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Supplementary Material Available: Full details for the synthesis of **4**, **5**, and their complexes, tables of crystal and refinement data, positional and thermal parameters, and bond distances and angles, and figures depicting the structures and numbering schemes of Ag(**4**)$^+$ and the two cations of Cu(**4**)$^+$ (27 pages); tables of observed and calculated structure factors for Cu(**4**)$BF_4 \cdot (CH_3)_2CO$ and Ag(**4**)O_2CCF_3 (33 pages). Ordering information is given on any current masthead page.

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Preparation and Characterization of [*closo*-1,1,1-$(MeCN)_3$-1,2,4-$SrC_2B_{10}H_{12}]_n$: The First Structural Characterization of a Polymeric Self-Assembling Metallacarborane

There has been considerable current research interest in the organometallic chemistry of alkaline-earth metals.[1-11] In particular, the beautiful cyclopentadienyl chemistry of these metals has shown novel structural arrangements.[1-7] We have recently reported the solid state structure of the first calcium carborane,[12] *closo*-1,1,1,1-$(MeCN)_4$-1,2,4-$CaC_2B_{10}H_{12}$, in which the Ca$(MeCN)_4{}^{2+}$ unit caps the open hexagonal face of the [*nido*-7,9-$C_2B_{10}H_{12}]^{2-}$ ligand. In this communication, we report the synthesis and characterization of a strontium carborane, [*closo*-1,1,1-$(MeCN)_3$-1,2,4-$SrC_2B_{10}H_{12}]_n$, which has been shown by X-ray diffraction to possess a novel polymeric structure. To our knowledge, it represents the first structurally characterized example of a polymeric metallacarborane.

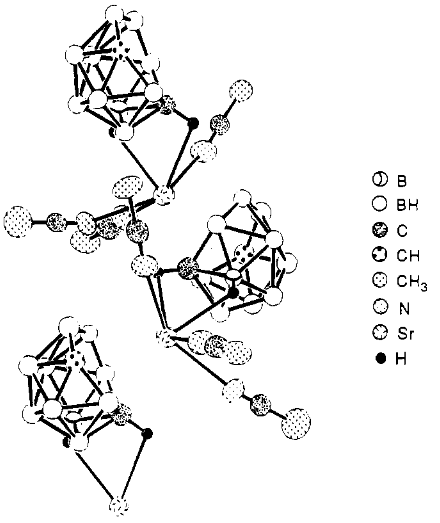

Figure 1. Three units of one of the spiral polymeric chains of [*closo*-1,1,1-$(MeCN)_3$-1,2,4-$SrC_2B_{10}H_{12}]_n$ (**2**).

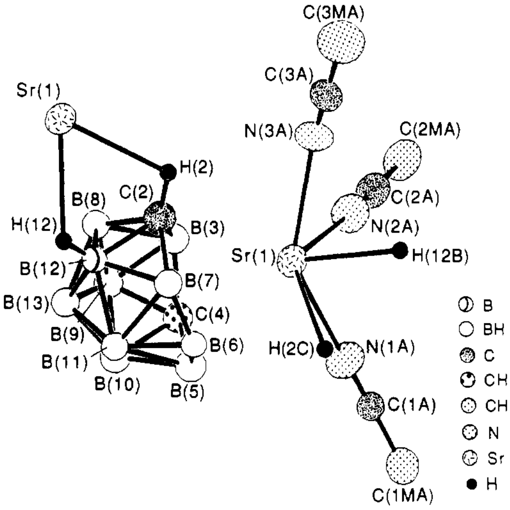

Figure 2. Closer view of the metal to carborane interactions in the polymeric complex [*closo*-1,1,1-$(MeCN)_3$-1,2,4-$SrC_2B_{10}H_{12}]_n$ (**2**). All terminal hydrogen atoms have been omitted for clarity. Selected interatomic distances (Å): Sr(1)–N(1A), 2.630 (9) [2.688 (9)]; Sr(1)–N(2A), 2.777 (10) [2.703 (9)]; Sr(1)–N(3A), 2.682 (8) [2.695 (9)]; Sr(1)–C(2)*, 2.997 (10) [3.064 (10)]; Sr(1)–B(3)*, 2.873 (10) [2.948 (13)]; Sr(1)–C(4)*, 3.176 (10) [3.142 (11)]; Sr(1)–B(5)*, 3.129 (10) [3.032 (13)]; Sr(1)–B(6)*, 2.909 (10) [2.826 (10)]; Sr(1)–B(7)*, 3.082 (10) [3.061 (13)]; C(2)–B(3), 1.716 (14) [1.731 (14)]; C(2)–B(7), 1.791 (14) [1.821 (14)]; C(4)–B(3), 1.695 (14) [1.604 (13)]; C(4)–B(5), 1.609 (14) [1.624 (15)]; B(5)–B(11), 2.003 (15) [1.99 (2)]; B(5)–B(10), 1.806 (16) [1.83 (2)]; C(2)–B(8), 1.732 (15) [1.730 (16)]; B(3)–B(8), 1.787 (15) [1.781 (16)]; C(2)–B(12), 1.731 (14) [1.719 (15)]; B(7)–B(12), 1.775 (15) [1.804 (16)]; Sr(1)–H(2), 2.62 (9) [2.70 (8)]; Sr(1)–H(12), 2.56 (9) [2.87 (9)]; C(2)–H(2), 1.12 (9) [1.43 (9)]; B(12)–H(12), 0.88 (9) [0.94 (9)]; Sr(1)–C(2), 3.153 (10) [3.166 (10)]. Asterisks denote atoms of the open hexagonal face of the carborane fragment that interacts directly with Sr(1). Distances in brackets are those of a second molecule. Note: Lines are for the purpose of orientation only and do not imply covalent bonding.

The reaction of SrI_2 with Na_2[*nido*-7,9-$C_2B_{10}H_{12}$][13] in THF affords a colorless complex (**1**), which precipitates from THF. Complex **1** is soluble in other coordinating solvents such as MeCN or DMF. Recrystallization of complex **1** from $MeCN/Et_2O$ produces colorless needlelike crystals; the X-ray study showed it to have the composition $Sr(C_2B_{10}H_{12})(MeCN)_3$ (**2**).[14] Complex **2** reverts to **1** in the presence of THF. On the basis of these

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(13) This dianion has been generated by the 2-electron reduction of 1,2-$C_2B_{10}H_{12}$ and has been formulated as Na_2[*nido*-7,9-$C_2B_{10}H_{12}$] with carbon atoms occupying the 7- and 9-positions. This assignment is further supported by the fact that the [*nido*-$C_2B_{10}H_{13}]^-$ monoanion (kinetic isomer) and all of the metallacarboranes derived from this dianion contain carbon atoms in these positions.

(14) Data for **1**: IR (Nujol mull, NaCl) ν_{B-H} 2524 s, 2472 vs, br cm^{-1}, ν_{Sr-H-E} 2390 m cm^{-1} (E = B or C), ν_{THF} 1032 s, 884 m cm^{-1}. Data for **2**: IR (Nujol mull, NaCl) ν_{B-H} 2512 s, br, 2429 s, br cm^{-1}, ν_{MeCN} 2300 m, 2265 s cm^{-1}; ^1H NMR (CD_3CN, 20 °C, ppm) 3.99 (s, br, carboranyl C–H); ^{11}B NMR (in MeCN, 20 °C, chemical shifts referenced to external $BF_3 \cdot OEt_2$, peaks upfield of the reference are designated as negative, areas given in parentheses) 2.6 (4), $^1J_{BH}$ = 111 Hz, −7.2 (3), $^1J_{BH}$ = 143 Hz, −18.1 (3), $^1J_{BH}$ = 129 Hz.

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observations, complex **1** is formulated as $Sr(C_2B_{10}H_{12})(THF)_3$.[14] Both these complexes are extremely air- and moisture-sensitive, but can be stored in an inert atmosphere over extended periods of time. Complex **2** decomposes to produce the known anion[15-17] $[\textit{nido}\text{-}9,12\text{-}C_2B_{10}H_{13}]^-$ (^1H and ^{11}B NMR vide infra) upon exposure to moist air or water. Both complexes **1** and **2** serve as a source of $[\textit{nido}\text{-}7,9\text{-}C_2B_{10}H_{12}]^{2-}$ in their reaction with YbI_2L_2 in the presence of a coordinating solvent L to afford the known[18,19] *closo*-1,1,1,1-$(L)_4$-1,2,4-$YbC_2B_{10}H_{12}$ (where L = THF or MeCN) in quantitative yield.

The molecular structure[20] of **2** was established by an X-ray diffraction study. Suitable single crystals of **2** were grown from a $MeCN/Et_2O$ solution at room temperature. The crystal is composed of two crystallographically independent, but structurally similar, spiral chains. Three units of one of the spiral polymeric chains are shown in Figure 1. A more detailed view of the metal to carborane interactions can be seen in Figure 2 along with selected interatomic distances. Each carborane fragment serves as a ligand to two strontium atoms, bonded to one through an open hexagonal face and to the other via upper- and lower-belt M–H–E (where E = B or C) interactions. The coordination geometry about each strontium is completed by three acetonitrile ligands. This arrangement of metal and carborane ligand is repeated to give a polymeric structure. To our knowledge, this is the first structurally characterized example of a polymeric metallacarborane.

The Sr–N distances fall in the range 2.63–2.77 Å and strontium–carborane (η^6) distances range from 2.87 to 3.17 Å. The Sr(1)–C(2) and Sr(1)–C(4) distances (2.997 and 3.176 Å, respectively) are much longer than the 2.81-Å distance found in the complex $\{C_5H_3\text{-}1,3\text{-}(SiMe_3)_2\}_2Sr(THF)$.[5] The C_2B_{10} fragment in **2** can be compared with related transition-metal metallacarborane complexes.[12,21-23] In complex **2**, the entire upper belt is distorted in order to accommodate the perturbed 13-vertex polyhedron. The polyhedron is somewhat similar to that observed in the complex *closo*-1,1-$(PPh_3)_2$-1-H-1,2,4-$RhC_2B_{10}H_{12}$.[22] However, in complex **2**, C(2) and C(4) lie on the same side in the upper belt of the carborane fragment. This is in contrast to other related metallacarboranes containing the C_2B_{10} unit,[12,21-23] where one carbon atom lies above and another lies below the plane defined by the remaining four borons in the upper belt. In complex **2**, B(3) and B(6) lie above the plane defined by C(2), C(4), B(5), and B(7) (maximum deviation of defining atoms from plane is 0.05 Å) in the upper belt. The upper belt thus adopts a boatlike shape. Both carbon atoms C(2) and C(4) interact asymmetrically with the adjacent borons in the upper belt [C(2)–B(3), C(2)–B(7), C(4)–B(3), and C(4)–B(5) distances are 1.716 (14), 1.791 (14), 1.695 (14), and 1.609 (14) Å, respectively] similar to the interaction reported for the complex[21] 1,1-$(PPh_3)_2$-1-H-3-OMe-1,2,4-$IrC_2B_{10}H_{11}$ [C(2)–B(3), C(2)–B(7), C(4)–B(3), and C(4)–B(5) distances are 1.50 (3), 1.62 (3), 1.69 (3), and 1.74 (3) Å, respectively]. In contrast, in the complex[12] *closo*-1,1,1,1-$(MeCN)_4$-1,2,4-$CaC_2B_{10}H_{12}$, the carbon atom that lies above the plane defined by four borons in the upper belt interacts nearly symmetrically with the adjacent borons [C(2)–B(3) and C(2)–B(7) distances are 1.519 (8) and 1.510 (7) Å, respectively] whereas the other carbon, which lies below the plane, interacts asymmetrically with the adjacent borons [C(4)–B(3) and C(4)–B(5) distances are 1.645 (8) and 1.697 (7) Å, respectively] in the upper belt. Another unique feature of the structure of **2** is the absence of a trapezoidal face in the carborane fragment. This is in contrast to the C_2B_{10} fragment in the complex *closo*-1,1,1,1-$(MeCN)_4$-1,2,4-$CaC_2B_{10}H_{12}$,[12] which contains a trapezoid consisting of the C(2) B(3), B(8), and B(9) atoms.

It is noteworthy that one of the C–H vertices of each carborane fragment interacts with the strontium. Since the B–H vertices of the carborane fragment are certainly more basic than the C–H vertices, one would anticipate that a second M–H–B interaction would be preferred over the observed M–H–C interaction. Consequently, the M–H–C interaction is not yet understood.

The solid-state IR spectrum of **1** exhibits a split pattern due to the existence of a unique B–H stretching mode. This pattern has previously been observed in the complexes *closo*-1,1,1,1-$(THF)_4$-1,2,3-$LnC_2B_9H_{11}$,[18,19] *closo*-1,1,1,1-$(THF)_4$-1,2,4-$LnC_2B_{10}H_{12}$ (Ln = Sm or Yb),[18,19] and *closo*-1,1,1,1-$(L)_4$-1,2,4-$CaC_2B_{10}H_{12}$[12] (where L = THF or MeCN) in which the bonding of the metal atom and the carborane ligand is believed to be largely ionic in nature. In addition to the split pattern, a band at 2390 cm^{-1} is also observed in the IR spectrum of **1** which can be attributed to a M–H–E (where E = B or C) stretch and compares very well with that observed in the structurally characterized complex[24] $Ag(CB_{11}H_{12})$ (M–H–B stretching frequency is 2380 cm^{-1}).

It is interesting to note that the calcium carborane complex *closo*-1,1,1,1-$(MeCN)_4$-1,2,4-$CaC_2B_{10}H_{12}$[12] exists as a monomer whereas the strontium carborane complex **2** exists as a polymer in the solid state, even though both were synthesized under similar reaction conditions. The complex *closo*-1,1,1,1-$(MeCN)_4$-1,2,4-$CaC_2B_{10}H_{12}$ may lose a MeCN ligand at higher temperature to produce a polymeric complex with the formulation $Ca(C_2B_{10}H_{12})(MeCN)_3$. The observed self-assembly of the metal with the carborane unit in the complex **2** may be due to the larger size of strontium compared to calcium. It is anticipated that complex **2** exists as a monomer in solution. These and related problems are presently under investigation.

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Supplementary Material Available: Tables of the details of the crystallographic data collection, atom coordinates, bond distances and angles, and anisotropic thermal parameters (10 pages); a table of observed and calculated structure factors (20 pages). Ordering information is given on any current masthead page.

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