# Crystal and Molecular Structure of a Paramagnetic Hydridotetrahydroborato-complex of Cobalt: Hydridotetrahydroboratobis(tricyclohexylphosphine)cobalt

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The crystal structure of the title compound has been determined by single-crystal X-ray diffraction techniques. Crystals are monoclinic, space group $P2_1/a$, with cell dimension $a = 23.391(10)$, $b = 12.614(4)$, $c = 13.195(6)$ Å, $\beta = 106.93(3)°$, $Z = 4$. The cobalt atom is co-ordinated by two tricyclohexylphosphine ligands in the *trans*-positions, a hydride hydrogen, and two bridging hydrogen atoms of the tetrahydroborato-ligands in a deformed square pyramid.

WE have synthesized a paramagnetic cobalt tetrahydroborato-complex, which seemed to be a cobalt hydride from an i.r. study of the deuteriated compound, and formulated it as $[CoH(BH_4)\{P(C_6H_{11})_3\}_2]$.[1] This composition is similar to that of the diamagnetic nickel analogue $[NiH(BH_4)\{P(C_6H_{11})_3\}_2]$.[2]

The transition-metal tetrahydroborato-complexes [3] have either doubly (I) or triply hydrogen-bridged (II) structures and the BH_4^- ligand is usually fluxional in solution, except in the iridium and rhodium complexes reported recently.[4] Structure determinations of $[Cu(BH_4)(PPh_3)_2]$ (ref. 5), $[Ti(BH_4)(C_5H_5)_2]$ (ref. 6), and $[Nb(BH_4)(C_5H_5)_2]$ (ref. 7) by single-crystal X-ray diffraction techniques have shown that they have doubly hydrogen-bridged structures. The crystal structure of the present cobalt complex has been investigated to obtain the definitive information on the Co–H and Co–BH₄ bonding. The results, a preliminary report of which has appeared,[1] confirm the existence of the Co–H bond and structure (I) for the BH₄-ligand.

(I)   (II)
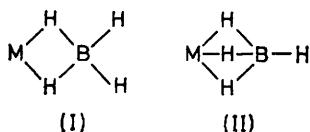
EXPERIMENTAL

The preparation and handling of the crystal were carried out under nitrogen.

Synthesis.—An ethanol solution (30 ml) of $CoCl_2 \cdot 6H_2O$ (1.4 g) was mixed with a toluene solution (200 ml) of tricyclohexylphosphine (8 g) and filtered. To the filtrate, an ethanol solution (50 ml) of sodium tetrahydroborate (0.44 g) was added slowly with stirring. The reaction mixture was then poured into methanol (430 ml) and cooled (refrigerator). After 3 h the yellowish brown crystals which had precipitated were washed (× 3) with methanol (40 ml) and dried *in vacuo* (32%, based on cobalt).

Preparation of the Crystal.—$[CoH(BH_4)\{P(C_6H_{11})_3\}_2]$ (1.5 g, 2.4 mmol) was dissolved in a toluene (65 ml) solution of tricyclohexylphosphine (2.1 g, 7.5 mmol) and filtered. The filtrate was slowly added to methanol (140 ml) and the mixture then cooled (refrigerator). After 6 days, yellowish brown crystals which grew along the crystallographic *b* axis were washed with methanol and dried *in vacuo.*

[1] M. Nakajima, H. Moriyama, A. Kobayashi, T. Saito, and Y. Sasaki, *J.C.S. Chem. Comm.,* 1975, 80.

[2] M. L. H. Green, H. Munakata, and T. Saito, *J. Chem. Soc. (A),* 1971, 469.

[3] B. D. James and M. G. H. Wallbridge, *Progr. Inorg. Chem.,* 1970, **11,** 99.

[4] H. D. Empsall, E. Mentzer, and B. L. Shaw, *J.C.S. Chem. Comm.,* 1975, 861.

Data Collection.—A single crystal with dimensions *ca.* $0.6 \times 0.25 \times 0.2$ mm was sealed in a glass capillary under nitrogen and used for measurement of diffraction intensities and dimensions on a Rigaku automated four-circle diffractometer, by use of graphite-monochromated Mo-K_α radiation. Unit-cell dimensions were obtained by a least-squares refinement of the angular measurements of 12 reflections.

Crystal Data.—$C_{36}H_{71}BCoP$, $M = 635.7$, Monoclinic, $a = 23.39(1)$, $b = 12.614(4)$, $c = 13.195(6)$ Å, $\beta = 106.93(3)°$, $U = 3\,724.7$ Å³, $D_c = 1.13$ g cm⁻³, $Z = 4$. Mo-K_α radiation $\lambda = 0.710\,7$ Å; $\mu(\text{Mo-}K_\alpha) = 6.5$ cm⁻¹. Space group $P2_1/a$ from systematic absences: $h0l$, $h = 2n + 1$, $0k0$, $k = 2n + 1$. D_m was not measured because of the reactivity of the compound. Intensity data were recorded by the ω—2θ scan technique with scan speed 2° min⁻¹ and background counts of 10 s taken at each end of the scan. The intensities of 3 standard reflections measured every 50 reflections during the data collection did not vary by >3%. Intensities were measured up to 2θ 50°, and 3 707 reflections having $F_o \geqslant 3\sigma$ were considered significant and used for the structure analysis. Intensities were corrected for Lorentz and polarization effects, but not for absorption.

Determination of the Structure.—The position of the cobalt atom was deduced from a three-dimensional Patterson map and the positions of all non-hydrogen atoms were determined by the usual heavy-atom method. Block-diagonal least-squares refinement, with anisotropic temperature factors reduced R to 0.081. At this stage, a difference-Fourier synthesis revealed the positions of almost all the hydrogen atoms. In further refinements, where the parameters of all non-hydrogen atoms were fixed, the parameters of all the cyclohexyl hydrogen atoms were refined with isotropic thermal parameters. In several cycles of block-diagonal least-squares refinement and difference-Fourier synthesis, all the cyclohexyl hydrogen atoms were located and R was reduced to 0.069. The peak height of the hydrido-hydrogen was 0.39 eÅ⁻³ and of the tetrahydroborato-hydrogen atoms 0.37—0.51 eÅ⁻³ from a difference-Fourier map calculated at this stage. There were no peaks >0.39 eÅ⁻³ around the hydrido-hydrogen. The hydrido- and tetrahydroborato-hydrogen atoms were then included in the least-squares refinement with isotropic thermal parameters, and the final R was 0.062.

Atomic scattering factors were taken from ref. 8, those of cobalt and phosphorus being corrected for the real part of anomalous dispersion, using values estimated from ref. 9.

[5] S. J. Lippard and K. M. Melmed, *Inorg. Chem.,* 1967, **6,** 2223.

[6] K. M. Melmed, D. Coucouvanis, and S. J. Lippard, *Inorg. Chem.,* 1973, **12,** 232.

[7] N. I. Kurillova, A. I. Gusev, and Yu. T. Struktov, *Zhur. strukt. Khim.,* 1974, **15,** 718.

[8] ' International Tables for X-Ray Crystallography,' vol. III, 3rd edn., Kynoch Press, Birmingham, 1969, p. 202.

[9] D. J. Cromer, *Acta Cryst.,* 1965, **18,** 17.

A weighting scheme with $w = 1$ for $|F_o| \geqslant 14.16$ on an absolute scale and $w = 0.5$ otherwise was employed.

Final positional and isotropic thermal parameters are given in Table 1, with their estimated standard deviations. The numbering system of the atoms is shown in the Figure.
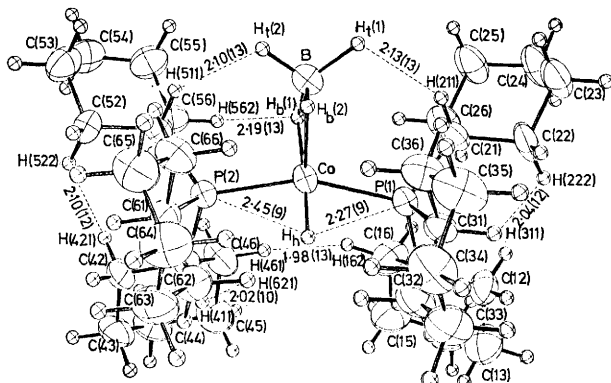
Molecular structure, illustrating the thermal ellipsoids at 50% probability. H atoms have an arbitrary radius of 0.10Å. Some intramolecular short contacts are shown as broken lines. Maximum H · · · H distance 2.2 Å and H · · non-hydrogen atoms 2.5 Å

Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21912 (10 pp., 1 microfiche).*

The calculation was performed on the HITAC 8700/8800 computer at the computer center of the University of Tokyo, using a local version of the UNICS [10] programs.

RESULTS AND DISCUSSION

The crystal consists of discrete molecules of [CoH-$(BH_4)\{P(C_6H_{11})_3\}_2]$ as shown in the Figure. Bond lengths and angles, best planes, dihedral angles, and vector-plane angles are summarized in Tables 2 and 3. All atoms are in general positions but the molecule has a pseudo-mirror plane which involves the Co–B bond and is perpendicular to the $P(1) \cdot \cdot \cdot P(2)$ vector. The cobalt atom is on the plane defined by H_h, $H_b(1)$, and $H_b(2)$, five-co-ordination being completed by the three hydrogen and two phosphorus atoms.

Trigonal-bipyramidal co-ordination is common among five-co-ordinated hydrides,[11] but the structure of the present complex is very much deformed from this. The co-ordination around cobalt may be described rather as a deformed square pyramid in which H_h, $H_b(1)$, $P(1)$, and $P(2)$ form a basal plane [plane (1) in Table 3] and $H_b(2)$ is axial.

The angle $P(1)–Co–P(2)$ is $157.8(1)°$, and the hydride hydrogen H_h is located such that it is held between the two tertiary phosphines. This type of bending of two phosphines towards a hydride hydrogen seems to be common in other transition-metal hydride complexes.[11]

Another characteristic feature of the complex is the large deformation of the BH_4^- ligand from ordinary

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

[10] ' The Universal Crystallographic Computation Program System,' Crystallographic Society of Japan, 1969.

[11] B. A. Frenz and J. A. Ibers, ' Transition-metal Hydrides,' ed. E. L. Muetterties, Dekker, New York, 1971, ch. 3.

TABLE 1

Positional parameters, with estimated standard deviations in parentheses

(a) For non-hydrogen atoms ($\times 10^4$)

Atom	X/a	Y/b	Z/c
Co	1 521(1)	2 223(1)	1 758(1)
P(1)	1 865(1)	947(2)	936(2)
P(2)	1 272(1)	3 026(2)	3 065(2)
B	1 519(6)	3 545(10)	745(10)
C(11)	1 489(4)	−323(8)	997(8)
C(12)	1 675(5)	−1 293(8)	456(8)
C(13)	1 387(6)	−2 320(10)	736(10)
C(14)	715(6)	−2 222(10)	441(11)
C(15)	526(6)	−1 261(10)	994(11)
C(16)	805(5)	−231(9)	671(10)
C(21)	1 853(4)	1 259(8)	−451(7)
C(22)	2 240(5)	555(9)	−964(7)
C(23)	2 232(5)	1 079(11)	−2 058(8)
C(24)	1 588(5)	1 151(11)	−2 785(8)
C(25)	1 195(5)	1 807(11)	−2 260(8)
C(26)	1 201(4)	1 307(9)	−1 192(7)
C(31)	2 674(4)	634(7)	1 562(7)
C(32)	2 788(4)	82(9)	2 648(7)
C(33)	3 476(5)	−111(10)	3 127(9)
C(34)	3 824(5)	914(11)	3 218(8)
C(35)	3 702(5)	1 462(11)	2 134(9)
C(36)	3 027(4)	1 684(9)	1 674(8)
C(41)	799(4)	2 133(8)	3 622(7)
C(42)	539(5)	2 627(8)	4 461(8)
C(43)	210(5)	1 755(9)	4 922(8)
C(44)	−283(5)	1 228(10)	4 047(9)
C(45)	−7(6)	713(10)	3 212(10)
C(46)	295(5)	1 618(9)	2 729(8)
C(51)	903(4)	4 338(8)	2 731(7)
C(52)	878(5)	5 100(9)	3 650(8)
C(53)	643(5)	6 195(9)	3 174(9)
C(54)	25(5)	6 096(9)	2 333(10)
C(55)	45(5)	5 304(9)	1 473(9)
C(56)	275(4)	4 226(8)	1 930(8)
C(61)	1 925(4)	3 323(7)	4 248(7)
C(62)	2 239(4)	2 306(8)	4 759(7)
C(63)	2 780(5)	2 614(9)	5 740(8)
C(64)	3 224(5)	3 336(10)	5 420(9)
C(65)	2 890(5)	4 351(9)	4 904(8)
C(66)	2 359(4)	4 066(9)	3 925(8)

(b) Final positional ($\times 10^3$) and isotropic thermal parameters ($Å^2$) for hydrogen atoms

Atom	X/a	Y/b	Z/c	B
H_h	175(4)	150(7)	250(6)	5(2)
$H_b(1)$	101(4)	299(7)	75(6)	5(2)
$H_b(2)$	200(4)	331(7)	150(6)	5(2)
$H_t(1)$	181(4)	356(7)	0(6)	5(2)
$H_t(2)$	156(4)	444(7)	112(7)	5(2)
H(111)	164(3)	−49(6)	182(6)	3(2)
H(121)	214(3)	−137(6)	74(6)	4(2)
H(122)	153(3)	−118(7)	−38(6)	4(2)
H(131)	156(4)	−247(7)	157(7)	6(3)
H(132)	150(4)	−298(7)	34(7)	6(3)
H(141)	55(4)	−293(8)	67(7)	6(3)
H(142)	54(4)	−212(7)	−41(7)	5(2)
H(151)	69(4)	−135(7)	184(7)	6(3)
H(152)	6(4)	−118(7)	74(7)	6(3)
H(161)	64(4)	−14(7)	−18(7)	5(2)
H(162)	69(4)	44(7)	106(7)	5(2)
H(211)	207(4)	203(7)	−37(6)	5(2)
H(221)	206(4)	−24(7)	−109(6)	5(2)
H(222)	270(4)	52(7)	−47(6)	4(2)
H(231)	249(4)	60(7)	−242(7)	5(2)
H(232)	242(4)	187(7)	−192(6)	5(2)
H(241)	141(4)	36(7)	−295(7)	5(2)
H(242)	159(4)	153(7)	−351(6)	5(2)
H(251)	76(4)	182(7)	−276(6)	5(2)
H(252)	135(4)	261(7)	−215(6)	5(2)
H(261)	95(3)	178(6)	−82(6)	4(2)
H(262)	103(4)	52(6)	−132(6)	4(2)
H(311)	282(4)	8(7)	106(6)	5(2)
H(321) *	256(4)	−67(7)	254(6)	4(2)
H(322) *	263(4)	59(7)	317(6)	5(2)

TABLE 1 (Continued)

Atom	X/a	Y/b	Z/c	B
H(331)	362(4)	−65(7)	262(7)	5(2)
H(332)	356(4)	−47(7)	388(7)	5(2)
H(341)	429(4)	75(7)	351(7)	6(2)
H(342)	369(4)	144(7)	376(7)	5(2)
H(351)	384(4)	95(7)	160(6)	5(2)
H(352)	393(4)	219(7)	221(7)	6(2)
H(361)	289(3)	222(7)	218(6)	4(2)
H(362)	295(3)	205(7)	93(6)	4(2)
H(411)	111(3)	153(6)	403(6)	4(2)
H(421)	23(4)	325(7)	410(6)	5(2)
H(422)	89(3)	297(6)	509(6)	4(2)
H(431)	53(4)	116(7)	532(6)	5(2)
H(432)	1(4)	212(7)	547(6)	5(2)
H(441)	−49(4)	62(7)	438(7)	6(2)
H(442)	−61(4)	181(7)	365(7)	6(3)
H(451)	32(4)	11(8)	357(7)	6(3)
H(452)	−35(4)	36(8)	260(7)	6(3)
H(461)	48(4)	129(7)	217(6)	5(2)
H(462)	−4(4)	222(7)	237(6)	5(2)
H(511)	121(3)	473(6)	238(6)	3(2)
H(521)	132(3)	519(6)	420(6)	4(2)
H(522)	59(4)	476(6)	406(6)	4(2)
H(531)	60(4)	670(7)	379(7)	5(2)
H(532)	95(4)	653(7)	281(7)	5(2)
H(541)	−29(4)	583(7)	270(7)	5(2)
H(542)	−10(4)	686(7)	198(6)	5(2)
H(551)	−39(4)	521(8)	96(7)	6(3)
H(552)	33(4)	563(8)	104(7)	7(3)
H(561)	−3(4)	390(7)	232(6)	5(2)
H(562)	30(4)	369(7)	131(6)	4(2)
H(611)	177(3)	370(6)	483(6)	3(2)
H(621)	239(3)	187(6)	420(6)	4(2)
H(622)	194(3)	181(6)	500(6)	4(2)
H(631)	301(4)	191(7)	609(6)	5(2)
H(632)	260(4)	301(7)	630(7)	6(3)
H(641)	341(4)	294(7)	488(7)	5(2)
H(642)	357(4)	355(7)	611(7)	5(2)
H(651)	319(4)	486(7)	466(7)	5(2)
H(652)	273(4)	478(7)	546(7)	5(2)
H(661)	213(3)	477(6)	359(6)	4(2)
H(662)	252(3)	369(6)	336(6)	4(2)

* Atoms H(321) and H(322) are attached to atom C(32).

C_{2v} symmetry. The two planes $B,H_t(1),H_t(2)$ and B, $H_b(1),H_b(2)$ are almost perpendicular. However, the former plane does not contain the $Co\cdots B$ vector and forms an angle [with it] as large as 29°; the angle between the planes $B,H_b(1),H_b(2)$ and $H_h,Co,H_b(1),H_b(2)$ is 11°.

The angle $H_t(1)-B-H_t(2)$ [106(6)°] is considerably smaller than corresponding angles in $[Ti(BH_4)(\eta^5-C_5H_5)_2]$ [129(9)° (ref. 6)] and $[Cu(BH_4)(PPh_3)_2]$ [121(5)°

TABLE 2

Bond distances (Å) and angles (°) in the co-ordination sphere

(a) Distances *

Co−P(1)	2.219(3)	Co−P(2)	2.219(3)
Co−B	2.14(1)	Co−H_h	1.34(8)
Co−H_b(1)	1.80(8)	Co−H_b(2)	1.87(9)
B−H_b(1)	1.39(9)	B−H_b(2)	1.30(7)
B−H_t(1)	1.35(10)	B−H_t(1)	1.22(9)

(b) Angles

P(1)−Co−P(2)	157.8(1)	P(2)−Co−B	100.2(4)
P(1)−Co−B	101.3(4)	P(2)−Co−H_h	83(3)
P(1)−Co−H_h	75(3)	P(2)−Co−H_b(1)	93(2)
P(1)−Co−H_b(1)	107(2)	P(2)−Co−H_b(2)	96(3)
P(1)−Co−H_b(2)	97(3)	B−Co−H_b(1)	40(3)
B−Co−H_h	157(3)	B−Co−H_b(1)	77(4)
B−Co−H_b(2)	37(3)	H_b(1)−Co−H_b(2)	77(4)
Co−B−H_h(1)	57(4)	H_h−Co−H_b(1)	163(4)
Co−B−H_t(1)	124(4)	H_h−Co−H_b(2)	120(4)
H_b(1)−B−H_b(2)	116(5)	Co−B−H_b(2)	60(3)
H_b(1)−B−H_t(1)	129(6)	Co−B−H_t(2)	119(4)
H_b(1)−B−H_t(2)	115(6)	H_t(1)−B−H_t(2)	106(5)
Co−H_b(1)−B	83(4)	H_b(2)−B−H_t(1)	93(5)
Co−H_b(2)−B	83(4)	H_b(2)−B−H_t(2)	87(5)

* Mean dimensions in C_6H_{11} groups: P−C 1.87(1) and C−C 1.55(2) Å; P−C−C 113(1) and C−C−C 110(1)°.

TABLE 3

Displacements (Å) of relevant atoms from least-squares planes

Plane (1): P(1), P(2), H_h, H_b

$-0.805\ 67X - 0.585\ 38Y - 0.090\ 64Z + 3.986\ 35 = 0$

[P(1) −0.045, P(2) −0.046, H_h 0.065, H_b(1) 0.028, Co −0.178]

Plane (2): H_b, H_b(1), H_b(2)
[Co 0.025]

Plane (3): B, H_b(1), H_b(2)

Plane (4): B, H_t(1), H_t(2)

Dihedral angles (°) between planes: (1)−(3) 82, (2)−(3) 11, (3)−(4) 94.

Vector–plane angles (°): $Co\cdots H_b(2)$−(1) 70, $Co\cdots$ B−(4) 29, $Co\cdots$ B−(3) 8.

(ref. 5)]. The cobalt–hydrido-hydrogen bond length [1.34(8) Å] appears to be shorter than is usual for transition-metal—hydrogen distances (1.4—1.7 Å),[11] although the difference may not be significant considering the large values of the standard deviations. The cobalt–boron distance [2.14(1) Å] is shorter than those in the

TABLE 4

Comparison of metal–boron distances d/Å with sums of relevant ionic and atomic radii from different sources (r/Å), and the difference ($\Delta = d - r$) between them

Compound	d	r(1) [a]	Δ(1)	r(2) [b]	Δ(2)	r(3) [c]	Δ(3)
(a) Bidentate BH₄							
[U(BH₄)₄] [d]	2.86	1.19	1.67	1.75	1.11		
[Nb(BH₄)(C₅H₅)₂] [e]	2.26	0.83	1.43	1.45	0.81	1.34	0.92
[Cu(BH₄)(PPh₃)₂] [f]	2.18	0.60	1.58	1.35	0.83	1.17	1.01
[CoH(BH₄){P(C₆H₁₁)₃}₂] [g]	2.14	0.79	1.35	1.35	0.79	1.16	0.98
[Ti(BH₄)(C₅H₅)] [h]	2.37	0.81	1.56	1.40	0.97	1.32	1.05
[Al(BH₄)₃(NMe₃)] [i]	2.25	0.67	1.58	1.25	1.00	1.25	1.00
[Al(BH₄)₃] [j]	2.14	0.67	1.47	1.25	0.89	1.25	0.89
[Be(BH₄)₂] [k]	1.96	0.41	1.55	1.05	0.91	0.89	1.07
(b) Terdentate BH₄							
[U(BH₄)₄] [d]	2.52	1.19	1.33	1.75	0.77		
[Zr(BH₄)₄] [l]	2.34	0.98	1.36	1.55	0.79	1.45	0.89

[a] Ionic radii of ref. 12.   [b] Atomic radii of ref. 13.   [c] Single-bond metallic radii of ref. 14.   [d] E. R. Bernstein, W. C. Hamilton, T. A. Keiderling, S. J. La Placa, S. J. Lippard, and J. J. Mayerle, Inorg. Chem., 1972, 11, 3009; the complex contains both bi- and ter-dentate BH₄⁻.   [e] Ref. 7.   [f] Ref. 5.   [g] This work.   [h] Ref. 6.   [i] N. A. Bailey, P. H. Baird, and M. G. H. Wallbridge, Inorg. Chem., 1968, 7, 1575.   [j] A. Almenningen, G. Gundersen, and A. Haaland, Acta Chem. Scand., 1968, 22, 328.   [k] D. S. Marynick and W. N. Lipscomb, Inorg. Chem., 1972, 11, 820.   [l] P. H. Baird and M. R. Churchill, Chem. Comm., 1967, 403.

tetrahydroborato-complexes of copper[5] (2.37 Å) and titanium[6] (2.18 Å). Table 4 lists known metal–boron distances (d), metal radii (r) from three different sources,[12-14] and the differences (Δ) between these distances. The present Co–B distance is definitely short even when differences in metal radii are taken into account. Table 4 also shows that in general the boron atom in the triply hydrogen-bridged BH_4 complexes approaches closer to the central metal than that in the doubly hydrogen-bridged BH_4 complexes. The shorter Co–B distance (Table 4) may be an indication that rather strong interactions exist between the metal and boron atoms,[15] and that M–BH_4 bonding has significant covalent character.

All cyclohexyl rings of the phosphine ligands have the chair conformation and are equatorially bonded to phosphorus as is usual.[16] The mean P–C (1.87 Å) and C–C (1.55 Å) bond lengths are also unexceptional.

Since there are few short intermolecular contacts,

interactions between the molecules may not be strong. The Figure shows some short intramolecular contacts. Steric hindrance within the molecule by bulky tricyclohexylphosphines seems to play an important role in the distortion of the five-co-ordination geometry around cobalt from the ordinary trigonal bipyramid and to the stabilization of the paramagnetic hydride. The short contacts of $H_t(1)$ with $H(211)$ and $H_t(2)$ with $H(511)$ explain the comparatively small $H_t(1)$–B–$H_t(2)$ angle.

Two bridging hydrogens, $H_b(1)$ and $H_b(2)$, are held between hydrogens of cyclohexyl rings, $H(562)$, $H(261)$, $H(662)$, and $H(361)$. These contacts might also be correlated with the deformation of the BH_4 ligand and stabilization of tetrahydroborato-complexes.

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