Inorganica Chimica Acta, 81 (1984) 147–150

Crystal and Molecular Structure of μ-Tetrahydroborato-bis[bis(triphenylphosphine)-copper(I)] Perchlorate

BRUCE E. GREEN, COLIN H. L. KENNARD*
Department of Chemistry, University of Queensland, Brisbane, Qld. 4067, Australia
GRAHAM SMITH
Department of Chemistry, Queensland Institute of Technology, Brisbane, Qld. 4000, Australia
BRUCE D. JAMES
Department of Inorganic and Analytical Chemistry, La Trobe University, Bundoora, Vic. 3083, Australia
PETER C. HEALY
School of Science, Griffith University, Nathan, Qld. 4111, Australia
and ALLAN H. WHITE
Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, W.A. 6009, Australia

Received May 17, 1983

μ-Tetrahydroborato-bis[bis(triphenylphosphine)-copper(I)] perchlorate, $C_{72}H_{64}BClCu_2O_4P_4$, is orthorhombic, space group Pnnb with $a = 23.17(1)$, $b = 18.90(1)$, $c = 14.94(1)$ Å, $Z = 4$. The structure was refined to $R = 0.045$ by full matrix least squares using 2203 observed reflections. Two tetrahedral Cu(I) atoms are linked by a tetrahedral BH_4^- group through bidentate hydrogen bridges. The coordination sphere about each copper is completed by two triphenylphosphines. The P–Cu–P angles are distorted [119.7(1) and 124.5(1)°]. The former is the smallest angle observed for this type of structure.

Introduction

Cariati and Naldini [1] reported the first group of compounds in which all the hydrogens in BH_4^- are involved in bridging two Cu(I) atoms. Because there were no ν_{B-H_t} absorbances in the infrared spectrum, a structure with four bridging hydrogens between boron and copper atoms was proposed. This paper reports the crystal structure of one of these bridged compounds, $[(Cu(TPP)_2)_2BH_4]^+[ClO_4]^-$ (*1*), where TPP = triphenylphosphine (Fig. 1).

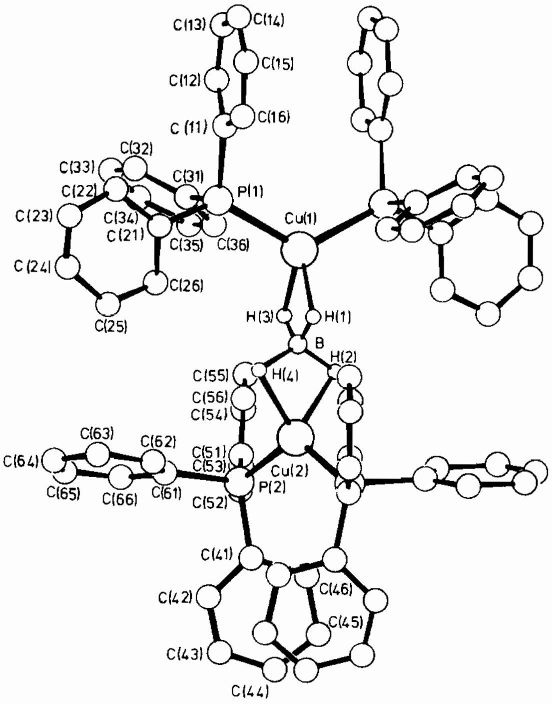

Fig. 1. Designations of the atoms in μ-tetrahydroborato-bis-[bis(triphenylphosphine)copper(I)] perchlorate.

Experimental

(a) Complex Preparation

(i) The complex was prepared by a modification of [1]. Dry absolute ethanol (25 cm^3) containing perchloric acid (0.17 g, 1.67 mmole) was added to a suspension of tetrahydroboratobis(triphenylphosphine)copper(I) (2 g, 3.33 mmoles) in ethanol (40 cm^3). The solution cleared after stirring for 10 min with evolution of H_2. After a further 10 min, a white suspension of the complex appeared. Addition of

---

*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

n-decane precipitated the remainder. The complex was recrystallized from methylene chloride and n-decane, and dried in vacuo at room temperature, m.p. 180 °C (Yield 84%). *Anal.* Found: C, 66.89; H, 5.22; Cl, 2.70; P, 9.18%. Calc. for $C_{72}H_{64}BClCu_2O_4P_4$: C, 67.0; H, 4.96; Cl, 2.75; P. 9.60%. ν_{B-H_b} 2140 cm^{-1} (s); $\nu_{as}(ClO_4)$ 1090–1120 cm^{-1}.

(b) Crystal Data

$C_{72}H_{64}BClCu_2O_4P_4$, M = 1289, orthorhombic, space group Pnnb (variant of Pnna, D_{2h}^{6}, No. 52), a = 23.17(1), b = 18.90(1), c = 14.94(1) Å, V = 6543(7) $Å^3$. D_m = 1.31(1), Z = 4, D_c = 1.31 g cm^{-3}. F(000) = 2376, μ(Mo-Kα) = 8.23 cm^{-1}. Crystal size: 0.20 X 0.24 X 0.36 mm. T = 295 K.

(c) Collection of X-Ray Data and Structure Solution

A data set ($2\theta_{max}$ = 45°) was collected on a Syntex $P2_1$ four circle diffractometer (graphite monochromatized Mo-Kα radiation, λ = 0.7107 Å yielding 4267 independent reflections, of which 2203 with $I > 3\sigma(I)$ were considered 'observed'. Data were corrected for absorption. The structure was solved using heavy atom methods, and the atomic parameters refined in a 9 X 9 block diagonal least squares refinement to R = 0.045 and R_w = 0.052. The temperature factors for non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from a difference electron density synthesis. The hydrogen atoms, other than those located on the B atom were constrained at idealized tetrahedral or trigonal positions. For all atoms the isotropic U was set at U_{ii} of the parent B or C atoms. Neutral atom scattering factors were used and the non-hydrogen atoms were corrected for anomalous dispersion. Computation was carried out using the X-RAY 76 [2] program system on a Perkin-Elmer 3240 computer. Final positional parameters are listed in Table I, while bond distances and angles are given in Table II.

Material available from the authors comprises: structure factor amplitudes, thermal parameters and hydrogen atoms parameters for the cation. Hydrogen atom numbering follows that of the parent ring carbon.

Discussion

In this complex the BH_4^- group is tetrahedral and bonded through four three-centred hydrogen bridges to two tetrahedral copper(I) atoms. Two TPP ligands

TABLE I. Atomic Co-ordinates. Hydrogen Atom Estimates are Included Only for BH_4^- Species.

	Ligand 1			Ligand 2		
Atom	x	y	z	x	y	z
Cu	0.2500(-)	0.43702(5)	0.2500(-)	0.2500(-)	0.20229(5)	0.2500(-)
Phosphine ligand						
P	0.32432(8)	0.49699(9)	0.1888(1)	0.33040(7)	0.14662(9)	0.2988(1)
C(11)	0.3089(2)	0.5890(3)	0.1628(4)	0.3219(3)	0.0524(3)	0.3197(4)
C(12)	0.3337(3)	0.6464(4)	0.2039(6)	0.3598(3)	0.0019(4)	0.2889(6)
C(13)	0.3196(4)	0.7141(4)	0.1800(7)	0.3517(4)	–0.0687(4)	0.3071(7)
C(14)	0.2795(4)	0.7250(5)	0.1142(8)	0.3041(4)	–0.0889(4)	0.3558(8)
C(15)	0.2535(5)	0.6713(5)	0.0745(6)	0.2652(4)	–0.0426(5)	0.3850(7)
C(16)	0.2673(2)	0.6012(4)	0.0977(6)	0.2737(3)	0.0310(4)	0.3671(5)
C(21)	0.3558(3)	0.4624(4)	0.0862(5)	0.3640(3)	0.1790(4)	0.4003(4)
C(22)	0.3863(4)	0.5073(4)	0.0267(5)	0.3866(4)	0.1364(5)	0.4668(6)
C(23)	0.4136(4)	0.4773(4)	–0.0472(5)	0.4122(4)	0.1667(6)	0.5417(6)
C(24)	0.4090(4)	0.4090(4)	–0.0645(5)	0.4149(5)	0.2365(7)	0.5520(7)
C(25)	0.3802(4)	0.3635(4)	–0.0083(6)	0.3914(5)	0.2798(5)	0.4878(7)
C(26)	0.3526(2)	0.3922(4)	0.0670(5)	0.3672(4)	0.2506(5)	0.4127(6)
C(31)	0.3867(3)	0.4998(3)	0.2636(5)	0.3877(3)	0.1551(3)	0.2150(5)
C(32)	0.4382(4)	0.5331(5)	0.2397(5)	0.3711(3)	0.1685(3)	0.1277(5)
C(33)	0.4848(4)	0.5328(5)	0.2978(7)	0.4120(4)	0.1756(4)	0.0602(5)
C(34)	0.4803(5)	0.4972(6)	0.3769(7)	0.4690(5)	0.1676(4)	0.0810(7)
C(35)	0.4307(6)	0.4649(6)	0.4031(7)	0.4866(3)	0.1537(5)	0.1679(8)
C(36)	0.3827(4)	0.4660(5)	0.3452(6)	0.4456(3)	0.1481(4)	0.2367(5)
Borohydride						
B	0.2500(-)	0.3189(6)	0.2500(-)			
H	0.220(-)	0.354(-)	0.211(-)	0.224(-)	0.286(-)	0.302(-)
Perchlorate						
Cl	0.0000(-)	0.2500(-)	0.6963(2)			
O	0.0340(4)	0.2946(4)	0.7447(5)	0.0314(4)	0.2095(5)	0.6388(6)

TABLE II. Comparison between $[(\mathrm{Cu(TPP)_2})_2\mathrm{BH_4}]^+[\mathrm{ClO_4}]^-$ [1] and $\mathrm{Cu(TPP)_2BH_4}$ [2] of:

(a) Interatomic Distances (Å).

Bond	[1]		[2]	Bond	[1]		[2]
Cu–P	2.256(2)	2.260(2)	2.276(1)	C(22)–C(23)	1.39(1)	1.39(1)	
Cu–B	2.23(1)	2.20(1)	2.184(9)	C(23)–C(24)	1.32(1)	1.33(2)	
Cu–H	1.810	1.864	2.02(5)	C(24)–C(25)	1.37(1)	1.37(2)	
P–C(11)	1.818(7)	1.819(6)	1.817(4)	C(25)–C(26)	1.40(1)	1.37(1)	
P–C(21)	1.819(7)	1.812(7)	1.814(5)	C(31)–C(32)	1.40(1)	1.38(1)	
P–C(31)	1.828(8)	1.831(7)	1.829(4)	C(31)–C(36)	1.38(1)	1.39(1)	
C(11)–C(12)	1.37(1)	1.38(1)		C(32)–C(33)	1.38(1)	1.39(1)	
C(11)–C(16)	1.39(1)	1.38(1)		C(33)–C(34)	1.36(2)	1.37(2)	
C(12)–C(13)	1.37(1)	1.37(1)		C(34)–C(35)	1.36(2)	1.39(2)	
C(13)–C(14)	1.37(1)	1.38(1)		C(35)–C(36)	1.41(2)	1.40(1)	
C(14)–C(15)	1.32(1)	1.33(1)		B–H	1.31	1.66	1.26(4)
C(15)–C(16)	1.41(1)	1.43(1)		Cl–O	1.36(1)	1.36(1)	
C(21)–C(22)	1.42(1)	1.38(1)					
C(21)–C(26)	1.38(1)	1.37(1)					

(b) Bond Angles (°).

Bond	[1]		[2]	Bond	[1]		
P(1)–Cu–P(3)	119.67(9)	124.52(9)	123.2(6)	P–C(21)–C(26)	120.4(5)	118.0(6)	
P(1)–Cu–B	120.16(5)	117.74(5)	118.4(1)	C(22)–C(21)–C(26)	118.7(7)	117.4(7)	
H–Cu–H	61	64	69(3)	C(23)–C(22)–C(21)	118.7(7)	119.9(9)	
Cu–P–C(11)	114.7(2)	115.0(2)	111.1(2)	C(22)–C(23)–C(24)	121.0(8)	121.5(10)	
Cu–P–C(21)	117.9(2)	111.9(2)	115.0(2)	C(23)–C(24)–C(25)	122.1(8)	119.5(10)	
Cu–P–C(31)	111.7(2)	109.7(2)	117.6(1)	C(24)–C(25)–C(26)	118.0(7)	119.6(9)	
C(11)–P–C(21)	104.1(3)	103.5(3)	103.9(2)	C(25)–C(26)–C(21)	121.4(7)	122.1(8)	
C(11)–P–C(31)	105.0(3)	106.3(3)	104.0(2)	P–C(31)–C(32)	122.2(6)	117.3(5)	
C(21)–P–C(31)	102.0(3)	103.3(3)	103.8(2)	P–C(31)–C(36)	118.3(6)	122.3(6)	
P–C(11)–C(12)	125.3(6)	123.5(5)		C(32)–C(31)–C(36)	119.5(7)	120.5(7)	
P–C(11)–C(16)	116.4(5)	117.5(5)		C(33)–C(32)–C(31)	120.2(8)	120.8(7)	
C(12)–C(11)–C(16)	118.3(7)	119.0(6)		C(32)–C(33)–C(34)	119.1(9)	118.9(8)	
C(13)–C(12)–C(11)	121.5(8)	121.3(7)		C(33)–C(34)–C(35)	122.5(10)	121.3(9)	
C(12)–C(13)–C(14)	119.3(8)	118.9(8)		C(34)–C(35)–C(36)	118.9(10)	120.0(8)	
C(13)–C(14)–C(15)	121.2(9)	122.3(8)		C(35)–C(36)–C(31)	119.8(9)	118.5(7)	
C(14)–C(15)–C(16)	120.6(9)	119.0(8)		O–Cl–O	115.8(5)	107.2(5)	–
C(15)–C(16)–C(11)	119.1(8)	119.4(7)		O–Cl–O	107.2(5)	101.8(6)	–
P–C(21)–C(22)	120.9(5)	124.6(6)		H–B–H	108	116	

complete the co-ordination about each metal ion. There is a crystallographically imposed two fold axis through the boron and copper atoms. The orientation of the TPP with respect to the Cu(I) is different from that in $\mathrm{Cu(TPP)_2BH_4}$ (*2*) [3], [torsion angles B–Cu(1)–P(1)–C(11), +162.0(8)°; –C(21), +39.0(8)°; –C(31), –78.7(8)°; B–Cu(2)–P(2)–C(41), +167.3(8)°; –C(51), +44.8(8)°; –C(61), –73.0(8)° and equivalent B–Cu–P–C(1), –7.7(1), +115.1(1), –125.3(1)°]. In (2) the molecule has a two-fold axis with boron and copper atoms at special positions in *C*2/*c*. It may be possible to form another isomer of (*1*) with the conformation of TPP groups analogous to that found in (*2*). Although the Cu–B distances are comparable for (*1*): 2.20(1), 2.23(1) Å and (*2*): 2.184(9) Å respectively there seems to be a marked difference in H–B–H angle (*1*): 107.6(8), 115.5(9)° and (*2*): 132(5)° respectively. The coordination around the metal atom is grossly distorted and according to Lippard [4] this arises from the distribution of bulk about the metal to minimize nonbonded contacts. However, one P–Cu–P angle in this case is significantly smaller (119.7(1), 124.5(1)°) compared to 123.26(1)° for (*2*). In fact it is the smallest so far found for $\mathrm{(TPP)_2ML}$ type complexes. Further similarities are found in the comparison in Table II (a) and (b) of bond distances and angles for compounds (*1*) and (*2*). The interatomic distances and angles are comparable to other related compounds [4], [5] and [6].

Other examples of BH_4^- bound to two metal atoms via double hydrogen bridges are $Be(BH_4)_2$ (*3*) [7], $U(BH_4)_4$ (*4*) [8], $U(BH_4)_4 \cdot (n\text{-}C_3H_7)O_2$ [9]. A summary on metal borohydride bonding is in [10]. The molecules are held together by van der Waals interactions (Fig. 2). The anisotropic thermal parameters of the perchlorate oxygens are large as expected. The presence of the ClO_4^- has an effect similar to solvated C_6H_6 in [4]. When it is absent as in $[(TPP)_3Cu_2Cl_2]$ [5, 6], the Cu–P distance is shorter.

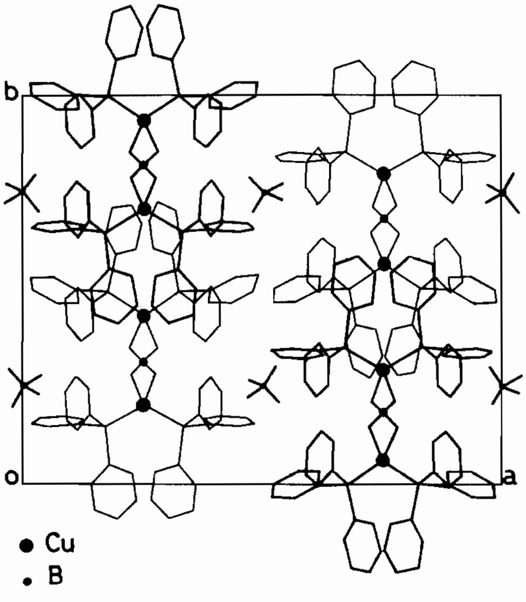

Fig. 2. Packing diagram about the *ab* plane.

Acknowledgements

The authors wish to thank the Australian Research Grants Committee and the University of Queensland for support, the University of Western Australia for the use of data collection and computing facilities, and the Queensland Institute of Technology for leave to work on this project (GS).

References

1 F. Cariati and L. Naldini, *J. Inorg. Nucl. Chem., 28,* 2243 (1966).
2 J. M. Stewart, 'X-Ray 76' TR-446, 'The X-Ray System of Crystallographic Programs', Computer Science Centre, University of Maryland, College Park, Maryland (1976).
3 S. J. Lippard and K. M. Melmed, *Inorg. Chem., 6,* 2223 (1967).
4 J. T. Gill, J. J. Mayerle, P. S. Welcker, D. F. Lewis, D. A. Ucko, D. J. Barton, D. Stowens and S. J. Lippard, *Inorg. Chem., 15,* 1155 (1976).
5 S. J. Lippard and G. J. Palenik, *Inorg. Chem., 10,* 1322 (1971).
6 V. G. Albano, P. L. Bellon, G. Ciani and M. Manassero, *J.C.S. Dalton,* 171 (1972).
7 D. S. Marynick and W. N. Lipscomb, *Inorg. Chem., 11,* 820 (1972).
8 E. R. Bernstein, W. C. Hamilton, T. A. Keiderling, S. J. La Placa, S. J. Lippard and J. J. Mayerle, *Inorg. Chem., 11,* 3009 (1972).
9 A. Zalkin, R. R. Rietz, D. H. Templeton and N. M. Edelstein, *Inorg. Chem., 17,* 661 (1976).
10 N. M. Edelstein, *Inorg. Chem., 20,* 299 (1981).