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Synthesis and Crystal Structure of [7,8-(Ethane-1′,2′-dithiolato-*S,S′*)-dicarba-*nido*-undecaborate]bis(triphenylphosphine)copper(I)

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The synthesis and crystal structure of $[Cu\{7,8\text{-}\mu\text{-}(SCH_2CH_2S)\text{-}7,8\text{-}C_2B_9H_{10}\}(PPh_3)_2]$ have been reported. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 15.207(3)$, $b = 10.531(3)$, $c = 26.592(6)$ Å, $\beta = 99.29(2)°$, $V = 4203(2)$ Å^3, $Z = 4$, final $R = 0.076$ ($R_w = 0.051$). The sulfur atoms of the carbaborane ligand and the phosphorus atoms of two PPh_3 groups are coordinated to the metal in a highly distorted tetrahedral environment. The bond lengths in the coordination sphere are Cu(1)–S(1) = 2.375(3), Cu(1)–S(2) = 2.483(3), Cu(1)–P(1) = 2.302(3) and Cu(1)–P(2) = 2.303(3) Å, and the bond angles vary from 76.1(1) to 124.8(1)°.

The present work forms a part of our chemical and structural studies of metal complexes of 7,8-dithio-7,8-dicarba-*nido*-undecaborate(1 –) derivatives incorporating exocyclic *S,S′*-connected strings. These macrocyclic ligands have several coordination sites, but generally *S,S′*-coordination is preferred in the presence of phosphines. In a few cases [Hg(II), Ag(I)] the open-face C_2B_3–M coordination has been found.[1,2] Our recent results suggested that the length of the exocyclic string modulates the B(3)–M distance; the shorter the string the smaller the B(3)–M distance.[3] Following this hypothesis a novel B(3)–Rh σ-interaction and agostic B(3)–H→Ru bond have been obtained using short strings.[4,5] In reactions of derivatives of 1,2-dithia-1,2-dicarba-*closo*-dodecaborane with $MCl(PPh_3)_2$ [M = Cu(I), Ag(I)] partial degradation of the carbaborane cage took place and *nido*-carbaborane complexes were obtained.[6] The crystal structure of the Cu(I) complex formed with a long external *S,S′*-connected string, $[Cu\{7,8\text{-}\mu\text{-}(SCH_2CH_2OCH_2CH_2OCH_2CH_2S)\text{-}7,8\text{-}C_2B_9H_{10}\}(PPh_3)]$, is partially disordered and exhibits two different configurations around the metal. In order to study further the coordination behaviour of Cu(I) with 7,8-dithio-7,8-dicarba-*nido*-undecaborate(1 –) derivatives we have now synthesized a copper(I) complex using a *nido*-carbaborane derivative with a short external *S,S′*-connected string as starting material.

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Experimental

Synthesis. Before use 1,2-dicarba-*closo*-dodecaborane (Dexsil Chemical Corp.) was sublimed. From this 1,2-dithiol-*o*-carborane and $[N(CH_3)_4][7,8\text{-}(ethane\text{-}1',2'\text{-}dithiolato\text{-}S,S')\text{-}dicarba\text{-}nido\text{-}undecaborate]$ were prepared according to the literature.[7,8] A 1.7 M solution of n-butyllithium in hexane from Fluka was used as supplied. $CuCl(PPh_3)_2$ was synthesized according to the literature.[9] Ethanol was reagent grade. All other reagents were from Fluka or Aldrich and were used as supplied.

To deoxygenated absolute ethanol (40 cm^3) containing $[N(CH_3)_4][7,8\text{-}\mu\text{-}(SCH_2CH_2S)\text{-}C_2B_9H_{10}]$ (100 mg, 0.336 mmol) was added $CuCl(PPh_3)_3$ (246 mg, 0.366 mmol). Under the dinitrogen atmosphere the mixture was refluxed for 2 h. The resulting solution was concentrated and allowed to rest at room temperature, after which a crystalline solid appeared. It was filtered, washed with ethanol and dried under vacuum to yield an analytically pure solid $[Cu\{7,8\text{-}\mu\text{-}(SCH_2CH_2S)\text{-}7,8\text{-}C_2B_9H_{10}\}(PPh_3)_2]$. Yield 210 mg (77%). FTIR (KBr): $\nu(cm^{-1}) = 3057$, $\nu(C_{aryl}–H)$; 2932, ν(C–H); 2526, ν(B–H), 1434, 742, 695, 521, $\nu(PPh_3)$. ^{13}C-FTNMR (100 MHz, d_6-acetone, 25 °C, TMS): 137.2, 133.6, 128.4, 128 (s, -C_6H_5-), 30.4 (s, S-CH_2-). Anal. Calcd. for $C_{40}H_{44}B_9CuP_2S_2$: C, 59.19; H, 5.46. Found: C, 58.2; H, 5.52. Elemental analysis were performed using a Perkin-Elmer 240-B microanalyser. The ^{13}C-NMR and

^{11}B-NMR spectra were obtained by using a Bruker AM 400WB instrument, and IR spectra were obtained on KBr pellets using a Perkin-Elmer 240FT spectrophotometer.

Crystal data. $C_{40}H_{44}B_9CuP_2S_2$, $M_r = 811.7$, monoclinic, $P2_1/c$, $a = 15.207(3)$, $b = 10.531(3)$, $c = 26.592(6)$ Å, $\beta = 99.29(2)°$, $V = 4203(2)$ Å, $Z = 4$, $D_x = 1.283$ Mg m^{-3}, $\lambda(MoK\alpha) = 0.710\ 69$ Å, colourless needles, $0.10 \times 0.12 \times 0.28$ mm, $\mu = 0.74$ mm^{-1}, transmission coefficient 1.00–0.97, $T = 295$ K, final $R = 0.076$ and $R_w = 0.051$ for 3089 unique reflections and 487 variables.

The unit-cell parameters were determined by least-squares refinement of 25 carefully centered reflections ($15 < 2\theta < 24°$) measured on a Nicolet P3F diffractometer. The compound crystallizes in the monoclinic crystal system, and systematic absences indicated space group $P2_1/c$. The data were corrected for Lorentz and polarization effects and for dispersion.

Data collection, structure solution and refinement. A total of 9569 reflections were collected ($2\theta_{max} = 53°$), giving 8717 unique reflections ($R_{int} = 0.029$). Of those, 3089 were considered as observed according the criteria $F > 4\sigma(F)$. The three check reflections monitored after every 100 reflections showed only statistical fluctuations during the course of the data collection. The structure was solved by direct methods by using the *SHELXS86* program.[10] Least-squares refinements and all subsequent calculations were performed using the *XTAL* program system,[11] which minimized the function $\Sigma w(\Delta F)^2$ $[1/w = \sigma^2(F_0)]$. Refinement of the non-hydrogen atoms anisotropically yielded an *R*-factor 0.102. A subsequent difference Fourier map revealed only five of the hydrogen atoms of the carbaborane cage. Those five hydrogen atoms were included in the final structure factor calculation but were not refined. The hydrogen atoms bonded to the carbon atoms were placed at their calculated positions (C–H = 0.95 Å) and not refined. Further anisotropic refinement of the non-hydrogen atoms, with fixed isotropic temperature factors for the hydrogen atoms, reduced the *R*-value to 0.076 ($R_w = 0.051$). The somewhat high *R*-value is due to the fair crystal quality and poor statistics of weak reflections. The greatest maximum in the final ΔF map was 0.65 *e* Å^{-3} at the vicinity of the metal. Scattering factors for neutral atoms were those included in the programs.

Table 1. Non-Hydrogen coordinates and isotropic thermal parameters for $C_{40}H_{44}B_9CuP_2S_2$.

Atom	*x/a*	*y/b*	*z/c*	U_{eq} [a]
Cu(1)	0.22129(8)	0.3250(1)	0.10741(5)	0.0355(8)
S(1)	0.1376(2)	0.1339(3)	0.1035(1)	0.044(2)
S(2)	0.0905(2)	0.3699(3)	0.0409(1)	0.045(2)
P(1)	0.2453(2)	0.4136(3)	0.1876(1)	0.032(2)
P(2)	0.3406(2)	0.3463(3)	0.0646(1)	0.035(2)
C(1)	0.1256(8)	0.112(1)	0.0353(5)	0.07(1)
C(2)	0.1037(8)	0.231(1)	0.0033(4)	0.062(9)
C(10)	0.1909(6)	0.331(1)	0.2343(3)	0.029(6)
C(11)	0.1965(7)	0.200(1)	0.2379(4)	0.043(8)
C(12)	0.1524(8)	0.134(1)	0.2708(5)	0.055(8)
C(13)	0.0956(8)	0.197(1)	0.2984(4)	0.057(9)
C(14)	0.0868(7)	0.324(1)	0.2944(4)	0.054(8)
C(15)	0.1327(7)	0.394(1)	0.2627(4)	0.050(8)
C(20)	0.2115(7)	0.579(1)	0.1892(4)	0.034(7)
C(21)	0.1531(8)	0.629(1)	0.1489(4)	0.048(8)
C(22)	0.1284(9)	0.755(1)	0.1495(5)	0.07(1)
C(23)	0.1591(9)	0.833(1)	0.1892(6)	0.065(9)
C(24)	0.2162(8)	0.784(1)	0.2298(5)	0.059(9)
C(25)	0.2436(7)	0.658(1)	0.2298(4)	0.048(8)
C(30)	0.3619(7)	0.416(1)	0.2181(4)	0.038(7)
C(31)	0.4205(8)	0.492(1)	0.1964(4)	0.051(8)
C(32)	0.5087(9)	0.488(1)	0.2149(5)	0.06(1)
C(33)	0.5448(8)	0.413(2)	0.2539(7)	0.09(1)
C(34)	0.489(1)	0.343(1)	0.2769(5)	0.08(1)
C(35)	0.3969(8)	0.340(1)	0.2598(5)	0.057(8)
C(40)	0.3723(7)	0.515(1)	0.0654(4)	0.032(7)
C(41)	0.3065(8)	0.603(1)	0.0608(4)	0.051(8)
C(42)	0.325(1)	0.732(1)	0.0645(5)	0.07(1)
C(43)	0.411(1)	0.770(1)	0.0723(5)	0.060(9)
C(44)	0.4783(8)	0.686(2)	0.0768(4)	0.061(9)
C(45)	0.4598(8)	0.556(1)	0.0729(4)	0.051(8)
C(50)	0.3232(6)	0.305(1)	−0.0026(4)	0.038(7)
C(51)	0.2959(7)	0.393(1)	−0.0404(4)	0.046(8)
C(52)	0.2715(8)	0.358(1)	−0.0904(4)	0.064(9)
C(53)	0.2753(9)	0.232(2)	−0.1034(5)	0.064(9)
C(54)	0.3031(7)	0.143(1)	−0.0670(5)	0.055(9)
C(55)	0.3263(6)	0.178(1)	−0.0173(4)	0.044(7)
C(60)	0.4415(7)	0.260(1)	0.0889(4)	0.035(7)
C(61)	0.5106(8)	0.248(1)	0.0620(4)	0.050(7)
C(62)	0.5868(7)	0.188(1)	0.0827(5)	0.065(9)
C(63)	0.5952(8)	0.134(1)	0.1301(6)	0.08(1)
C(64)	0.525(1)	0.143(1)	0.1570(5)	0.08(1)
C(65)	0.4477(7)	0.204(1)	0.1359(4)	0.049(8)
B(1)	−0.1041(9)	0.310(1)	0.1412(5)	0.06(1)
B(2)	−0.0329(8)	0.175(1)	0.1511(5)	0.046(8)
B(3)	0.0099(8)	0.326(1)	0.1329(5)	0.038(8)
B(4)	−0.0789(8)	0.402(1)	0.0897(5)	0.045(9)
B(5)	−0.1692(8)	0.294(1)	0.0794(5)	0.053(9)
B(6)	−0.1408(8)	0.157(1)	0.1185(5)	0.049(9)
C(7)	0.0239(6)	0.183(1)	0.1012(3)	0.033(6)
C(8)	−0.0003(6)	0.3055(9)	0.0682(4)	0.032(6)
B(9)	−0.0980(8)	0.295(1)	0.0347(5)	0.047(9)
B(10)	−0.1472(9)	0.147(1)	0.0513(5)	0.045(9)
B(11)	−0.0553(8)	0.079(1)	0.0943(5)	0.035(8)

[a] $U_{eq} = 1/3\,\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

Results and discussion

Fractional atomic coordinates and U_{eq}-values for the non-hydrogen atoms are given in Table 1, and a drawing of the monomeric molecule is shown in Fig. 1. Selected bond lengths and angles are listed in Table 2. In the title compound, [Cu{7,8-μ-(SCH_2CH_2S)-7,8-$C_2B_9H_{10}$}-(PPh_3)$_2$], the metal atom is in a trigonally distorted tetrahedral environment with two vertices occupied by the sulfur atoms of the bidentately acting *nido*-carbaborane ligand. The other two vertices are occupied by two phosphorus atoms of the PPh_3 groups. The Cu–P distances are identical [2.302(3) and 2.303(3) Å], but atom S(1) is more strongly bonded to Cu(1) than S(2), as can be seen from Cu–S bond lengths, which are 2.375(3) and 2.483(3)

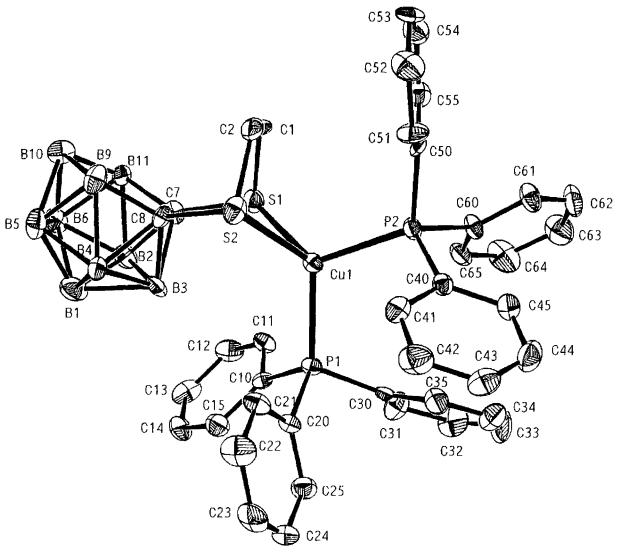

Fig. 1. An ORTEP drawing of [7,8-(ethane-1′,2′-dithiola-to-*S,S′*)-dicarba-*nido*-undecaborate]bis(triphenylphosphine)-copper(I). Thermal ellipsoids are drawn at 30% probability. Hydrogen atoms have been omitted.

Table 2. Selected bond lengths (in Å) and angles (in °).

Cu(1)–S(1)	2.375(3)	P(2)–C(40)	1.84(1)
Cu(1)–S(2)	2.483(3)	P(2)–C(50)	1.82(1)
Cu(1)–P(1)	2.302(3)	P(2)–C(6)0	1.81(1)
Cu(1)–P(2)	2.303(3)	C(1)–C(2)	1.52(2)
S(1)–C(1)	1.81(1)	C(7)–C(8)	1.57(1)
S(1)–C(7)	1.80(1)	C(7)–B(3)	1.76(2)
S(2)–C(2)	1.80(1)	C(7)–B(11)	1.61(2)
S(2)–C(8)	1.79(1)	C(8)–B(3)	1.72(2)
P(1)–C(10)	1.82(1)	C(8)–B(9)	1.61(1)
P(1)–C(20)	1.81(1)	B(9)–B(10)	1.82(2)
P(1)–C(30)	1.83(1)	B(10)–B(11)	1.80(2)
S(1)–Cu(1)–S(2)	76.6(1)	S(1)–C(7)–C(8)	113.2(7)
S(1)–Cu(1)–P(1)	112.8(1)	S(1)–C(7)–B(11)	120.5(8)
S(1)–Cu(1)–P(2)	121.3(1)	B(3)–C(7)–C(8)	61.7(7)
S(2)–Cu(1)–P(1)	124.8(1)	B(3)–C(7)–B(11)	119.3(8)
S(2)–Cu(1)–P(2)	103.5(1)	C(8)–C(7)–B(11)	112.8(7)
P(1)–Cu(1)–P(2)	113.5(1)	S(2)–C(8)–B(3)	113.9(6)
Cu(1)–S(1)–C(1)	96.8(4)	S(2)–C(8)–C(7)	114.2(6)
Cu(1)–S(1)–C(7)	105.3(4)	S(2)–C(8)–B(9)	120.3(7)
C(1)–S(1)–C(7)	93.5(5)	B(3)–C(8)–C(7)	64.6(7)
Cu(1)–S(2)–C(2)	95.3(4)	B(3)–C(8)–B(9)	119.5(9)
Cu(1)–S(2)–C(8)	102.7(3)	C(7)–C(8)–B(9)	111.4(8)
C(2)–S(2)–C(8)	94.5(5)	C(8)–B(9)–B(10)	107.8(9)
S(1)–C(1)–C(2)	115.8(9)	B(9)–B(10)–B(11)	100.6(8)
S(2)–C(2)–C(1)	113.1(8)	C(7)–B(11)–B(10)	107.2(9)

Å, respectively. The angles around the Cu(I) ion vary from 76.6(1) to 124.8(1)°. The S(1)–Cu(1)–S(2) angle of 76.6(1)° can be assumed as a consequence of the short S–S distance of the obviously rigid carbaborane ligand. Also, the variation of the S–Cu–P angles [103.5(1)–124.8(1)°] may be due to the rigidity of the carbaborane ligand.

A comparison of the coordination spheres of the title compound and [Cu{7,8-μ-($SCH_2CH_2OCH_2CH_2OCH_2CH_2S$)-7,8-$C_2B_9H_{10}$}($PPh_3$)][6] reveals considerable differences. The compared structure is partly disordered and exhibits two configurations, labelled **A** and **B**. In **A** the two sulfur atoms of the carbaborane ligand, the phosphorus atom of the PPh_3 group and two oxygen atoms of the exocluster macrocyclic chain are coordinated to copper in a highly distorted square-pyramidal arrangement [Cu–S = 2.351(6) and 2.29(1) Å; Cu–P = 2.199(4) Å; Cu–O = 2.31(2) and 2.56(2) Å]. In **B** the metal atom is only three-coordinated [Cu–S distances 2.327(9) and 2.33(1); Cu–P = 2.199(4) Å]. Thus, in addition to the different coordination spheres, the Cu–S and Cu–P distances are also different in the two compounds. Even though some differences in the Cu–S and Cu–P bonds could be expected, taking into account the considerable differences in the coordination spheres of the three compared complex units, the large variations observed may still be considered somewhat surprising.

Metal atoms can coordinate to the sulfur atoms of 7,8-dithio-7,8-dicarba-*nido*-undecaborate(1 –) derivatives in an *anti* or *syn* disposition with regard to the pentagonal C_2B_3 open face, but *anti* is preferred, as in the title compound and in [Cu{7,8-μ-($SCH_2CH_2OCH_2CH_2OCH_2CH_2S$)-7,8-$C_2B_9H_{10}$}($PPh_3$)].[6] The *syn* form has been observed in [Ag{7,8-μ-(SCH_2CH_2S)-7,8-$C_2B_9H_{10}$}(PPh_3)]·0.5 CH_2Cl_2[12] and [$N(CH_3)_4$][Ru{7,8-μ-(SCH_2CH_2S)-7,8-$C_2B_9H_{10}$}$_2$Cl],[13] in which the cages are disordered and also exist in the *anti* form. The orientations of the cages in the title compound having a short *S,S′*-connecting string and in [Cu{7,8-μ-($SCH_2CH_2OCH_2CH_2OCH_2CH_2S$)-7,8-$C_2B_9H_{10}$}($PPh_3$)][6] having a longer string are markedly different. In the title compound the cage is more bent towards the metal, which can be seen in the dihedral angle values through the planes S(1),C(7),C(8),S(2) and Cu(1),S(1),S(2), which are 133.2(3)° in the title compound and 178.1(5) and 176.7(6)° in the compared complex. This confirms our hypothesis that the length of the exocyclic string modulates the B(3)–M distance.[3]

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