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(2,9-Dimethyl-1,10-phenanthroline)tetrahydroboratocopper(I)*

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Abstract. $[Cu(BH_4)(C_{14}H_{12}N_2)]$, $C_{14}H_{16}BCuN_2$, orthorhombic, *Pnma*, $a = 18{\cdot}761$ (11), $b = 6{\cdot}799$ (3), $c = 10{\cdot}489$ (5) Å, $M_r = 286{\cdot}6$, $Z = 4$, $D_x = 1{\cdot}42$ (3) Mg m^{-3}, μ(Mo $K\alpha$) = 1·68 mm^{-1}, $R = 0{\cdot}062$, 656 observed reflexions. Cu^I has distorted tetrahedral stereochemistry and is coordinated to two bidentate ligands, 2,9-dimethyl-1,10-phenanthroline [Cu—N 2·023 (9), 2·049 (8) Å; N—Cu—N 81·8 (3)°] and BH_4 [Cu—H 1·58 (5) Å; H—Cu—H′ 77 (2)°]. The Cu—B distance is short at 2·08 (2) Å. The molecule, Cu(dmp)(BH_4), possesses *m* point symmetry with Cu, B, and the dmp ligand in the crystallographic mirror planes at $y = \frac{1}{4}, \frac{3}{4}$. The molecules are stacked perpendicular to the *b* axis with 3·40 Å separation.

Introduction. The title compound, Cu(dmp)BH_4, was prepared by the method of Green, Hawkins, James & Payne (1980) and recrystallized as orange air-stable crystals from methylene chloride. The structure was determined by X-ray diffraction. A total of 656 reflections with $I > 2\sigma(I)$ were considered observed out of 1075 in a unique set collected from one crystal (0·12 × 0·12 × 0·18 mm) mounted on a Syntex $P2_1$ four-circle diffractometer ($2\theta_{max} = 50°$, graphite-monochromated Mo $K\alpha$ radiation). No corrections were made for absorption or extinction.

The structure was solved by multisolution Σ_2 sign expansion (Sheldrick, 1976). Full-matrix least-squares refinement, with all non-hydrogen atoms having anisotropic temperature factors, reduced R $[= \sum ||F_o| - |F_c||/\sum |F_o|]$ from an initial value of 0·447 to 0·062 and R_w $[= \sum w||F_o| - |F_c||^2/\sum w|F_o|^2)^{1/2}]$ to 0·057 with $w = 1{\cdot}856/[\sigma^2(F_o) + 0{\cdot}000484F_o^2]$. The H atoms were located in a difference-Fourier synthesis and were included in the refinement at fixed positions with the exception of those of the BH_4 group which were allowed to refine. All the H atoms were assigned isotropic thermal parameters set invariant at $U = 0{\cdot}05$ Å^2. A final difference-Fourier synthesis revealed no features larger than 0·12 e Å^{-3}. Atomic positional parameters are listed in Table 1.‡

Table 1. *Fractional atomic coordinates* (×10^4) *with estimated standard deviations* (*in parentheses*)

(a) Atoms on the mirror plane, $y = \frac{1}{4}$

	x	z		x	z
Cu	6105 (1)	2017 (2)	C(14)	5718 (7)	−594 (12)
N(1)	5077 (5)	1352 (10)	C(21)	4460 (7)	3374 (11)
C(2)	4464 (7)	1977 (15)	C(91)	7587 (6)	343 (14)
C(3)	3813 (8)	1341 (16)	B	6569 (9)	3817 (18)
C(4)	3796 (8)	55 (16)	H(B2)	6245 (50)	4444 (95)
C(5)	4462 (7)	−2007 (16)	H(B3)	6978 (52)	4039 (102)
C(6)	5077 (9)	−2646 (14)	H(3)	3440	1906
C(7)	6396 (9)	−2499 (14)	H(4)	3357	−567
C(8)	7003 (8)	−1775 (16)	H(5)	4031	−2320
C(9)	6939 (7)	−437 (13)	H(6)	5073	−3868
N(10)	6322 (5)	128 (10)	H(7)	6434	6492
C(11)	5046 (7)	48 (13)	H(8)	7472	−2397
C(12)	4420 (7)	−650 (15)	H(912)	7729	848
C(13)	5725 (8)	−1924 (12)	H(212)	4870	4062

(b) Atoms in general positions

	x	y	z
H(B1)	6391 (27)	3943 (91)	3080 (60)
H(911)	7901	3944	130
H(211)	4538	1360	3828

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‡ Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35300 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* Stereochemistry of Rigid Chelate–Metal Complexes. V. Part IV: Smith, O'Reilly, Kennard & White (1977).

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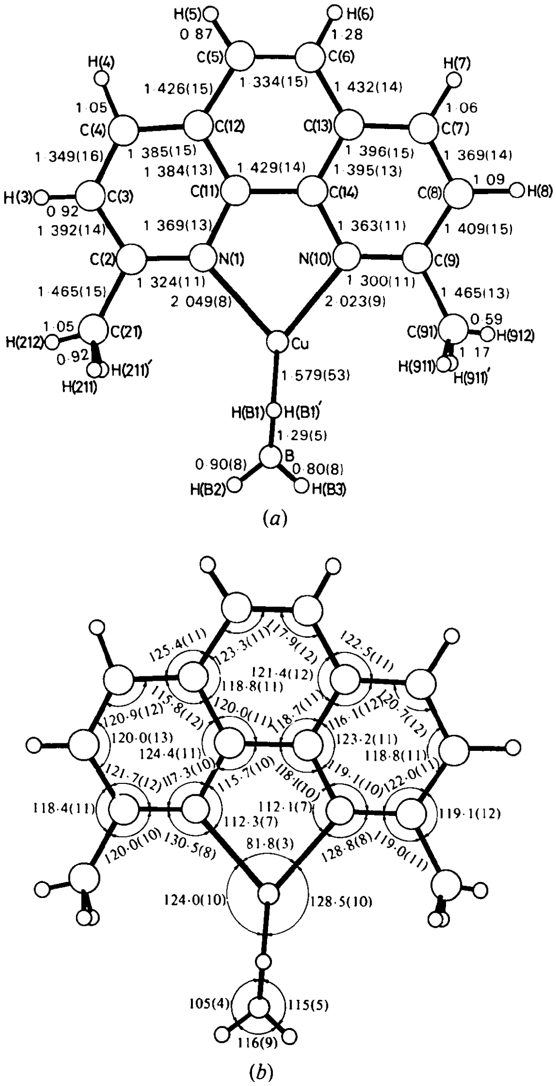
Discussion. With four molecules of $Cu(dmp)(BH_4)$ per unit cell, the Cu, B and dmp are confined to the crystallographic mirror planes at $y = \frac{1}{4}, \frac{3}{4}$ (Fig. 1). The complex units have a very distorted tetrahedral stereochemistry involving two N atoms from dmp [Cu—N 2·023 (9), 2·049 (8) Å] and two H atoms from BH_4 ligands [Cu—H 1·58 (5) Å] while the Cu—B distance is short at 2·080 (15) Å. Because the angles about the tetrahedron [N—Cu—N 81·8 (3)°; H—Cu—H′ 77 (2)°] are contracted from the normal tetrahedral values, the N—Cu—H angles are expanded to 124·0 (10) and 128·5 (10)° (Fig. 2).

The Cu—N and N—Cu—N angles found for the title compound are similar to those found for bis(2,9-dimethyl-1,10-phenanthroline)copper(I) perchlorate (Dessy & Fares, 1979) [2·025 (5), 2·077 (6) Å, 81·3 (2)°; and 2·053 (6), 2·060 (6) Å, 81·7 (2)°] and nitrate (Hämäläinen, Ahlgren, Turpeinen & Raikas, 1979) [2·059 (8), 2·083 (7) Å, 82·7 (3)°].

In the title compound, BH_4^- behaves as a bidentate ligand. This is comparable to tetrahydroboratobis(triphenylphosphine)copper(I) (Lippard & Melmed, 1967) [Cu—H 2·02 (5); Cu—B 2·184 (9) Å; H—Cu—H 69 (3)°]; tris(tetrahydroborato)trimethylaminealuminium(III) (Bailey, Bird & Wallbridge, 1966) [Al—H 1·97 (1); Al—B 2·23 (1) Å]; hydridotetrahydroboratobis(tricyclohexylphosphine)cobalt(II) (Nakajima, Moriyama, Kobayashi, Saito & Sasaki, 1975) [Co—H 1·80, 1·87 (9); Co—B 2·13 (1) Å]; tetrahydroborato-1,1,1-tris(diphenylphosphinomethyl)ethanecobalt(I) (Dapporto, Midollini, Orlandini & Sacconi, 1976) [Co—H 1·45 (15), 1·55 (15); Co—B 2·21 (3) Å; H—Co—H 76·2 (1·0)°]; tetrakis(tetrahydroborato)zirconium(IV) (BH_4 as a tridentate) (Bird & Churchill, 1967) [Zr—B 2·34 (3) Å] and bis(methylcyclopentadienyl)bis(tetrahydroborato)hafnium(IV) (Johnson, Cohen, Marks & Williams, 1978) [Hf—H 2·069 (7), 2·120 (8); Hf—B 2·553 (6) Å; H—Hf—H 57·0 (3)°]. In tetrakis(tetrahydroborato)uranium(IV) (Bernstein, Hamilton, Keiderling, LaPlaca, Lippard & Mayerle, 1972), BH_4 acts as both a tridentate and a bridging bidentate ligand, while it is unidentate in tetrahydroboratotris(methyldiphenylphosphine)copper(I) (Atwood, Roger, Kutal & Gratsch, 1977) [Cu—H 1·47; Cu—B 2·650 (5) Å].



(a)

(b)

Fig. 2. (a) Bond distances (Å) and atom numbering in Cu(dmp)(BH_4). (b) Bond angles (°).

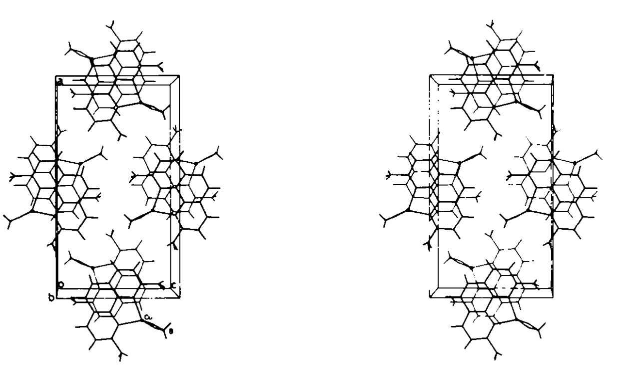


Fig. 1. Stereoview perpendicular to the *ac* plane.

The intramolecular distances for the dmp ligand are similar to those already published. The shortness of C(2)—N(1) or C(9)—N(10) compared to N(1)—C(11) or N(10)—C(14) is reflected in the other dmp Cu^I complexes and in 1,10-phenanthroline bis(thiourea)copper(I) iodide 1,10-phenanthroline adduct (Hall, Kepert, Raston & White, 1977) [coordinated phen 1·328 (8), 1·330 (9) to 1·359 (7), 1·370 (6) Å; and uncoordinated phen 1·322 (6), 1·325 (6) to 1·365 (6), 1·349 (7) Å]. The methyl carbon–dmp carbon distance [1·46 (1) Å] is shorter than the normal C—C single-bond distance (1·54 Å) but is of the same order as in $Cu(dmp)_2ClO_4$ [1·52 (1) Å] and $Cu(dmp)_2NO_3$ [1·50 (2) Å].

Molecules of the title compound are stacked perpendicular to the *b* axis with 3·40 Å separation between dmp residues. Viewed down this axis, the 2,9-dimethyl groups in alternate layers adopt a *trans* configuration. In the isostructural tetraaquabis(1,10-phenanthroline)-strontium(II) perchlorate 1,10-phenanthroline adduct and the barium(II) complex (Smith, O'Reilly, Kennard & White, 1977), the separation is similar (3·53, 3·52 Å respectively) but the 1,10-phenanthroline residues have the *cis* relationship.

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Dichlorobis(triphenylphosphine oxide)zinc(II)

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Abstract. $[Zn\{(C_6H_5)_3PO\}_2Cl_2]$, $C_{36}H_{30}Cl_2O_2P_2Zn$, orthorhombic, *Fdd*2, $a = 20{\cdot}728$ (3), $b = 33{\cdot}042$ (7), $c = 9{\cdot}769$ (2) Å, $Z = 8$, $D_o = 1{\cdot}38$ (1), $D_c = 1{\cdot}38$ Mg m^{-3}. The structure contains $[Zn\{(C_6H_5)_3PO\}_2Cl_2]$ molecules with point symmetry 2. Each Zn atom is ligated by two Cl and two O atoms having an approximately tetrahedral arrangement as indicated by the Cl—Zn—Cl′/O—Zn—O′ dihedral angle [87·7 (2)°]. Bond angles within the coordination polyhedron are: O—Zn—O′, 96·8 (3); Cl—Zn—O, 112·0 (2); Cl—Zn—O′, 109·0 (2); and Cl—Zn—Cl′, 116·4 (1)°. The Zn—Cl and Zn—O distances are 2·204 (2) and 1·984 (5) Å, respectively.

Introduction. The spectroscopic properties of approximately tetrahedral Cu^{II} complexes are of considerable current interest. A coordination polyhedron of this type was reported for the $[Cu\{(C_6H_5)_3PO\}_2Cl_2]$ analogue of the title complex (Bertrand & Kalyanaraman, 1971). The neat Cu^{II} complex displayed electronic spectral and EPR features appropriate for a flattened tetrahedral $Cu^{II}Cl_2O_2$ chromophore having point symmetry 2 (Bertini, Gatteschi & Martini, 1973). The title complex has been used as a host lattice for EPR studies of Mn^{II} and Cu^{II} ions (Vivien & Gibson, 1975). On the basis of these EPR studies and space-group analyses, the structures

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