Crystal and Molecular Structure of Hydrido(tetrahydroborato)bis(tricyclohexylphosphine)nickel(II)

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The crystal structure of the title complex has been determined by single-crystal *X*-ray diffraction techniques. Crystals are monoclinic, space group $P2_1/a$, with cell dimensions $a = 23.168(6)$, $b = 12.664(4)$, $c = 13.107(3)$ Å, $\beta = 105.75(3)°$, and $Z = 4$. The nickel atom is co-ordinated by two tricyclohexylphosphine ligands in *trans* positions, a hydride hydrogen, and two bridging hydrogen atoms of the tetrahydroborate ligand to give a deformed trigonal bipyramid. The structure of the compound is less distorted than that of the cobalt analogue having the same set of ligands, and the difference between the structures is discussed in terms of the *d*-electron configurations of the nickel and cobalt complexes.

THE bonding of the $[BH_4]^-$ group in transition-metal tetrahydroborate complexes poses interesting chemical and spectroscopic problems.[1] In particular, the establishment of the co-ordination mode in these complexes as tri-, bi-, or uni-dentate is important in confirming the assignments of the vibrational spectra. We have determined the crystal structure of a paramagnetic cobalt complex $[CoH(BH_4)\{P(C_6H_{11})_3\}_2]$ and found that the $[BH_4]^-$ ligand is bidentate but is rather distorted.[2]

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[1] T. J. Marks and J. R. Kolb, *Chem. Rev.*, 1977, **77**, 263.

[2] M. Nakajima, T. Saito, A. Kobayashi, and Y. Sasaki, *J.C.S. Dalton*, 1977, 385.

Recent publications of a few interesting BH_4 complexes of rhodium, iridium, cobalt, and copper[3] have prompted us to study the crystal structure of a known diamagnetic nickel complex $[NiH(BH_4)\{P(C_6H_{11})_3\}_2]$ having the same set of ligands as the above cobalt complex. This complex was reported by Green *et al.*[4] and the bidentate nature of the $[BH_4]^-$ group was inferred from i.r. spectra. The present crystallographic study sought to confirm this conclusion and to determine the Ni–H-(hydride) distance. The results have shown that the nickel complex is isomorphous with and essentially similar to the cobalt analogue, but that it is more symmetric. The difference between the structures is discussed with reference to the *d*-electron configurations of Ni^{II} and Co^{II}.

EXPERIMENTAL

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

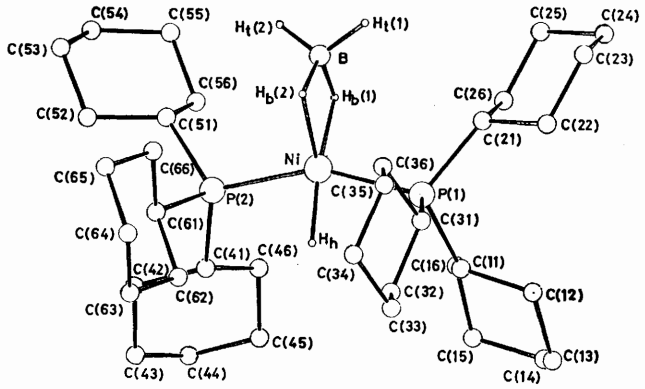

FIGURE 1 Molecular structure, illustrating the atom-numbering scheme. Cyclohexyl hydrogen atoms have been omitted for clarity

Synthesis.—The complex $[NiH(NO_3)\{P(C_6H_{11})_3\}_2]$[5] (2.6 g) was treated with $Na[BH_4]$ (0.4 g) in ethanol (50 cm^3)–acetone (50 cm^3) at 30 °C for 24 h. The product was filtered off and washed with water (50 cm^3) and methanol (50 cm^3) and dried *in vacuo* (2.0 g).

Preparation of the Crystal.—The complex $[NiH(BH_4)\{P(C_6H_{11})_3\}_2]$ (2.0 g) was dissolved in toluene (100 cm^3), methanol (150 cm^3) was added, and the solution filtered. After 24 h at *ca.* 5 °C the orange crystals which formed were filtered off, and washed with methanol (10 cm^3), and dried *in vacuo* (1.1 g).

Data Collection.—A single crystal with dimensions *ca.* 0.5 × 0.4 × 0.3 mm was sealed in a glass capillary under nitrogen and used for measurement of diffraction intensities and dimensions on a Rigaku automatic 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 17 reflections.

Crystal Data.—$C_{36}H_{71}BNiP_2$, $M = 635.4$, Monoclinic, $a = 23.168(6)$, $b = 12.664(4)$, $c = 13.107(3)$ Å, $\beta = 105.75(3)°$, $U = 3\,701.0$ Å^3, $D_m = 1.14$ g cm^{-3}, $Z = 4$, $D_c = 1.14$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 6.3 cm^{-1}. Space group $P2_1/a$ from systematic absences: $h0l$, $h = 2n + 1$; $0k0$, $k = 2n + 1$. Intensity data were recorded by the ω—2θ scan technique with a scan speed of 2° min^{-1} and background counts of 10 s were taken at each end of the scan. The intensities of three standard reflections measured every 50 reflections during the data collection did not vary by $>3\%$. Intensities were measured up to 2θ 60°, and 4 314 independent reflections having $F_o \geqslant 3\sigma$ were used for the structure analysis. Intensities were corrected for Lorentz and polarization effects, but not for absorption.

Determination of the Structure.—The structure was solved by the heavy-atom method. The position of the nickel atom was deduced from three-dimensional Patterson maps and the positions of all the non-hydrogen atoms were determined by subsequent Fourier syntheses. Block-diagonal

TABLE 1

Positional parameters, with estimated standard deviations in parentheses

Atom	x	y	z
(*a*) For non-hydrogen atoms (× 10^4)			
Ni	1 540(0)	2 265(1)	1 746(1)
P(1)	1 862(1)	972(1)	936(1)
P(2)	1 271(1)	3 010(1)	3 050(1)
B	1 513(1)	3 613(7)	675(6)
C(11)	1 467(3)	−287(5)	975(5)
C(12)	1 670(3)	−1 254(5)	459(5)
C(13)	1 365(4)	−2 261(7)	711(7)
C(14)	717(4)	−2 166(7)	485(8)
C(15)	529(4)	−1 238(7)	1 024(8)
C(16)	805(4)	−213(7)	685(7)
C(21)	1 856(3)	1 284(5)	−450(4)
C(22)	2 262(3)	638(6)	−970(5)
C(23)	2 250(4)	1 131(7)	−2 046(5)
C(24)	1 616(4)	1 184(7)	−2 771(5)
C(25)	1 206(4)	1 815(7)	−2 254(5)
C(26)	1 218(3)	1 329(5)	−1 186(4)
C(31)	2 662(3)	663(5)	1 565(4)
C(32)	2 775(3)	86(6)	2 633(5)
C(33)	3 450(3)	−110(6)	3 098(6)
C(34)	3 811(3)	895(7)	3 216(6)
C(35)	3 698(3)	1 443(6)	2 160(6)
C(36)	3 030(3)	1 675(5)	1 690(5)
C(41)	786(2)	2 138(4)	3 611(4)
C(42)	537(3)	2 596(5)	4 478(5)
C(43)	208(3)	1 754(6)	4 941(5)
C(44)	−285(3)	1 240(6)	4 094(6)
C(45)	−37(3)	783(6)	3 227(6)
C(46)	272(3)	1 633(5)	2 748(5)
C(51)	904(3)	4 321(5)	2 736(4)
C(52)	884(3)	5 074(5)	3 645(5)
C(53)	654(3)	6 166(5)	3 199(6)
C(54)	47(3)	6 086(6)	2 395(7)
C(55)	51(3)	5 310(6)	1 503(6)
C(56)	284(3)	4 229(5)	1 952(5)
C(61)	1 918(2)	3 287(4)	4 212(4)
C(62)	2 242(3)	2 289(5)	4 712(5)
C(63)	2 772(3)	2 557(6)	5 664(5)
C(64)	3 214(3)	3 299(6)	5 357(6)
C(65)	2 895(3)	4 304(6)	4 850(5)
C(66)	2 363(3)	4 043(5)	3 903(5)
(*b*) For hydrogen atoms (× 10^3)			
H_h	168(3)	143(5)	257(5)
H_b (1)	110(2)	297(4)	69(4)
H_b (2)	196(2)	331(4)	145(4)
H_t (1)	163(3)	358(6)	−9(5)
H_t (2)	135(3)	437(5)	78(5)

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[3] H. D. Empsall, E. M. Hyde, E. Mentzer, B. L. Shaw, and M. F. Uttley, *J.C.S. Dalton*, 1976, 2069; P. Dapporto, S. Midollini, A. Orlandini, and L. Sacconi, *Inorg. Chem.*, 1976, **15**, 2768; J. C. Bommer and K. W. Morse, *J.C.S. Chem. Comm.*, 1977, 137.

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

[5] H. Imoto, H. Moriyama, T. Saito, and Y. Sasaki, *J. Organometallic Chem.*, 1976, **120**, 453.

least-squares refinement with anisotropic temperature factors reduced R to 0.101. A difference-Fourier synthesis at this stage revealed the positions of the hydride and BH_4 hydrogen as well as 58 of the 66 cyclohexyl hydrogen atoms. In further refinements, where the calculated positions of the unlocated eight hydrogen atoms were included, with isotropic temperature factors for the hydrogen and anisotropic temperature factors for non-hydrogen atoms, the final R was 0.075. The peak height of the hydride hydrogen was 0.40 e Å^{-3} and of BH_4 hydrogen atoms 0.40—0.60 e Å^{-3} from a difference-Fourier map calculated at this stage. There were no peaks >0.3 e Å^{-3} near the hydride hydrogen.

Atomic scattering factors were taken from ref. 6, those of nickel and phosphorus being corrected for the real part of anomalous dispersion, using values estimated from ref. 7. A weighting scheme, with $w = 1$ for reflections having $|F_o| \geqslant 19.81$ on an absolute scale and $w = 0.5$ in other cases, was employed, since the counting reliability of reflections having lower intensities was uncertain. We regard the final R value obtained using this weighting scheme as reasonable. Calculations were performed on the HITAC 8700/8800 computer at the Computer Center of the University of Tokyo, using a local version of the UNICS programs.[8]

Final positional parameters are given in Table 1, with their estimated standard deviations. Those for cyclohexyl hydrogen atoms are omitted. The numbering system of the atoms is shown in Figure 1. Observed and calculated structure factors, thermal parameters, and parameters for cyclohexyl hydrogen atoms are listed in Supplementary Publication No. SUP 22214 (21 pp.).†

RESULTS AND DISCUSSION

Molecular Structure.—Selected bond lengths, bond angles, best planes, dihedral angles, and vector-plane angles are summarized in Tables 2 and 3. All the atoms are in general positions. The nickel atom is co-ordinated by two tricyclohexylphosphines in the *trans* positions, the hydride hydrogen (H_h), and two bridging hydrogen atoms (H_b) of the BH_4 group. The Ni, P(1), P(2), B, and H_h atoms are coplanar to within 0.11 Å [plane (1)]. The Ni, H_h, $H_b(1)$, $H_b(2)$, and B atoms are coplanar to within 0.01 Å [plane (2)]. Plane (2) is perpendicular to plane (1) and is a pseudo-mirror plane of the molecule. The four hydrogen atoms of the BH_4 group are arranged tetrahedrally around the boron. Plane (3) [B, $H_t(1)$, $H_t(2)$] is almost parallel to plane (1) and has a dihedral angle of 3°.

TABLE 2

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

(*a*) Distances *

Ni–P(1)	2.188(2)	Ni–P(2)	2.187(2)
Ni–B	2.201(8)	Ni–H_h	1.48(7)
Ni–$H_b(1)$	1.73(5)	Ni–$H_b(2)$	1.76(6)
B–$H_b(1)$	1.27(5)	B–$H_b(2)$	1.30(5)
B–$H_t(1)$	1.12(8)	B–$H_t(2)$	1.05(6)

(*b*) Angles

P(1)–Ni–P(2)	155.4(7)	P(2)–Ni–B	101.5(2)
P(1)–Ni–B	103.0(2)	P(2)–Ni–H_h	78(3)
P(1)–Ni–H_h	77(3)	P(2)–Ni–$H_b(1)$	100(2)
P(1)–Ni–$H_b(1)$	102(2)	P(2)–Ni–$H_b(2)$	98(2)
P(1)–Ni–$H_b(2)$	100(2)	B–Ni–$H_b(1)$	35(2)
B–Ni–H_h	168(3)	$H_b(1)$–Ni–$H_b(2)$	71(2)
B–Ni–$H_b(2)$	36(2)	H_h–Ni–$H_b(1)$	157(3)
Ni–B–$H_b(1)$	52(3)	H_h–Ni–$H_b(2)$	132(3)
Ni–B–$H_t(1)$	125(4)	Ni–B–$H_b(2)$	53(2)
$H_b(1)$–B–$H_b(2)$	104(4)	Ni–B–$H_t(2)$	125(3)
$H_b(1)$–B–$H_t(1)$	112(5)	$H_t(1)$–B–$H_t(2)$	110(5)
$H_b(1)$–B–$H_t(2)$	107(4)	$H_b(2)$–B–$H_t(1)$	110(5)
Ni–$H_b(1)$–B	93(3)	$H_b(2)$–B–$H_t(2)$	114(4)
Ni–$H_b(2)$–B	91(3)		

* Mean dimensions in C_6H_{11} groups: P–C 1.86(1) and C–C 1.52(1) Å; P–C–C 114(1) and C–C–C 111(1)°.

TABLE 3

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

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

$$-0.862\,19X - 0.263\,29Y - 0.432\,79Z + 4.346\,69 = 0$$

[P(1) 0.080, P(2) 0.076, H_h −0.108, B −0.042, Ni 0.097]

Plane (2): Ni, H_h, $H_b(1)$, $H_b(2)$

$$0.497\,97X - 0.593\,84Y - 0.631\,96Z + 1.634\,73 = 0$$

[Ni 0.007, H_h −0.004, $H_b(1)$ −0.002, $H_b(2)$ −0.001, B 0.005]

Plane 3: B, $H_t(1)$, $H_t(2)$

Plane 4: B, $H_b(1)$, $H_b(2)$

Dihedral angles (°) between planes: (1)–(2) 90, (1)–(3) 3, (3)–(4) 87

Vector-plane angles (°): Ni · · · B–(3) 4, Ni · · · B–(4) 1

The angle P(1)–Ni–P(2) is 155.4(7)°, and the hydride hydrogen is located such that it is held between the two tricyclohexylphosphines with an Ni–H distance [1.48(7) Å] which is nearly equal to the sum of the covalent radii of nickel and hydrogen (1.48 Å),[9] and a little longer than the Ni-H distance (1.37 Å) in $[NiH(Cl)(PPr^i_3)_2]$.[10] The Ni-B distance (2.20 Å) is a little longer than the sum of the covalent radii of nickel and boron (1.98 Å).[9]

The co-ordination around the nickel atom may be described as a deformed trigonal bipyramid with the two phosphine ligands axial and the three hydrogen atoms equatorial. The bond angles between the three equatorial hydrogen atoms are significantly distorted from the ideal value of 120°, and the two phosphine ligands bend towards the hydride hydrogen atom. Therefore the actual symmetry is at best C_{2v} rather than the D_{3h} of a trigonal bipyramid. Alternatively, the co-ordination can be described as square planar with four ligating atoms, H_h, P(1), P(2), and B, which are almost coplanar, if we ignore the hydrogen atoms of the BH_4 group.

A projection of the atoms on plane (1), together with the similar one for the atoms in $[CoH(BH_4)\{P(C_6H_{11})_3\}_2]$, is shown in Figure 2. The projections of the atoms on plane (2) are illustrated in Figure 3. In a previous paper [2] we described the co-ordination of the cobalt complex as a deformed square pyramid, but the same complex can be described also as deformed square planar

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† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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

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

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

[9] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960, p. 256.

[10] U. A. Gregory and B. T. Kilbourn, referred to in B. A. Frenz and J. A. Ibers, 'Transition Metal Hydrides,' ed. E. L. Muetterties, Marcel Dekker, New York, 1971, p. 45.

if the hydrogen atoms of the BH_4 group are neglected. Figures 2 and 3 indicate that the structure of the cobalt complex is much more deformed than that of the nickel analogue. Distortion of the BH_4 group in the cobalt complex from C_{2v} symmetry is particularly noteworthy.

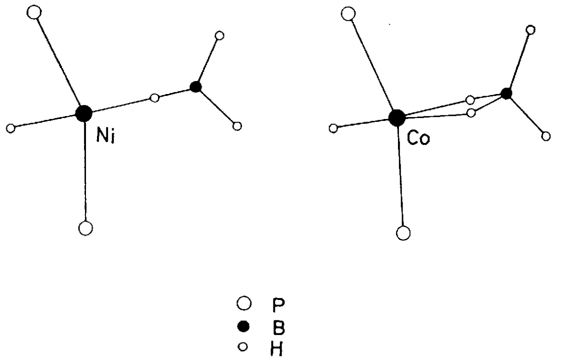

FIGURE 2 Projections of atoms on the least-squares plane (1) [P(1), P(2), H_h, B]

All the cyclohexyl rings of the phosphine ligands have the chair conformation and the bond lengths and bond angles are normal.

Because of the same set of ligands and of the similarity of the ionic radii of Ni^{II} and Co^{II}, non-bonded interactions between the ligands in these nickel and cobalt BH_4 complexes should be similar. Thus the different geometries of the complexes can only be rationalized in terms of the different *d*-electron configurations. The nickel complex is low-spin d^8 (diamagnetic) and the cobalt complex is low-spin d^7 ($\mu_{eff.}$ 2.15 B.M.*).[11]

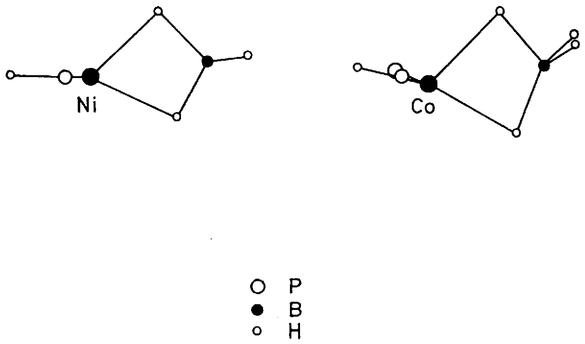

FIGURE 3 Projections of atoms on the least-squares plane (2) [Ni or Co, H_h, $H_b(1)$, $H_b(2)$]

Prediction of the stereochemistry of low-spin d^7 and d^8 transition-metal complexes $[MY_n]$ by the angular-overlap method[12] indicates that a square-pyramidal (s.p.) structure is more favourable energetically than a trigonal-bipyramidal (t.b.p.) structure for five-co-ordination. The energy difference between the two structures is larger for d^7 (210) than for d^8 (220) configurations, and it is conceivable that low-spin d^7 complexes tend to exhibit s.p. structures. In the case of four-co-ordination, the s.p. structure is more favourable than *cis*-divacant octahedral and the energy difference is larger for d^8 (220) than for d^7 (210) configurations. Hence the s.p. structure is more likely in low-spin d^8 complexes. Although the above results have been derived in the case of simple binary compounds like metal carbonyls $[M(CO)_n]$, it is tempting to apply them to the present nickel and cobalt BH_4 complexes. Thus if we regard these complexes as five-co-ordinate it is understandable that the low-spin d^8 nickel complex adopts a t.b.p. and the low-spin d^7 cobalt complex a s.p. structure. If we ignore the hydrogen atoms of the BH_4 group, the square-planar structure of the nickel complex and the distortion from it in the cobalt complex may also be associated with the *d*-electron configurations. If the coincidence is more than fortuitous, this suggests the wider applicability of the simple angular-overlap method to the prediction of the stereochemistry of transition-metal complexes of lower symmetries.

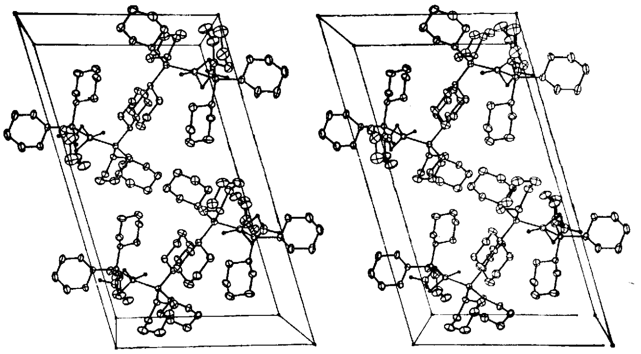

FIGURE 4 Stereoview of a unit cell of $[NiH(BH_4)\{P(C_6H_{11})_3\}_2]$. The *a* axis is vertically downwards, the *c* axis is horizontal to the left, and the *b* axis is perpendicular to the paper. The thermal ellipsoids are drawn at the 30% probability level (ORTEP). Cyclohexyl hydrogen atoms have been omitted

Crystal Structure.—A stereoprojection of the crystal structure along the *b* axis is shown in Figure 4. The structure is similar to that of the cobalt analogue, but there are slight differences in the cell constants of the nickel and cobalt complexes.[2] Bulky tricyclohexylphosphines seem to determine the gross structures, in spite of the slightly different molecular structures due to the different *d*-electron configurations of Ni^{II} and Co^{II}.

[7/1099 *Received, 24th June,* 1977]

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* Throughout this paper: 1 B.M. ≈ 9.27×10^{-24} A m^2.

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

[12] J. K. Burdett, *Inorg. Chem.*, 1975, **14**, 375.