

## Structure of 8,8'- $\mu$ -(Methoxycarbonylmethylthio)-3,3'-*commo*-bis[1,2-dicarba-3-cobaltacloso-dodecaborane(11)]

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**Abstract.**  $C_7H_{25}B_{18}CoO_2S$ ,  $M_r = 427$ , orthorhombic, *Pbca*,  $a = 13.982$  (4),  $b = 13.417$  (3),  $c = 22.202$  (4) Å,  $V = 4165$  (2) Å<sup>3</sup>,  $Z = 8$ ,  $D_m = 1.358$ ,  $D_x = 1.361$  Mg m<sup>-3</sup>, Mo  $K\alpha$ ,  $\lambda = 0.71073$  Å,  $\mu = 0.926$  mm<sup>-1</sup>,  $F(000) = 1728$ , room temperature,  $R = 0.053$  for 3627 observed independent reflections. The two dicarbaborane ligands are coordinated to the Co atom to form a 'sandwich' compound linked by pentagonal faces. The ligands are also linked together by a monoatomic sulfur bridge to which a methoxycarbonylmethyl group is bound [B–S bond lengths 1.925 (4) and 1.926 (4) Å]. The position of the Co atom is intermediate between those of unbridged and oxygen-bridged cobaltabis(dicarbaborane) molecules.

**Introduction.** The present study reports the result of the X-ray investigation of 8,8'-CH<sub>3</sub>OCOCH<sub>2</sub>S-3-Co(1,2C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub> and forms part of our continuing study of the structure of metallocarbaboranes prepared in the Institute of Inorganic Chemistry of the Czechoslovak Academy of Sciences (Janoušek, Plešek, Heřmánek & Baše, 1981).

**Experimental.** Red transparent crystal, 0.6 × 0.7 × 0.7 mm;  $D_m$  by flotation; Hilger & Watts diffractometer; Mo  $K\alpha$  radiation, Zr filter; cell parameters and standard deviations by least squares from 35 reflections ( $3 < \theta < 21^\circ$ ) (Shoemaker, 1970); 5021 independent reflections measured by  $\omega/2\theta$  scans to  $\sin \theta/\lambda = 0.6606$  Å<sup>-1</sup> ( $h$ : 0 to 18,  $k$ : 0 to 17,  $l$ : 0 to 29); intensity measurements by learnt profile method (Clegg, 1981); 1394 reflections with  $I < 1.96\sigma(I)$  regarded as unobserved. Intensities of three standards (322, 060, 114) measured every 30 reflections, no significant variation; data corrected for Lorentz and polarization effects, not for absorption or extinction; coordinates of Co atom determined from Patterson map, Fourier synthesis based on these input parameters provided positions of all remaining non-hydrogen atoms. Refinement with local version of full-matrix least-squares program *ORFLS* (Busing, Martin & Levy, 1962), anisotropic temperature factors for non-H atoms; H atoms from difference Fourier synthesis refined with common isotropic temperature factor fixed at  $B = 3$  Å<sup>2</sup>; function minimized  $\sum w(|F_o| - |F_c|)^2$  with  $w^{-1} = \sigma^2(|F_o|) +$

$(0.015|F_o|)^2$ ; in final cycle  $R = 0.053$ ,  $wR = 0.081$ ,  $S = 1.49$  (for observed reflections),  $(\Delta/\sigma)_{av} = 0.01$ ,  $(\Delta/\sigma)_{max} = 0.12$ ; max. and min. peak heights in final difference Fourier synthesis: +0.27 and -0.34 e Å<sup>-3</sup>. Scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations performed on Siemens 7536 computer.

**Discussion.** Final atomic coordinates are given in Table 1\* and bond lengths for non-hydrogen atoms in Table 2.

\* Lists of structure amplitudes, anisotropic thermal parameters, bond angles, H-atom parameters and bond lengths involving H have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42726 (52 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Hamilton, 1959), with *e.s.d.*'s in parentheses

$$B_{eq} = \frac{1}{3} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	$B_{eq}$ (Å <sup>2</sup> )
Co	0.07156 (3)	0.19913 (3)	0.12723 (2)	2.09 (1)
S	-0.04614 (6)	0.02502 (6)	0.08046 (4)	2.57 (2)
O(1)	-0.1170 (3)	-0.1508 (2)	0.2102 (1)	5.26 (9)
O(2)	-0.0646 (2)	-0.1772 (2)	0.1174 (1)	3.88 (7)
C(3)	-0.1249 (3)	-0.0191 (3)	0.1403 (2)	3.29 (9)
C(4)	-0.1021 (3)	-0.1229 (3)	0.1610 (2)	3.07 (8)
C(5)	-0.0415 (4)	-0.2799 (4)	0.1322 (2)	5.5 (1)
C(1)	0.2197 (2)	0.1823 (3)	0.1288 (2)	2.90 (8)
C(2)	0.1724 (2)	0.1752 (3)	0.1943 (2)	2.89 (8)
B(4)	0.1646 (3)	0.1076 (3)	0.0778 (2)	2.73 (8)
B(5)	0.2765 (3)	0.0738 (4)	0.1100 (2)	3.3 (1)
B(6)	0.2822 (3)	0.1189 (4)	0.1838 (2)	3.7 (1)
B(7)	0.0786 (3)	0.0938 (3)	0.1968 (2)	2.62 (8)
B(8)	0.0733 (3)	0.0473 (3)	0.1214 (2)	2.33 (8)
B(9)	0.1828 (3)	-0.0163 (3)	0.1057 (2)	3.00 (9)
B(10)	0.2551 (3)	-0.0078 (4)	0.1708 (2)	3.7 (1)
B(11)	0.1926 (3)	0.0613 (3)	0.2259 (2)	3.4 (1)
B(12)	0.1305 (3)	-0.0238 (3)	0.1784 (2)	3.02 (9)
C(1')	0.0009 (3)	0.3283 (3)	0.1532 (2)	2.95 (8)
C(2')	0.0500 (3)	0.3390 (2)	0.0892 (2)	3.14 (8)
B(4')	-0.0669 (3)	0.2256 (3)	0.1595 (2)	2.86 (9)
B(5')	-0.1199 (3)	0.3438 (4)	0.1488 (2)	4.0 (1)
B(6')	-0.0437 (4)	0.4182 (3)	0.1055 (2)	4.1 (1)
B(7')	0.0223 (3)	0.2429 (3)	0.0421 (2)	2.75 (8)
B(8')	-0.0562 (3)	0.1678 (3)	0.0867 (2)	2.41 (8)
B(9')	-0.1587 (3)	0.2408 (3)	0.1046 (2)	3.5 (1)
B(10')	-0.1435 (4)	0.3603 (3)	0.0708 (2)	4.0 (1)
B(11')	-0.0322 (4)	0.3621 (3)	0.0344 (2)	3.5 (1)
B(12')	-0.1034 (3)	0.2519 (3)	0.0320 (2)	3.3 (1)

The title molecule (see Fig. 1) consists of two dicarbaborane ligands which form a 'sandwich' *via* their pentagonal faces with Co as the central atom. In this molecule, unlike the anion Co(C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)<sub>2</sub><sup>-</sup> (I) (Borodinsky, Sinn & Grimes, 1982), the ligands are bridged by a >SCH<sub>2</sub>COOCH<sub>3</sub> group.

It is of interest to compare geometric parameters derived from our molecule (II), and the anions (I) and Co(C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>O<sup>-</sup> (III), which is oxygen bridged (Petřina, Petřicek, Malý, Šubrtová, Líněk & Hummel, 1981), to study changes caused by the bridge. The bridge does not affect significantly the distances of the central Co atom from the 'best' planes through the atoms C(1), C(2), B(4), B(7), B(8) and C(1'), C(2'), B(4'), B(7'), B(8'), which are 1.4665 (5), 1.4753 (6); 1.4791 (4), 1.4828 (4); and 1.456 (2), 1.467 (1) Å for (I), (II) and (III), respectively. Significant differences were, however, found in the angles between these planes which are 3.8 (2), 16.6 (1) and 28.2 (3)°, respectively. Another significant difference is in the individual distances involving the Co atom. The average Co—C distances tend to increase from (I) to (III), 2.045 (9), 2.079 (4), 2.09 (1) Å, respectively, and the average Co—B(8) and Co—B(8') distances have the opposite

tendency, becoming shorter [2.105 (4), 2.043 (2), 2.028 (8) Å, respectively]. This means that the position of Co is changed, moving towards the bridge, and this effect seems to be larger for the oxygen bridge.

Mean cage bond distances, B—B = 1.776 (14), B—C = 1.709 (14), C—C = 1.593 (10), B—H = 1.05 (5), C—H = 0.90 (3) Å and also the mean B—S distance 1.926 (1) Å are in a good agreement with those derived from similar compounds (Churchill & Gold, 1971;

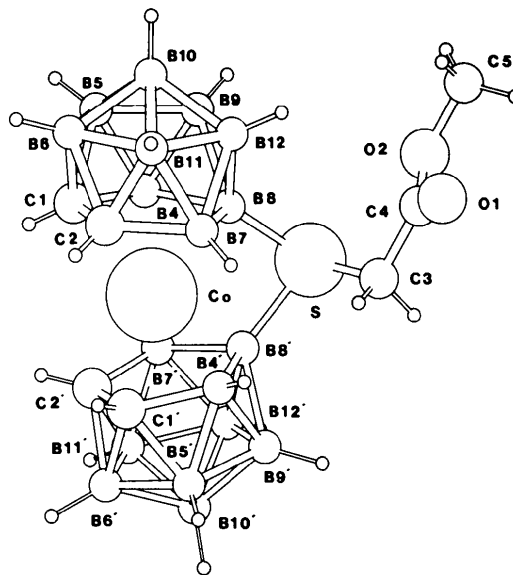


Fig. 1. View of the CH<sub>3</sub>OCOCH<sub>2</sub>SCo(C<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub> molecule with atom numbering.

Table 2. Interatomic distances (Å) with *e.s.d.*'s in parentheses

(a) Metal-cage distances

Co—C(1)	2.084 (3)	Co—C(1')	2.077 (4)
Co—C(2)	2.076 (4)	Co—C(2')	2.080 (3)
Co—B(4)	2.099 (4)	Co—B(4')	2.095 (4)
Co—B(7)	2.096 (4)	Co—B(7')	2.096 (4)
Co—B(8)	2.041 (4)	Co—B(8')	2.044 (4)

(b) Cage distances

C(1)—C(2)	1.600 (6)	C(1')—C(2')	1.585 (6)
C(1)—B(4)	1.697 (6)	C(1')—B(4')	1.678 (6)
C(1)—B(5)	1.710 (6)	C(1')—B(5')	1.705 (6)
C(1)—B(6)	1.726 (6)	C(1')—B(6')	1.722 (6)
C(2)—B(6)	1.727 (5)	C(2')—B(6')	1.725 (6)
C(2)—B(7)	1.708 (5)	C(2')—B(7')	1.705 (5)
C(2)—B(11)	1.705 (6)	C(2')—B(11')	1.702 (7)
B(4)—B(5)	1.779 (6)	B(4')—B(5')	1.767 (7)
B(4)—B(8)	1.795 (6)	B(4')—B(8')	1.799 (6)
B(4)—B(9)	1.792 (6)	B(4')—B(9')	1.782 (6)
B(5)—B(6)	1.748 (6)	B(5')—B(6')	1.748 (7)
B(5)—B(9)	1.785 (6)	B(5')—B(9')	1.780 (7)
B(5)—B(10)	1.764 (7)	B(5')—B(10')	1.777 (6)
B(6)—B(10)	1.765 (7)	B(6')—B(10')	1.773 (7)
B(6)—B(11)	1.744 (6)	B(6')—B(11')	1.756 (6)
B(7)—B(8)	1.788 (6)	B(7')—B(8')	1.789 (6)
B(7)—B(11)	1.774 (6)	B(7')—B(11')	1.780 (6)
B(7)—B(12)	1.784 (6)	B(7')—B(12')	1.776 (6)
B(8)—B(9)	1.787 (6)	B(8')—B(9')	1.781 (6)
B(8)—B(12)	1.775 (6)	B(8')—B(12')	1.784 (6)
B(9)—B(10)	1.767 (6)	B(9')—B(10')	1.783 (6)
B(9)—B(12)	1.775 (6)	B(9')—B(12')	1.794 (6)
B(10)—B(11)	1.766 (6)	B(10')—B(11')	1.754 (8)
B(10)—B(12)	1.763 (6)	B(10')—B(12')	1.781 (6)
B(11)—B(12)	1.780 (6)	B(11')—B(12')	1.783 (6)

(c) SCH<sub>2</sub>COOCH<sub>3</sub>-group distances

S—B(8)	1.925 (4)	O(1)—C(4)	1.173 (5)
S—B(8')	1.926 (4)	O(2)—C(4)	1.320 (5)
S—C(3)	1.824 (4)	O(2)—C(5)	1.453 (6)
		C(3)—C(4)	1.501 (6)

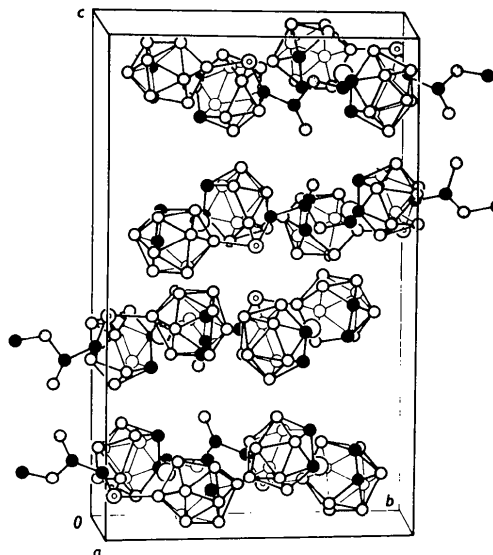


Fig. 2. Packing of the molecules within the unit cell. Large open, small open, double, dotted and filled circles represent Co, B, S, O and C atoms, respectively.

Zalkin, Hopkins & Templeton, 1967). The distances in the methoxycarbonylmethyl moiety are in good agreement with those in  $\text{CH}_3\text{COOCH}_3$  (Barrow, Scradock, Ebsworth & Rankin, 1981). The packing of the molecules within the unit cell is shown in Fig. 2.

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## Octacarbonyl-bis{ $\mu$ -[pentacarbonylrhenio(–I)]gallio(III)}-dirhenium(–II)(Re–Re)

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**Abstract.**  $[\text{Re}_2(\text{CO})_8\{\text{Ga}[\text{Re}(\text{CO})_5]_2\}]$ ,  $M_r = 1388.4$ , tetragonal,  $I4_1/a$ ,  $a = 13.894$  (4),  $c = 28.836$  (9) Å,  $U = 5566.6$  Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 3.312$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 185.7$  cm<sup>-1</sup>,  $F(000) = 4912$ ,  $T = 294$  (1) K, final  $R = 0.058$  for 1420 unique reflections. The central fragment of the molecule consists of a planar  $\text{Ga}_2\text{Re}_2$  rhombus with an Re–Re bond [ $r(\text{Re}–\text{Re}) = 3.139$  (2) Å]. The Re atoms of the two  $\text{Re}(\text{CO})_5$  ligands have a *trans* configuration with respect to the plane of the  $\text{Ga}_2\text{Re}_2$  ring. The mean value of the Ga–Re bond length is 2.589 (5) Å.

**Introduction.** In the course of our investigations on the influence of packing forces on the geometry of molecules we have prepared the compound  $\text{Re}_2(\text{CO})_8[\mu\text{-GaRe}(\text{CO})_5]_2$  and determined its crystal structure. The title substance shows a thermal cluster condensation process at 573 K  $\{2\text{Re}_2(\text{CO})_8[\mu\text{-GaRe}(\text{CO})_5]_2(s) \rightarrow \text{Re}_4(\text{CO})_{12}[\mu_3\text{-GaRe}(\text{CO})_5]_4(s) + 2(\text{CO})(g)\}$  (Haupt & Balsaa, 1985). Such a condensation of preformed clusters offers interesting synthetic possibilities to obtain a polyhedral heteronuclear metal-atom cluster with main-group metals and transition-metal carbonyls.

The analogous compound  $\text{Re}_2(\text{CO})_8[\mu\text{-InRe}(\text{CO})_5]_2$  (Preut & Haupt, 1975) does not show this expected cluster condensation. Perhaps a complete set of structural information can allow us to explain the different reaction behaviour.

**Experimental.** The yellow crystals were prepared by a reaction of  $\text{GaI}_3$  with  $\text{Re}_2(\text{CO})_{10}$  in the presence of gallium metal and xylene at 413 K for 4 d (Haupt & Balsaa, 1985). Crystal size 0.20 × 0.25 × 0.25 mm; Nonius CAD-4 diffractometer;  $\omega/2\theta$  scan, scan speed 0.74–3.33° min<sup>-1</sup> in  $\theta$ ; graphite-monochromated Mo  $K\alpha$ ; lattice parameters from least-squares fit with 25 reflections in the range  $8.0 \leq \theta \leq 17.0^\circ$ ; three standard reflections, recorded every 4 h: only random deviations measured; 2735 reflexions measured,  $1 \leq \theta \leq 25^\circ$ ,  $0 \leq h \leq 16$ ,  $0 \leq k \leq 16$ ,  $0 \leq l \leq 34$ ; after merging ( $R_{\text{int}} = 0.026$ ) 2068 unique reflections; 648 reflections considered unobserved  $I < 2\sigma(I)$ ; Lorentz-polarization correction, absorption correction *via*  $\psi$  scans, min./max. correction factor 0.76/1.00; systematic absences:  $hkl$   $h + k + l = 2n + 1$ ,  $hk0$   $h = 2n + 1$  and  $00l$   $l = 4n + 1$ ; space group  $I4_1/a$ ; structure solution with Patterson and Fourier methods