SYNTHESIS AND CHARACTERISTICS OF SULFUR INTERLIGAND BRIDGE-DERIVATIVES AND OF SOME S-SUBSTITUTED COMPOUNDS IN THE $(C_2B_9H_{11})_2Co^-$ SERIES. CONFORMATIONS OF $(C_2B_9H_{11})_2M^{x-}$ METALLOCARBORANES

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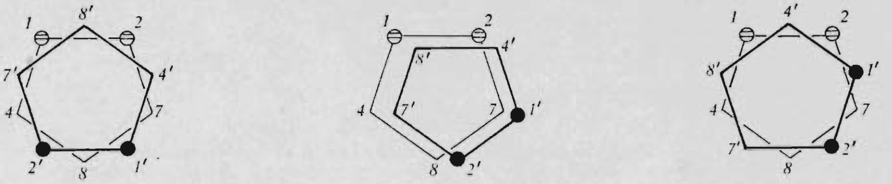
Dedicated to Professor J. Klikorka on the occasion of his 60th birthday.

Synthesis, properties and chemical behaviour of the $(C_2B_9H_{11})_2Co^-$ derivatives, namely anions with —S— or —SS— bridges and of neutral species with —SR— (R = H, alkyl, aryl) or —S—SR— bridges as well as with $—\overset{(+)}{S}(CH_3)_2$ group are described. The analysis of ^{11}B-NMR spectra indicates in solution and in the ^{11}B-NMR time scale a free rotation at $(C_2B_9H_{11})_2Co^-$, oscillations at $—S_2—$, —S⎓CH⎓S— and rigid conformations at —S—, $—\overset{(+)}{S}R—$, $(CH_3)_2\overset{(+)}{S}—$ and $—S—\overset{(+)}{S}R—$ derivatives. For description of different conformations a combination of locants and descriptors *e* (eclipsed), *s* (staggered) is proposed. The (*s*-1,4′,2,1′) conformation was found by X-Ray study of $(8\text{-}CH_3OC_2B_9H_{10})_2Ni$.

In the basic studies on transition metal π-complexes of the general formula M^{n+}. $.(1,2\text{-}C_2B_9H_{11})_2^{n-4}$, Hawthorne and his coworkers[1,2] considered a free rotation of unsubstituted dicarbollide $C_2B_9H_{11}$ units round the longitudinal axis intersecting the central M atom, *i.e.* rotation similar to that of cyclopentadiene ligands in ferrocene[3]. In the case of bis-dicarbollide sandwiches (Fig. 1) with central Fe, Co or Ni atoms in d^5, d^6 or d^7 electron configurations, the free rotation allows the ligands to prefer in the solid state an optimal conformation with most remoted positively charged C-atom couples[4].

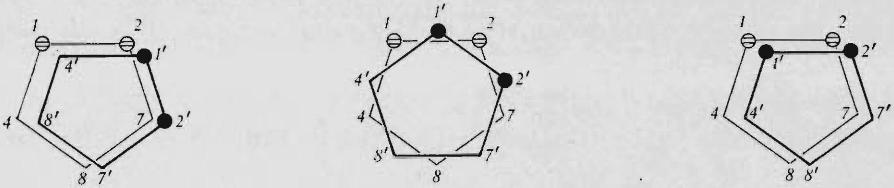
The free rotation existing for instance in solutions of 3-commo-3-cobalta-bis[undecahydro-1,2-dicarbadodecaborate(1−)] $(C_2B_9H_{11})_2Co^-$ (*I*), is not present in compounds with two dicarbollide π-ligands connected between B(8)—B(8′) atoms by the three-membered —S⎓CH⎓S— or $—O⎓C(CH_3)⎓O—$ bridges[5] and especially by the two-membered —S—S—[5] or $1,2\text{-}C_6H_4$ bridges[6,7]. Of these compounds, only the exact structure of the —S⎓CH⎓S— derivative was described[8] in which the *cis*-artiprismatic positions of both π-faces with C-couples on the same side of the molecule [*i.e.* (*s*-1,1′,2,2′) conformation in Scheme 1] was found.



(*s*-1,8′,2,4′) *trans*-antiprismatic

(*e*-1,8′,2,4′) *trans*-prismatic

(*s*-1,4′,2,1′)



(*e*-1,4′,2,1′)

(*s*-1,1′,2,2′) *cis*-antiprismatic

(*e*-1,1′,2,2′) *cis*-prismatic

SCHEME 1

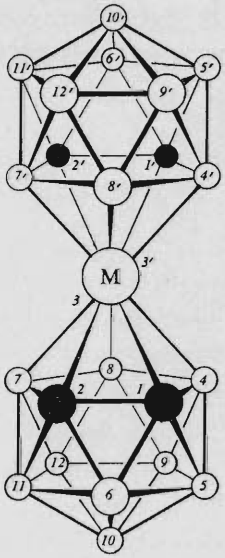


FIG. 1

The "frozen" structure and numbering of the bis-dicarbollylcomplexes of d^5, d^6 and d^7 transition metal ions; in solution, a free rotation around the longitudinal B(10)-M-B(10′) axis is present

This paper reports in detail on preparation, properties and chemistry of the 8,8'-$S(C_2B_9H_{10})_2Co^-$ anion[9] (*II*) and of further B-substituted S-derivatives[9,10], and pays an attention to the factors which make the rotation of the dicarbollide ligands difficult or impossible, forming oscillating or "frozen" conformations.

RESULTS AND DISCUSSION

Preparation and Chemical Behaviour of the Anion II

In view of bond-angle strains and in view of the electrostatic repulsions of C-couples in both pentagons facing to the Co atom, the compounds with one-atom bridge can be expected as sterically less preferred than those with two- or three-membered bridges. Despite these unfavorable factors, the first representative of the one-atom bridge series, the 8,8'-$CH_3S(C_2B_9H_{10})_2Co^{III}$ metallocarborane (*IIIa*) was obtained according to the following scheme:

$$\underset{\mathit{Ia}}{(C_2B_9H_{11})_2Co^-Cs^+} + (CH_3)_2SO \rightarrow \underset{\mathit{IV}}{8\text{-}(CH_3)_2SC_2B_9H_{10}{-}Co{-}C_2B_9H_{11}} \rightarrow$$

$$\xrightarrow{AlCl_3} \underset{\mathit{IIIa}}{8,8'\text{-}CH_3S(C_2B_9H_{10})_2Co} + \underset{\mathit{V}}{ClC_2B_9H_{10}{-}Co{-}C_2B_9H_{10}S(CH_3)_2}$$

The disadvantages of this preparation were a low yield of c. 10% and the necessity to separate products by the column chromatography. More rational way to the preparation of this series was found in the reaction of the anion *I* with disulfur dichloride[9]:

$$\underset{\mathit{I}}{(C_2B_9H_{11})_2Co^-} + S_2Cl_2 \xrightarrow[2.\,KOH-CH_3OH]{1.\,CH_2Cl_2,\,reflux} \underset{\mathit{II}}{8,8'\text{-}S(C_2B_9H_{10})_2Co^-}$$

A high yield of the pure anion *II* was achieved only in the case when dimethylsulfoxonium salt $[(C_2B_9H_{11})_2Co]^- [HOS(CH_3)_2.OS(CH_3)_2]^+$ (*Ib*) was used as the starting material. Other types of cations gave a mixture of anions with one and two S-atom/s in the bridge.

S-*Substituted Derivatives of the Anion II*

The anion *II* can be methylated with dimethyl sulfate to yield a neutral, in high vacuum volatile S-methyl derivative *IIIa*. Similar alkylations with ethyl bromide, allyl bromide, butyl bromide, benzyl bromide, chloroacetic acid and methyl chloroacetate afford in a high yield the red S-substituted zwitterionic derivatives *IIIb*–*IIIg*:

$$\begin{array}{ccl} 8,8'\text{-S}(C_2B_9H_{10})_2Co^- + RX & \rightarrow & 8,8'\text{-RS}(C_2B_9H_{10})_2Co \\ \mathit{II} & & \mathit{IIIa},\ R = CH_3 \\ & & \mathit{IIIb},\ R = C_2H_5 \\ & & \mathit{IIIc},\ n\text{-}C_4H_9 \\ & & \mathit{IIId},\ \text{—}CH_2\text{—}CH\text{=}CH_2 \\ & & \mathit{IIIe},\ \text{—}CH_2\text{—}C_6H_5 \\ & & \mathit{IIIf},\ \text{—}CH_2COOH \\ & & \mathit{IIIg},\ \text{—}CH_2COOCH_3 \end{array}$$

Protonization of the anion *II* generates an unique zwitterionic conjugated acid *IIIh* with a three-coordinated S-atom:

$$\begin{array}{ccc} 8,8'\text{-S}(C_2B_9H_{10})_2Co^- + H^+ & \rightarrow & 8,8'\text{-H}\overset{(+)}{\text{S}}(C_2B_9H_{10})_2Co^- \\ \mathit{II} & & \mathit{IIIh} \end{array}$$

The conjugated acid *IIIh* can be extracted into benzene, it is stable in the crystalline form at room temperature and shows a relevant mass spectrum with the cut-off m/e 358 corresponding to ${}^1H^{32}S({}^{12}C_2{}^{11}B_9{}^1H_{10})_2{}^{59}Co$. The relatively low pK_a value of 3·18 (50% ethanol) of the $>\overset{(+)}{S}\text{—}H$ group can be explained as a result of a donation of electron density from the B(8) and B(8′) positions.

The conjugated acid *IIIh* is very reactive as documented by two reactions, the first of which reminds the Michael addition, whereas the second one is an analogy of an aldol-type condensation:

$$\begin{array}{ccc} 8,8\text{-HS}(C_2B_9H_{10})_2Co & \xrightarrow{CH_2=CH-CN} & 8,8'\text{-CN—}CH_2\text{—}CH_2\text{—S}(C_2B_9H_{10})_2Co \\ \mathit{IIIh} & & \mathit{IIIi} \end{array}$$

$$\begin{array}{ccc} \mathit{IIIh} & \xrightarrow{CH_2O + CH_3OH} & 8,8'\text{-}CH_3OCH_2S(C_2B_9H_{10})_2Co \\ & & \mathit{IIIj} \end{array}$$

In both cases, the reaction has a reversible character. In an acid medium, the equilibrium is almost quantitatively shifted to the products, whereas in an alkaline medium the products decompose back to the parent anion *II*. As proved by TLC, the decomposition proceeds very easily and almost quantitatively even by a treatment with ammonia vapors. On the other hand, compound *IIIj* is converted during prolonged standing in methanol to the S-methyl derivative *IIIa*. This transformation demonstrates a high nucleophility of the bridge S-atom which undergoes probably an intramolecular methylation.

The reaction of *II* with bromine in acetic acid yielded an unstable $>\overset{(+)}{S}\text{—}Br$ derivative which was immediately converted with benzene in the presence of $AlCl_3$ into $8,8'\text{-}C_6H_5S(C_2B_9H_{10})_2Co$ (*IIIk* $R = C_6H_5$).

As shown, the S-bridge anion *II* represents an ideal precursor for the introduction of a metallo-heteroborane system into an arbitrary position of an organic molecule.

Two-Sulfur Derivatives of the $(C_2B_9H_{11})_2Co^-$ *Anion*

In contrast to the dimethylsulfoxonium salt *Ib*, the caesium salt *Ia* of the same anion reacts with S_2Cl_2 affording the 8,8'-$S_2(C_2B_9H_{10})_2Co^-$ anion (*VI*) prepared earlier

TABLE I

Some characteristic of 8,8'-substituted $(C_2B_9H_{10})_2Co^-$ derivatives *I*—*IV*, *VI*—*IX* and of (8-$CH_3OC_2B_9H_{10})_2Ni$ (*X*)

Compound Substituent	^{1}H-NMR δ^a (intensity)		Electronic spectra $\lambda(\varepsilon)$			
	C—H$_{carb.}$	C—H				
I —H; —H	3·95	—	—			
II —S—	3·34	—	213^b (21 300)	283 (16 615)	405 sh	575 (635)
IIIa —S(CH_3)—	4·11	2·64	289^c (27 380)	—	440 (643)	—
IIIh —S(H)—	2·41^d	2·74 (S—H)	287^c (19 480)	—	425 (718)	490 (583)
IIIk —S(C_6H_5)—	4·17 (4)	7·63 (5)	234^c (11 780)	297 (17 150)	440 (451)	495 (440)
IV —S($CH_3)_2$; —H	4·18 (2) 4·46 (2)	2·67 (6)	289^c (30 500)	—	440 (684)	492 (638)
VI —S_2—	3·82	—	283^b (11 400)	322 (8 770)	450 sh	558 (1 230)
VIIa —S(CH_3)S—	4·21 (1) 4·41 (3)	3·21 (3)	300^c (18 370)	—	475 sh	—
VIIb —S(C_6H_5)S—	4·27 (2) 4·58 (2)	7·71 (5)	—	—	—	—
VIII —S⩵CH⩵S—	4·65^e	—	—	—	—	—
IX —SH; —SH	4·47^f	—	—	—	—	—
X (8-$CH_3OC_2B_9H_{10})_2$Ni	—	—	240 (10 900)	317 (13 500)	400 (1 600)	510 sh

[a] In hexadeuterioacetone; [b] in CH_3CN; [c] in CH_2Cl_2; [d] in C_6D_6; [e] ref.[17]; [f] ref.[5].

in a different way[5]. Methylation has transformed this anion possesing a two-membered sulfur bridge to a new yellow zwitterionic species 8,8'-$CH_3S_2(C_2B_9H_{10})_2Co$ (*VIIa*) in which the methyl group is located on one of the S-atoms in the bridge, as shown by the ESCA method[10].Analogously to *IIIk*, the $C_6H_5S_2$- derivative *VIIb* was prepared from the anion *VI*. Some properties and characteristics of discussed compounds are collected in Tables *I–III*.

Structures and Conformations of the S-Substituted Derivatives of the Parent $(C_2B_9H_{11})_2Co^-$ *Skeleton*

^{11}B-NMR spectra of compounds *I–IX*, measured at 70·6 MHz are collected in Table III. The comparison of individual ^{11}B-NMR spectra of compounds *II–IX* with that of the parent compound *I* has shown that the substituent is in all cases located in the position B(8) and a bridge is between the B(8) and B(8') atoms. At first sight, however, it is also possible to deduce from the ^{11}B NMR spectra that two compounds, *i.e.* *VI* and 8,8'-$SCHS(C_2B_9H_{10})_2Co$ (*VIII*) have higher symmetry than expected, whereas *IV* and *VII* have no element of symmetry (except identity) even in individual dicarbollide units. These facts indicated that a detailed analysis of the ^{11}B-NMR spectra can provide us with valuable information on the conformations of individual substituted bis-dicarbollide complexes.

TABLE II

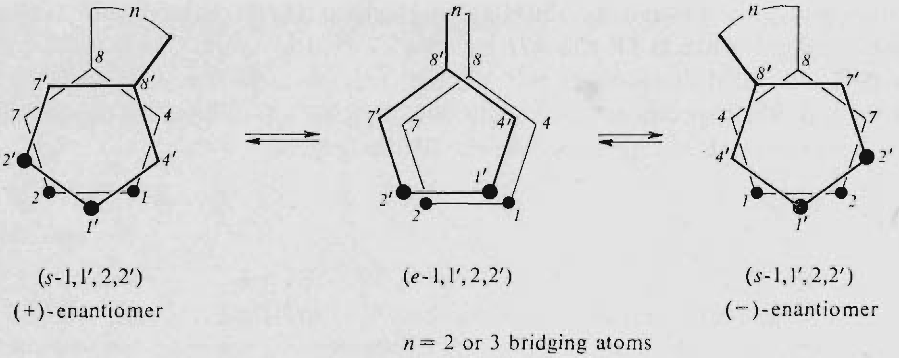
Chromatographic characteristics of some alkyl derivatives *IIIa—IIId*, *IIIg*, *IIIk*, *VIIa* and *VIIb*

Compound	Substituent	k'(HPLC)[a]	R_F rel.[b]
IIIa	—$S(CH_3)$—	2·23	100
IIIb	—$S(C_2H_5)$—	1·93	119
IIIc	—$S(C_4H_9)$—	1·77	138
IIId	—$S(C_3H_5)$—	2·04	116
IIIg	—$S(CH_2COOCH_3)$—	4·48	34
IIIk	—$S(C_6H_5)$—	2·35	103
VIIa	—$S(CH_3)S$—	2·04	100
VIIb	—$S(C_6H_5)S$—	1·65	103

[a] $k' = t_r - t_0/t_0$ where t_r and t_0 are the retention times of the carbaborane complexes and unretained solute-tetrachloroethylene, respectively. HPLC operating conditions: column 250 × × 4 mm packed with Separon Si VSK 6—10 µml (Laboratory Works, Prague, Czechoslovakia); eluent heptane–CH_2Cl_2 9 : 1 with 0·2% 2-propanol; flow-rate 1·2 ml/min. Detection UV at 254 nm. A home-made HPLC apparatus used was described elsewhere[18]. [b] TLC on Silufol, eluent benzene–hexane 1 : 1, R_F (*IIIa*) 0·32 = 100.

Two dicarbollide cages connected by a central metal atom can assume an infinite number of conformations by a free rotation around the logitudinal axis. The presence of two positively charged $C^{\delta+}$ atoms in both π-faces bound to the Co atom evoques distinct charge repulsions which are the cause that the internal energy changes during one revolution show several maxima and minima. Of all possible arrangements, only six conformations are of a practical importance (Scheme 1). Among these, the highest potential energy belongs to the (*e*-1,1′,2,2′) and the lowest one to the (*s*-1,8′,2,4′) conformations*.

The one-atom bridged derivatives *II* and *III* show in the ^{11}B-NMR spectra only six signals of the intensities 2 : 2 : 4 : 4 : 4 : 2, which is in harmony with the (*e*-1,1′,2,2′) conformation. This arrangement can be considered as almost rigid due to the fact that a connection of B(8) and B(8′) positions by a monoatomic bridge requires not only deviations of the radially directed bonds but, largely, inclinations of both



SCHEME 2

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* A generalization of this nomenclature proposal will be published elsewhere[11]. The leadings rules of this concept are as follows:
1) Each ligand is numbered independently according to the nomenclature rules[12]. *2*) In compounds named in this paper, the more substituted ligand is considered as the senior π-ligand (non-primed locants). *3*) The relative geometrical arrangement of both ligands is described by a four-membered set of locants of atoms *w*, *x*, *y*, *z* selected in an alternating manner (zig-zag) from both sandwiching faces (π and π′). The sequence starts from the lowest-numbered atom in the π-face (*w*) and continues towards the lower-numbered neighboring atom in the same face (*y*). *x* is the atom in the π′-face either opposing the atom *w* (eclipsed conformation) or located nearest to the atoms *w* and *y*, *z* is the atom neighboring *x* in the π′-face in the same direction as *w* → *y*; *4*) Where is a choice, the set of lowest possible numbers is used; if still two possibilities are numerically equivalent, that of lower number for *x* is preferred. *5*) The full configurational descriptor is composed of a letter symbol *e* (for eclipsed) or *s* (for staggered) followed by a hyphen and locants of the atoms *w*, *x*, *y*, *z*, The descriptor is enclosed in brackets (Scheme 1) and placed in front of the full name specifying the constitution.

pentagonal faces connected with the Co atom (*cf.* the crystal structure of 8,8-$CH_3O(C_2B_9H_{10})_2Co$ (ref.[13]) and 8,8′-$O(C_2B_9H_{10})_2Co^-$ (ref.[14]), which reduces oscillations of dicarbollide units to a minimum.

In contrast to the above series, a similar character of ^{11}B-NMR spectra of B(8), B(8′) substituted compounds *VI* with the two-atom S_2 bridge and of *VIII* with the three-atom —S=CH=S— bridge is very likely of a different origin. In these compounds, the bonding lengths of two- and three-membered bridges are greater than it is needed for the connection of B(8) – B(8′) positions and therefore a zig-zag character, fitting better with the conformation (*s*-1,1′,2,2′) can be expected (Scheme 2).

TABLE III

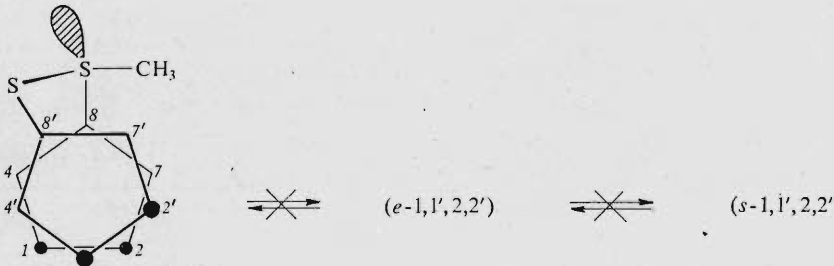
Chemical shifts of ^{11}B-NMR signals at 70·6 MHz of the 8,8′-substituted $(C_2B_9H_{11})_2Co^-$ derivatives *I—IV* and *VI—IX* (ppm rel. to $BF_3.O(C_2H_5)_2$, + sign means shift to the lower magnetic field, solvent : acetone)

Compound	Substituent		B(8)	B(10)	B(4,7)	B(9,12)	B(5,11)	B(6)
	B(8)	B(8′)						
I	—H; —H		6·5	1·5	—7·1	—7·1	—16·9	—22·3
II	—S—		3·2[a]	—0·8	—2·9	—7·6	—14·2	—24·2
IIIa	—S(CH_3)—		—3·4[a]	1·5	—6·0	—7·9	—14·0	—21·5
IIIh	—S(H)—		—6·0[a]	2·4	—6·3	—7·2	—14·1	—22·3
IIIk	—S(C_6H_5)—		2·5[a]	1·7	—5·5	—7·3	—13·6	—21·2
IV	—S(CH_3)$_2$; —H		8·6 7·4[a]	6·2 —0·9	—3·5 (1)[b] —3·7 (3)[b] —6·1 (1)[b] —8·1 (3)[b]		—14·4 —16·5	—20[c] —21[c]
VI	—S_2—		29·8[a]	—3·3	—3·3	—7·1	—16·6	—28·8
VIIa	—S(CH_3)S—		21·7[d]	1·3	—2·0 (1)[b] —4·0 (6)[b] —7·0 (1)[b]		—21·1 —13·0 —14·2 —14·5	—22·7 —24·1
VIIb	—S(C_6H_5)S—		21·9[a] 17·8[a]	2·0 1·0	—4·2 (6)[b] —6·5 (2)[b]		—13·2 (3)[b] —15·4 (1)[b]	—22·5 —23·4
VIII	S=CH=S—		13·0[a]	3·0	—0·2	—6·1	—14·3	—20·2
IX	—SH; —SH		11·6[a]	0·1	—4·5[c] (8)[b]		—16·8	—22·5

[a] Singlet; [b] intensity; [c] approximately; [d] coincidence of two singlets,

This conformation has been confirmed by the X-Ray diffraction analysis[8] of *VIII* which has shown in the crystalline state a structure having no plane of symmetry, *i.e.* (−) and (+) enantiomeric forms (Scheme 2). The NMR equivalence of both dicarbollide fragments in the above compounds can be therefore explained as a result of oscillations between two enantiomers that pass through the unfavorable symmetrical (*e*-1,1′,2,2′) conformation in which both repulsions of δ^+ charged C-atoms and increased strains of bridge-atoms bonding-angles exist. The easy oscilaltion indicates, however, that $C^{\delta+}$ repulsions in both compounds are not sufficiently great to stop a passage through the (*e*-1,1′,2,2′) stage. The considered equilibrium could also explain our previous unsuccessful attempts at resolving the $S_2(C_2B_9H_{10})_2Co^-$ anion to the enantiomers.

In contradistiction to the $S_2(C_2B_9H_{10})_2Co^-$ anion, the methylated 8,8′-CH_3S_2.$(C_2B_9H_{10})_2Co$ species (*VIIa*) shows surprisingly four signals belonging to the B(5,11) positions, which indicates not only a non-equivalency of both dicarbollide moities but also a loss of a plane of symmetry in them. The derivative *VIIa* exists therefore either in the "frozen" conformation (*s*-1,1′,2,2′) (Scheme 3) or its dicarbollide fragment oscillate too slowly in the NMR time-scale. A presence of the methyl group in the —S_2— bridge brings thus further hindrance which makes an inversion of (*s*-1,1′,2,2′) conformation to its enantiomer more difficult or impossible. An identity of chemical shifts of B(8) and B(8′) singlets (Table III) has been found to be only an accidental coincidence, because the ESCA measurement has proved that particular atoms are δ^+ and δ^- charged[10]. This was also confirmed by the different antipodal shift of B(6) and B(6′) atoms. Further support for this statement is the fact that the 8,8′-$C_6H_5S_2$— analogue *VIIb* shows two distinct singlets of B(8) and B(8′) atoms in the ^{11}B-NMR spectrum.



VIIa

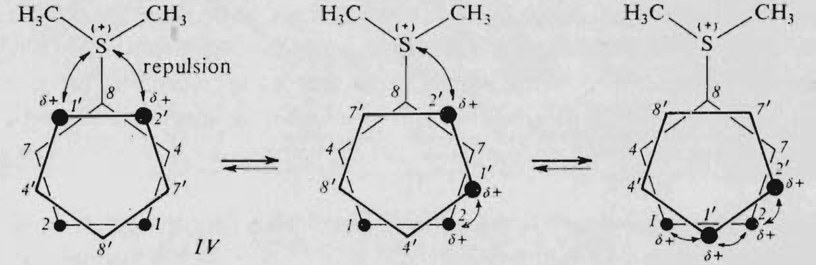
(*s*-1,1′,2,2′)
(−)-*cis*-antiprismatic

cis-prismatic

(+)-*cis*-antiprismatic

SCHEME 3

Conformationally unique seems to be the monosubstituted 8-$(CH_3)_2SC_2B_9H_{10}$—Co—$C_2B_9H_{11}$ derivative (*IV*) with 14 signals in the ^{11}B-NMR spectrum, which indicates a suppression or cancelation of the rotation round the longitudinal axis (two signals of intensity 3 are a result of a coincidence of two to three signals). Compound *IV* is thus the first non-bridged π-metalloheteroborane with which a dramatically restricted rotation of a π-ligand has been observed in solution. The reason can be found in suitably strong repulsions among the charged $S^{(+)}$ atom and the partially δ^+ charged C-atoms in the opposite face to stop (in the ^{11}B-NMR time-scale) a rotation in one of the non-symmetrical (*s*-1,4',2,1') or (*s*-1,1',2,2') conformations (Scheme 4). Which of these two conformations is really present is



IV

(*s*-1,8',2,4')
trans-antiprismatic

(*s*-1,4',2,1')

(*s*-1,1',2,2')
cis-antiprismatic

SCHEME 4

difficult to determine. However, if a rotation of CH_3 groups round the S—B axis is absent (as it is with 4-$(CH_3)_2SC_2B_9H_{10}$—Co—$C_2B_9H_{11}$ where two CH_3 signals at δ 2·77 and 2·88 ppm have been found in the ^{1}H-NMR spectrum), a single methyl signal at δ 2·67 ppm with *IV* allows to prefer the conformation (*s*-1,1',2,2') in which the counterparts to both methyl groups are two BH vertices in the opposite π-face.

Up to now, only *cisoid, i.e.* (*s*-1,8',2,4'), (*e*-1,8',2,4') and *transoid, i.e.* (*s*-1,1',2,2'), (*e*-1,1',2,2') conformations were considered. The existence of a "frozen" conformation of non-bridged bis-dicarbollide sandwiches with medium remoted carbon couples is, however, also possible. The (*s*-1,4',2,1') conformation was recently found by the single crystal X-Ray diffraction analysis[15] of the $(8\text{-}CH_3OC_2B_9H_{10})_2Ni$ species (*X*) (Fig. 2) which was prepared together with the partially methoxylated compound 8-$CH_3OC_2B_9H_{10}$—Ni—$C_2B_9H_{11}$ (*XI*) by the reaction of $(C_2B_9H_{11})_2Ni^-$ with formaldehyde in strongly acidic medium.

The above examples show that despite a low energy rotation barrier in the parent $[(C_2B_9H_{11})_2M^n]^{n-4}$ metallocarborane, a substitution of H in the pentagonal π-face can either lower or stop the rotation round the longitudinal axis of the molecule. What conformation prevails is controlled both by the charges on individual atoms in the opposite pentagons and by steric interactions of substituent/s with the opposite radially directed pentagonal ring protons or substituent/s.

The geometry of the intermediate prismatic form between two antiprismatic boundary stages is still obscure. A distinct mutual inclination α of the pentagonal π-faces connected with the Co atom, evoked either by the presence of a relatively short $\mathrm{O}\langle$ bridge ($\alpha = 28°$, ref.[13,14]) or by mere Van der Waals repulsions of methyls bonded to the C-atoms in these π-faces as in $[(CH_3)_2C_2B_9H_9]_2Ni^{IV}$ ($\alpha = 15°$, ref.[16]) documents that a mutual tilting of these π-faces is easy. Considering this, we prefer a "waving" of the π-faces rather than a distortion of radially pointing B—S bonds in the course of oscillations of bridge-connected bis-dicarbollide sandwiches.

The NMR behaviour of some of the discussed compounds (*i.e. VI, VIII*) has indicated that the mutual repulsions of C-couples in both pentagonal π-faces are relatively low and do not inhibit a passage through the less favourable (*e*-1,1′,2,2′) conformation in a solution. This allows to assume a sufficient fast (in the NMR time-scale) free rotation of dicarbollide units round the longitudinal axis also in the unsubstituted anion *I*.

The above considerations allow to state that with pentahapto-bis-dicarbollide transition metal π-complexes: *1*) Rotation or oscillation of dicarbollide units is not significantly suppressed by mutual repulsions of $C^{\delta+}$ couples. *2*) Strongly positively charged substituent in one of the present dicarbollide units can stop the rotation and brings a preference of a conformation in which this substituent is remoted from the C-couples of the opposite π-face (see Scheme 4). *3*) Even the R—$\underset{|}{\overset{(+)}{\mathrm{S}}}$— substituent

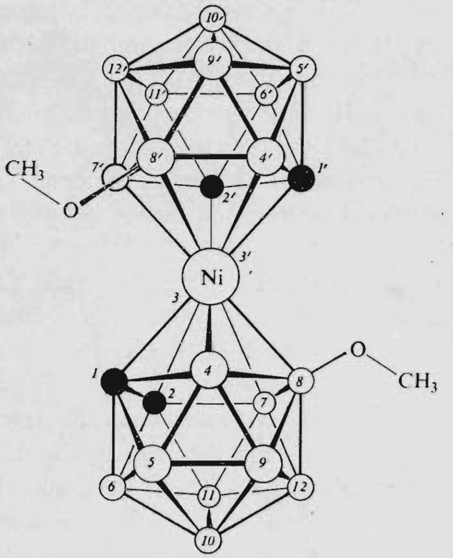


FIG. 2

The molecular structure of $(8\text{-}CH_3O\text{-}1,2\text{-}C_2B_9H_{10})_2Ni^{IV}$

Note added in proof: numbers in couples 1′-2′, 4′-7′, 5′-11′ and 9′-12′ should be mutually exchanged.

(R $\neq$ H) evoques a sufficiently great hindrance which can stop not only rotation of dicarbollide units as in *IV* but also oscillation about the "equilibrium" prismatic position (*cf. VI vs VII*). *4*) In the course of oscillation, a mutual tilting of the dicarbollide π-faces rather than a distortion of B – X bond can be preferred.

EXPERIMENTAL

^{1}H-NMR spectra at 100 MHz were measured on a Varian XL-100 instrument. The ^{11}B-NMR spectra at 70·6 MHz were recorded on an instrument consisting of a pulsed NMR apparatus (built at Indiana University, Bloomington, U.S.A.), a Varian 51·7 kG superconducting magnet, and a 20K Nicolet 1 080 series computer. UV and visible spectra were recorded on a Beckman Acta M IV device and IR spectra on a Beckman IR-20 A spectrometer. Mass spectra were measured on LKB 9000 instrument. The solvents were of a spectral grade for measurements and of chemical purity for preparative operations. The purity of individual compounds was checked by thin-layer chromatography on Silufol (silica gel on aluminum foil, starch as binder, Kavalier, Votice, Czechoslovakia). Melting points were measured in sealed capillaries in the Kofler stage. Compounds *VIII* and *IX* were prepared according to literature[5].

Preparation of Dimethylsulfoxonium Salt of $(C_2B_9H_{11})_2Co^-$ (*Ib*)

To the suspension of 43 g (0·3 mol) of *o*-carborane in 150 ml of methanol was added 60 g (1 mol) of potassium hydroxide. Degradation of *o*-carborane proceeded under violent hydrogen evolution and therefore the mixture had to be occasionally cooled. When the hydrogen evolution stopped, 150 ml of methanol was added to the mixture and the solution was refluxed for 2 h. A portion of methanol (c. 50 ml) was then distilled off and 200 ml of water were added to the solution. The remaining methanol was removed by distillation, a next portion of 100 ml of water was added and further 100 ml of liquid was distilled off. The resulting solution was poured into 51 g (0·22 mol) of $CoCl_2.6\,H_2O$ in 100 ml of water and while stirring a hot solution of 60 g KOH in 100 ml of water was added. The mixture was heated in boiling water bath for 5 min and then brought to room temperature. The cool mixture was diluted with 300 ml of water, saturated with CO_2 and separated cobalt was removed by filtration. The orange solution was extracted with three 100 ml portions of diethyl ether, the ether extracts were combined and extracted twice with 50 ml portions of 30% H_2SO_4, the ether layer was washed with 100 ml of water and ether was distilled off. The residue was diluted with 300 ml of water and the remaining ether was pumped off. The aqueous orange-colored solution was filtered and 30 ml of dimethyl sulfoxide was added to the filtrate. The mixture was left overnight, the separated crystals were filtered, washed with water and dried *in vacuo* to yield 52 g (72%) of $(C_2B_9H_{11})_2.Co^-[HOS(CH_3)_2OS(CH_3)_2]^+$. For $C_8H_{35}B_{18}CoO_2S_2$ (481·2) calculated: 40·35% B, 12·19% Co, 13·25% S; found: 39·98% B, 12·12% Co, 13·32% S.

8,8′-$S(C_2B_9H_{10})_2Co^-$ Anion (*II*)

To the suspension of *Ib* (5g, 10 mmol) in 40 ml of dichloromethane was added 5 ml of disulfur dichloride and the mixture was refluxed under nitrogen. After 4 h all solid compound dissolved and the mixture turned red. The solution was evaporated *in vacuo* and to a residue was added 50 ml of methanol, 50 ml of water and 10 g of NaOH. After stirring for 30 min, the mixture was saturated with carbon dioxide and the separated solid was filtered. To the violet filtrate was added cesium chloride, and precipitated cesium salt was recrystallized from aqueous methanol; yield 3·2 g (63%) of the anion *II*. For $C_4H_{20}B_{18}CoCsS$ (486·8) calculated: 12·10% Co, 6·79% S; found: 11·62% Co, 6·63% S.

Alkylation of the Anion *II*

Synthesis of IIIa: To the cesium salt of *II* (4·8 g, 10 mmol) dissolved in 25 ml of acetone, 2·5 ml of dimethyl sulfate was added. When the green solution turned dark red (in c. 5 min), the excess dimethyl sulfate was decomposed with aqueous ammonia, the mixture was diluted with water and extracted with benzene. The benzene layer was separated, benzene evaporated and a red-brown solid residue was recrystallized from benzene–hexane (1 : 2). Yield: 3 g (82%) of red compound *IIIa* (m.p. 302—304°C, dec.) which exhibits a molecular cut-off at *m/e* 372, corresponding to $^{12}C_5\,^{11}B_{18}H_{23}\,^{59}Co\,^{32}S$.

Synthesis of IIIe: Cesium salt of *II* (1·0 g, 2 mmol) was dissolved in 20 ml of acetone and benzyl bromide (2 ml) was added. After standing for 1 h at room temperature, the mixture was diluted with water and extracted with benzene. The benzene extracts were combined and the solvent was distilled off *in vacuo*. A solid residue was recrystallized from hexane, yielding 0·7 g (58%) of red derivative *IIIe*, m.p. 233—235°C, *m/e* 448 corresponds to $^{12}C_{11}\,^{11}B_{18}\,^{1}H_{27}\,^{59}Co\,^{32}S$.

Synthesis of IIIb: Alkylation of *II* with ethyl bromide was performed in the same way as with *IIIe*. Yield: 65% of red compound *IIIb*, m.p. 258—259°C, *m/e* 386 corresponds to $^{12}C_6\,^{11}B_{18}.\,^{1}H_{25}\,^{59}Co\,^{32}S$.

Synthesis of IIIc: The procedure was the same as above but refluxing with n-butyl bromide for 3 h was required for completing the reaction. Yield: 60% of red compound *IIIc*, m.p. 266 to 268°C (dec.), *m/e* 414 corresponds to $^{12}C_8\,^{11}B_{18}\,^{1}H_{29}\,^{59}Co\,^{32}S$.

Synthesis of IIId: Under similar conditions as with *IIIe*, allyl chloride reacted giving 60% of the red derivative *IIId*, m.p. 217—218°C, *m/e* 398 corresponds to $^{12}C_7\,^{11}B_{18}\,^{1}H_{25}\,^{59}Co\,^{32}S$.

Synthesis of IIIf: To the cesium salt of *II* (4·8 g, 10 mmol) dissolved in 20 ml of methanol, 40 ml of 5% NaOH solution containing 2·3 g (20 mmol) of sodium chloroacetate was added. After standing for several hours at room temperature, the mixture was acidified with diluted hydrochloric acid and extracted with benzene. The benzene extracts were combined, the solvent distilled off and a solid residue was recrystallized from benzene–hexane (1 : 1), yielding 2·2 g (50%) of the red substance *IIIf*, m.p. 184—185°C, *m/e* 416 which corresponds to $^{12}C_6\,^{11}B_{18}.\,^{1}H_{23}\,^{59}Co\,^{16}O_2\,^{32}S$; pK_a (50% C_2H_5OH) 3·70.

Synthesis of IIIg: The acid *IIIf* was esterified with methanol in the presence of sulfuric acid affording the methyl ester *IIIg* which after recrystallization from benzene–hexane (1 : 1) had m.p. 190—191°C and *m/e* 430, corresponding to $^{12}C_7\,^{11}B_{18}\,^{1}H_{25}\,^{59}Co\,^{16}O_2\,^{32}S$.

Preparation of IIIh: A solution of cesium salt of *II* (1 g, 2 mmol) in aqueous methanol was acidified with diluted hydrochloric acid and after few minutes the mixture was extracted with benzene. Benzene extracts were combined, the solvent was distilled off and a solid residue was extracted with hexane which dissolved reaction by-products. The resulting red solid was dried *in vacuo* leaving 0·7 g (98%) of *IIIh* of *m/e* 358 which corresponds to $^{12}C_4\,^{11}B_{18}\,^{1}H_{21}\,^{59}Co\,^{32}S$.

Reaction of IIIh *with acrylonitrile*: To the solution of *III h* (0·4g, 1·4 mmol) in 15 ml of benzene, 2 ml of acrylonitrile was added. After standing for 24 h at room temperature, the benzene and unreacted acrylonitrile were removed under reduced pressure. The residue was chromatographed on a silica gel column using the 1 : 1 benzene–hexane mixture as an eluent. Yield: 0·2 g (44%) of red crystals of *IIIi*, m.p. 242—244°C (dec.), *m/e* 411 corresponds to $^{12}C_7\,^{11}B_{18}\,^{1}H_{24}\,^{59}Co.\,^{14}N^{32}S$. ^1H-NMR (100 MHz, C_6D_6): δ 2·36 (br, CH_{carb}) and 1·38 ppm (br, CH_2).

Synthesis of IIIj: The cesium salt of *II* (2·22 g, 4·5 mmol) was suspended in 50 ml of benzene and the solution was shaken with 30 ml of concentrated hydrochloric acid. Benzene solution was separated, benzene and HCl were removed *in vacuo* and the residue was again dissolved in 50 ml of benzene. The resulting red solution was treated with 0·3 g (10 mmol) of paraformaldehyde and 10 ml of methanol. The mixture turned immediately violet. The presence of a distinct amount of the red *IIIj* was revealed by means of TLC. Using preparative TLC on silica gel with benzene–hexane (1 : 1) as an eluent, the compound *IIIj* was isolated; m.p. 132—134°C, *m/e* 370, ^{1}H-NMR (100 MHz, C_6D_6): δ 4·68 (CH_2), 2·65 (CH_3) and 2·42 ppm (CH_{carb}).

Reaction of S_2Cl_2 with *Ia*

To the suspension of *Ia* in 20 ml of 1,2-dichloroethane, 5 ml of disulfur dichloride was added. The further procedure was the same as in the preparation of *II*. The reaction afforded 3·4 g of a mixture of the Cs salts of *II* and *VI* which dissolves in acetone forming a blue solution. This mixture was methylated similarly to *II* yielding 1·2 g of an orange solid which was — according to TLC — composed of two compounds. Several times repeated chromatography on a silica gel column (benzene–hexane 1 : 3) afforded 0·5 g of the red compound *IIIa* and 0·5 g of the yellow substance *VIIa* of *m/e* 404 which corresponds to $^{12}C_5\,^{11}B_{18}\,^{1}H_{23}\,^{59}Co\,^{32}S_2$. Methylation of the anion *VI*, prepared according to Francis and Hawthorne[5], gave the identical methyl derivative *VIIa*.

Preparation of *IV*

Acetanhydride (13 ml) was added to a solution of *Ib* (9·0 g, 18 mmol) in 80 ml of benzene. The mixture was refluxed for 1 h under nitrogen, evaporated and separated by the chromatography on a silica gel column (benzene–hexane 1 : 1). The first solute was a red compound (0·07 g) which was according to the mass and IR spectra identical with *IIIa*. The second fraction was the yellow substance *IV* (3·3 g, 50%); m.p. 278—280°C, *m/e* 388 corresponds to $^{12}C_6\,^{11}B_{18}$. $^{1}H_{27}\,^{59}Co\,^{32}S$.

Reaction of *IV* with $AlCl_3$

To the substance *IV* (1 g, 2·6 mmol) dissolved in 20 ml of benzene, 1·5 g (11 mmol) of anhydrous aluminum chloride was added and the suspension was refluxed for 4 h under nitrogen. The mixture was diluted with water, benzene layer was separated, several times washed with water, benzene was evaporated, and a solid residue was chromatographed on a silica gel column (benzene–hexane 1 : 9), yielding 0·12 g (14%) of the red compound *IIIa* and 0·35 g (32%) of the orange substance *V* of m.p. 239—241°C and of *m/e* 422 which corresponded to $^{12}C_6\,^{11}B_{18}\,^{1}H_{26}$. .$^{59}Co\,^{35}Cl\,^{32}S$.

Bromination of *II*

To the solution of 2 g (4 mmol) of cesium salt of *II* in 30 ml of concentrated acetic acid, 4 g of bromine were dropwise added. After the addition of first drops of bromine, the solution turned turbid and an orange substance started to separate. When all bromine was added, the mixture changed again clear. Acetic acid was distilled off *in vacuo*, a solid remnant was dissolved in a necessary amount of benzene and the benzene solution was carefully covered with pentane. The double-layer system was allowed to stand undisturbed for 2 days at room temperature. Separated crystals were filtered and dried *in vacuo*, yielding 1·0 g (57%) of yellow-orange substance which showed the molecular cut-off at m/e 418 corresponding to $^{12}C_4\,^{11}B_{18}\,^{1}H_{20}\,^{81}Br\,^{59}Co\,^{32}S$. The bromoderivative appeared to be unstable and hydrolysed rapidly in air. TLC on Silufol showed R_F 0·53 in benzene.

Synthesis of *IIIk*

To the solution of 1 g (2·4 mmol) of the above bromo derivative in 50 ml of benzene, 0·2 g of $AlCl_3$ was added and the mixture was heated for 2 h on a boiling water bath. After this period, 50 ml of water was slowly added under stirring and cooling. The benzene layer was extracted with 20 ml of 1M-NaOH. The alkaline solution was precipitated by cesium chloride recovering 0·5 g (45%) of cesium salt of *II*. The benzene solution was evaporated and the residue was chromatographed on a column of silica gel with benzene–hexane (1 : 1) as an eluent, affording 0·2 g (20%) of the red compound *IIIk*, m.p. 275°C (dec.); *m/e* 446 corresponds to $^{12}C_{10}\,^{11}B_{18}\,^{1}H_{25}.\,^{59}Co\,^{32}S$.

Synthesis of *VIIb*

Compound *VIIb* was prepared similarly to *IIIk*, using the cesium salt of *VI* as the starting compound. In this way, the yellow compound *VIIb* (15%) of m.p. 240°C (dec.) and of *m/e* 446 corresponding to $^{12}C_{10}\,^{11}B_{18}\,^{1}H_{25}\,^{59}Co\,^{32}S_2$ was obtained.

Synthesis of *X* and *XI*

A suspension of 10 g of $(C_2B_9H_{11})_2NiCs$ in 50 ml of 30% H_2SO_4 was extracted with 50 ml of diethyl ether. The ether layer was separated, 50 ml of water were added and diethyl ether was distilled off. The remaining water solution together with 50 ml of concentrated hydrochloric acid and 50 ml of c. 30% aqueous formaldehyde solution was heated for 2 h in boiling water bath, cooled to ambient temperature, extracted with benzene and the benzene extract was chromatographed on a silica gel column with benzene–hexane (1 : 1) mixture as an eluent. It was isolated 1·5 g (18%) of a red compound *X* (m.p. 186—187°C, dec., R_F in benzene 0·59) and 1·0 g (13%) of derivative *XI* (m.p. 203—204°C, dec., R_F in benzene 0·30).

The mass spectra were measured by Drs V. Kubelka and J. Mitera, Prague Institute of Chemical Technology, Prague, the electronic spectra were recorded by Drs F. Hanousek and F. Haruda and the ^{1}H-NMR *spectra were obtained by Dr F. Mareš, Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Řež. All these colleagues are thanked for their assistance.*

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