ASYMMETRIC COBALTACARBORANES [6,6′-μ-R-S(1,7-$C_2B_9H_{10}$)$_2$-2-Co] WITH A MONOSULFUR BRIDGE BETWEEN LIGANDS AND HPLC RESOLUTION OF THE ENANTIOMERS

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On treatment of the [2-Co-(1,7-$C_2B_9H_{11}$)$_2$]$^-$ ion with elemental sulfur and $AlCl_3$ only the racemic form of the [6,6′-μ-S(1,7-$C_2B_9H_{10}$)$_2$-2-Co]$^-$ ion is obtained in high yield. Methylation of this ion proceeds at the sulfur bridge giving rise to the zwitterionic complex [6,6′-μ-MeS(1,7-$C_2B_9H_{10}$)$_2$-2-Co]. Constitution of both species has been established by high-field NMR methods and confirmed by resolution to enantiomers by HPLC on chiral stationary phase.

The first sandwich complex with an intramolecular monoatomic bridge between both ligands has been discovered twenty years ago[1]. It became apparent that it was only one member of a large family of the [8,8′-μ-R-E(1,2-$C_2B_9H_{10}$)$_2$-3-Co] type (Fig. 1) in which the bridging atoms were O, S, Se, Te, N, Br and I (refs[2-5]). Several structure determinations by X-ray diffraction analysis revealed that the short monoatomic bridge dramatically influenced the ligand arrangement around the central metal vertex. *Following remarkable features have been found*: forced *cis* prismatic (eclipsed) conformation of both pentagonal ligand planes, their remarkable inclination, lengthening of some and shortening of other bonds, noticeable shift of the central ion towards the bridging atom[6-9], and the presence of at least one symmetry plane.

In this paper we discuss the preparation and properties of bridged sandwiches of the type [6,6′-μ-R-E(1,7-$C_2B_9H_{10}$)$_2$-2-Co] (*Ia*, *Ib*, Fig. 2), which are entirely asymmetric.

Starting with the highly symmetric [2-Co-(1,7-$C_2B_9H_{11}$)$_2$]$^-$ ion[10] and applying the same method as that used earlier[3] for the preparation of the isomeric [8,8′-μ-S(1,2-$C_2B_9H_{11}$)$_2$-3-Co]$^-$ ion (Eq. (*A*)), we were able to insert a monoatomic bridge between both ligands under the formation of the racemic form of *Ia* in 80% yield.

$$[2\text{-Co-}(1,7\text{-}C_2B_9H_{11})_2]^- + S_x \xrightarrow[60\ °C,\ 2\ h]{AlCl_3,\ \text{benzene}} [6,6'\text{-}\mu\text{-}S(1,7\text{-}C_2B_9H_{10})_2\text{-}2\text{-Co}]^- + H_2S \qquad (A)$$

Methylation of the *Ia* anion led to the corresponding zwitterion with a three-coordinate sulfur bridge (*Ib*, Fig. 2).

For a better understanding of the following discussion it seems reasonable to neglect the six distant {B-H} vertices in each ligand (positions 4, 5, 8, 9, 10, 12) and consider only conformation of both pentagonal ligand planes according to Fig. 3 (the Co^{3+} ion sandwiched between both pentagons in the position 2 = 2′ is not shown).

In the starting $[2\text{-Co-}(1,7\text{-}C_2B_9H_{11})_2]^-$ ion the ligands can freely rotate in solution, possibly prefering the conformation depicted in Fig. 3*a* (due to the best alignments of the dipole moment vectors to achieve the least Coulomb repulsion). Also apparent from this figure is that the equivalent vertices B(6,11) and B(6′,11′) are negative and consequently prone to substitution under electrophilic conditions.

For connection by a monoatomic bridge both ligands should attain a prismatic conformation with eclipsed vertices B(6) and B(6′) which is possible either with conformation 3*b* (meso-form) or with conformation 3*c* (racemic form). As in the case 3*b*, both dipole vectors are parallel (maximum Coulomb repulsion) and this conformation ought to be less favourable than the conformation 3*c*. This is probably the main reason why the meso-form is completely missing in the real experiment.

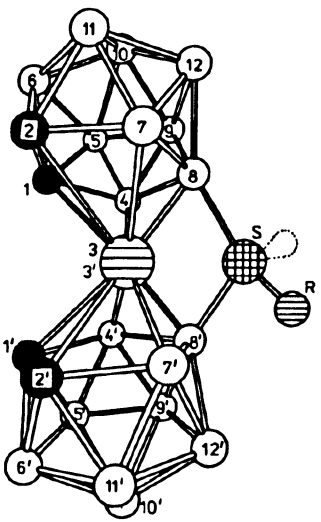

FIG. 1
Structure of the [8,8′-μ-R-S(1,2-$C_2B_9H_{10})_2$-3-Co] species. Terminal hydrogen atoms are omitted for clarity

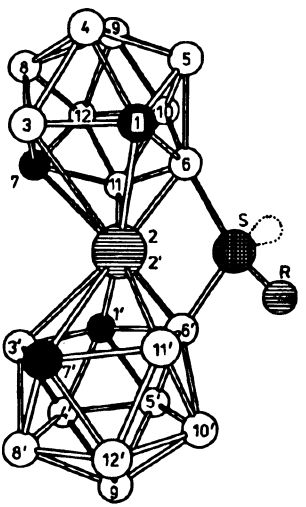

FIG. 2
Proposed structure of [6,6′-μ-R-S(1,7-$C_2B_9H_{10})_2$-2-Co] species. Terminal hydrogen atoms are omitted for clarity

On methylation of the meso-form of *Ia* at the sulfur bridge two isomeric zwitterions of the *Ib* type might be expected; one with the methyl group inclined to both carbon atoms and the other with the methyl group inclined to the vertices B(11,11′). It is highly improbable for both isomers to be formed in the 1 : 1 ratio since in one case the positively charged CH_3^+ moiety would approach from the side of relatively positive C–H vertices, while it would attack from the side of relatively negative vertices B(11,11′) in the other case, respectively.

Methylation of one enantiomer of the racemic form of *Ia* should afford a single Me–S< zwitterion of the *Ib* type because on turning the molecule "bottom up" nothing would changed but the methyl group would appear at the opposite side of the sulfur bridge. However, in one ligand, the methyl group points to C(1) whereas it is inclined to B(11′) in the other. This renders both ligands magnetically nonequivalent from the viewpoint of NMR shielding behaviour. The expected ^1H and ^{11}B NMR features for racemic and meso-forms are shown in Table I.

The measured NMR parameters (Table II) confirm exclusive formation of the racemic form; the ^1H NMR spectrum of *Ia* shows two {CH} carborane signals whereas that of the zwitterion *Ib* displays four signals. A little more complex is the ^{11}B NMR spectrum of *Ia*. Despite the highest available resolution (160.4 MHz), two signals in *Ia* remain overlapped; fortunately the [^{11}B-^{11}B]-COSY measurements make possible unequivocal assignments of most signals to individual {BH} vertices. Only the signals belonging to the B(5,12) and B(4,8) pairs remain ambiguous, but it is apparent that the latter pair resonates at the highest field (see Table II).

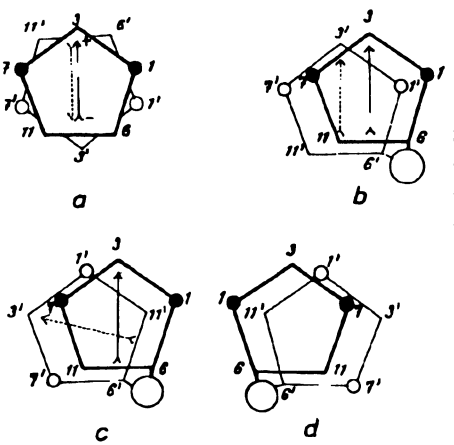

FIG. 3

Schematic drawing of the possible conformations of both pentagonal ligand planes adjacent to the cobalt atom in the [6,6′-μ-R-S(1,7-$C_2B_9H_{10})_2$-2-Co] species. *a* Symmetric *anti* prismatic; *b* eclipsed meso-form, upper ligand ρ, bottom ligand σ; *c*, *d* ENANTIOMERS – staggered prismatic; in left both ligands ρ, in right both ligands σ. Numbering of the frameworks is based on least-number locant principle and the σ, ρ-convention for chiral molecules[11]. (Symbols σ and ρ indicate the direction of unfolding of the numbering spirals from the defined position 1)

Still worse is the situation with the zwitterion *Ib* where of the expected eighteen ^{11}B signals only fifteen are seen, three of them showing a double intensity due to a coincidental overlap. Due to the extremely narrow span of the ^{11}B NMR spectrum and a high number of signals, corresponding [^{11}B-^{11}B]-COSY NMR data are nearly worthless. But the correlation diagram (Fig. 4) clearly indicates how the S-bridge methyl

TABLE I
Expected NMR patterns for the meso- and racemic forms in the [6,6′-μ-R-S(1,7-$C_2B_9H_{10}$)$_2$-2-Co] system

Bridge	meso-Form		Racemic form	
	^{1}H NMR	^{11}B NMR	^{1}H NMR	^{11}B NMR
S<$^{(-)}$	2 CH	9 signals 1 singlet	2 CH	9 signals 1 singlet
CH_3–S<	2 CH	9 signals 1 singlet	4 CH	18 signals 2 singlets
	1 CH_3		1 CH_3	

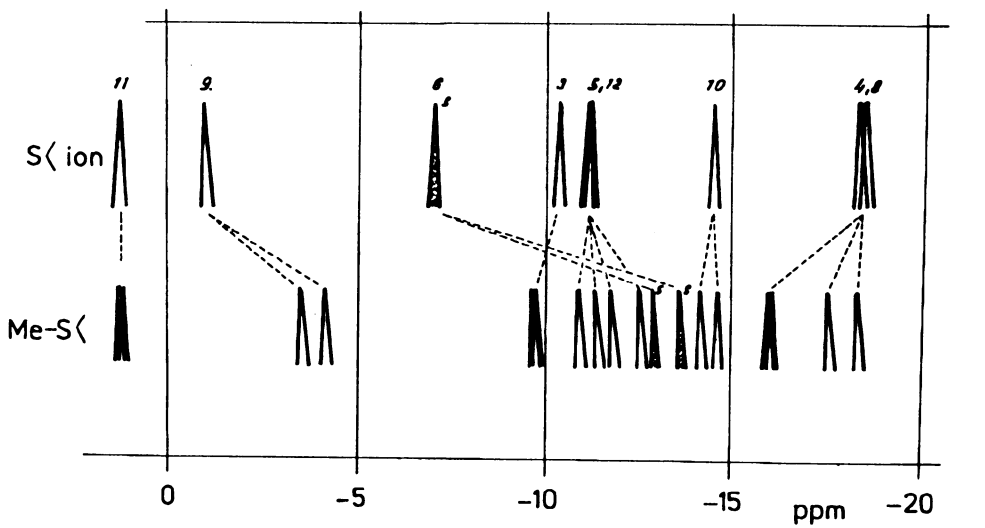

FIG. 4
Correlation of chemical shifts in idealized ^{11}B NMR spectra of the [6,6′-μ-S(1,7-$C_2B_9H_{10}$)$_2$-2-Co]$^-$ anion and its methyl derivative [6,6′-μ-MeS(1,7-$C_2B_9H_{10}$)$_2$-2-Co] at 160 MHz

group affects the chemical shifts in both ligands and allows for the most probable assignment of all signals to individual {BH} vertices in the zwitterion.

Further support for this interpretation of the NMR data is afforded by the resolution of both enantiomers of *Ia* and *Ib* by HPLC on column with bonded β-cyclodextrin (β-CD) chiral stationary phase using aqueous methanol as mobile phase. Figure 5 shows analytical chromatogram of *Ib*. Anion *Ia* was separated on β-CD in aqueous methanol as the mobile phase with a lower methanol content. Semipreparative modification of the chromatographic method, recently used in separation of chiral deltahedral borane compounds of the L-R-$C_2B_9H_{10}$ type[12], enabled us to isolate pure enantiomers of *Ia* and *Ib* in submilligram quantities. Figure 6 shows the circular dichroism spectra (CD) with the curves *1* and *2* representing the CD spectra of the first eluted enantiomers of *Ia* and *Ib*. A detailed description of the chromatographic method for the separation of the sulfur substituted zwitterionic species of the [6,6′-μ-R-S(1,7-$C_2B_9H_{10}$)$_2$-2-Co] type will be subject of a separate article[13].

TABLE II
^{1}H and ^{11}B NMR spectra (δ, ppm) of compounds *Ia* and *Ib*

Species	^{1}H NMR[a,b]	^{11}B NMR[a,c,d]
Ia	C–H	1.30 [3.06] B(11);
	4.35	−1.05 [2.75] B(9);
S<$^{(-)}$	2.73	−7.12 s B(6); −10.5 [3.07] B(3);
		−11.7 [1.910, 1.80] B(5,12);
		−14.56 [1.723] B(10);
		−18.44 [1.78, 1.68] B(4,8)
Ib	C–H	1.26 (2) [3.13];
	4.28	−3.65, −4.13 [3.18, 3.00];
	4.06	−9.83 (2) [3.32];
CH_3–S<	3.22	−11.11, −11.49 [2.00];
	3.13	−11.97, −12.69 [2.09];
	CH_3	−12.96 (s); −13.76 (s);
	2.59	−14.22 [2.02]; −14.88 [1.97];
		−16.06 (2) [2.00, 1.920];
		−17.77 [1.97]; −18.46 [1.94]

[a] Additional NMR spectra are available on request, e.g. [^{11}B-^{11}B]-COSY NMR of *Ia*, ^{11}B-{^{1}H} NMR, ^{1}H-{^{11}B} NMR data, etc. [b] Measured at 500 MHz in deuterioacetone. [c] Measured at 160.4 MHz in deuterioacetone; assignments based on [^{11}B-^{11}B]-COSY. [d] Followed by cluster proton chemical shifts (in square brackets) and assignments in parentheses.

EXPERIMENTAL

Analytical TLC were performed on silica sheets Silufol (Kavalier, Votice). The NMR spectra (δ, ppm) were measured with a Varian XL-500 spectrometer at 500 MHz (^{1}H) and 160.4 MHz (^{11}B) in deuterioacetone (relative to $B(OCH_3)_3$ as internal standard, −18.2 ppm). Mass spectra were recorded with a Jeol HP-5985 equipment by electron impact ionization at 70 eV. Circular dichroism spectra were recorded on an Auto Dichrographe Mark V device (Jobin Yvon, France) driven by a microcomputer (Silex, France) loaded with our own software. The measurements were performed in methanol in quartz cells with the optical pathlength 1 and 0.1 cm. The spectra are computer averages over 2 – 3 instrument scans and the data are presented as $\Delta A/l$, where l is the cell pathlength in cm.

The simple isocratic chromatographic system was described elsewhere[12]. The chromatographic separations were performed on stainless steel semipreparative column (250 × 8 mm) filled with CSP based on β-CD directly bonded to silica gel Separon SGX (7 μm, TESSEK, Prague). The chromatographic conditions used for the separation of the *Ib* enantiomers are described in the Fig. 5 caption. Enantiomers of the *Ia* anion were separated in 52% aqueous methanol (flow rate 1.6 ml/min, detection UV 290 nm with capacity factor of the first eluted enantiomer k_1 8.55, high selectivity value α 1.39, but with a relatively low resolution value R_s 0.83 due to extensive peak broadening. In the semipreparative separations for CD measurements, the 50 μl of samples of concentration 1 mg/ml were injected and the front part of the first and back part of the second peaks were collected from 10

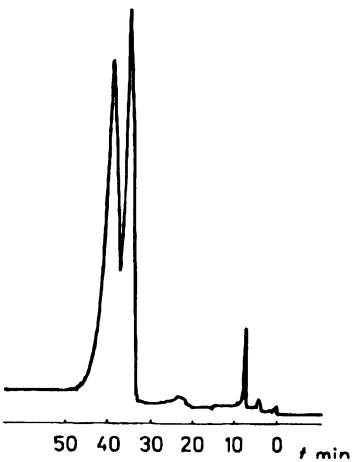

FIG. 5
Analytical HPLC separation of enantiomers of [6,6′-μ-MeS(1,7-$C_2B_9H_{10}$)$_2$-2-Co] on 250 × 8 mm β-cyclodextrin semipreparative column (TESSEK, Prague). Mobile phase: 85% aqueous methanol, flow rate 1.2 ml/min, detection: UV at 290 nm, sensitivity 0.04 A.U.F.S., injection: 2 μl of the methanolic solution of the compound *Ib* of concentration 1 mg/ml

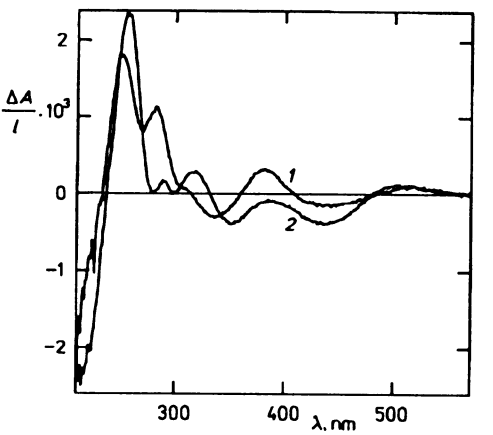

FIG. 6
Circular dichroism spectra of the first eluted enantiomers of [6,6′-μ-S(1,7-$C_2B_9H_{10}$)$_2$-2-Co]$^-$ (*1*) and [6,6′-μ-MeS(1,7-$C_2B_9H_{10}$)$_2$-2-Co] (*2*)

successive injections. The mobile phase was then evaporated in vacuum and the samples were dissolved in 4 ml of methanol.

$M^+[6,6'$-μ-S(1,7-$C_2B_9H_{10})_2$-2-Co$]^-$ Ion (*Ia*; M = Na and NMe_4)

A mixture of 2-Co-(1,7-$C_2B_9H_{11})_2$. Cs (4.6 g, 0.01 mol), S_x (0.96 g, 0.03 mol) and of $AlCl_3$ (4.0 g, 0.03 mol) in benzene (50 ml) was stirred for 1 h at 60 °C. The solids were filterred off from the turbid red-brown solution, washed with benzene (2 × 10 ml) and then discarded. The combined benzene extracts were stirred with 50 ml of 5% hydrochloric acid for 5 min. From the resulting three-layer system, upper benzene layer was separated, washed twice with 50 ml of water and discarded. The aqueous extracts were combined with both bottom layers previously separated. The residual benzene was removed in vacuum from the combined aqueous extracts, the resulting red-brown water solution filtered and the product extracted with two 50 ml portions of diethyl ether. The combined ether extracts were neutralized with 1.0 g of Na_2CO_3 and the diethyl ether was evaporated in vacuum after the addition of 100 ml of water. The resulting water solution of the *Ia*-Na salt was concentrated to a 50 ml volume. The *Ia*-NMe_4 salt was precipitated from 10 ml of this solution by adding of 0.1 M Me_4N^+ . Cl^- (10 ml) and the precipitate recrystallized from hot 30% ethanol to give brown leaflets, 0.65 g (81%), R_F = 0.28 (Silufol, acetonitrile–chloroform 1 : 2). For ^1H and ^{11}B NMR properties see Table II.

[6,6'-μ-MeS(1,7-$C_2B_9H_{10})_2$-2-Co] (*Ib*)

To 20 ml of the above solution of *Ia*-Na salt was added $(CH_3)_2SO_4$ (1.0 ml) and Na_2CO_3 (1.0 g) and the mixture was stirred for 10 min at ambient temperature. Excess dimethyl sulfate was decomposed by stirring with of 15% aqueous NH_4OH (5 ml), the product was extracted with benzene (10 ml) and the orange solution was poured onto a dry silica gel column. The pure product was eluted with a benzene–hexane mixture (1 : 2). The solvents were evaporated from the orange eluate and the residue was recrystallized from hot hexane to yield a crystalline orange powder, 1.21 g (91%), m.p. 234 °C, *m/z* 372 (for $^{12}C_5{}^{11}B_{18}{}^1H_{23}{}^{32}S^{59}Co$ calculated 372); R_F 0.39 (Silufol, benzene–hexane 1 : 2), for ^1H and ^{11}B NMR shifts see Table II. It is noteworthy that the methylation of *Ia*-Na salt with methyl iodide is considerably slower as indicated by TLC monitoring of the reaction, the reaction being still incomplete after 4 days at ambient temperature.

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