

[1,1,2,2-(CO)₄-1,2- μ -(CO)-4,11-(SMe₂)₂-*closo*-1,2-Co₂B₁₀H₈]¹

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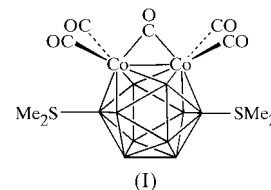
The title compound, 1,1,2,2-tetracarbonyl-1,2- μ -carbonyl-4,11-dimethylsulfido-*closo*-1,2-dicobaltadodecaborane, [Co₂(C₄H₂₀B₁₀S₂)(CO)₅], has a *closo* 12-vertex {1,2-Co₂B₁₀H₈} structure with SMe₂ ligands at the *exo*-4- and 11-positions. The cluster displays close structural similarities to the SEt₂ analogue.

Comment

We have an interest in developing the chemistry of bis(ligand) 'adducts' of decaborane, 6,9-*L*₂-*arachno*-B₁₀H₁₂, where *L* is a two-electron ligand such as a phosphorus, sulfur or nitrogen base (Crook *et al.*, 1984; Fontaine & Kennedy, 1987; Dörfler *et al.*, 1997, 1998; Londesborough *et al.*, 1999; Plešek *et al.*, 1994). In particular, we have contemporary interest in the incorporation, without the displacement of the two boron-to-ligand bonds, of transition-element centres into the {L₂B₁₀} matrix. This, for example, would introduce the possibility of generating boron-only analogues of the interesting {MC₂B₈} species (Kennedy *et al.*, 1993), and of doping new types of boron-based polymers (Londesborough *et al.*, 1999) with selected metal centres. In this context, we note that Hawthorne and colleagues have introduced a bimetallic {Co₂(CO)₅} unit into the [B₁₀H₁₂(SEt₂)₂] molecule by treatment with [Co₂(CO)₈] (Schubert *et al.*, 1988). This reaction gives isomers of [(CO)₅Co₂B₁₀H₈(SEt)₂] with a closed 12-vertex constitution. In order to assess this reaction type, and to develop our techniques, we have repeated the reaction, but now using the SMe₂ complex [B₁₀H₁₂(SMe₂)₂] as a starting substrate. Under essentially the same reaction and separatory conditions, we have isolated one of the analogous SMe₂ complexes, [1,1,2,2-(CO)₄- μ -1,2-(CO)-4,11-(SMe₂)₂-*closo*-1,2-Co₂B₁₀H₈], (I), in *ca* 7% yield, for which we here report the crystal and molecular structure as established by single-crystal X-ray diffraction analysis.

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In terms of the common features of molecular structure, the differences between the SMe₂ and SEt₂ compounds are principally those of B(SMe₂) versus B(SEt₂) rotamer differences.



Other dimensions are very comparable, *e.g.* intercobalt at 2.4913 (4) compared to 2.490 (1) Å in the SEt₂ species, although a detailed comparison is inappropriate because of differences in s.u.'s and different temperatures of data collection. Within the cluster, there are minor differential interboron cluster flexings associated with the sulfur-substituted positions, *e.g.* distances centred on the substituted B11 and B4 sites are up to *ca* 0.040 (4) Å shorter than otherwise equivalent distances associated with the unsubstituted B5 and B7 sites. The shortening is mimicked by variations in the cobalt–boron distances, *e.g.* Co1–B4 is 2.116 (3) Å and Co1–B5 is some 0.05 Å longer at 2.169 (3) Å.

There is an interesting aspect of the cluster constitution of [(CO)₅Co₂B₁₀H₈(SMe₂)₂] that warrants comment (Fig. 1). Although it has a closed icosahedral {Co₂B₁₀} skeleton that merits the classical *closo* geometrical descriptor, the cluster is not in complete accord with the useful Williams–Wade *closo/nido/arachno* paradigm which classifies and relates geometry and cluster electron count in boron-containing cluster compounds (Williams, 1976; Wade, 1976). Using an isolobal vertex-replacement model in conjunction with the regular icosahedral [*closo*-B₁₂H₁₂]²⁻ exemplar, two neutral {B(SMe₂)} vertices would formally compensate for two anionic {BH}⁻ vertices, leaving the {Co₂(CO)₅} unit to compensate for two neutral {BH} vertices. Since a neutral {BH} unit is a two-electron cluster contributor (Wade, 1976), this would imply that each cobalt vertex also contributes two electrons which would in turn imply two cobalt(II) centres. The compound, however, is not paramagnetic. A direct intercobalt bond must therefore be additionally invoked. This is in accord with the intercobalt distance of 2.49 Å, which is in the range generally taken to be indicative of a direct Co–Co bond, *e.g.* compare

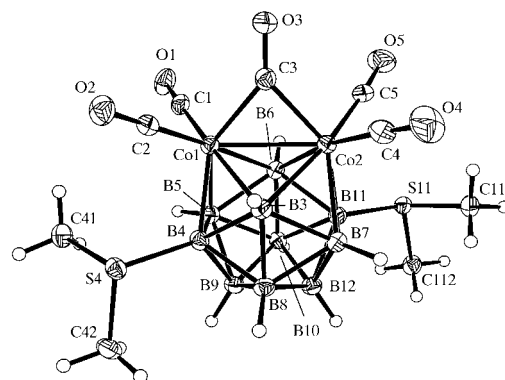


Figure 1

A perspective view of a single molecule of (I) drawn with 40% probability ellipsoids and H atoms shown as small circles of arbitrary radii for clarity.

2.47 Å in $[\text{Co}_2(\text{CO})_8]$ (Sumner *et al.*, 1964) and 2.51 Å in cobalt metal. Since the intercobalt vector is part of the icosahedral cluster, then the two electrons in the intercobalt bond constitute part of the cluster electron count, which would thereby total 14 electron pairs, corresponding to a formal *nido* electron count, rather than the 13 electron pairs that would be classically associated with the 12-vertex *closo* structure. The 14 pairs would thereby constitute a count in excess of *closo* – a ‘hyper’-*closo* count, as it were (Kennedy, 1998). This interesting apparent paradox is closely related to the one encountered with similar intermetallic bonding in the ten-vertex ‘*isocloso*’-structured species $[\text{1,6-}(\eta^5\text{-C}_5\text{H}_5)_2\text{-1,6,2,3-Fe}_2\text{C}_2\text{B}_6\text{H}_8]$ (Callahan *et al.*, 1975), in which conventional electron counting would dictate a ten-electron-pair sub-*closo* count – a ‘hypo’-*closo* count. In the Callahan structure, the electron pair in the additional intracluster Fe–Fe bond (Nishimura, 1978) would engender an 11-electron-pair count, which is classically associated with ten-vertex *closo*. Most recently, in this general area, the relationship between intermetallic bonding and anomalous cluster electron count has been discussed by Fehlner and co-workers in the context of metallaborane clusters that are rich in metal atoms, as in ‘cubane’ species such as $[(\text{C}_5\text{Me}_5)_3\text{Ru}_3\text{B}_3\text{H}_3\text{Co}(\text{CO})_3]$ (Lei *et al.*, 2000)

Experimental

The title compound was prepared essentially according to the method published for the preparation of the SeT_2 analogue (Schubert *et al.*, 1988). Single crystals were obtained from hexane diffusion into a methylene chloride solution of the compound.

Crystal data

$[\text{Co}_2(\text{C}_4\text{H}_{20}\text{B}_{10}\text{S}_2)(\text{CO})_5]$	Mo $K\alpha$ radiation
$M_r = 498.33$	Cell parameters refined using 52070 reflections
Orthorhombic, <i>Pbca</i>	$\theta = 2.0\text{--}27.5^\circ$
$a = 12.2978(2) \text{ \AA}$	$\mu = 1.836 \text{ mm}^{-1}$
$b = 10.9183(2) \text{ \AA}$	$T = 150(2) \text{ K}$
$c = 30.5900(5) \text{ \AA}$	Prism, yellow
$V = 4107.35(12) \text{ \AA}^3$	$0.21 \times 0.18 \times 0.15 \text{ mm}$
$Z = 8$	
$D_x = 1.612 \text{ Mg m}^{-3}$	

Data collection

Nonius KappaCCD area-detector diffractometer	3276 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (Blessing, 1995)	$R_{\text{int}} = 0.077$
$T_{\text{min}} = 0.699$, $T_{\text{max}} = 0.770$	$\theta_{\text{max}} = 26.00^\circ$
48 902 measured reflections	$h = -13 \rightarrow 15$
4029 independent reflections	$k = -13 \rightarrow 13$
	$l = -37 \rightarrow 34$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0223P)^2 + 2.5684P]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.061$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.026$	$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
4029 reflections	$\Delta\rho_{\text{min}} = -0.48 \text{ e \AA}^{-3}$
289 parameters	
H atoms: see below	

Cluster H atoms were located *via* Fourier difference syntheses and positional and isotropic displacement parameters were freely refined and resulted in B–H dimensions in the range 1.03(2)–1.13(2) Å. Methyl H atoms were included in calculated positions with a refined

Table 1

Selected geometric parameters (Å, °).

C1–O1	1.142(3)	Co1–B4	2.116(3)
C1–Co1	1.774(3)	Co1–B3	2.163(3)
C2–O2	1.142(3)	Co1–B5	2.169(3)
C2–Co1	1.779(2)	Co1–B6	2.189(3)
C3–O3	1.171(3)	Co1–Co2	2.4913(4)
C3–Co1	1.913(2)	Co2–B11	2.113(3)
C3–Co2	1.917(2)	Co2–B7	2.160(3)
C4–O4	1.142(3)	Co2–B6	2.161(3)
C4–Co2	1.771(3)	Co2–B3	2.200(3)
C5–O5	1.133(3)	B4–S4	1.917(3)
C5–Co2	1.780(3)		
Co1–C3–Co2	81.16(9)		

rotational parameter for each methyl group and isotropic displacement parameters of $1.2U_{\text{eq}}$ of the parent C atom.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1996); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (McArdle, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1001). Services for accessing these data are described at the back of the journal.

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