COBALT BIS(1,2-DICARBOLLIDE) ION WITH A DISULFUR BRIDGE BETWEEN B(8) AND B(8′). X-RAY STRUCTURE, ABSOLUTE CONFIGURATION OF ONE ENANTIOMER, AND IMPLICATIONS

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The structure and absolute configuration of one enantiomer of the $[3\text{-Co-}(1,2\text{-C}_2B_9H_{10})_2\text{-}8,8'\text{-}\mu\text{-S}_2][NEt_4]$ salt was established by X-ray diffraction. A spontaneous resolution took place during crystallization but attempts at resolution in solution *via* chiral HPLC and chiral capillary electrophoresis failed. The probable cause is discussed and successful resolution of less racemisable 8,8′-bridged metallacarboranes of this type is predicted. The criterion of resolvability ought to be the observation of two $C\text{-}H_{carborane}$ signals in ^1H NMR of the respective compound with a symmetric bridge. The geometry of the disulfur-bridged title compound is discussed in terms of accessibility of the central ion to external moieties. The central ion is apparently screened from the environment by terminal hydrogens at the rim of the pentagonal ligand planes in any kind of *commo*-bis-icosahedral sandwich complexes.

Keywords: Carboranes; Metallacarboranes; Cobalt bis(dicarbollide) complexes; Disulfur bridge; X-Ray diffraction; Absolute configuration; Spontaneous resolution of enantiomers; Solid state chirality.

The cobalt bis(dicarbollide) ions $[3\text{-Co-}(1,2\text{-C}_2B_9H_{11})_2]^-$ (**1**) and $[2\text{-Co-}(1,7\text{-C}_2B_9H_{11})_2]^-$ (**2**) (ref.[1]) are probably the most important representatives of the metallaheteroboranes. Substitution chemistry of both ions is similar and very extensive. However, due to better accessibility of **1** its chemistry is by far more developed. Moreover, several derivatives of **1** have found technological application in solvent extraction of radionuclides. In the recent comprehensive review[2] on chemistry of **1** and **2**, 132 papers are recorded and briefly commented although a majority of several dozens of papers and patents dealing with solvent extractions are explicitly omitted. More than one quarter of all recorded papers deals with **1** and **2** derivatives in which both deltahedral ligands are connected by an intramolecular exopolyhedral bridge, spanning the shortest possible distance of 2.94 Å between both

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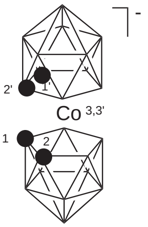
ligand planes[3]. Compounds with C–C, C–B and B–B bridges are known, most of them being these with B(8) and B(8′) as bridgeheads (family of **1** derivatives). Up to ten membered C–C bridges were constructed; mono-, di- and triatomic bridges are known with B(X) and B(Y′) bridgeheads in both families **1** and **2**. Even several double-bridged cobaltacarboranes were reported. Such bridging implies some new stereochemical features: It cancels the original free rotation of both deltahedral ligands around the longest axis (connecting the vertices B(10), Co and B(10′) in the **1** family) and may even restrict their mutual oscillations; it forces both pentagons to the mutual *prismatic* or *antiprismatic* conformation (clearly, distorted structures between both pure archetypes are conceivable) and eventually forces both ligand planes to an appreciable inclination. In structures with inclined ligand planes the central ion becomes shifted from the symmetric central position (above and below the centers of both pentagons) towards the bridging moiety. These features are briefly commented in the Sivaev–Bregadze review[2] and more thoroughly discussed in the original papers[3–8]. X-Ray structures of many bridged metallacarboranes are known and mentioned in the review[2], three others were added recently[9,10]. Some general conclusions can be drawn from these X-ray investigations: In all species with monoatomic bridges, the pentagonal ligand planes are arranged *prismatically* and are mutually inclined; the dihedral angles decrease with increasing size of the bridging atom in the series O > N > S > P (28° → 12° in the **1** family, in the **2** family this inclination is only 75% of the former[6]). In the arylene (pyrazolediyl)-bridged cobaltacarboranes, the ligand planes have also a *prismatic* conformation but are nearly parallel. In all species with triatomic and larger bridges the conformation is *antiprismatic* and except the C–C bridged compounds, the ligand planes are essentially parallel (ref.[2] and references therein). The compounds with *antiprismatic* conformation are inherently prochiral.



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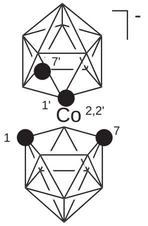

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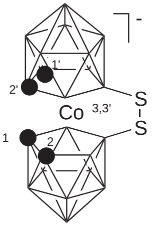

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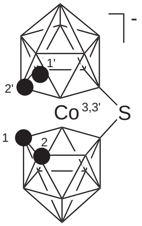

4

● = CH, other vertices = BH

The arylene (pyrazolediyl)-bridged cobaltacarboranes can be considered as special examples of compounds with diatomic bridges. The specificity is due to a very short distance between both neighbours within the aromatic ring and its planarity. No X-ray structure has been known so far of any cobaltacarborane with a non-aromatic diatomic bridge. Here we report on the X-ray structure of the $[3\text{-Co-}(1,2\text{-C}_2B_9H_{10})_2\text{-}8,8'\text{-}\mu\text{-S}_2]^-$ ion (**3**) and on absolute configuration of one of its enantiomers, as well as discuss some implications.

RESULTS AND DISCUSSION

The disulfur-bridged cobaltacarborane **3** was first prepared by oxidation of its precursor $[3\text{-Co-}(8\text{-HS-}1,2\text{-C}_2B_9H_{10})_2]^-$ (ref.[11]), so its constitution has been unambiguously known from the very beginning. Several years later we have found its alternative synthesis by reaction of **1** with S_2Cl_2 (ref.[5]); depending on conditions, the monoatomically bridged $[3\text{-Co-}(1,2\text{-C}_2B_9H_{10})_2\text{-}8,8'\text{-}\mu\text{-S}]^-$ ion (**4**) might prevail over **3** but both species can be easily separated. The ion **3** was the first reported cobaltacarborane with a diatomic bridge. Some of its properties are rather conspicuous. For instance, its solutions in water, alcohols and ethers are deep purple in contrast to the notorious yellow to orange colour of conventional **1** derivatives[11]; we have subsequently found that in acetonitrile and acetone solutions of **3** are deep blue. Still more peculiar is the enormous span of its ^{11}B NMR spectrum (58.6 ppm, contrasting with 28.8 ppm with **1** and 27.4 ppm with **4** (ref.[5])). This huge span is due essentially only to the large downfield shift of the bridgehead borons. These peculiarities remained unexplained, among other things, because the exact structure of **3** was not known. From the assumed S–S distance near 2.08 Å it was clear that an *antiprismatic* conformation of the pentagonal ligand planes in **3** would better accommodate such long bridge than a *prismatic* one (the B(8)–B(8′) distance increases by 23.5% on going from *prismatic* to *antiprismatic* arrangement). This is why an *antiprismatic* arrangement of both pentagons in **3** was assumed from the beginning[11] and afterwards[5]. In this case, however, one would expect to find two $\text{C-H}_{\text{carborane}}$ signals in the ^{1}H NMR, and the system should be prochiral. But only one $\text{C-H}_{\text{carborane}}$ signal (intensity 4) was found in ^{1}H NMR and all attempts at resolution of enantiomers by classic methods failed[5].

Now appropriate crystals of NEt_4 salt of **3** were grown and subjected to the X-ray analysis. A spontaneous resolution of enantiomers took place during crystallization and the randomly chosen crystal was in fact that of one enantiomer. Such spontaneous resolution is apparently a quite common case because the same was already observed several times before[9,10]. The structure of **3** is shown in Fig. 1. The essential features are shown in Figs 2 and 3, selected bond lengths and angles are gathered in Table I.

The main features are: The conformation of both ligand pentagons is not entirely *antiprismatic* the torsion angle being only 22.35° instead of 36°, the dihedral angle is just 2.2(1)° and the centers of both pentagons are 2.961 Å apart. The bridge area, defined by the vertices –Co1–B18–S1–S2–B28–, can be viewed as an irregular nonplanar pentagon (see lengths and angles in Table I). The distortion off planarity is apparent from comparison of the sum of actual internal angles (527.54°) with that calculated for a planar pentagon (540.00°). The top sulfur atom in Fig. 3 is behind and the bottom atom in front of the plane of the picture (the plane defined by vertices B18, Co1 and B28). Noteworthy are the eight terminal hydrogens at the circumference of the pentagonal ligand planes resembling the eyelashes. They screen the central ion from approach of essentially any external moiety. When taking into account the van der Waals's radius of hydrogen (1.2 Å), the length of the B(C)–H bond (1.1 Å) and the inward declination of this bond (B–H = 23° and C–H = 28° off the ligand plane), the distance between the hydrogens of both pentagonal rims should be at most 0.9 Å (less than 0.8 Å between the C–H hydrogens). No monovalent ion is that small. The bare proton is not considered because it hardly exists in any solution. The

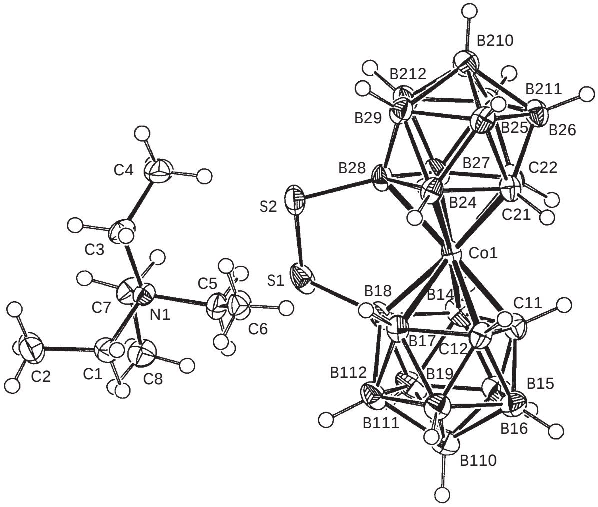

FIG. 1
Overall view of structure of the NEt_4 salt of compound **3**. The thermal ellipsoids are drawn on 50% probability level (PLATON)[18]

same should apply generally to any sandwich complex of this kind, bridged or non bridged. On the other hand, with both pentagons in *prismatic* conformation, the space between, *e.g.*, B(4)-H and B(8)-H in one pentagon and B(4′)-H–B(8′)-H in the counterpart is large enough (radius *ca* 1.1 Å) not only for Li^+ but even for Na^+ to penetrate to a close proximity to the central ion. Such arrangement, however, would block free rotation of both deltahedral ligands as effectively as an intramolecular bridge.

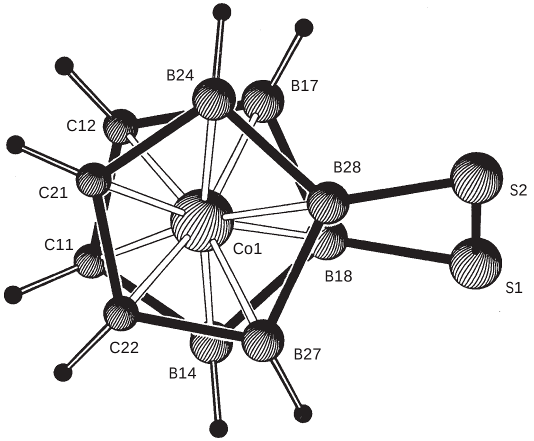

FIG. 2
Conformation of the pentagonal ligand planes in compound **3** above and below the central ion, observed from above

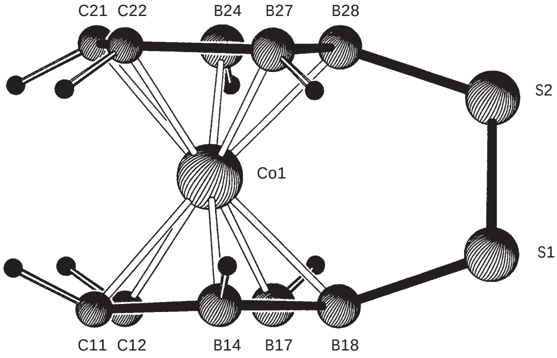

FIG. 3
Arrangement of the ligand planes, central ion, the S–S bridge, and terminal hydrogens in compound **3**, observed from the side

The actual enantiomer of **3** shows a σ-configuration[12]. For the more or less *antiprismatic* bridged species of this type a still more fitting designation is conceivable because the mutual arrangement of the four carbon atoms in both pentagons resembles the capital letters either **Z** or **S**, if observed from the side (Fig. 4).

Our σ-enantiomer can be identified with the **S** configuration. The situation is quite peculiar. Now we know the absolute configuration of one enantiomer of **3** but we do not know its optical activity because we are not

TABLE I
Selected lengths (in Å) and angles (in °) in compound **3**

Atoms	Length	Atoms	Angle
Co1–B18	2.0969(18)	S1–B18–Co1	117.16(10)
Co1–B28	2.1012(14)	S2–B28–Co1	117.48(10)
B18–S1	1.8696(19)	B18–S1–S2	101.28(7)
B28–S2	1.8637(18)	B28–S2–S1	100.86(7)
S1–S2	2.0741(8)	B18–Co1–B28	90.76(7)
Interplane	2.961	Torsion angle	22.35
Average B–H	1.1000	Dihedral angle	2.2(1)
Average C–H	1.1000		

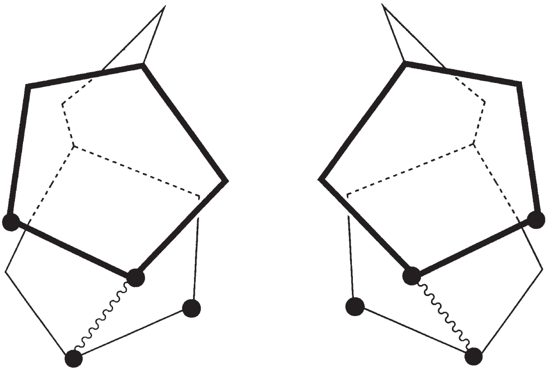

FIG. 4
Configurations **Z** (ρ-, ref.[12]), left and **S** (σ-, ref.[12]), right in enantiomers of compound **3**. The pentagons represent both ligand planes, with black circles indicating the C–H vertices; the rest is omitted for clarity

able to obtain a larger sample for, *e.g.*, circular dichroism and, moreover, we do not know whether a resolution in solution is possible at all. Earlier attempts *via* a classic crystallization of diastereomeric salts failed[5] and the recent attempts *via* chiral HPLC (ref.[13]) and even *via* chiral capillary electrophoresis[14] were unsuccessful even though both the methods were very reliable in other cases[12,15]. It seems that an easy racemization of **3** in solution is the real cause. A potential mechanism of such racemization was already suggested; oscillation from one *antiprismatic* arrangement to the opposite one through a *prismatic* conformation of both pentagons was assumed to be the true cause[5]. This view was supported by the fact that only one C-$H_{carborane}$ signal appeared in the ^{1}H NMR of **3** in any solution[5]. On the other hand, the appearance of two C-H signals in any 8,8′-bridged derivative of **1** (with a symmetric bridge) should indicate its resolvability to enantiomers by some efficient method.

EXPERIMENTAL

Compound **3** was prepared as described[5]; its Et_4N^+ salt was precipitated from water solution of the K salt with a slight excess of Et_4NCl. Crystals were grown from saturated solution in acetonitrile (5 ml) carefully covered with diethyl ether (l5 ml) in a stoppered test tube (i.d. 15 mm) by standing undisturbed for two weeks at ambient temperature. A randomly chosen blue-black crystal was subjected to X-ray diffraction.

X-Ray Diffraction Analysis

Crystal data for **3**: $[C_4H_{20}B_{18}CoS_2][C_8H_{20}N]$, M = 516.08, orthorhombic, $P2_12_12_1$ (No. 19), a = 11.88300(10) Å, b = 13.09700(10) Å, c = 17.2510(2) Å; V = 2 684.80(4) $Å^{-3}$, Z = 4, D_x = l.277 Mg m^{-3}; a dark blue black crystal with dimensions 0.4 × 0.37 × 0.2 mm was mounted with epoxy glue on a glass capillary and measured on a KappaCCD diffractometer with monochromatized MoKα radiation (λ = 0.71070 Å) at 150(2) K. Absorption was neglected (μ = 0.801 mm^{-1}); a total of 48 207 measured reflections in the range $h = -15 \rightarrow +15$, $k = -17 \rightarrow +16$, $l = -22 \rightarrow +22$ (θ_{max} = 27.5°), of which 6 154 were unique (R_{int} = 0.041) and 6 037 observed according to the $I > 2\sigma(I)$ criterion. Cell parameters from 30 546 reflections ($\theta = l - 27.5°$). The structure was solved by direct methods (SIR92)[16] and refined by full-matrix least squares based on F^2 (SHELXL97)[17]. The hydrogen atoms were fixed in idealized positions (riding model) and temperature factors were assigned either $H_{iso}(H) = 1.2\ U_{eq}$ (pivot atom) or $H_{iso}(H) = 1.5\ U_{eq}$ (pivot atom) for the methyl group. The refinement converged (Δ/ρ_{max} = 0.002) to R = 0.0235 for observed reflections and wR = 0.060, GOF = 1.057 for 311 parameters and all 6 154 reflections. The final difference map displayed no peaks of chemical significance ($\Delta\rho_{max}$ = 0.335 e $Å^{-3}$, $\Delta\rho_{min}$ = –0.356 e $Å^{-3}$). The absolute configuration was determined unambiguously since the chiral parameter is equal to zero within two esd (Flack parameter is 0.017(8)).

The results are shown in a condensed form in Figs 1–3 and Table I. CCDC 184432 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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