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Bis(*N*,*N*-diethyldithiocarbamato)gold(III) 3,3′-Bis(1,2-dicarbollyl)aurate, $[3,3'\text{-Au}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-[(\text{Et}_2\text{NCS}_2)_2\text{Au}]^+$

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Abstract. $C_4H_{22}AuB_{18}^-.C_{10}H_{20}AuN_2S_4^+$; monoclinic, $P2_1/c$; $a = 8{\cdot}3786\,(9)$, $b = 20{\cdot}6068\,(22)$, $c = 10{\cdot}0656\,(11)$ Å, $\beta = 105{\cdot}346\,(8)°$, $Z = 2$, $D_m = 1{\cdot}89\,(1)$, $D_x = 1{\cdot}891\,(2)$ g cm^{-3}, $\mu(\text{Mo}\,K\alpha) = 89{\cdot}7$ cm^{-1}. R was refined to 0·022 on 1486 observed reflections. While the distances of the metal ion from the C_2B_3 facial cage atoms conform to the conventional 'slipped sandwich' description, the novel distortions of the cage itself are shown to be of importance in the description of both this and related structures.

Introduction. Single-crystal X-ray studies of the electron-rich bis(dicarbollyl) complexes containing $[3,3'\text{-Cu}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^{n-}$ [Cu^{II} (d^9), $n = 2$; Cu^{III} (d^8), $n = 1$] have revealed the 'slipped sandwich' structure, the Au^{III} derivative having been shown to be isomorphous with that of Cu^{III} (Wing, 1967, 1968). The structure determination of $[(\text{C}_6\text{H}_5)_3\text{PCH}_3]^+[3,3'\text{-Cu}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-$ ($R = 0{\cdot}125$ for 1559 independent reflections estimated from Weissenberg films) by Wing (1968) did not allow the bis(dicarbollyl)Cu^{III} anion to be recognized as being significantly different from the Cu^{II} analogue [$R = 0{\cdot}091$, 2039 observed reflections, film data (Wing, 1967)], while the cage H atoms were placed in calculated positions, radially directed with B—H = 1·2 Å and C—H = 1·1 Å.

In view of the necessity to acquire accurate descriptions of both the distortions in the open C_2B_3 face and the H positions, to facilitate, for example, MO calculations as reported recently for related systems (Mingos, 1977), we have undertaken the single-crystal structure analysis of the Au^{III} complex $[3,3'\text{-Au}(1,2\text{-C}_2\text{B}_9\text{H}_{11})_2]^-[(\text{Et}_2\text{NCS}_2)_2\text{Au}]^+$. The synthesis, crystal data and some average bond lengths and angles for the C_2B_3 face and the metal–cage interactions have been given by Colquhoun, Greenhough & Wallbridge (1976).

Crystals suitable for examination were obtained by recrystallization from THF/diethyl ether. The Laue symmetry $2/m$, the systematic absences $h0l$, $l = 2n$; $0k0$, $k = 2n$ and an initial unit cell were obtained from a series of precession photographs. Accurate lattice parameters were calculated by least-squares calculations from the 2θ values of 26 reflections ($2\theta = 28$–$35°$) measured at 20°C on a Syntex $P2_1$ computer-controlled diffractometer using Mo $K\alpha$ radiation ($\lambda = 0{\cdot}70926$ Å). Intensities were measured on a crystal of approximate axial dimensions $0{\cdot}18 \times 0{\cdot}12 \times 0{\cdot}22$ mm using the θ–2θ scan technique out to $2\theta = 51°$. 1621 observations included 1486 independent intensities with $I > 3\sigma(I)$ (variances based on counting statistics) which were classified as observed. Three standard reflections measured periodically during the data collection showed no significant change in intensity. Lorentz and polarization corrections were carried out. Morphological examination of the crystal revealed the bounding planes to be {100} and {111}, accurate measurements of the interplanar distances being used in a local version of *ABSCOR* (Alcock, 1970) where the analytical absorption correction gave maximum and minimum transmission factors for the correction of $|F_o|$ of 0·786 (10,0,0) and 0·718 (020).

A very marked tendency for reflections with h, k and l all odd or even to be of high intensity led to the two independent Au atoms being placed on centres of symmetry at 0,0,0 and $\frac{1}{2}$,0,$\frac{1}{2}$. Chemically satisfactory positions for the S atoms were found from a Fourier synthesis phased on the Au atoms. The expected

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symmetry complications caused only minor difficulties. Full-matrix least-squares refinement of the Au and S atoms with anisotropic temperature factors allowed the remaining non-hydrogen atoms to be located from a Fourier synthesis. The scattering factors were taken from Cromer & Mann (1968). Least-squares refinement of all the non-hydrogen atoms gave $R = 0{\cdot}032$ ($R = \Sigma\,|\Delta F_o|/\Sigma\,|F_o|$) using anisotropic temperature factors, unit weights, the anomalous scattering components given by Cromer & Liberman (1970) for Au and S, and an extinction parameter r^* (Larson, 1970). The H atoms were located from a difference Fourier map, and were assigned isotropic temperature factors; their scattering factors were taken from Stewart, Davidson & Simpson (1965). All parameters except the H temperature factors were refined in the final cycles of least squares which gave the final R index 0·022, the function minimized being $\Sigma\,w(|F_o| - |F_c|)^2$ with $w = 1/[\sigma(F_o)^2 + 0{\cdot}02|F_o| + 0{\cdot}00005(|F_o|)^2]$: weighting analyses confirmed the suitability of this function. The final value of $R_w = [\Sigma\,w(|F_o| - |F_c|)^2/\Sigma\,wF_o^2]^{1/2}$ was 0·024, and the standard deviation of an observation of unit weight $\sigma_1 = [\Sigma\,w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ was

Table 1. *Atomic coordinates with e.s.d.'s in parentheses*

	x	*y*	*z*
Au(1)	0	0	0
Au(2)	$\frac{1}{2}$	0	$\frac{1}{2}$
S(1)	0·5583 (3)	0·1080 (1)	0·5647 (3)
S(2)	0·7288 (3)	0·0266 (1)	0·4206 (2)
N	0·7847 (8)	0·1547 (3)	0·4486 (7)
C(21)	0·7060 (9)	0·1057 (4)	0·4759 (8)
C(22)	0·9171 (10)	0·1482 (4)	0·3758 (9)
C(23)	0·7463 (11)	0·2225 (5)	0·4843 (9)
C(24)	0·6459 (12)	0·2591 (5)	0·3609 (11)
C(25)	1·0863 (11)	0·1480 (5)	0·4743 (11)
C(2)	0·3195 (9)	0·0465 (4)	0·0887 (9)
C(3)	0·2802 (10)	0·0465 (4)	−0·0658 (8)
B(4)	0·0787 (11)	0·0737 (5)	−0·1383 (9)
B(5)	−0·0053 (13)	0·1069 (5)	−0·0022 (11)
B(6)	0·1493 (12)	0·0751 (5)	0·1431 (10)
B(7)	0·4247 (11)	0·1011 (5)	0·0169 (11)
B(8)	0·2652 (12)	0·1184 (5)	−0·1360 (11)
B(9)	0·0986 (12)	0·1585 (5)	−0·0908 (10)
B(10)	0·1461 (13)	0·1594 (5)	0·0924 (11)
B(11)	0·3399 (11)	0·1200 (5)	0·1540 (10)
B(12)	0·3076 (13)	0·1730 (5)	0·0110 (12)

Table 2. *Hydrogen positional coordinates and assigned thermal parameters* (× 10²)

	x	*y*	*z*	*U*(Å²)
H(221)	0·915 (8)	0·104 (4)	0·332 (7)	5·95
H(222)	0·908 (9)	0·186 (4)	0·316 (7)	5·95
H(231)	0·703 (10)	0·219 (4)	0·563 (8)	7·85
H(232)	0·847 (10)	0·240 (4)	0·521 (8)	7·85
H(241)	0·611 (10)	0·289 (4)	0·393 (8)	7·60
H(242)	0·700 (10)	0·263 (4)	0·287 (8)	7·60
H(243)	0·543 (10)	0·231 (4)	0·337 (8)	7·60
H(251)	1·077 (9)	0·111 (4)	0·520 (7)	7·09
H(252)	1·096 (9)	0·190 (4)	0·503 (8)	7·09
H(253)	1·180 (11)	0·147 (4)	0·437 (9)	7·09
H(2)	0·367 (9)	0·007 (3)	0·126 (7)	5·32
H(3)	0·311 (8)	0·006 (3)	−0·103 (7)	4·81
H(4)	0·030 (8)	0·062 (3)	−0·240 (7)	4·69
H(5)	−0·160 (8)	0·114 (3)	−0·021 (7)	5·19
H(6)	0·155 (9)	0·062 (4)	0·255 (7)	6·21
H(7)	0·544 (8)	0·101 (4)	0·027 (7)	5·32
H(8)	0·296 (8)	0·127 (4)	−0·237 (6)	5·83
H(9)	0·036 (9)	0·198 (3)	−0·143 (7)	6·08
H(10)	0·105 (9)	0·196 (4)	0·143 (7)	6·46
H(11)	0·419 (8)	0·126 (4)	0·260 (7)	6·59
H(12)	0·364 (9)	0·217 (4)	0·008 (7)	5·83

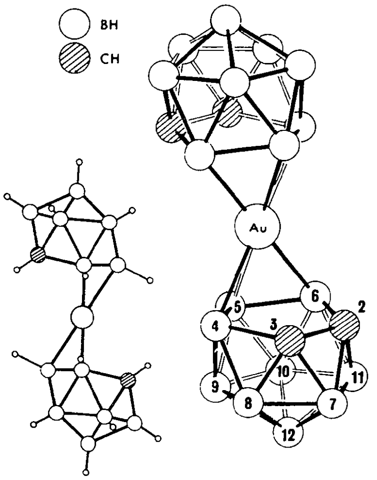

Fig. 1. Molecular structure of the $\text{Au}(\text{C}_2\text{B}_9\text{H}_{11})_2^-$ anion. H atoms are omitted for clarity. A projection of the anion, parallel to the cage C—C bonds, is shown in the inset.

Table 3. *Bond distances* (Å) *for* $\text{Au}(\text{C}_2\text{B}_9\text{H}_{11})_2^-$ *with e.s.d.'s in parentheses*

Au(1)–C(2)	2·760 (7)	B(7)–B(12)	1·768 (15)
Au(1)–C(3)	2·774 (9)	B(8)–B(12)	1·817 (15)
Au(1)–B(4)	2·273 (10)	B(9)–B(12)	1·804 (13)
Au(1)–B(5)	2·204 (11)	B(10)–B(12)	1·781 (18)
Au(1)–B(6)	2·254 (9)	B(11)–B(12)	1·770 (15)
		B(7)–B(8)	1·787 (13)
C(2)–C(3)	1·502 (12)	B(7)–B(11)	1·755 (16)
C(2)–B(6)	1·759 (12)	B(8)–B(9)	1·782 (15)
C(3)–B(4)	1·745 (12)	B(10)–B(11)	1·774 (14)
B(4)–B(5)	1·831 (16)	B(9)–B(10)	1·781 (15)
B(4)–B(6)	1·801 (13)		
		C(2)–H(2)	0·93 (6)
C(2)–B(7)	1·703 (12)	C(3)–H(3)	0·97 (7)
C(3)–B(7)	1·701 (12)	B(4)–H(4)	1·03 (6)
C(2)–B(11)	1·642 (13)	B(5)–H(5)	1·27 (7)
C(3)–B(8)	1·632 (13)	B(6)–H(6)	1·14 (7)
B(4)–B(8)	1·809 (14)	B(7)–H(7)	0·98 (7)
B(4)–B(9)	1·807 (14)	B(8)–H(8)	1·13 (7)
B(5)–B(9)	1·758 (16)	B(9)–H(9)	1·14 (7)
B(5)–B(10)	1·744 (14)	B(10)–H(10)	0·93 (6)
B(6)–B(10)	1·809 (14)	B(11)–H(11)	0·97 (7)
B(6)–B(11)	1·823 (14)	B(12)–H(12)	1·04 (8)

1·02 for $m = 1486$ and $n = 249$. The final positional parameters for the non-hydrogen atoms are given in Table 1. H atom coordinates and assigned values of U are given in Table 2.*

Discussion. Bond distances in the anion are given in Table 3, according to the atomic labels shown in Fig. 1 (*cf.* Wing, 1967, 1968). Bond angles for the anion and bond distances and angles for the cation, whose geometry is normal as compared with that of other thiocarbamates (Willemse, Cras, Steggerda & Keijzers, 1976), are available.* In view of the large standard deviations on the bond lengths in the bis(dicarbollyl)Cu^{III} anion (Wing, 1968), a comparison with the bond lengths in the present structure is not justified. In the case of the bis(dicarbollyl)Cu^{II} anion (Wing, 1967), however, there appear to be significant differences from the present structure, although the bond-length standard deviations (0·01 Å) for the former structure may have been underestimated. The C—B bond lengths in the C_2B_3 face here are 1·759 (12) and 1·745 (12) Å, whereas in the Cu^{II} analogue they are 1·71 (1) and 1·67 (1) Å (Wing, 1967). The other C—B bonds in the cage are all shorter here than in the Cu^{II} bis(dicarbollyl) (Wing, 1967) being 1·703 (12), 1·701 (12) Å and 1·632 (13), 1·642 (13) Å here, and 1·74 (1), 1·76 (1) Å and 1·71 (1), 1·71 (1) Å for the Cu^{II} analogue (Wing, 1967).

Some best least-squares planes are given in Table 4, showing dihedral angles of 166° [C_2B_2 (plane 2)–B_3 (plane 1)] and 172° [B_4 (plane 4)–B_3 (plane 3)]. These distortions may be clearly seen in the inset to Fig. 1. The corresponding angles in the Cu^{II} analogue are 172 and 176° respectively.

While large variations of the cage C—C bond distance in 1,2-C_2B_9 metal dicarbollyls have previously been recognized (Wing, 1968) {values of *ca* 1·6 Å for symmetrical structures such as $[C_2B_9H_{11}Re(CO)_3]^-$ (Zalkin, Hopkins & Templeton, 1966) being compared with values of *ca* 1·5 Å for distorted structures}, sufficient attention has not been drawn to the distinct non-planarity of the C_2B_3 face which occurs when a symmetrically bonded structure is not adopted. Indeed, this non-planarity has not previously been evaluated in terms of the dihedral angles given above. Further, in going from $[C_2B_9H_{11}Re(CO)_3]^-$ (Zalkin, Hopkins & Templeton, 1966) to the distorted d^8 complex described here, the cage distortions also include a shortening of the C(2)—B(11), C(3)—B(8) distances from 1·74 (1), 1·72 (1) Å, a lengthening of the C—B facial bond lengths from 1·71 (1), 1·71 (1) Å, a shortening of the B(5)—B(9),B(10) distances from 1·80 (1), 1·80 (1) Å and a narrowing of the facial B—B—B angle from 106 to 97·8 (7)°.

Using the mean C_2B_3 plane and describing the metal-cage interaction in terms of 'slip' from a centroid (Wing, 1967) give a value of 0·7 Å for the present structure. However, using 'slip' to describe the deviations from the symmetrically bonded case gives no indication of the significant differences between the C_2B_9 frameworks in the two types of structure, and these additional distortions must be accounted for in any rationalization of the bonding in bis(dicarbollyl) complexes. It is emphasized that a full description of this and related structures is only possible in terms of distances of the metal from the facial B and C atoms, *and* the distortions within the cage.

It is interesting to note that, despite the large deviations from icosahedral geometry, the cage H atoms remain approximately radially directed. There are no (non-H) intramolecular contacts of less than 3·5 Å.

Table 4. *Some best least-squares planes and atom deviations* (Å) *in the* Au^{III} *bis(dicarbollyl) anion* (C *and* B *unit weight,* Au *and* H *zero weight*)

Plane 1		Plane 2		Plane 3		Plane 4	
B(4)	0·000	B(6)	−0·003	B(11)	0·000	B(8)	0·002
B(5)	0·000	C(2)	0·005	B(7)	0·000	B(9)	−0·004
B(6)	0·000	C(3)	−0·005	B(8)	0·000	B(10)	0·004
H(4)	0·305	B(4)	0·003	H(11)	−0·253	B(11)	−0·002
H(5)	0·584	H(6)	0·314	H(7)	−0·337	H(8)	−0·396
H(6)	0·328	H(2)	0·653	H(8)	−0·344	H(9)	−0·514
Au(1)	1·801	H(3)	0·652	Au(1)	3·177	H(10)	−0·438
		H(4)	0·295			H(11)	−0·305
		Au(1)	1·769			Au(1)	3·363

Angles between the planes

1–2	166·4°	3–4	171·6°
1–3	166·2	2–4	171·7
1–4	174·6	2–3	179·6

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* Lists of structure factors, anisotropic thermal parameters, bond angles for the anion, and distances and angles for the cation have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32865 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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Refinement of Aluminium Orthoborate

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Abstract. $AlBO_3$, high-pressure phase, calcite-like structure, trigonal, $R\bar{3}c$, $a = 4{\cdot}4638\ (3)$, $c = 13{\cdot}745\ (1)$ Å, $Z = 6$, $D_x = 3{\cdot}60$ g cm^{-3}, $\mu_{\text{Mo}} = 8{\cdot}66$ cm^{-1}. The B–O bond length is 1·3796 (4) Å. The six crystallographically equivalent Al–O distances are 1·9230 (4) Å. The oxygen arrangement is closer to hexagonal close packing than in the isostructural $NaNO_3$ and $CaCO_3$.

Introduction. The growth of $AlBO_3$ single crystals was achieved under hydrothermal conditions at high pressure. Details of this synthesis have been published by Capponi (1973), whom we thank for providing the crystals. The crystal selected was a rhombohedron whose edge measured about 0·2 mm. Intensities for 1504 reflections were measured within a hemisphere, up to $\theta = 50°$ with monochromated Mo $K\alpha$ radiation. The moduli of 288 averaged independent reflections were used in the refinement. Of these, 278 were significant and 10 were considered as unobserved by the criterion $I \leq 3\sigma(I)$.

The scattering factors were from *International Tables for X-ray Crystallography* (1974) for Al, Al^{3+}, O, O^- and B. Most of the calculations were made with the XRAY system (Stewart, Kundell & Baldwin, 1970).

Least-squares refinement on F was started from the parameters reported by Abrahams, Bernstein & Keve (1971) for $LuBO_3$. The structure was refined assuming two models: the first with neutral atoms and the second

Table 1. *Final R values and atomic parameters with their standard deviations*

The U_{ij} ($\times 10^5$) conform to the expression $[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^* + \cdots)]$. The symmetry requirements are: for B and Al, $U_{11} = U_{22} = 2U_{12}$, $U_{13} = U_{23} = 0$; for O, $U_{11} = U_{12} = 2U_{12}$, $U_{13} = \frac{1}{2}U_{23}$. Al and B occupy the special positions (0,0,0) and $(0,0,\frac{1}{4})$ respectively. O is located at $(x,0,\frac{1}{4})$.

	0–50° B, Al, O	0–50° B, Al^{3+}, O^-	0–30° B, Al, O	0–30° B, Al^{3+}, O^-	30–50° B, Al, O	30–50° B, Al^{3+}, O^-
R (%)	1·5	1·6	1·6	1·7	1·2	1·2
R_w (%)	1·6	1·8	1·6	1·6	1·2	1·2
x(O)	0·69093 (6)	0·69095 (6)	0·69096 (13)	0·69064 (13)	0·69098 (5)	0·69099 (5)
U_{33} (O)	420 (9)	427 (10)	352 (20)	404 (25)	449 (9)	458 (9)
U_{12} (O)	148 (3)	150 (4)	136 (8)	145 (9)	156 (4)	160 (4)
U_{13} (O)	−33 (2)	−33 (3)	−36 (7)	−39 (8)	−30 (2)	−30 (2)
U_{33} (Al)	318 (8)	313 (9)	262 (21)	266 (26)	332 (9)	333 (9)
U_{12} (Al)	145 (3)	143 (4)	135 (7)	148 (8)	153 (4)	154 (4)
U_{33} (B)	428 (17)	436 (18)	355 (60)	301 (63)	455 (16)	465 (16)
U_{12} (B)	163 (6)	165 (6)	167 (17)	216 (19)	168 (6)	173 (5)