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Silver Coordination to *exo*-Dithio-7,8-dicarba-*nido*-undecaborate Derivatives. Sulfur to Metal and Open Face to Metal: Two Ways of Bonding

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exo-Dithiocarbaborane compounds display two different silver coordinations (Ag–S and AgC_2B_3) depending on the length of the *exo*-cluster chain.

Our research on the coordination chemistry of macrocyclic derivatives of *exo*-dithiocarbaborane compounds[1] has shown the singularity of their chemistry, which is modulated by the length of the *exo*-cluster (*S*,*S*′) macrocyclic chain.[2,3] Examples of silver coordination to boranes are rare. Muetterties and coworkers[4] found that $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ formed water-insoluble salts with polarizing cations (Ag^+, Cu^+, Hg^{2+}).[5] Other notable examples are $[\{(Ph_3P)AgC_2B_8H_{11}\}_2]$,[6] $AgCB_{11}H_{12}\cdot 2C_6H_6$,[7] $(Ph_3P)_2AgBH_4$ or $(Ph_3P)_3AgHBH_2CO_2Et$.[8] However, little is known about complex derivatives of $C_2B_9H_{12}^-$. In 1968[9] it was reported that treatment of $C_2B_9H_{12}^-$ with $AgNO_3$ produced the black complex $[(C_2B_9H_{11})_2Ag]^{2-}$, but doubt was later cast on the nature of this solid.[10]

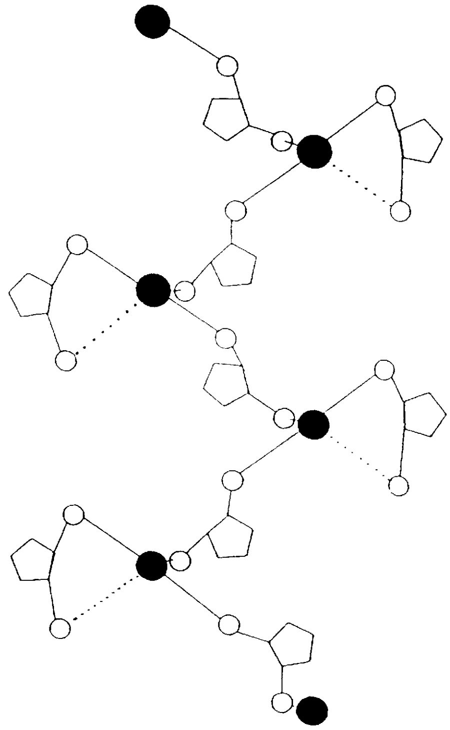

Fig. 1 Schematic view of **2**, representing the sequence ···Ag-S-carb-S-(ScarbS)Ag-S-carb-S-Ag(ScarbS)-S-carb-S-Ag···

Two different modes of Ag^+ coordination to *exo*-dithiocarbaborane are reported here, Ag–S and Ag-open face (C_2B_3). When the number of links in the *exo*-cluster cycle is six, Ag–S coordination is observed, but when the number is five, a C_2B_3–Ag coordination is seen.

The reaction of $[NMe_4][7,8\text{-}\mu\text{-}(SCH_2CH_2S)\text{-}7,8\text{-}C_2B_9H_{10}]$ **1** with $AgNO_3$, in solvents such as EtOH, MeOH, H_2O-acetone, produces a fine precipitate of silver metal. However, the compound $[NMe_4][Ag\{7,8\text{-}\mu\text{-}(SCH_2CH_2S)\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$ **2**† is obtained when $\{7,8\text{-}\mu\text{-}(SCH_2CH_2S)\text{-}7,8\text{-}C_2B_9H_{10}\}^-$ and $AgNO_3$ are mixed with $Co(NO_3)_2\cdot 6H_2O$ in water–acetone in a 2:1:1 molar ratio, respectively. Resonances with the ratio 2:1:2:2:1:1 are observed in the $^{11}B\{H\}$ NMR spectrum. The chemical shifts are comparable with those found in the free ligand, thus indicating no boron-cage to metal interaction. The X-ray analysis of **2**‡ shows the chain nature of the compound (Fig. 1), which can be schematically represented as ···Ag-S-carb-S-(ScarbS)Ag-S-carb-S-Ag(ScarbS)-S-carb-S-Ag···, where (ScarbS) represents a chain pendant fragment. Fig. 2 shows the fragment -S-carb-S-Ag(ScarbS)-S-carb-S-. The Ag is three-coordinated

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† *Spectroscopic data* for $[NMe_4][Ag\{7,8\text{-}\mu\text{-}(SCH_2CH_2S)\text{-}7,8\text{-}C_2B_9H_{10}\}_2]$ **2**: IR (KBr) ν(B–H)/cm^{-1} 2587, 2550 and 2538. ^1H NMR (in [$^2H_6$] acetone; chemical shifts referenced to Me_4Si): δ 3.45, s, —, 12; 3.30–3.05, m, —, 8; −2.6, b, —, 1. $^{11}B\{H\}$NMR (in acetone; chemical shifts, referenced to external $BF_3\cdot OEt_2$, upfield of the reference are designated as negative): δ −6.6 (2), −8.0 (1); −15.5 (2), −18.0 (2), −31.9 (1), −35.4 (1).

‡ *Crystal data*: space group $P2_12_12_1$; $Z = 4$; $a = 7.710(3)$, $b = 13.437(3)$, $c = 28.127(4)$ Å; $V = 2913.9$ Å^3. Data collection parameters: maximum 2θ range 50°, μ(Mo-Kα) = 9.87 cm^{-1}, λ = 0.71069 Å. The structure was solved with the OMEGA tangent formula (J. Rius and C. Miravitlles, *Acta Crystallogr., Sect. A.*, 1989, **45**, 490) and refined with SHELX76 (G. M. Sheldrick, SHELX76. Program for crystal structure determination. Univ. of Cambridge, England 1978) to $R = 0.049$ for 1776 independent reflections having $I > 2.5\sigma$. A full report of the structure determination will be given later. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

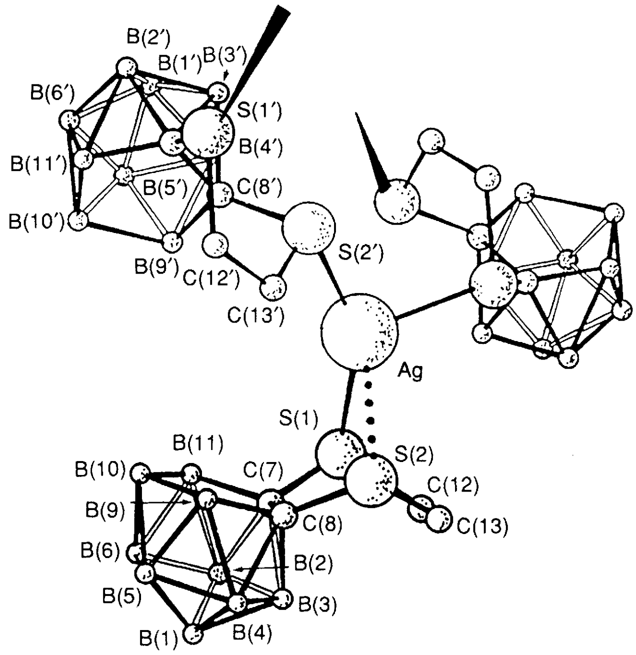

Fig. 2 Structure of **2** (hydrogens and the cation omitted; primes do not indicate, in this case, a symmetry related fragment). The fragment -S-carb-S-Ag(ScarbS)-S-carb-S- of the general sequence ···Ag-S-carb-S-(ScarbS)Ag-S-carb-S-Ag(ScarbS)-S-carb-S-Ag··· is represented. Selected intramolecular distances (Å) angles (°) are as follows: S(1)–Ag, 2.520(4); S(2)–Ag, 2.939(4); S(2′)–Ag, 2.546(3); S(1′)–Ag, 2.600(3). S(2)–Ag–S(1), 70.5(1); S(2′)–Ag–S(2), 101.4(1); S(2′)–Ag–S(1), 148.1(1).

to one S of three carbaborane units (2.52; 2.54 and 2.60 Å) with a further close separation of 2.94 Å. Consequently, the Ag is trigonally coordinated with an additional weak S–Ag interaction, due to the chain's pendant carborane. This represents the first example of a non-symmetrical chelating mode found in these dithio compounds.

Treatment of [NMe$_4$]{7,8-μ-(SCH$_2$S)-7,8-C$_2$B$_9$H$_{10}$} **3** with AgNO$_3$ in water–acetone: 1:3, produces a yellow precipitate.§ The IR spectrum shows absorptions at the B–H stretching regions from 2598 to 2450 cm^{-1}, which differs from that of the free ligand. The ^{1}H NMR spectrum does not display the typical B–H–B absorption at δ *ca.* −2.5. This resonance is very informative in [C$_2$B$_9$H$_{10}$RR′]$^{1-}$ chemistry.[11] Its absence supports a reformulation of the carbaborane ligand as the dianion [7,8-μ-(SCH$_2$S)-7,8-C$_2$B$_9$H$_9$]$^{2-}$. However, it is highly unlikely that such species exist in protic solvents (H$_2$O). To our understanding, an Ag–C$_2$B$_3$ coordination is in accordance with the spectroscopic data, and the ionic species [Ag{7,8-μ-(SCH$_2$S)-7,8-C$_2$B$_9$H$_9$}]$^{1-}$ is postulated. The analyses agree well with the formulation [Ag$_2${7,8-μ-(SCH$_2$S)-7,8-C$_2$B$_9$H$_9$}] **4**. In the solid state the compound is stable, even when exposed to light, but decomposes quite rapidly in solution. Highly coordinating solvents such as dimethylformamide, pyridine or dimethyl sulfoxide (DMSO) are required to dissolve the compound. The ^{11}B-{H} NMR spectrum of **4** is very different from that of the free ligand and varies from one solvent to another, making good comparison with other spectra of 'structurally similar complexes' difficult *e.g.* the order of the signals is 1:2:4:2 for Me$_2$SO, but 2:3:2:1:1 for tetrahydrofuran–pyridine 1:1. An attempt to compare this ^{11}B NMR spectra with others in the literature to support the Ag-open face coordination is difficult, owing to the thioether and metal influence on the resonances' distribution and position. When Lewis bases are added to a suspension of **4** in acetone, tetrahydrofuran or CH$_2$Cl$_2$, in which the compound is insoluble, the chain is broken and discrete species can be found, *e.g.* with PPh$_3$ the complex [Ag(PPh$_3$)$_4$][Ag(7,8-μ-(SCH$_2$S)-7,8-C$_2$B$_9$H$_9$)(PPh$_3$)] **5** is produced.¶

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§ *Spectroscopic data* for [Ag$_2${7,8-μ-(SCH$_2$S)-7,8-C$_2$B$_9$H$_9$}] **4**: IR (KBr) ν(B-H)/cm^{-1} 2598, 2565, 2539, 2477 and 2450. ^{1}H NMR ([^{2}H$_6$]DMSO; chemical shifts referenced to Me$_4$Si: 4.22, d, 11.4, 1; 3.66, d, 11.4, 1. ^{11}B{^{1}H} NMR (in DMSO; chemical shifts, referenced to external BF$_3$·OEt$_2$, upfield of the reference are designated as negative): −10.9 (1), −16.7 (2); −24.7 (4), −36.1 (2).

¶ *Spectroscopic data* for [Ag(PPh$_3$)$_4$][Ag(7,8-μ-(SCH$_2$S)-7,8-C$_2$B$_9$H$_9$)(PPh$_3$)] **5**: IR (KBr) ν(B-H)/cm^{-1} 2520. ^{1}H NMR (in CD$_2$Cl$_2$, chemical shifts referenced to Me$_4$Si: 7.28–7.12, m, —, 75; 3.39, d, 10.1, 1; 3.21, d, 10.1, 1. ^{11}B{H} NMR (in CH$_2$Cl$_2$; chemical shifts, referenced to external BF$_3$·OEt$_2$, upfield of the reference are designated as negative): −19.2 (3), −21.2 (4); −27.4 (1), −40.6 (1).