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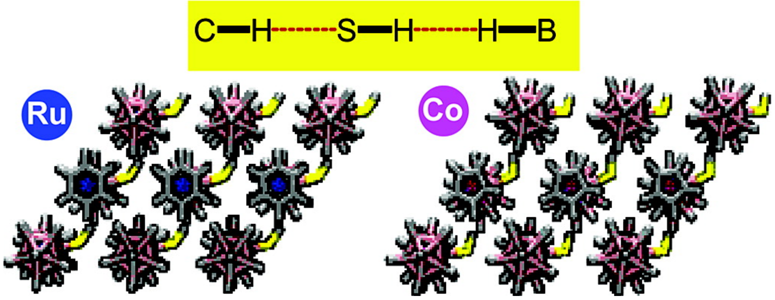

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Self-Assembly of Mercaptane−Metallacarborane Complexes by an Unconventional Cooperative Effect: A C−H···S−H···H−B Hydrogen/Dihydrogen Bond Interaction

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Abstract: The existence of a dihydrogen bond (S−H···H−B) and its combination with a C−H···S hydrogen bond in an unusual cooperative effect are demonstrated from a combination of experimental and theoretical methods. This cooperative effect seems to be responsible for self-assembly of mercaptane−metallacarborane complexes such as *closo*-[3-Ru(η^6-C_6H_6)-8-HS-1,2-$C_2B_9H_{10}$] (**1**) and *closo*-[3-Co(η^5-C_5H_5)-8-HS-1,2-$C_2B_9H_{10}$] (**3**), which present identical supramolecular two-dimensional polymeric networks. The findings, besides documenting structurally the first S−H···$(H-B)_2$ dihydrogen bond and the unconventional cooperative ability of a boron-attached SH group, prove that substituted carboranes have the potential to serve as building blocks for assembling complex structures.

Introduction

The dihydrogen bond[1,2] (DHB) is possibly the most astonishing unconventional hydrogen bond,[3] because of the opposing nature presented by the two hydrogen atoms facing each other. It has been demostrated to be able to influence structure, reactivity, and selectivity in solution and the solid state,[1] thus finding potential utility in catalysis[4] and crystal engineering and materials chemistry.[5] DHBs are usually described as X−H···H−M, where X is a typical electronegative atom and M is a transition metal or boron atom. Structurally, the crystallographic data show that the contact distance between the two interacting hydrogens is substantially shorter than the sum of their van der Waals radii (2.4 Å) and typically between 1.8 and 2.3 Å. Whereas X−H···H angles tend to be close to linear, those for H···H−M are close to bent; the directionality of weak hydrogen bonds is, however, much softer than that of conventional hydrogen bonds.[1] The most usual hydrogen donors are the NH and OH groups, whereas a DHB with a SH group acting as hydrogen donor has not yet been characterized.

Carbon-containing polyhedral boranes, the carboranes, are extremely stable cage molecules that have been known for over 30 years. Carborane-containing organic functional groups have applications in a number of diverse fields such as materials science, boron carriers for boron neutron capture therapy, agents for the extraction of metal ions, ligands for metals, and more recently supramolecular chemistry.[6,7] The three-dimensional nature of icosahedral carborane *closo*-$C_2B_{10}H_{12}$ cages has been shown to give them great potential as building blocks in supramolecular systems.[8] Carborane supramolecular chemistry

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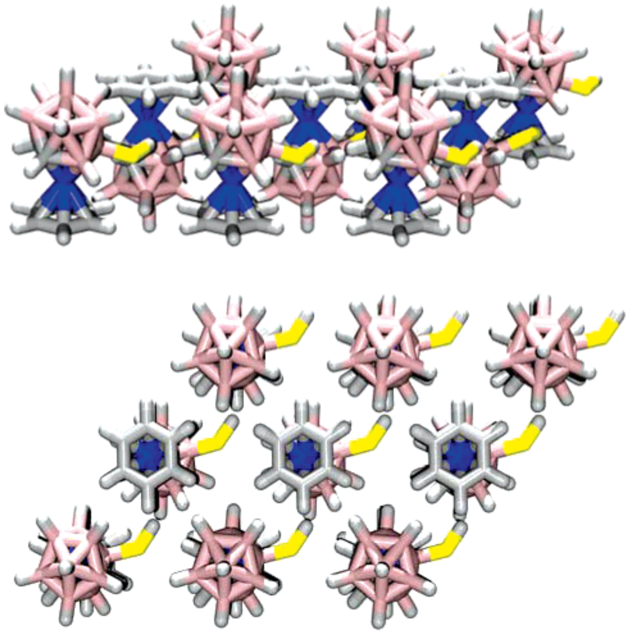

Figure 1. Top: A crystal packing diagram of the X-ray structure of **1** showing the planar two-dimensional sheet structure along a perspective between the crystallographic *a* and *c* axes. Bottom: Crystal packing of **1** along the crystallographic *c* axis showing the 2D network and directionality. Atom colors: B (pink), C and H (gray), Ru (blue), S (yellow).

is mainly directed by the carboranes' acidic C*c*−H (C*c* = cage carbon) vertexes as proton donors of the type C*c*−H···X with classical (X = O, N, S, F, Cl, Br, I)[7,9] and weak nonclassical (X = alkynes, arenes)[7,10] proton acceptors.

As part of our ongoing research on icosahedral metallacarborane chemistry, we previously communicated the formation and X-ray crystal structure of the first mercaptane−ruthenacarborane complex, *closo*-[3-Ru(η^6-C_6H_6)-8-HS-1,2-$C_2B_9H_{10}$] (**1**).[11] The low acidity of the thiol group in **1** is expected to make this particular "boron-attached" SH group an extremely weak hydrogen bond donor,[3] and consequently, we did not anticipate its involvement in any significant hydrogen bond interaction. However, the solid-state structure of **1** reveals a surprising supramolecular architecture in which the SH group participates in a C−H···S−H···$(H-B)_2$ cooperative hydrogen/bifurcated DHB interaction (Figures 1 and 2). Here we describe the first structural characterization and accurate DFT calculations of a new dihydrogen bond (S−H···H−B) and its combination with a C−H···S hydrogen bond interaction in a unprecedented cooperative effect. This unconventional cooperative effect seems to be responsible for the self-assembly of **1** into a supramolecular two-dimensional polymeric network and allowed us to anticipate the solid structure of the related cobaltocarborane complex *closo*-[3-Co(η^5-C_5H_5)-8-HS-1,2-$C_2B_9H_{10}$] (**3**).

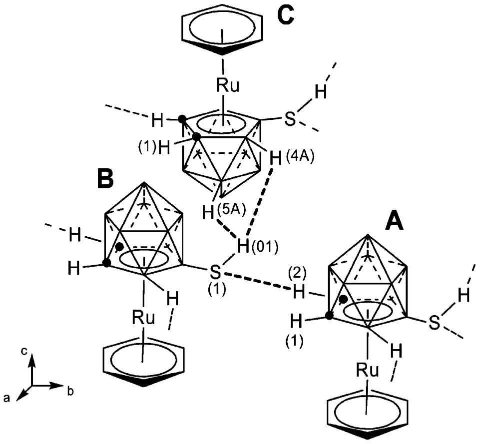

Figure 2. Drawing for the trimer structure repeated in the 2D network of **1** showing the unconventional cooperative hydrogen/bifurcated dihydrogen bond chain C*c*−H···S−H···$(H-B)_2$ (numbering shown in parentheses). Black dots represent cage carbon atoms (C*c*), and the rest of the vertexes are B−H, except those having the SH group.

Experimental Section

General Procedures. In our analysis of the structural data we have normalized all C−H bonds to a distance of 1.083 Å[3] and S−H bonds to 1.388 Å.[12] As for the boron cage compounds we have chosen to normalize all cage B−H bonds to a distance of 1.191 Å.[3] Cambridge Structural Database searches for nonbonded contacts were carried out using the program ConQuest (version 1.7).[13] The search criteria (CSD dated February 2005) were error- and disorder-free structures (organic and organometallic) only with *R* factors less than 0.1 (H normalized). Normalized structures were retrieved from the Cambridge Structural Database as mol2 files and analyzed using Mercury (version 1.4).[12] Complex **3** was prepared as previously reported.[14]

Theoretical Calculations. Calculations were performed using the GAUSSIAN03[15] series of programs. The density functional theory was used with the BHandH[16] functional, which combines a gradient-corrected correlation functional with an exchange functional formed from equal parts of the Hartree−Fock and its gradient-corrected exchange terms. All geometry optimizations were made without restrictions. Effective core potentials and their associated double-ζ LANL2DZ basis set were used for ruthenium and sulfur atoms.[17] An extra series of d-polarization functions were also added for S (experimental, 0.503) atoms.[18] The 6-31G basis set was used for C, B, and H atoms. For the interaction energy analysis an augmented basis set, 6-311++G(3df,3pf), was used for all the atoms directly involved in the cooperative hydrogen/bifurcated DHB interaction (S, H, B, and C); basis set superposition errors (BSSEs) were corrected by means of the counterpoise method as implemented in Gaussian.[19] Charge analysis was made using natural population analysis.[20] The topological properties of the electron density were investigated using the XAIM 1.0 program.[21]

X-ray Structure for 3. Orange slabs of **3** were obtained by slow evaporation of an acetone solution under air at room temperature. Cell

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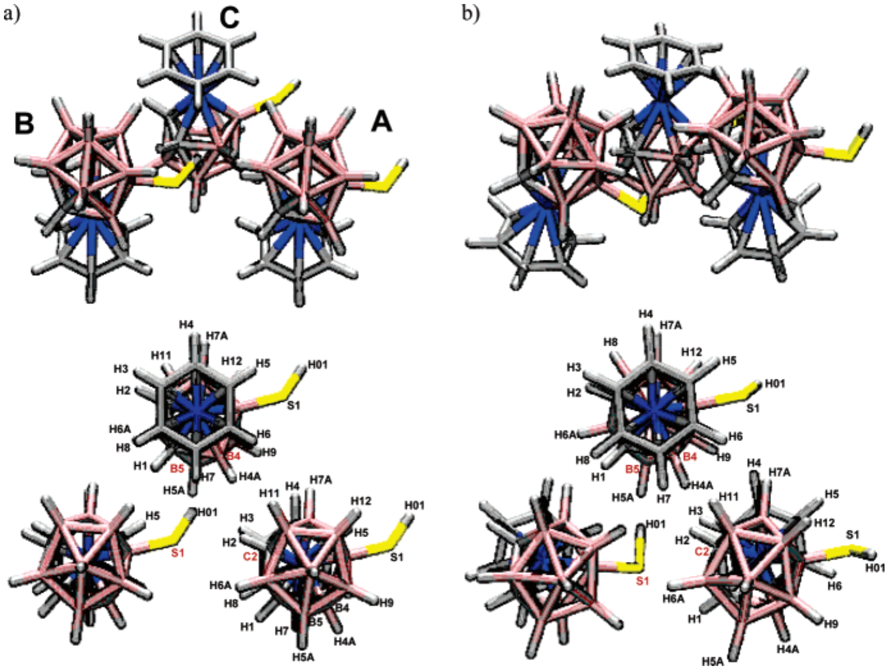

Figure 3. (a) An X-ray diagram for a trimer of the ruthenium complex **1** showing a perspective along the diagonal between the *a* and *c* axes (top) and viewed along the *a* axis (bottom, showing relevant atom labeling). (b) A diagram for a DFT-calculated trimer of **1** viewed as in (a). Atom colors: B (pink), C and H (gray), Ru (blue), S (yellow).

parameters and intensity data were collected on a Bruker Nonius Kappa CCD diffractometer mounted at the window of a molybdenum rotating anode following standard procedures. The structure was solved by direct methods and refined using full matrix least squares with shelx97.[22] The structure contains a pseudo center of inversion, but refinement in the higher symmetry space group $P2_1/m$ was unsuccessful (R1 = 20.0); the structure was refined as a racemic twin, BASF = 0.46. The aromatic and carborane hydrogens were placed in idealized positions and refined using a riding model; the distances were normalized as indicated above. The distance of the S−H bond was restrained to the calculated value, and the angle and torsion were refined.

Crystal data for **3**: $C_7H_{16}B_9CoS$, M_r = 288.48, orange slab, monoclinic, $P2_1$, $a = 7.8092(12)$ Å, $b = 10.3674(6)$ Å, c = 15.709(3) Å, $\beta = 90.967(12)°$, $Z = 4$, 120(2) K, final R indices $[F^2 > 2\sigma(F^2)]$ R1 = 0.0425 and wR2 = 0.0966. Further details for the crystal structure of **3** may be obtained from the Cambridge Crystallographic Data Centre (CCDC; 12 Union Rd., Cambridge CB2 1EZ, U.K.; fax (+44) 1223-336-033; e-mail deposit@ccdc.cam.ac.uk) on quoting the depository number 262664.

Results and Discussion

In the solid-state structure, molecules of **1** form a two-dimensional polymeric network in which all SH groups point in the same direction as shown in Figure 1. The trimer of molecules shown in Figures 2 and 3 is the repeated unit in this two-dimensional polymeric network. The complexes are all interacting through a large number of close intermolecular contacts, with the SH group being particularly involved. The analysis of these interactions was carried out by means of theoretical calculations and solid-state infrared spectra. The trimer structure repeated in the crystal 2D network of **1** was fully optimized using DFT methods. The optimized minimum proved to be the structure shown in Figure 3 and provides a reasonable reproduction of the experimental results. Tables 1 and 2 show selected interatomic distances for the trimer structure of **1**. Calculated intermolecular distances among relevant heavy atoms in the trimer (those closely related to the studied interactions S1···B5 (4.064 Å), S1···B4 (4.006 Å), C2···S1 (3.646 Å), and C2···B4 (4.254 Å); see Figures 2 and 3) are in

Table 1. Experimental and Calculated (in Parentheses) Values for Selected Distances (Å) and Angles (deg) of **1** Related to DHB Complexes

entry	X–H···H–B	H···H	X···B	X–H···H	H···H–B	molecules[c]
1	$S_1-H_{01}\cdots H_{4A}-B_4$	[a]	3.719	[a]	[a]	B/C
		(2.246)	(4.006)	(126.76)	(103.21)	
2	$S_1-H_{01}\cdots H_{5A}-B_5$	[a]	4.044	[a]	[a]	B/C
		(2.230)	(4.064)	(140.49)	(102.59)	
3	$C_4-H_4\cdots H_9-B_9$[b]	2.152	3.871	135.14	132.10	A/C
		(2.399)	(3.657)	(111.06)	(106.10)	
4	$C_5-H_5\cdots H_{5A}-B_5$[b]	2.195	3.948	165.65	114.49	B/C
		(2.027)	(3.902)	(160.04)	(134.32)	
5	$C_8-H_8\cdots H_{12}-B_{12}$[b]	2.261	3.871	121.36	118.42	C/B
		(2.012)	(3.829)	(129.49)	(155.55)	
6	$C_6-H_6\cdots H_{11}-B_{11}$[b]	2.272	4.025	130.54	127.50	C/A
		(2.164)	(3.566)	(110.72)	(110.50)	
7	$C_3-H_3\cdots H_{5A}-B_5$[b]	2.323	3.940	161.67	108.72	A/C
		(2.609)	(3.963)	(170.05)	(94.54)	

[a] See the text for details. [b] All CH donors correspond to the benzene fragment. [c] See Figures 2 and 3 for labeling of the molecules in the trimer.

Table 2. Calculated (in Parentheses) and/or Experimental Values for Selected Distances and Angles of **1** and **3** Related to Hydrogen Bond Interactions

compd	C*c*–H···S	*d*[a] (Å)	*D*[b] (Å)	*θ* (deg)	molecules[c]
1	$\mathrm{C}c_2-\mathrm{H}_2\cdots\mathrm{S}_1$[c]	2.628	3.617	151.49	A/B
		(2.862)	(3.646)	(129.50)	
	$\mathrm{C}c_1-\mathrm{H}_1\cdots\mathrm{S}_1$[c]	2.872	3.614	125.73	C/B
		(3.632)	(4.146)	(111.11)	
3	$\mathrm{C}c_{107}-\mathrm{H}_{107}\cdots\mathrm{S}_{101}$[d]	2.652	3.514	136.14	
	$\mathrm{C}c_{208}-\mathrm{H}_{208}\cdots\mathrm{S}_{201}$[d]	2.597	3.656	165.67	

[a] Interatomic H···S distances. [b] Interatomic C*c*···S distances. [c] See Figures 2 and 3 for labeling of the molecules in the trimer. [d] See Figure 6 for labeling.

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(22) SHELX97, Programs for Crystal Structure Analysis (Release 97-2): Sheldrick, G. M., Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.

very good agreement with the X-ray distances 4.044, 3.719, 3.617, and 4.346 Å, respectively. The major discrepancy observed in the S1⋯B4 interatomic distance (0.287 Å) is due to a slight tilt of molecules in the gas-phase trimer as can be seen in Figure 3b; packing effects in the solid state probably prevent the small tilting observed in gas-phase calculations. To date, most of the computational studies on the properties of DHBs refer to isolated models (i.e., in the gas phase) which in general closely resemble the crystal structures. We have therefore carried out the present computational studies on a trimer of **1** in the gas phase. The absence of "other molecules" apart from those of the trimer in the calculations is certainly reflected in the minima obtained that show a slight tilt of the molecules. It is however important to realize that calculated intermolecular distances in the closest region to the three molecules in the trimer (around the SH group) are reproduced to within 0.1−0.3 Å and angles within 6−24°, which we consider a reasonable agreement taking into account the complexity of our system. Although the position of the H atom in the SH group was tentatively located on a difference electron density map, its position could not be unequivocally refined.[23] Nevertheless, its position within the optimized trimer structure (and in the isolated monomer) gives values similar to those obtained by neutron diffraction on a related structure. The computed S−H distance and B−S−H angle are 1.351 Å and 98.4°, respectively, whereas the neutron diffraction values for a C−S−H group are 1.338 Å and 96.9°, respectively.[24]

Interestingly, short H⋯H contacts were observed between the SH of a metallacarborane and two hydrides on boron from an adjacent molecule, forming a bifurcated DHB (molecules B and C in Figures 2 and 3). The calculated H⋯H contact distances (entries 1 and 2, Table 1) are shorter than 2.4 Å, and they are qualified as dihydrogen bonds.[1] The S−H⋯H interactions deviate from linear due to interaction of the SH with two hydride atoms from the boron cage, and the H⋯H−B angles averaging around 100° are typical for dihydrogen-bonded complexes. Distances and donor angles are consistent with other bifurcated DHBs formed between amines or phenol and boron hydrides.[1e,25] The weak nature of this S−H⋯H−B interaction is probably the reason for the H⋯H interactions being at the upper limit of the accepted distance values for DHB interactions. DFT calculations have demonstrated that H⋯H distances in DHBs depend on the strength of the XH proton donor.[1g] It has also been determined experimentally that, e.g., a weak CH donor forms weaker DHBs with MH acceptors (DHB distances, M = Ru (2.1 Å), Os (2.2 Å)) than the stronger NH donor (1.7 Å for both Ru and Os).[26] The existence of the S−H⋯H−B interactions in **1** has been further confirmed by means of Bader's atoms in molecules (AIM) theory.[27] Two bond critical points (bcp's) were identified for $S_1-H_{01}\cdots H_{4A}-B_4$ and $S_1-H_{01}\cdots H_{5A}-B_5$ (Figure 4). The electronic charge densities $\rho(r)$ at these bcp's are 0.010 au for both, whereas the Laplacians of the charge density $\nabla^2\rho(r)$ are positive with values of 0.032 for both. These values for $\rho(r)$ and $\nabla^2\rho(r)$ are within the common accepted values for DHB interacions.[2,28] In addition, a ring critical point for the $(S_1)H_{01}-H_{4A}-B_4-B_5-H_{5A}-H_{01}(S_1)$ ring was also identified, with values for $\rho(r)$ and $\nabla^2\rho(r)$ of 0.008 and 0.030 au, respectively. This analysis further supports the existence of a bifurcated DHB[28] between the SH group and two HB groups of the adjacent metallacarborane. Thus, our findings prove to be the first SH⋯HB DHB and bifurcated SH⋯(HB)$_2$ DHB interactions ever reported in the solid state. This S−H⋯H−B interaction is a rare motif: Examination of the Cambridge Structural Database reveals only one example of boron cluster intermolecular S−H⋯H−B interactions for $[(CH_3)_3NH]_2[B_{10}H_9\text{-}SH]$ with an H⋯H distance of 2.325 Å (S−H⋯H = 141.52° and H⋯H−B = 126.66°). Even though all hydrogen atoms of the anion were located, no mention was made of this short contact in the original paper.[29] In addition to the above-mentioned AIM analysis of our molecule, experimental interatomic distances between heavy atoms S1 (molecule B) and B4A and B5A (molecule C) are slighty shorter than the calculated ones (vide supra), further supporting the AIM analysis. Moreover, charge analysis also supports the presence of a bifurcated S−H⋯(H−B)$_2$ DHB. Atomic charges of the isolated monomer and the trimer are listed in Table 3. A necessary criterion for the formation of hydrogen bonds is the loss of the charge of the H atoms involved.[2] As shown in Table 3, this trend is clearly observed in all H atoms involved in the bifurcated SH⋯(HB)$_2$ DHB (entries 4, 6, and 8). Positive (though small) atomic charges for the H atoms in both BH groups might drive the reader to the wrong conclusion that

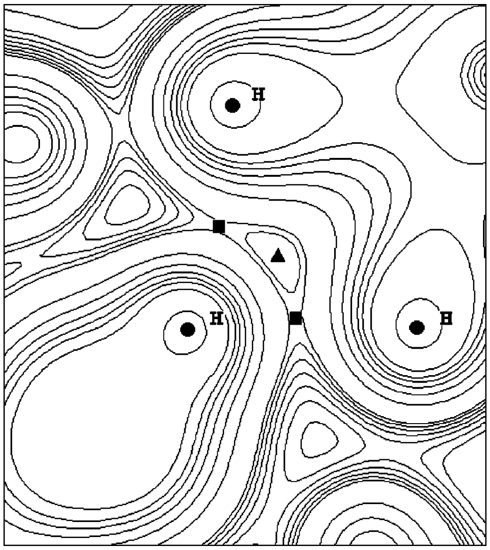

Figure 4. Contour plot of the electron density for the bifurcated S−H⋯(H−B)$_2$ dihydrogen bond in the plane containing the H atoms involved in the interaction. Bond critical points are depicted by squares, the ring critical point is depicted by a triangle, and hydrogens are depicted by circles.

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[23] The refinement would not completely converge due to a small oscillation about the mean position/value of a small number of parameters, mainly the SH hydrogen. The rest of the H atoms were calculated as previously described.[10] H atoms can normally be independently located by reference to the heavy atom positions, making the error in H positions less problematic. This is the case with the H position for BH and CH in *closo* boron cages.

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Table 3. Atomic Charges (NPA) for the Isolated Monomer and Trimer of **1**

entry	atom	trimer charge[a]	monomer charge[b]	Δcharges[c]
1	Cc_2	−0.562	−0.568	0.006
2	H2	0.356	0.358	−0.002
3	S1	−0.149	−0.176	0.027
4	H01	0.135	0.164	−0.029
5	B4	−0.055	−0.031	−0.024
6	H4A	0.063	0.081	−0.018
7	B5	−0.070	−0.045	−0.025
8	H5A	0.067	0.101	−0.034

[a] Atomic charges in the trimer structure. [b] Atomic charge for the equivalent atoms in the monomer structure. [c] Difference between trimer and monomer atomic charges.

DHBs will not form because of the positive charge. An explanation lies in the large negative charges carried by the boron atoms, compared to the small charge carried by the hydrogens. To take advantage of the charge distribution, the H atom of SH points toward the B−H bond rather than toward H analogously to that found in aminoboranes.[1a]

In addition to the previous SH$\cdots$(HB)$_2$ DHB interaction in compound **1**, the SH group is also involved in another classical C−H$\cdots$S hydrogen bond interaction. The observed Cc_2−$H_2\cdots S_1$ distance of 2.628 Å is substantially shorter than the 3.0 Å distance corresponding to the sum of the van der Waals radii of hydrogen and sulfur atoms (Table 2, entry 1), and the near-linear C*c*−H$\cdots$S angle (151.49°) qualifies it to be a hydrogen bond (between units A and B in Figures 2 and 3).[3,30] Another longer and nondirectional contact is also seen in the structure (between molecules B and C), Cc_1−$H_1\cdots S_1$ (2.872 Å, 125.73°), so that it is probably less attractive and consequently contributes less to the crystal packing effects.[3,30] Experimental evidence for the presence of these bonding interactions in the solid state is obtained from the solid-state infrared spectra of **1**. The IR spectrum of **1** in KBr exhibits two stretching frequencies for carborane C*c*−H (3074 and 3047 cm^{-1}), whereas only one C*c*−H band is observed experimentally for *closo*-[3-Ru(η^6-C_6H_6)-1,2-$C_2B_9H_{11}$] (**2**) (3073 cm^{-1}), which is the result of substituting the SH group in **1** by a H atom.[31] For **1**, only one of the C*c*−H stretching modes is significantly shifted to lower frequency in comparison with that of **2**. This observation of two stretching modes in **1** and the shift to lower frequency[1f,32] of only one is consistent with the solid-state structure and the conclusion that only one of the C*c*H groups of the carborane is involved in hydrogen bonding as a proton donor or both C*c*H groups form hydrogen bonds of different strengths. Therefore, it is straighforward to suggest that the stretching band shifted to lower frequency corresponds to the strongest hydrogen interaction, Cc_2−$H_2\cdots S_1$, in **1**.[33] Bader analysis on the Cc_2−$H_2\cdots S_1$ interaction also indicates the existence of a hydrogen bond by the presence of a bond critical point within the bond path with values for $\rho(r)$ and $\nabla^2\rho(r)$ of 0.009 and 0.029 au, respectively. Experimental interatomic distances are slightly shorter than calculated ones, further supporting the AIM analysis of hydrogen bond interactions. Consistently, a loss of calculated charge is also observed for the H atom involved in this conventional hydrogen interaction (Table 3, entry 2).

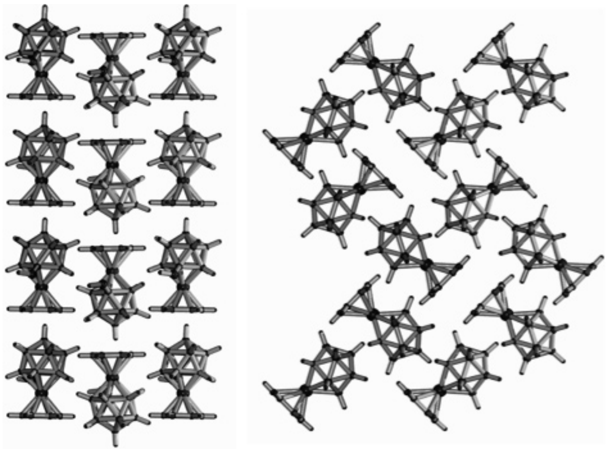

Figure 5. Left: Crystal packing of **1** along the *b* axis. Right: Crystal packing of **2** along the *c* axis.

Regarding other nonconventional interactions, five C−H$\cdots$H−B contacts (2.152−2.323 Å, Table 1) are also found among molecules in the trimer of **1**. Here it is interesting to make a comparison with the related neutral ruthenacarborane complex **2**. In the absence of the SH group only C−H$\cdots$H−B interactions (six contacts, 2.225−2.251 Å) are observed in the solid-state structure for **2**.[34] More importantly, the absence of directionality in the solid-state structure of **2** compared to **1** (Figure 5) suggests that there is a relation between the directionality found in the network of **1** and the SH group being present. Thus, although the C−H$\cdots$H−B interactions should contribute in some measure to the overall crystal stabilization in **1**, interactions involving the SH group seem to play a more important role in its self-assembly.

The above hydrogen/bifurcated DHB description is consistent with the SH group acting simultaneously as donor and acceptor in an *unconventional cooperative effect* of the type C*c*−H$\cdots$S−H$\cdots$(H−B)$_2$ in **1** (Figure 2). The SH group is acting as a hydrogen acceptor from the C*c*−H bond through the sulfur atom,[35] making the S−H bond more polar. As a consequence, the SH group becomes a better donor than in the absence of a C*c*−H$\cdots$S interaction. More importantly is that the acceptors of the polarized SH hydrogen are two hydrogen atoms from two different H−B bonds (therefore the "unconventional cooperative effect"). The effect can also be regarded as a flow of charges from the C*c*−H bond to two H−B bonds through the S−H bond. Calculated charges show that the residual charges on hydrogens decrease in the order C*c*−H > S−H > B−H (Table 3, entries 2, 4, 6, and 8) and are fully consistent with the observed cooperative effect. Consequently, this new unconventional cooperative effect exerted by the SH group seems to favor the construction of two-dimensional supramolecular networks of self-assembled neutral **1**.

The interaction energy among the three molecules after BSSE correction is −27.2 kcal/mol. This energy accounts for all the

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(33) The S−H stretch appears at the same frequency as that for B−H (2596−2511 cm^{-1}, vs br) in the solid-state infrared spectrum of **1**, preventing its analysis.

(34) See the Supporting Information.

(35) This boron-attached S atom is probably a better acceptor than a related carbon-attached one as reflected by the much lower acidity of a B−SH thiol in comparison with a related C−SH thiol.[14]

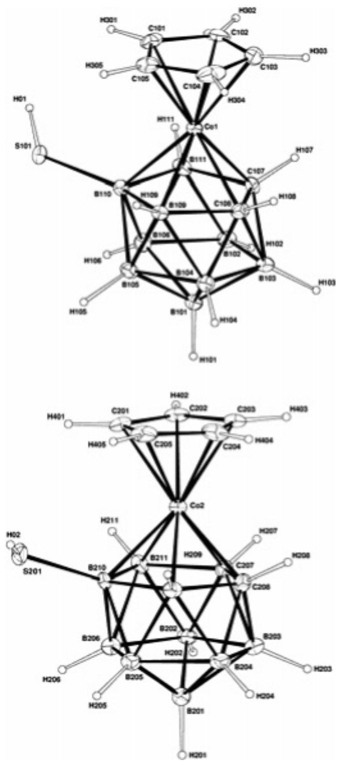

Figure 6. Molecular structure (thermal ellipsoids set at 35% probability) showing both independent molecules of **3**.

interactions among the three molecules (vide supra). To estimate the energy corresponding to the hydrogen/bifurcated DHB interaction, an additional set of calculations were performed. Hence, the interaction energy of an analogous trimer where the SH group involved in the cooperative effect is substituted by a H (i.e., S_1-H_{01} of molecule B was suppressed, Figure 2) was also evaluated.[36] The interaction energy after BSSE correction for this new system is -25.8 kcal/mol. Thus, assuming that the energy difference between the two systems is due to the interactions where the SH is involved, the hydrogen/bifurcated DHB interactions can be estimated at 1.4 kcal/mol.

Another icosahedral mercaptocobaltacarborane analogous to **1**, namely, **3**, has been previously synthesized but only characterized by elemental analysis and NMR.[14] Given that **3**, on the basis of spectrocopic characterization, has nearly the same shape as **1**—especially with respect to the important C*c*H, SH, and BH groups—we predicted that its crystal structure would contain the same two-dimensional polymeric network as in **1**. More importantly, the IR spectrum for **3** shows, like in the case of **1**, the presence of two streching frequencies for both C*c*−H bonds at 3107 and 3044 cm^{-1}, supporting the existence of a cooperative effect analogous to that of **3**. In an effort to confirm our prediction, we have now crystallized complex **3** and determined its structure by X-ray difraction (Figure 6). The asymmetric unit contains two independent molecules related by a pseudo center of inversion. Figure 6 shows a perspective view and the atom labeling of both molecules. Mercaptacobaltocarborane **3** has a molecular geometry comparable with that of **1**, and more importantly, its packing motif is identical to that of **1** as shown in Figure 7.

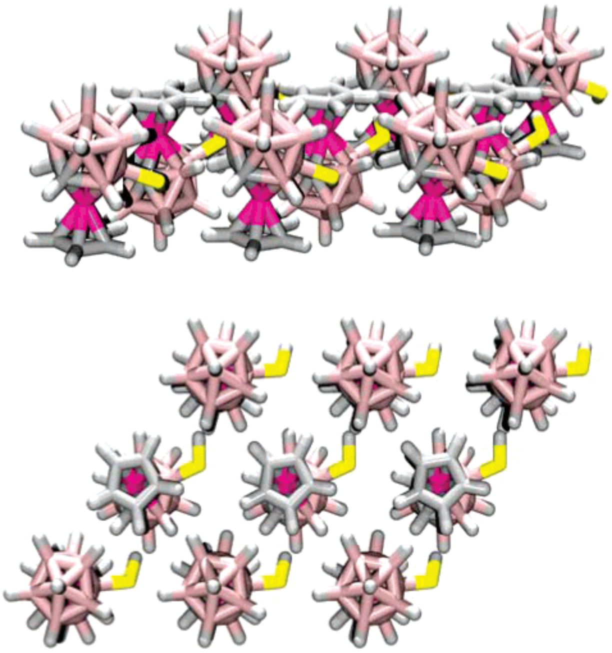

Figure 7. Top: A crystal packing diagram of the X-ray structure of a molecule of **3** showing the planar two-dimensional sheet structure along a perspective between the crystallographic *b* and *c* axes. Bottom: Crystal packing of **3** along the crystallographic *c* axis showing the 2D network and directionality. Atom colors: B (pink), C and H (gray), Co (deep pink), S (yellow).

Both molecules of **3** show conventional C*c*−H···S hydrogen bond interactions, structurally very similar to that found in the mercaptaruthenacarborane complex **1** (Table 2). Although the positions of H atoms in the SH groups were tentatively located in a difference electron density map, their positions could not be unequivocally refined. In any case, interatomic S101···B211 and S101···B202 distances of 3.804 and 3.928 Å, respectively, for one molecule in the unit cell or S202···B109 and S202···B104 distances of 3.487 and 3.806 Å for the other one are in agreement with those for the related ruthenacarborane complex **1** (entries 1 and 2, Table 1) and suggest the existence of bifurcated DHBs of the type $S-H\cdots(H-B)_2$ analogous to that found in **1**.

Conclusions

The combined evidence from experimental and theoretical studies demonstrates the first example of a new DHB ($S-H\cdots H-B$) and its combination with a $C-H\cdots S$ hydrogen bond in a cooperative effect of the type $Cc-H\cdots S-H\cdots(H-B)_2$ in crystalline **1**. The energy for this hydrogen/bifurcated DHB interaction is estimated at 1.4 kcal/mol. This unconventional cooperative effect, which seems to be responsible for self-assembly of mercaptane complex **1**, allowed us to predict the crystal packing of a related mercaptane−cobaltacarborane compound. In both complexes, the observed 2D supramolecular networks would be difficult to rationalize without considering the cooperative effect through the boron-attached SH group. The findings, besides documenting structurally the first $S-H\cdots(H-B)_2$ dihydrogen bond and the unconventional cooperative ability of a boron-attached SH group, prove that substituted carboranes have the potential to serve as building blocks for assembling complex structures.

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[36] These are single-point calculations taking the optimized geometry for the trimer complex.

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Supporting Information Available: (i) ORTEP drawing of **2** showing atom labeling and a list of relevant intermolecular close contacts, (ii) ORTEP drawing of **3** showing atom labeling and a list of relevant intermolecular H···H close contacts, (iii) solid-state infrared spectra of **1** and **3**, (iv) computational details, (v) additional crystal data for **3**, and (vi) complete references. This material is available free of charge via the Internet at http://pubs.acs.org.

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