

Sulfur as a heteroatom in metallaborane structures: Cyclopentadienylcobalt thiaboranes



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ABSTRACT

The series of cobaltathiaboranes $\text{CpCoSB}_n\text{H}_n$ ($n = 6, 7, 8, 9, 10$) related to the experimentally known $\text{CpCoSB}_8\text{H}_8$ and $\text{CpCoSB}_{10}\text{H}_{10}$ have been investigated by density functional theory. The lowest energy $\text{CpCoSB}_n\text{H}_n$ ($n = 6-10$) structures are the *closo* deltahedra in accord with expectations for these $2n + 2$ Wadean skeletal electron systems. In the lowest energy such structures the sulfur atom is located at a lowest degree vertex and the cobalt atom at a highest degree vertex. An alternative bicapped octahedral $\text{CpCoSB}_6\text{H}_6$ structure having the sulfur atom at a degree 3 capping vertex lies only ~ 7 kcal/mol above the bisdisphenoid global minimum. For the 12-vertex $\text{CpCoSB}_{10}\text{H}_{10}$ system the three possible structures based on a B_{10}CoS regular icosahedron lie more than 50 kcal/mol in energy below any non-icosahedral structures. The relative energy ordering of ortho < meta < para for these icosahedral $\text{CpCoSB}_{10}\text{H}_{10}$ structures is the opposite of the relative energy ordering of para < meta < ortho for the well-known icosahedral dicarbaboranes $\text{C}_2\text{B}_{10}\text{H}_{10}$. One of the low-energy nine-vertex $\text{CpCoSB}_7\text{H}_7$ structures B7CoS-3 (Fig. 3) appears to be a frozen intermediate in the diamond-square-diamond process interconverting two isomeric tricapped trigonal prisms through a capped square antiprism intermediate.

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1. Introduction

Polyhedral metallaborane chemistry originated from the discovery by Hawthorne [1] that one or two boron vertices in polyhedral boranes can be replaced by transition metal units. In their original work they studied polyhedral metallacarboranes containing not only one or two transition metal vertices but also two carbon vertices. Especially stable derivatives were obtained using CpCo vertices ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) vertices, which are isoelectronic and isolobal with BH vertices, leading, for example, to a number of neutral cobaltadicarbaboranes of the type $\text{CpCoC}_2\text{B}_{n-3}\text{H}_{n-1}$. The polyhedra in such compounds are the most spherical *closo* deltahedra (Fig. 1) [2,3] similar to those found in the metal-free boranes $\text{B}_n\text{H}_n^{2-}$. These species have the $2n + 2$ skeletal electrons required by the Wade–Mingos rules [4–7] for such a most spherical deltahedral structure. Since BH as well as CpCo vertices are donors of only two Wadean skeletal electrons the replacement of two BH vertices with CH vertices donating three skeletal electrons each is necessary to provide structures for neutral cobaltaboranes having the requisite $2n + 2$ skeletal electrons.

A question of interest is whether main group heteroatoms other than carbon can be incorporated in metallaboranes to provide the $2n + 2$ skeletal electrons required by the Wade–Mingos rules [4–7] for the most spherical *closo* deltahedral structures (Fig. 1). Sulfur is of interest as such a heteroatom since a bare sulfur vertex can provide four Wadean skeletal electrons for a polyhedral borane structure. Thus cobaltathiaboranes of the type $\text{CpCoSB}_{n-2}\text{H}_{n-2}$, like the isoelectronic $\text{CpCoC}_2\text{B}_{n-3}\text{H}_{n-1}$, are $2n + 2$ skeletal electron systems and thus might be expected to exhibit such *closo* deltahedral structures. The relationship between the three-dimensional $2n + 2$ skeletal electron systems $\text{CpCoC}_2\text{B}_{n-3}\text{H}_{n-1}$ and $\text{CpCoSB}_{n-2}\text{H}_{n-2}$ is somewhat analogous to the relationship between the planar 6π electron systems benzene and thiophene in which two CH groups of benzene are replaced by a single sulfur atom to give thiophene.

The original syntheses of cobaltathiaboranes were unselective syntheses by Sneddon and co-workers [8] using condensation of cobalt metal vapor with a mixture of cyclopentadiene or pentamethylcyclopentadiene and various thiaboranes such as *nido*-6-SB₉H₁₁, *arachno*-4-SB₈H₁₂, or *nido*-SB₁₀H₁₂. Products from such reactions include the 10-vertex $\text{CpCoSB}_8\text{H}_8$ and the 12-vertex $\text{CpCoSB}_{10}\text{H}_{10}$. Recently, the anion [*nido*-7-SB₁₀H₁₁][−], which is readily available from B₁₀H₁₄, sulfur, and triethylamine, has been used by Welch and co-workers as a reagent in a selective synthesis of $\text{CpCoSB}_{10}\text{H}_{10}$ in good yield [9]. X-ray crystallography shows $\text{CpCoSB}_{10}\text{H}_{10}$ to have

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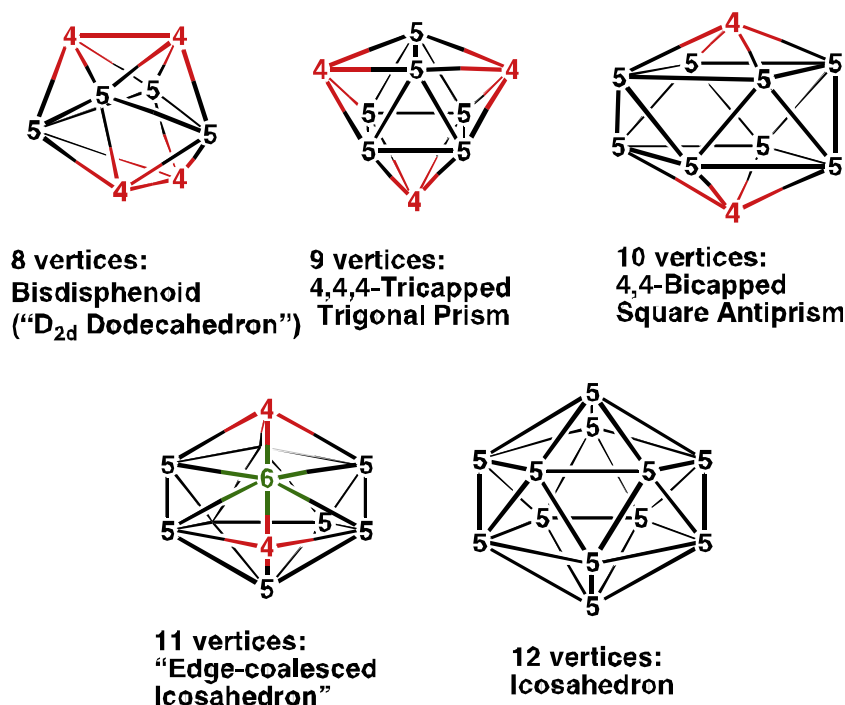


Fig. 1. The most spherical *closo* deltahedra having from 8 to 12 vertices found in *n*-vertex metallaboranes having $2n + 2$ Wadean skeletal electrons.

an icosahedral structure with the cobalt and sulfur atoms at adjacent vertices with a Co–S distance of 2.1770(7) Å.

We now report a density functional theory (DFT) on the complete series of cobaltathiaboranes CpCoSB_{*n*-2}H_{*n*-2} having from 8 to 12 vertices for comparison with the structures previously found for the related cobaltadecaboranes using similar DFT methods [10]. This allows an assessment of the effect on polyhedral geometry by replacing the two CH vertices in the cobaltathiaboranes with an S and a BH vertex in the cobaltadecaboranes.

2. Theoretical methods

Full geometry optimizations were carried out on the CpCoSB_{*n*-2}H_{*n*-2} systems (*n* = 8–12) at the B3LYP/6-31G(d) [11–14] level of theory. The lowest-lying structures were then reoptimized at a higher level i.e. M06L/6-311G(d,p) and the reported relative energies include zero-point corrections. The initial structures were chosen by systematic substitution of a boron atom in B_{*n*}H_{*n*}²⁻ with a sulfur atom followed by all possible substitution of a boron atom in the resulting thiaborane by a CpCo unit. This led to a large number of different starting structures. Thus 127 structures of the 8-vertex clusters CpCoSB₆H₆, 85 structures of the 9-vertex clusters CpCoSB₆H₆, 111 structures of the 10-vertex clusters CpCoSB₆H₆, 155 structures of the 11-vertex clusters, and 45 structures of the 12-vertex CpCoSB₁₀H₁₀ were chosen as starting points for the optimizations (see the Supporting Information). The natures of the stationary points after optimization were checked by calculations of the harmonic vibrational frequencies. If significant imaginary frequencies were found, the optimization was continued by following the normal modes corresponding to imaginary frequencies to insure that genuine minima were obtained.

All calculations were performed using the GAUSSIAN 09 package [15] with the default settings for the SCF cycles and geometry optimization, namely the fine grid (75302) for numerically evaluating the integrals, 10⁻⁸ hartree for the self-consistent field convergence, maximum force of 0.000450 hartree/bohr, RMS force of 0.000300 hartree/bohr, maximum displacement of 0.001800 bohr, and RMS displacement of 0.001200 bohr.

The CpCoSB_{*n*-2}H_{*n*-2} (*n* = 8–12) structures are numbered as B(*n* – 2)SCo-*x* where *n* is the total number of polyhedral vertices, and *x* is the relative order of the structure on the energy scale. The lowest energy optimized structures discussed in this paper are depicted in Figs. 2–6. Only the lowest energy and thus potentially chemically significant structures are considered in detail in this paper. More comprehensive lists of structures, including higher energy structures, are given in the Supporting Information.

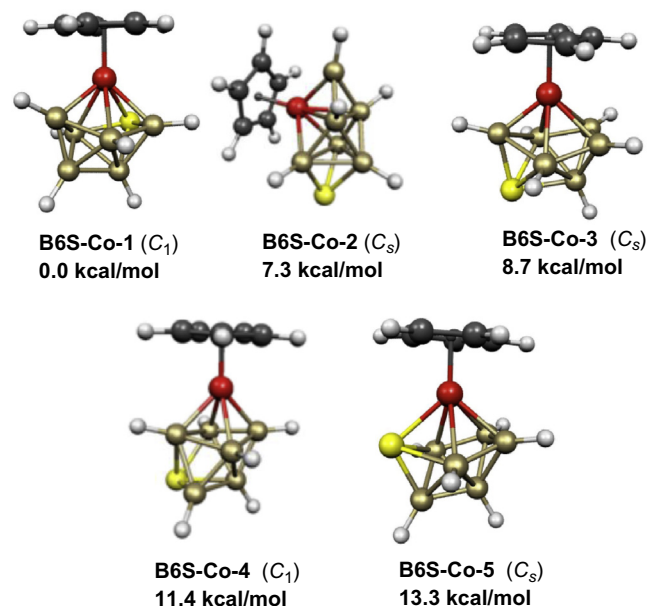


Fig. 2. The optimized CpCoSB₆H₆ structures within 15 kcal/mol of the global minimum.

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