−20.4 (4 B, *J* = 100)	−24.7 (2 B, *J* = 110)

Note. The signals of the $C_2B_8H_{10}^{4-}$ (I) and $C_2B_9H_{11}^{2-}$ (II) fragments in cobaltacarboranes are given (the signals were assigned as previously[9]). Numbering of the boron atoms is shown in Fig. 1.

* The signals overlap.

dicarbacanastide ligands grow continuously in the spectra of complexes **5**—**7**. In addition, in the spectra of the complexes **3**—**7** under consideration, the signals corresponding to both dicarballide ligands and the two types of dicarbacanastide ligands shift downfield as the chain length increases. Apparently, this trend is due to variations of the paramagnetic contributions to shielding. As the chain length increases, the signals of the protons of the two types of dicarbacanastide ligands approach each other: the difference between the chemical shifts of these signals in complex **4** is 0.24 ppm, while that for complex **7** is 0.16 ppm.

^{11}B NMR spectroscopy is now one of the most important methods for the investigation of structures and properties in the chemistry of metallocarboranes. In the present work we obtained the ^{11}B NMR spectra both for complexes known previously and for those synthesized for the first time, which allowed us to follow the character of variations caused by the increase in the chain length.

The ^{11}B NMR spectrum of complex **2** (Table 3) consists of eight doublets. Among them, a group of signals of the dicarbollide ligands can be distinguished, the positions and relative intensities of which correspond to those in the spectrum of the mononuclear complex **1**. The rest of the signals should be assigned to the nuclei of boron incorporated in the dicarbacanastide ligand. The relative intensities of these signals (2:4:2) conforms to the symmetrical structure of the ligand.

It is if interest to follow the variations occurring in the ^{11}B NMR spectra on the successive replacement of the $(BH)^{2+}$ fragments in the icosahedral *ortho*-carborane $C_2B_{10}H_{12}$ by cobalt-containing fragments, which results in the formation of a dicarbollide ligand and then of a dicarbacanastide ligand. It can be seen from the scheme (Fig. 4) that the replacement of the $[B(3)H]^{2+}$ fragment by a metal-containing fragment leads to a substantial downfield shift of the signals of B(4, 7, 8, 10), *i.e.*, of the atoms that constitute the open pentagonal surface, which is bound to the cobalt ion, and also of the atom that is located in the antipode position with respect to the metal-containing fragment (numbering of the boron atoms is shown in Fig. 1). The signals of the rest of the boron atoms shift upfield, which results in the retention of the "chemical shift of the cluster" (the mean value over the chemical shifts of all the signals in the spectrum). This is a general trend in the spectra of metallocarboranes.[9] The replacement of a further $[B(6)H]^{2+}$ fragment by the second cobalt-containing fragment is accompanied by an increase in the symmetry of the structure of the carborane cluster and, correspondingly, by the reduction in the number of signals to three, their relative intensities being 2:4:2. The signal with an intensity of 4 B is due to the B(4, 5, 7, 11) nuclei, which form the two open pentagonal surfaces in the cluster. This signal is displaced downfield with respect to that of the dicarbollide ligand. The B(8, 10) nuclei directly bound to the metal-containing fragment, are, at the same time, in the antipode position with respect to the second cobalt-containing fragment, which should lead to a substantial downfield displacement of this signal. Therefore, the signal at δ 22.3 can be assigned to the B(8, 10) nuclei, the downfield shift being equal to 17 and 25 ppm, respectively. In this case, the position of the signal of the B(9, 12) nuclei of the dicarbacanastide polyhedron (−6.4 ppm) remains virtually unchanged compared to those for the dicarbollide polyhedron. Thus, when the B—H fragment in the carborane polyhedron is replaced by the cobalt-containing fragment, the signals of the boron atoms bound directly to the metal-containing group, and also the signal of the boron atoms located in the antipode position with respect to it, shift downfield. The signals of the other boron atoms in the framework remain unchanged or shift upfield.

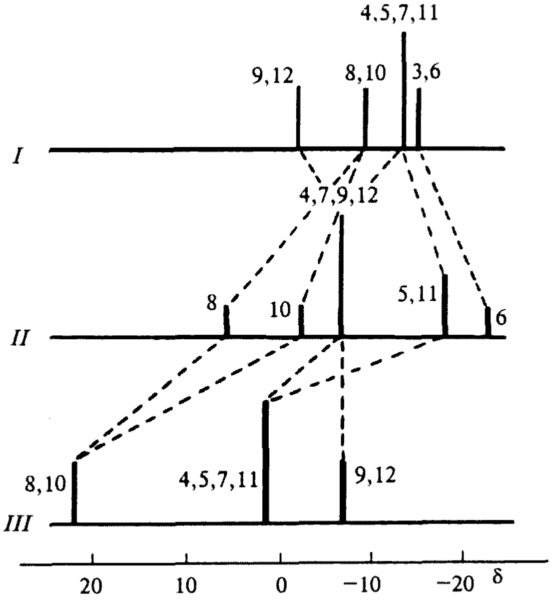


Fig. 4. Schemes of the ^{11}B NMR spectra: *ortho*-carborane(12), $C_2B_{10}H_{12}$ [9] (*I*); the $C_2B_9H_{11}^{2-}$ dicarbollide ligand in complex **2** (*II*); the $C_2B_8H_{10}^{4-}$ dicarbacanastide ligand in complex **2** (*III*). The signals in spectra *I* and *II* were assigned in accordance with published data.[9]

The structure of compound **3** incorporates two dicarbollide and two dicarbacanastide polyhedra. In the ^{11}B NMR spectrum of complex **3** (see Table 3), as in the spectrum of **2**, two groups of signals, corresponding to the two types of carborane ligands, can be distinguished. The signals of the boron atoms of the dicarbollide ligands shift ~2 ppm upfield with respect to those for complex **2**. The signals of the boron atoms of the dicarbacanastide ligands, which shift somewhat upfield, undergo substantial changes. The signal of B(4, 5, 7, 11) is broadened, which hampers the detection of the B—H spin-spin coupling. The signal corresponding to B(9, 12) is also broadened and is superimposed onto the signal of the B(4, 7, 9, 12) atoms of the dicarbollide ligand. In the region of the signals that we have assigned to B(8, 10) of the dicarbacanastide ligands, two new signals appear; they have identical intensities and their chemical shifts differ by 4 ppm. This indicates either the magnetic nonequivalence of the B(8, 10) nuclei belonging to two different dicarbacanastide ligands present in the complex, or the nonequivalence of the B(8) and B(10) nuclei incorporated in the same polyhedron. The suggestion that the two dicarbacanastide ligands present in **3** are nonequivalent has not been supported by the X-ray investigation of **3**.[8] In addition, the ^{1}H NMR spectrum of **3** exhibits only one signal for the C—H protons of the two dicarbacanastide ligands. This makes it possible to conclude that the B(8) and B(10) nuclei incorporated in the same dicarbacanastide cluster are magnetically nonequivalent. Broadening of the B(4, 5, 7, 11) signal also attests to the magnetic nonequivalence of the B(4, 7) and B(5, 11) pairs of nuclei, which form the two open pentagonal surfaces of the same polyhedron (see Fig. 1). This may be caused by the nonequivalent positions of these atoms in the polyhedron with respect to the terminal dicarbollide ligands (see Fig. 2): one of the open surfaces is involved in the bonding with the metal-containing $CoC_2B_9H_{11}$ fragment, and the other is bound to $CoC_2B_8H_{10}Co$.

In the spectrum of complex **4**, the intensities of the resonances of the boron nuclei in the dicarbacanastide ligands increase further. The spectrum of the dicarbollide ligands undergoes no substantial changes. Let us consider the variations of the signals corresponding to the boron atoms in the dicarbacanastide ligands in more detail. The signals of the B(4, 5, 7, 11) nuclei are broadened like those in the spectrum of complex **3**, and the signals of B(9, 12) are superimposed on the signals of the B(4, 7, 9, 12) atoms in the dicarbollide ligands. Now the B(8, 10) atoms are responsible for three signals: the positions of two resonances coincide with those in the spectrum of complex **3**, while the third signal is displaced somewhat upfield. Recall that the ^{1}H NMR spectrum of complex **4** exhibits signals corresponding to two types of dicarbacanastide ligands, **A** and **B**, which differ in the remoteness from the terminal fragments. Complexes **2** and **3** contain only type **A** ligands. Therefore, the signal at δ 16.3, which is missing from the spectra of compounds **2** and **3** but appears in the spectrum of **4**, can be assigned to the B(8, 10) nuclei incorporated in the type **B** dicarbacanastide ligand (see Fig. 3). In this case, the signal is degenerate, since the B(8) and B(10) nuclei are arranged symmetrically with respect to the plane of symmetry of this complex. In the ligands of type **A**, as has been noted above, the degeneracy of the signals of the B(8, 10) nuclei is eliminated. The signal at δ 22.3 in the spectrum of complex **2** was assigned to the B(8, 10) atoms in the type **A** ligand, *i.e.*, to the atoms located on the open pentagonal surface involved in the bonding with the $CoC_2B_9H_{11}$ fragment. It is quite probable that the signals at δ 21.1 in the spectra of complexes **3** and **4** can also be assigned to boron atoms of this type. Then the signals at δ 17.3 in the spectra of complexes **3** and **4** should be assigned to the boron atoms located on the open pentagonal surface bound to the $CoC_2B_8H_{10}Co$ fragment in the type **A** ligand.

The positions of signals in the spectrum of complex **5** remain virtually unchanged with respect to those in the spectrum of **4**; however, the intensity of the signal at δ 16.5 increases twofold compared to that in the spectrum of **4**, which corresponds to the elongation of the chain of the complex by one more dicarbacanastide ligand of type **B** (see Fig. 3). The intensity of the broadened signal associated with the B(4, 5, 7, 11) atoms in the dicarbacanastide ligand also increases. In the region of the signals of the B(4, 7, 9, 12) atoms in the dicarbollide ligands, a doublet occurs, which we assigned to the B(9, 12) atoms of the dicarbacanastide ligands. Apparently, these two atoms are magnetically equivalent in the dicarbacanastide ligands of both types, because they are far removed from the open pentagonal surface of the polyhedron, and this makes it possible to observe spin-spin coupling in his case.

The positions of signals in the spectrum of complex **6** are also the same as those in the spectra of **4** and **5**. The intensities of the signal at δ 16.5 (the signal of the B(8, 10) atoms of the type **B** ligand) and the broadened signal at δ −4 (the signal of the B(4, 5, 7, 11) atoms in the dicarbacanastide ligand) increase, and the signal of the B(9, 11) nuclei of the dicarbacanastide ligand, like that in the spectrum of **5**, is manifested as a doublet. Similar changes are observed in the spectrum of complex **7**. The positions of the signals of the dicarbacanastide ligands remain the same, while their intensities with respect to those of the signals of the dicarbollide ligands increase. The signal at δ 16.5, which we assigned to the B(8, 10) nuclei of the type **B** ligand, is broadened and superimposed on the signal of the B(8, 10) nuclei of the type **A** ligand, and the broad signal at δ −4.1 is superimposed on the signals of the B(10) nuclei of the dicarbollide ligands.

Thus, the following trends can be distinguished in the variation of the ^{11}B NMR spectra in the series of multinuclear cobaltacarboranes studied as a function of the elongation of their chains. The most substantial changes in the chemical shifts of the signals occur on going from the binuclear complex (**2**) to the trinuclear complex (**3**). All the signals in the spectrum of **3** shift upfield by 2 ppm. In this connection, note that in a previous X-ray photoelectron study of complexes **2** and **3**,[10] it has been found that the energy of bonding of the B1s and $Co2p_{3/2}$ electrons decreases somewhat on going from **2** to **3**, which indicates an increase in the electron density in the cobaltacarborane polyhedra of complex **3**. Apparently, this also accounts for the observed upfield shifts of signals in the ^{11}B NMR spectrum of complex **3** and of the signals corresponding to the C—H protons in the ^1H NMR spectrum of complex **3** (see Table 2). The main changes in the ^{11}B NMR spectra of cobaltacarboranes **3**—**7** are due to the magnetic nonequivalence of the boron nuclei in the dicarbacanastide ligands, occupying different positions with respect to the terminal $CoC_2B_9H_{11}$ fragments. The boron nuclei located on the open pentagonal surface of the dicarbacanastide polyhedra, bound directly to the terminal metal-containing $CoC_2B_9H_{11}$ fragments, are deshielded to a greater extent than the corresponding nuclei in the ligands, remote from the terminal fragments of the chains. The same situation was observed in the ^1H NMR spectra for the C—H protons belonging to two different types of dicarbacanastide ligands (see Table 2). This trend may be caused by both the increase in the electron density at the ligands remote from the terminal fragments of the chain and the variation of the paramagnetic contribution to the shielding of the boron atoms. To elucidate the reason for this tendency, further investigations are needed.

In conclusion, it may be said that the possibility of preparing chain multinuclear cobaltacarboranes with a specified length and also of modifying and varying the ligands and the cationic components in these compounds opens up substantial possibilities for the synthesis of numerous compounds of this class, and the study of their physicochemical properties is of obvious interest.

Experimental

IR spectra were recorded on a UR-20 spectrophotometer in pellets with KBr. The ^1H NMR spectra (400.13 MHz, cesium salts of the complexes in CD_3CN were studied using tetramethylsilane as the internal standard) and the ^{11}B NMR spectra (128.33 MHz, tetramethylammonium salts of the complexes in MeCN were studied using $BF_3 \cdot Et_2O$ as the internal standard) were recorded on a Bruker MSL-400 instrument. The UV/VIS spectra were obtained on a Specord UV-VIS instrument (for solutions in acetonitrile).

The multinuclear cobaltacarboranes were synthesized in the following way. A solution of 25 g of NaOH in 30 mL of water was added to 1.5 g of $[Me_3NH](C_2B_9H_{12})$, and the mixture was heated to 100 °C. After that, a solution of 3 g of

$CoCl_2 \cdot 6H_2O$ in 5 mL of water was added with vigorous stirring, and the reaction mixture was kept for 8 h at 105 °C and poured into 100 mL of cold water. The alkali was carefully neutralized with dilute hydrochloric acid, the mixture being cooled with ice. Then the suspension was filtered, and a mixture of the multinuclear complexes was precipitated from the dark-brown solution with $Me_3N \cdot HCl$. The precipitate was filtered off, washed with small portions of cold water, and dried. The resulting mixture of cobaltacarboranes was chromatographed on plates with unbound layer of L 40/100 silica gel (using a 1:1.1 mixture of CH_2Cl_2 and MeCN as the eluent). The individual fractions were eluted from the support, the solvent was evaporated, and the residue was recrystallized from aqueous acetonitrile. The following compounds were obtained:

$[Me_3NH]_2[(C_2B_9H_{11})_2Co_2(C_2B_8H_{10})]$ (**2**), yield 0.27 g (17 %);
$[Me_3NH]_3[(C_2B_9H_{11})_2Co_3(C_2B_8H_{10})_2]$ (**3**), yield 0.43 g (26 %);
$[Me_3NH]_4[(C_2B_9H_{11})_2Co_4(C_2B_8H_{10})_3]$ (**4**), yield 0.11 g (6 %);
$[Me_3NH]_5[(C_2B_9H_{11})_2Co_5(C_2B_8H_{10})_4]$ (**5**), yield 0.06 g (4 %);
$[Me_3NH]_6[(C_2B_9H_{11})_2Co_6(C_2B_8H_{10})_5]$ (**6**), yield 0.04 g (2 %);
$[Me_3NH]_7[(C_2B_9H_{11})_2Co_7(C_2B_8H_{10})_6]$ (**7**), yield 0.02 g (1 %).

Compounds **2**—**4** have been synthesized and characterized previously.[3,4] Salts containing the Me_3NH^+ cation can be converted into salts with Cs^+ or Me_4N^+ cations by the action of alkali, removal of triethylamine by evaporation *in vacuo*, subsequent neutralization of the alkali, and precipitation of the complex anions by the addition of CsF or Me_4NCl.

The elemental analysis data are presented for compounds **5**—**7** with the trimethylammonium cation. **5**. Found (%): B, 39.20; Co, 22.37. $C_{27}H_{112}B_{50}Co_5N_5$. Calculated (%): B, 40.26; Co, 21.92. **6**. Found (%): B, 38.75; Co, 22.44. $C_{32}H_{132}B_{58}Co_6N_6$. Calculated (%): B, 39.63; Co, 22.35. **7**. Found (%): B, 38.26; Co, 22.29. $C_{37}H_{152}B_{66}Co_7N_7$. Calculated (%): B, 39.17; Co, 22.65.

The IR spectra of the cesium salts of complexes **2**—**7** in the 800—1300 cm^{-1} region exhibit the bands associated with bending vibrations of the boron-carbon skeleton. The intense band at 2495 cm^{-1} corresponds to the B—H stretching vibrations, and the weak broadened bands recorded in the 3000 cm^{-1} region are due to the C—H stretching vibrations of the carborane fragments.[4]

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