

[(2-3)Pentaboran(9)yl](triphenylphosphine)gold(I), [Au(B₅H₈)(C₁₈H₁₅P)]

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Abstract. $M_r = 432.3$, triclinic, $P\bar{1}$; at 289 K: $a = 8.742$ (2), $b = 11.265$ (2), $c = 11.581$ (3) Å, $\alpha = 104.74$ (2), $\beta = 69.73$ (2), $\gamma = 95.23$ (2)°, $V = 1034.5$ (4) Å³; at 173 K: $a = 8.693$ (2), $b = 11.187$ (2), $c = 11.573$ (3) Å, $\alpha = 104.78$ (2), $\beta = 69.61$ (2), $\gamma = 95.32$ (2)°, $V = 1019.9$ (4) Å³; $Z = 2$, $D_x = 1.39$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 71.6$ cm⁻¹, $F(000) = 500$, final $R = 0.038$, $wR = 0.042$ for 3613 independent reflections [$I/\sigma(I) > 3.0$] measured at 289 K. The Au is attached to two basal B atoms of the square-pyramidal B₅H₈ cage; Au–B 2.269 (12), 2.281 (8) Å; B–B 1.647 (15)–1.782 (13) Å. The Au atom is virtually coplanar with the B(1), B(2), B(3) face {dihedral angle [B(1)–B(3)]–[Au–B(2)–B(3)] 175.1 (2)°}.

Introduction. It is well known that pentaborane(9), B₅H₉, can be deprotonated with bases such as the hydride ion to yield the B₅H₈⁻ anion (Gaines, 1973, and references therein). Reaction of this species with metal halide derivatives leads to complexes where the metal is often inserted into the B₅ framework system (Greenwood & Kennedy, 1982). In spite of the many metal derivatives reported there is still some uncertainty about their relative stabilities, and an order has been suggested as Ni > Pd > Pt and Cu > Ag >> Au (Greenwood & Kennedy, 1982; Greenwood & Staves, 1978). Indeed, it has been reported that the Au compound [Au(B₅H₈)(PPh₃)] (I) is unstable at 195 K and cannot be isolated (Greenwood & Staves, 1978). We have modified the preparative route to this compound, and have obtained a crystalline sample of (I).

Experimental. Pentaborane(9) (2.2 mmol) was distilled *in vacuo* into an ethereal solution (30 cm³) of methyl-lithium (2.7 cm³, 2.2 mmol) at 77 K. On warming to room temperature methane (2.0 mmol) was evolved, and LiB₅H₈ remained in the ethereal solution. To this solution at 198 K was added [Au(PPh₃)NO₃] (1.15 g, 2.2 mmol), and the mixture allowed to warm to room temperature with stirring. After 24 h the colourless precipitate was filtered off and, after concentration of the red filtrate, it was allowed to stand at 273 K. The pale-red solid which deposited from the solution was recrystallized from CH₂Cl₂/Et₂O to yield pale-red

crystals (0.44 g, 38%). Analysis: found: C, 41.0; H, 4.1%. AuB₅C₁₈H₂₃P requires C, 41.4; H, 4.4%. The 28.9 MHz ¹¹B NMR spectrum (CDCl₃ solution) of the product showed only two resonances at -12.4 (intensity 4) and -46.7 (intensity 1) with $J_{11\text{B-H}}$ values of 140 and 170 Hz respectively. The absence of any resolution of the low-field signal (intensity 4) on decoupling indicates either that the system is fluxional on the ¹¹B NMR time scale, or that the two sets of two basal B atoms possess essentially identical chemical-shift values. After standing for several days, in the absence of light, other signals are observed in the spectrum, and the solution darkens considerably. The infrared spectrum of (I) shows absorptions, due to the B–H bonds, at 2575, 2525 and 2480 cm⁻¹, as well as the expected bands from the triphenylphosphine ligand at 1090, 870, 700 and 680 cm⁻¹.

Crystal character: needles. D_m not determined. Data collected with a Syntex P2₁ four-circle diffractometer. Max. $2\theta = 50^\circ$; scan range $\pm 1.0^\circ$ (2θ) around the $K\alpha_1$ – $K\alpha_2$ angles; scan speed 1–29° min⁻¹, depending on the intensity of a 2 s pre-scan; backgrounds measured at each end of the scan for 0.25 of the scan time. h 0→7, k -13→13, l -12→12. Three standard reflections monitored every 100 reflections, no significant changes during data collection. Unit-cell dimensions and standard deviations obtained by least-squares fit to 15 high-angle reflections. 3613 observed reflections [$I/\sigma(I) > 3.0$] used in refinement, corrections for Lorentz, polarization and absorption effects, the last with *ABSCOR* (Alcock, 1970) (max. and min. transmission factors 0.37 and 0.16). Crystal dimensions 0.80 × 0.27 × 0.35 mm. No systematic absences, space group $P\bar{1}$ assumed. Structure solved by Patterson and Fourier techniques. All non-H atoms refined on F with anisotropic temperature factors; phenyl H atoms in calculated positions, not refined; borane H atoms located on a difference synthesis and refined. Empirical weighting scheme, down-weighting reflections of low $\sin\theta$ and high F , shown to be satisfactory by a weight analysis. $(\Delta/\sigma)_{\text{max}} = 2.1$ (H parameter). $\Delta\rho_{\text{max}} = 1.7 \text{ e } \text{Å}^{-3}$. Computing with the *XRAY76* system (Stewart, 1976), on a Burroughs B6700 computer. No correction for secondary extinction. Scattering factors in the analytical form and anomalous-dispersion factors taken from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic coordinates are given in Table 1, and bond lengths and angles in Table 2.*

* Lists of structure factors, anisotropic thermal parameters and calculated H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39986 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	x	y	z	U_{eq}
Au	3467.6 (3)	2575.0 (3)	543.8 (2)	50
P	3629 (2)	2813 (2)	-1415 (1)	43
B(1)	3130 (9)	1827 (8)	3396 (8)	64
B(2)	3754 (11)	1412 (8)	1793 (9)	64
B(3)	2631 (13)	2783 (9)	2682 (7)	61
B(4)	4026 (12)	3180 (11)	3561 (9)	84
B(5)	5132 (14)	1807 (13)	2684 (11)	97
C(11)	5708 (8)	2845 (6)	-2476 (6)	43
C(12)	6188 (10)	3570 (8)	-3346 (9)	64
C(13)	7812 (10)	3594 (9)	-4133 (9)	70
C(14)	8931 (9)	2901 (9)	-4024 (9)	63
C(15)	8489 (11)	2165 (10)	-3209 (9)	75
C(16)	6871 (11)	2130 (8)	-2425 (8)	67
C(21)	2656 (8)	1508 (6)	-2179 (6)	43
C(22)	1297 (9)	990 (7)	-1414 (7)	52
C(23)	507 (10)	6 (8)	-1955 (9)	66
C(24)	1056 (11)	-473 (8)	-3242 (9)	67
C(25)	2388 (10)	35 (7)	-4000 (7)	59
C(26)	3182 (9)	1021 (7)	-3479 (7)	54
C(31)	2647 (8)	4167 (6)	-1407 (6)	42
C(32)	2573 (9)	5224 (7)	-473 (7)	54
C(33)	1857 (11)	6272 (8)	-465 (8)	63
C(34)	1173 (10)	6265 (8)	-1361 (9)	62
C(35)	1224 (11)	5227 (8)	-2289 (8)	70
C(36)	1956 (10)	4168 (7)	-2317 (7)	56
H(1)	2418 (113)	1331 (83)	4075 (90)	100 (28)
H(2)	3681 (95)	490 (70)	1051 (75)	71 (22)
H(3)	1443 (55)	3268 (41)	2958 (43)	29 (11)
H(4)	4071 (130)	3842 (96)	4373 (104)	130 (33)
H(5)	6140 (117)	1396 (88)	2855 (93)	105 (29)
H(25)	5093 (145)	1450 (107)	1377 (113)	125 (38)
H(34)	3487 (100)	3728 (74)	2836 (79)	77 (23)
H(45)	5307 (116)	2958 (86)	2858 (92)	90 (29)

Table 2. Principal bond lengths (\AA) and angles ($^\circ$)

Au—P	2.306 (2)	Au—P—C(11)	112.9 (3)
P—C(11)	1.811 (6)	Au—P—C(21)	109.1 (2)
P—C(21)	1.816 (7)	Au—P—C(31)	115.8 (2)
P—C(31)	1.814 (8)	B(2)—Au—B(3)	46.1 (3)
Au—B(2)	2.269 (12)	B(2)—Au—P	150.8 (2)
Au—B(3)	2.281 (8)	B(3)—Au—P	161.2 (3)
B(1)—B(2)	1.692 (13)	B(2)—B(1)—B(3)	63.8 (6)
B(1)—B(3)	1.680 (16)	B(2)—B(1)—B(4)	98.4 (6)
B(1)—B(4)	1.647 (15)	B(2)—B(4)—B(5)	65.1 (6)
B(1)—B(5)	1.656 (13)	B(3)—B(1)—B(4)	65.6 (7)
B(2)—B(3)	1.782 (13)	B(3)—B(1)—B(5)	99.0 (8)
B(2)—B(5)	1.801 (18)	B(4)—B(1)—B(5)	65.0 (7)
B(3)—B(4)	1.803 (17)	B(1)—B(2)—B(3)	57.8 (5)
B(4)—B(5)	1.776 (17)	B(1)—B(2)—B(5)	56.5 (6)
H(1)—B(1)	1.07 (10)	B(3)—B(2)—B(5)	90.1 (7)
H(2)—B(2)	1.18 (7)	B(1)—B(3)—B(2)	58.4 (6)
H(3)—B(3)	1.12 (5)	B(1)—B(3)—B(4)	56.3 (6)
H(4)—B(4)	1.05 (11)	B(2)—B(3)—B(4)	89.7 (7)
H(5)—B(5)	1.13 (12)	B(1)—B(4)—B(3)	58.1 (6)
H(25)—B(2)	1.10 (12)	B(1)—B(4)—B(5)	57.7 (6)
H(25)—B(5)	1.48 (13)	B(3)—B(4)—B(5)	90.2 (7)
H(34)—B(3)	1.26 (8)	B(1)—B(5)—B(2)	58.4 (6)
H(34)—B(4)	1.38 (11)	B(1)—B(5)—B(4)	57.2 (6)
H(45)—B(4)	1.14 (8)	B(2)—B(5)—B(4)	89.9 (8)
H(45)—B(5)	1.26 (10)		

The structure (Fig. 1) shows that the Au atom forms a three-centre bond to two of the basal B atoms, replacing a bridging H of the parent B_5H_9 . This is closely similar to the only comparable structure, that of $[(Ph_3P)_2CuB_5H_8]$ (Greenwood, Howard & McDonald, 1977). The B_5 cage is virtually undistorted by the substitution of Au for H; the basal B—B distances are identical to within one standard deviation [average 1.791 (8) \AA], but the apex—base distances are just perceptibly lengthened on the side to which the Au is bound, average 1.686 (10) \AA , compared to 1.652 (10) \AA . The Cu compound appears to show a similar distortion, but its significance is obscured by the larger errors. The Au—B distances [average 2.276 (8) \AA] are indistinguishable from those in the three other known structures containing Au—B bonds [average 2.24 (4) \AA] (Colquhoun, Greenough & Wallbridge, 1977, 1978; Barker, Godfrey, Green, Parge, Stone & Welch, 1983). As in the Cu compound, the Au atom is virtually coplanar with the B(1), B(2), B(3) face {dihedral angle $[B(1)—B(3)]—[Au—B(2)—B(3)]$ 175.1 (2) $^\circ$ }.

Perhaps the most intriguing comparison between the title compound and the related Cu compound is in the stoichiometry. The $B_5H_8^-$ ion behaves as a two-electron donor to the metal atom, and thus in $[(Ph_3P)_2CuB_5H_8]$ the Cu^I is a 16-electron species. However, in $[(Ph_3P)AuB_5H_8]$, the Au^I has only 14 electrons. In view of the identical B_5 cage geometries, this difference shows very clearly that the metal cannot be treated as part of the borane cage. Therefore it would be reasonable to regard the stoichiometry of the Au compound to be related to the well known tendency of Au^I to assume linear coordination, compared with the situation in Cu^I compounds where trigonal or tetrahedral geometry is more commonly observed.

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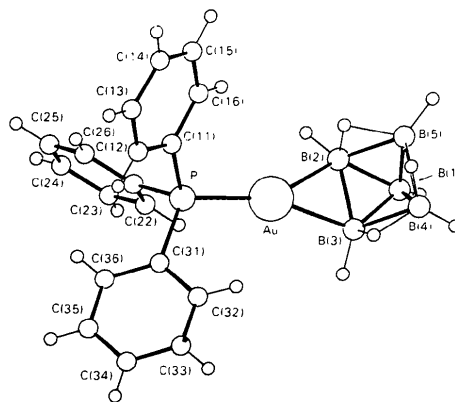


Fig. 1. View of the molecule showing the atomic numbering. H atoms are numbered to correspond to the atom to which they are attached, with H(24), H(35) and H(45) as the three bridging atoms of the B_5H_8 cage.

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Bis[*N*¹-(2-pyrimidinyl)sulphanilamido]zinc–Ammonia (1/2),* [Zn(C₁₀H₉N₄O₂S)₂].2NH₃

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Abstract. $M_r = 597.98$, orthorhombic, $Pn2_1a$ (non-standard setting of $Pna2_1$), $a = 13.887(4)$, $b = 14.217(4)$, $c = 12.603(4)$ Å, $V = 2488.23$ Å³, $Z = 4$, $D_m = 1.62(1)$, $D_x = 1.596$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 1.23$ mm⁻¹, $F(000) = 1232$, $T = 294$ K, $R = 0.041$ for 2407 observed diffractometer reflexions [$I > \sigma(I)$]. The Zn atom is coordinated tetrahedrally to four N atoms, one from each of the two sulphadiazine molecules and two of the ammonias of crystallization. The two rings of each molecule are inclined to each other at +95.71(5) and +85.57(5)°, and are linked to each other and to the two ammonia molecules by a three-dimensional system of hydrogen bonds, of lengths between 2.833 and 3.194(10) Å. Bond lengths and interbond angles are within the usual range.

Introduction. The title compound is one of a series of sulphonamides which have been investigated for the treatment and control of infection in burns. The structures of silver sulphadiazine (Cook & Turner, 1975), [*N*¹-(3-pyridyl)sulphanilamido]silver (Cook & Turner, 1976) and *N*¹-phenylsulphanilamide (Brown, Cook & Sengier, 1984) have already been published from these laboratories, and an extensive literature on the crystal structures of sulpha drugs has appeared in recent years. This investigation was undertaken to determine the coordination of the Zn atom and to

ascertain the role of the NH₃ of crystallization in the molecular structural arrangement.

Experimental. Samples supplied by both Professor C. L. Fox of Columbia University, New York, and by Smith & Nephew Ltd, Harlow, Essex; m.p. 509 K (dec.); analysis gave Zn 10.96, C 39.59, H 4.03, N 23.17% (required for C₂₀H₂₄N₁₀O₄S₂Zn: Zn 10.93, C 40.17, H 4.05, N 23.42%). White needle-shaped crystals ca 0.1 × 0.1 × 0.8 mm from 10% ammonia solution in the dark. D_m by flotation in NaI solution. Lattice parameters initially from rotation photographs, subsequently refined on the diffractometer. Intensities measured on CAD-4 diffractometer with Mo $K\alpha$ radiation; $2\theta_{\max} = 54^\circ$, index range h 0→17, k 0→18, l 0→16; 2 standard reflexions, no variation; 2814 observed reflexions, 407 of which with $I < \sigma(I)$; corrections for Lp but not for absorption or extinction; structure solved by Patterson synthesis followed by successive Fourier syntheses; refinement by least squares on F using NRC programs (Ahmed, Hall, Pippy & Huber, 1970) on our DEC-20 computer; NH₃ molecules from difference Fourier map, other H atoms by calculation by bisecting bond angles or on direct line of H bonds where appropriate; H used in F calculations with $B_{\text{iso}} = 7.0$ Å² but not refined; non-H atoms refined using B_{iso} initially and finally B_{ij} until all shifts $< 0.2\sigma$; residual $\Delta\rho$ in final difference Fourier synthesis within $0.2 e \text{ \AA}^{-3}$ (except +0.9 at Zn and +0.5 $e \text{ \AA}^{-3}$ at S atoms); scattering factors from *International Tables for X-ray Crystallography* (1974); $R = 0.041$, $wR = 0.094$, $\sqrt{w} = 1/F_o$.

* Bis[4-amino-*N*-(2-pyrimidinyl)benzenesulphonamido]zinc–ammonia (1/2); zinc sulphadiazine–ammonia (1/2).