Contribution from the Departments of Chemistry,
Barnard College and Columbia University, New York, New York 10027

Transition Metal Hydroborate Complexes. 9.[1] Preparation, Properties, and Structure of Di-μ-cyanotrihydroborato-bis(2,2′,2″-triaminotriethylamine)dinickel(II) Tetraphenylborate

BERNICE G. SEGAL[2a] and STEPHEN J. LIPPARD*[2b]

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The compound di-μ-cyanotrihydroborato-bis(2,2′,2″-triaminotriethylamine)dinickel(II) tetraphenylborate has been prepared and its molecular structure determined by a single-crystal x-ray diffraction study. The complex crystallizes in the space group $P2_1/c$ of the monoclinic system with two dimeric cations and four tetraphenylborate anions in the unit cell. Lattice parameters are $a = 15.027$ (6) Å, $b = 9.885$ (4) Å, $c = 20.923$ (9) Å, and $\beta = 100.17$ (1)°. By use of 4153 unique observed reflections collected by diffractometer, the structure was solved and refined on F to a final value for the discrepancy index R_1 of 0.048. The compound is a centrosymmetric cyanotrihydroborate-bridged dimer. The Ni···Ni distance within the dimer is 5.933 (2) Å. The Ni atoms are octahedrally coordinated with a hydrogen atom of the $-NCBH_3$ ligand occupying one of the coordination sites. The Ni–H bond distance is 2.1 (1) Å. The two dimeric cations in the unit cell are isolated from one another by two tetraphenylborate anions. The Ni–H–B stretching modes in the infrared region have been assigned by comparison with the spectrum of the deuterated compound containing the $-NCBD_3$ ligand. The infrared spectra of $[(Ph_3P)_2Cu(NCBH_3)]_2$ and $[(Ph_3P)_2Cu(NCBD_3)]_2$ have also been compared. Characteristic frequencies for the $-NCBH_3$ group as both a monodentate and a bridging ligand are summarized.

Introduction

Transition metal complexes of the cyanotrihydroborate anion containing the $M-NCBH_3$ linkage have been known for several years.[3-8] A single example in which the H_3BCN^- anion serves as a bridging ligand between two Cu(I) atoms has also been reported.[9] It was of interest to determine whether other transition metal bridged cyanotrihydroborate complexes could be synthesized. In particular, it was decided to investigate nickel(II) complexes (i) since $[(en)_2Ni(NCBH_3)_2]\cdot THF$ is already known,[3] (ii) since the number of compounds known to contain an Ni–H bond is not large (in the triad Ni, Pd, Pt, the metal with the least stable hydrides is Ni[10]), and (iii) since there is the possibility that spin exchange might occur in a compound containing two paramagnetic metal ions linked, inter alia, through a three-center M–H–B bridge bond. The present paper describes the synthesis and structural characterization of $[(tren)Ni(NCBH_3)]_2^{2+}$ as its tetraphenylborate salt. This cation is related to a family of ligand-bridged dimers of general formula $[(tren)MX]_2^{2+}$ characterized chiefly by Hendrickson and co-workers.[11-13] Magnetic studies have been carried out and will be reported separately.[14]

Experimental Section

Synthesis. The ligand 2,2′,2″-triaminotriethylamine (tren) was extracted from technical grade Fisher Scientific triethylenetetramine by fractional precipitation of the hydrochloride salt, tren·3HCl, according to literature procedures,[15,16] recrystallized from aqueous ethanol and stored in a desiccator.

A 1.0-mL portion of a 50% NaOH solution was added to 1.03 g (4 mmol) of recrystallized tren·3HCl and the mixture was stirred thoroughly and warmed on a steam bath. The free amine was extracted into two 12-mL portions of chloroform and the sodium chloride residue discarded. A 1.06-g (4-mmol) sample of $NiSO_4\cdot 6H_2O$ was dissolved in 30 mL of distilled water. A 20-mL sample of methanol was added to the chloroform solution of tren and this solution was then added to the green nickel solution which immediately turned deep royal blue. A colorless chloroform lower layer was formed. This mixture was stirred for about 1 h. A 0.277-g (4.4-mmol) sample of sodium cyanotrihydroborate (Aldrich, used without further purification) was dissolved completely in 20 mL of methanol, and this solution was added to the deep blue nickel solution. The resulting purple solution was filtered, decanting the upper layer. A small amount of pale gray residue was discarded. A 1.38-g (4-mmol) sample of sodium tetraphenylborate was dissolved in 25 mL of water and this solution was slowly filtered into the purple nickel solution. A pale precipitate appeared immediately, but after the entire sodium tetraphenylborate solution had been added and the mixture thoroughly stirred, there was a large curdy purple precipitate and a colorless supernatant. The precipitate was collected by filtration and washed with two small portions of water and two of methanol; yield of crude product 2.85 g (79.2%). The compound was recrystallized twice from boiling methanol to yield 0.904 g (31.8%) of dark purple crystals. Microchemical analysis was performed by Galbraith Laboratories, Knoxville, Tenn. Anal. Calcd for $NiC_{31}H_{41}N_5B_2$: C, 66.01; H, 7.33; N, 12.42. Found: C, 65.67; H, 7.20; N, 12.34.

The compound is readily soluble in acetonitrile and acetone, insoluble in toluene, slightly soluble in boiling water, and moderately soluble in boiling methanol. The addition of either methanol or water to the acetonitrile solution reprecipitates the compound. If the acetonitrile or acetone solutions are allowed to evaporate until crystals appear, the crystals so produced are not the original compound since their IR spectra contain peaks attributable to acetonitrile or acetone, respectively, and the peaks assigned (vide infra) to the Ni–H–B stretching modes are absent.

Physical Measurements. Infrared spectra were obtained with a Perkin-Elmer 467 grating spectrophotometer in the range 4000–600 cm^{-1}. Samples were mulled in Nujol and spread between NaCl plates. Polystyrene was used as the calibrant and the resulting frequencies are estimated to be accurate to ±2 cm^{-1}.

Collection and Reduction of the X-Ray Data. A clear purple crystal of dimensions 0.43 × 0.37 × 0.07 mm was mounted with nail polish on the end of a glass fiber parallel to the long axis. Preliminary precession photographs using Cu Kα radiation (λ 1.5418 Å) showed the lattice to have Laue symmetry $2/m$ with extinctions $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, which uniquely indicate the space group to be $P2_1/c$.[17] Before collection of data, the rotation axis was deliberately offset by ~10° from the mounting axis b^*. Details of the data collection and reduction are given in Table I.

Determination and Refinement of the Structure. The structure was solved by conventional Patterson, Fourier and least-squares refinement techniques. Scattering factors for neutral Ni, N, C, and B atoms and corrections for the anomalous dispersion effects for the Ni atoms were obtained from ref 18. Scattering factors for neutral hydrogen atoms were taken from Stewart et al.[19] Several cycles of unit weight and individual isotropic refinement for all the 39 nonhydrogen atoms in the asymmetric unit resulted in discrepancy values $R_1 = 0.110$ and $R_2 = 0.111$.[20] All atoms other than hydrogen were then assigned anisotropic temperature factors.[21] Since it requires 351 variables to refine 39 atoms with anisotropic temperature factors and 164 variables to refine 41 hydrogen atoms isotropically, subsequent refinements were carried out by varying the atoms of the cation on separate cycles from those of the tetraphenylborate anion. Hydrogen atoms were refined only when the atoms to which they were attached were also refined. All of the hydrogen atoms were located on difference Fourier maps following several successive cycles of refinement of different groups of atoms.

In order to verify that the Ni atom was bound to the nitrogen atom of the $-NCBH_3$ group and that no structural rearrangement had taken place which would result in an $Ni-CNBH_3$ linkage, the structure was

Table I. Experimental Details of the X-Ray Diffraction Study of $[(\text{tren})\text{Ni}(\text{NCBH}_3)]_2[\text{B}(\text{C}_6\text{H}_5)_4]_2$

(A) Crystal Parameters[a] at 23 °C

a = 15.027 (6) Å	β = 100.166 (12)
b = 9.885 (4) Å	V = 3059 (4) Å^3
c = 20.923 (9) Å	Space group $P2_1/c$
Z = 2	ρ(calcd) = 1.224 g/cm^3
Mol wt (dimer) 1128.1	ρ(obsd)[b] = 1.23 (1) g/cm^3

(B) Measurement of Intensity Data

Instrument: Picker FACS-I-DOS diffractometer
Radiation: Mo Kα (λ_{α_1} 0.70926 Å), graphite monochromatized
Takeoff angle: 2.0°
Detector aperture: 6 mm × 6 mm
Crystal–detector distance: 31 cm
Scan technique: coupled θ(crystal)–2θ(counter)
Scan range: 1.50° (symmetric, plus Kα_1–Kα_2 dispersion)
Scan rate: 1.0°/min
Maximum 2θ: 52°
Background measurements: stationary crystal, stationary counter; 10-s counts at each end of 2θ scan range
Standards: three reflections $[(12\bar{1}), (0\bar{1}5), (3\bar{2}3)]$ measured every 97 data reflections
No. of reflections collected: 7046

(C) Treatment of Intensity Data[c]

Reduction to preliminary F_o^2 and $\sigma(F_o^2)$: correction for background, attenuators, and Lorentz–polarization of monochromatized x-radiation in the usual manner;[d,e] ϵ[f] = 0.03
Absorption correction: μ = 6.65 cm^{-1}; transmission factors varied from 0.79 to 0.95
Averaging: 642 equivalent pairs in the inner sphere (2$\theta \leqslant$ 20°); agreement factor R_{av}[g] = 0.011
Scaling: Wilson's method[h]
Observed data: 4153 unique reflections for which $F_o^2 > 2\sigma(F_o^2)$

[a] From a least-squares fit to the setting angles of 27 reflections. [b] By suspension in a mixture of *n*-pentane and CCl_4. [c] Programs for an IBM 360/91 computer used in this work include the following: UMAT, the local version of the Brookhaven diffractometer setting and cell constant and orientation refinement program; AVERAGE, which computes a weighted average of equivalent reflections and was written by J. T. Gill; XDATA, the Brookhaven Wilson plot and scaling program; ORABS, the local version of the Oak Ridge absorption correction program; FOURIER, a modification of the Zalkin FORDAP program by R. J. Dellaca and W. T. Robinson, further modified by D. J. Hodgson; CULS, the Columbia University version of the Busing–Martin–Levy structure factor calculation and least-squares refinement program ORFLS; CUGLS, a local version of ORFLS modified by Ibers and Doedens for rigid-body refinement; ORFFE, the Busing–Martin–Levy molecular geometry and error function program; ORTEP II, the Johnson thermal ellipsoid plotting program; and various local data processing programs. [d] See ref 8. [e] See ref 1. [f] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967). [g] $R_{\text{av}} = \Sigma_{i=1}{}^N\Sigma_{j=1}{}^n|\bar{F}_i^2 - F_{ij}^2|/\Sigma_{i=1}{}^N\bar{F}_i^2$, where N is the number of reflections measured more than once and n is the number of observations of the Nth reflection. [h] A. J. C. Wilson, *Nature (London)*, **150**, 151 (1942).

refined in the following manner. All 80 atoms were refined isotropically in four cycles: in the first and third cycles the cation atoms were refined and in the second and fourth cycles the anion atoms were refined. In one of these four cycle refinements the linkage was assumed to be Ni–$NCBH_3$ and in the second it was assumed to be Ni–$CNBH_3$. When the N and C atoms of the cyanotrihydroborate group were interchanged, the temperature factor of the pseudocarbon atom decreased from 5.2 to 3.5 while the temperature factor of the pseudonitrogen atom increased from 5.7 to 8.3. In addition the discrepancy factors R_1 and R_2 increased slightly, from 0.091 and 0.092, respectively, to 0.095 for both when the linkage was taken as Ni–$CNBH_3$. In a separate test of the assignment both the N and C atoms were removed from the refinement cycles and a difference Fourier map based on the refinement of the remaining 78 atoms was obtained. The electron density at the positions of the nitrogen and carbon atoms was 6.4 and 5.2 e/Å^3, respectively, and the original assumption that the linkage is Ni–$NCBH_3$ is therefore considered to be correct.

During the last stages of refinement, the positional parameters and the isotropic temperature factors of the 41 hydrogen atoms and the positional parameters and anisotropic temperature factors of the other 39 atoms were refined, with alternate groups of atoms included in different cycles of refinement as described previously. With 3649 observables $[F^2 > 3\sigma(F^2)]$ R_1 = 0.044 and R_2 = 0.050; with 4153 observables $[F^2 > 2\sigma(F^2)]$ R_1 = 0.051 and R_2 = 0.053. The final cycle of refinement utilized CUGLS4, a program which can refine 400 variables at once; the temperature factors of the hydrogen and phenyl carbon atoms were held constant at the values obtained in the previous refinement, but all other variables were refined. No parameter varied by more than 0.1 of its estimated standard deviation except for one of the hydrogen atoms in an amino group of the tren ligand, the x and z coordinates of which varied by 0.12 and 0.18 of their estimated standard deviations, respectively. The N–H bond distance for this hydrogen atom is 0.67 (4) Å which is shorter than expected and the C···H contact distance to the adjacent methylene carbon atom is 1.84 (4) Å, a value that is also short. The discrepancy indices R_1 and R_2 converged at 0.049 and 0.048, respectively.

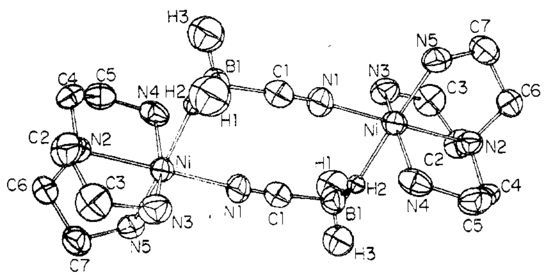

Figure 1. Structure of the dimeric cation $[(\text{tren})\text{Ni}(\text{NCBH}_3)]_2^{2+}$ indicating the atom-labeling scheme. Hydrogen atoms, other than those in the $-NCBH_3$ group, are not shown. The 40% probability thermal ellipsoids are depicted.

The $|F_o| - |F_c|$ values for strong, low-order reflections were randomly positive and negative and therefore no corrections for secondary extinction were applied.

In a test of the weighting scheme used, the function $w\Delta^2$ for data sectioned both with respect to $|F_o|$ and to $(\sin\theta)/\lambda$ showed reasonable consistency and the weighting scheme was therefore considered to be satisfactory. The standard deviation of an observation of unit weight was 1.63.[22] A final difference Fourier map showed only slight residual electron density of 0.54 e/Å^3 near one of the methylene groups in the tren ligand and ~0.4 e/Å^3 near the B, C, and N atoms of the $-NCBH_3$ group and also at the position of the Ni atom.

Table II contains the final atomic positional and thermal parameters for all atoms, with their standard deviations derived from the inverse matrix of the last least-squares refinement cycle. Table III summarizes the molecular geometry. Tables S1 and S2, listing the final observed and calculated structure factor amplitudes and the root-mean-square amplitudes of vibration for the atoms refined anisotropically, are available.[23] The sizes and orientations of the anisotropic ellipsoids are shown along with the atom-labeling scheme in Figure 1.

Results and Discussion

Crystal and Molecular Structure. The compound $[(\text{tren})\text{Ni}(\text{NCBH}_3)]_2(\text{BPh}_4)_2$ is a cyanotrihydroborate-bridged dimer with a crystallographic center of symmetry. The closest Ni···Ni approach is 5.933 (2) Å which may be compared with Ni···Ni distances of 5.385 (1) Å in the corresponding cyanate-bridged dimer,[11] 5.8 Å in the thiocyanate-bridged dimer,[24,25] and 5.220 (2) Å in the azide-bridged dimer.[13] The Ni···Ni distance observed in the cyanotrihydroborate-bridged dimer is somewhat larger because the nickel atoms are part of a ten-membered ring, whereas in the other three cations the ring is eight membered. Figure 2 shows the packing of molecules in the unit cell. The two dimeric cations in the unit cell are isolated from one another by two tetraphenylborate anions. The closest anion–cation contact distance is 2.69 Å between a carbon atom of ring "A" of the BPh_4^- anion and a hydrogen atom of an amino group of the tren ligand. There is one 3.53-Å and one 3.63-Å contact distance between a phenyl group carbon atom and a methylene carbon atom of the tren ligand. All other intermolecular contacts are greater than the sum of the van der Waals radii of the atoms.

Table II

Final Positional and Isotropic Thermal Parameters for the Dimeric Cation $[(\text{tren})\text{Ni}(\text{NCBH}_3)]_2^{2+}$[a, b]

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
Ni	0.15746 (3)	0.10074 (4)	0.09374 (2)		H21[c]	0.169 (3)	0.404 (4)	0.078 (2)	9 (1)
N1	0.0648 (2)	−0.0445 (3)	0.0681 (1)		H22	0.244 (2)	0.442 (4)	0.149 (2)	7 (1)
C1	0.0223 (3)	−0.1339 (4)	0.0491 (2)		H31	0.086 (2)	0.423 (4)	0.160 (2)	7 (1)
B1	−0.0403 (4)	−0.2573 (6)	0.0183 (3)		H32	0.160 (3)	0.338 (5)	0.215 (2)	9 (1)
H1	−0.008 (3)	−0.332 (5)	−0.003 (2)	9 (1)	H41	0.268 (2)	0.312 (3)	0.032 (2)	4.6 (8)
H2	−0.090 (2)	−0.210 (3)	−0.011 (1)	2.3 (6)	H42	0.355 (2)	0.313 (3)	0.079 (2)	4.8 (9)
H3	−0.043 (2)	−0.355 (4)	0.060 (2)	7.1 (9)	H51	0.356 (3)	0.128 (4)	0.005 (2)	8 (1)
N2	0.2555 (2)	0.2499 (3)	0.1214 (1)		H52	0.369 (2)	0.077 (4)	0.075 (2)	6 (1)
N3	0.0794 (3)	0.2285 (4)	0.1430 (2)		H61	0.329 (2)	0.280 (4)	0.210 (2)	7 (1)
N4	0.2421 (3)	0.0467 (3)	0.0297 (2)		H62	0.372 (2)	0.161 (4)	0.169 (2)	5.8 (9)
N5	0.2268 (2)	−0.0016 (3)	0.1731 (2)		H71	0.321 (2)	0.058 (4)	0.258 (2)	6.8 (9)
C2	0.2047 (3)	0.3750 (4)	0.1299 (2)		H72	0.223 (2)	0.135 (4)	0.243 (2)	7 (1)
C3	0.1319 (3)	0.3481 (5)	0.1683 (2)		H33[d]	0.060 (3)	0.197 (5)	0.165 (2)	6 (2)
C4	0.3064 (3)	0.2620 (5)	0.0670 (2)		H34	0.033 (3)	0.259 (5)	0.107 (2)	10 (1)
C5	0.3262 (3)	0.1242 (5)	0.0431 (2)		H43	0.210 (2)	0.064 (3)	−0.008 (2)	5.1 (9)
C6	0.3155 (3)	0.2045 (5)	0.1823 (2)		H44	0.251 (2)	−0.028 (4)	0.029 (2)	5 (1)
C7	0.2729 (3)	0.0971 (4)	0.2189 (2)		H53	0.195 (3)	−0.042 (4)	0.186 (2)	6 (1)
					H54	0.273 (3)	−0.048 (4)	0.160 (2)	8 (1)

Final Anisotropic Thermal Parameters for the Dimeric Cation[e]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	5.50 (2)	9.04 (5)	2.12 (1)	−1.18 (3)	0.51 (1)	−0.21 (2)	N5	6.4 (2)	11.6 (4)	2.62 (9)	−1.1 (2)	0.8 (1)	0.8 (2)
N1	7.2 (2)	10.9 (4)	3.22 (9)	−2.9 (2)	0.2 (1)	−0.4 (2)	C2	9.1 (3)	9.1 (5)	4.0 (1)	−1.9 (3)	1.6 (2)	−1.2 (2)
C1	6.0 (2)	15.0 (6)	2.7 (1)	−0.3 (3)	0.5 (1)	0.5 (2)	C3	8.5 (3)	11.9 (5)	4.3 (1)	1.1 (3)	1.7 (2)	−1.7 (2)
B1	6.2 (3)	14.6 (7)	3.2 (1)	−1.6 (4)	0.6 (2)	−1.5 (3)	C4	7.1 (3)	16.0 (6)	3.0 (1)	−4.0 (3)	1.7 (1)	0.4 (2)
N2	5.9 (2)	9.8 (3)	2.31 (7)	−1.4 (2)	1.02 (9)	−0.4 (1)	C5	7.2 (3)	20.0 (8)	3.0 (1)	−1.0 (4)	2.2 (1)	−0.9 (2)
N3	6.7 (2)	15.0 (5)	3.3 (1)	−0.2 (3)	1.7 (1)	−0.2 (2)	C6	6.0 (2)	17.4 (6)	2.4 (1)	−2.6 (3)	0.3 (1)	−0.9 (2)
N4	8.0 (2)	11.7 (4)	2.19 (8)	0.8 (3)	0.8 (1)	−0.8 (2)	C7	7.5 (3)	14.6 (5)	2.6 (1)	−0.8 (3)	−0.3 (1)	0.6 (2)

Final Positional and Isotropic Thermal Parameters for the Tetraphenylborate Anion[f]

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
B2	−0.2794 (2)	0.2264 (3)	0.1333 (2)		CD5	−0.3798 (3)	0.2455 (4)	−0.0532 (2)	
CA1	−0.2810 (2)	0.0607 (3)	0.1391 (1)		CD6	−0.3694 (2)	0.2305 (4)	0.0132 (2)	
CA2	−0.3581 (2)	−0.0154 (3)	0.1414 (2)		HA2	−0.407 (2)	0.032 (3)	0.141 (1)	3.4 (7)
CA3	−0.3580 (3)	−0.1555 (4)	0.1403 (2)		HA3	−0.410 (2)	−0.204 (3)	0.139 (1)	5.3 (9)
CA4	−0.2810 (3)	−0.2256 (4)	0.1361 (2)		HA4	−0.285 (2)	−0.314 (3)	0.131 (1)	4.9 (8)
CA5	−0.2037 (3)	−0.1557 (4)	0.1333 (2)		HA5	−0.152 (2)	−0.199 (3)	0.127 (1)	4.5 (8)
CA6	−0.2042 (2)	−0.0162 (3)	0.1353 (1)		HA6	−0.155 (2)	0.029 (3)	0.131 (1)	3.1 (7)
CB1	−0.1879 (2)	0.2908 (3)	0.1771 (1)		HB2	−0.188 (2)	0.470 (3)	0.125 (2)	5.7 (9)
CB2	−0.1566 (2)	0.4203 (3)	0.1644 (2)		HB3	−0.068 (2)	0.565 (3)	0.190 (1)	5.4 (9)
CB3	−0.0843 (2)	0.4808 (4)	0.2041 (2)		HB4	0.005 (2)	0.454 (4)	0.287 (2)	8 (1)
CB4	−0.0403 (2)	0.4173 (4)	0.2584 (2)		HB5	−0.049 (2)	0.251 (3)	0.308 (1)	4.8 (9)
CB5	−0.0692 (2)	0.2922 (4)	0.2734 (2)		HB6	−0.163 (2)	0.146 (3)	0.246 (1)	4.1 (7)
CB6	−0.1416 (2)	0.2294 (3)	0.2333 (2)		HC2	−0.349 (2)	0.187 (3)	0.244 (1)	3.7 (7)
CC1	−0.3623 (2)	0.2993 (3)	0.1622 (1)		HC3	−0.458 (2)	0.298 (4)	0.290 (2)	7 (1)
CC2	−0.3823 (2)	0.2621 (3)	0.2226 (2)		HC4	−0.538 (2)	0.483 (4)	0.241 (2)	6.4 (9)
CC3	−0.4464 (2)	0.3278 (4)	0.2512 (2)		HC5	−0.504 (2)	0.545 (3)	0.140 (1)	5.7 (9)
CC4	−0.4939 (2)	0.4345 (4)	0.2201 (2)		HC6	−0.402 (2)	0.436 (2)	0.091 (1)	2.8 (6)
CC5	−0.4772 (2)	0.4744 (4)	0.1611 (2)		HD2	−0.162 (2)	0.306 (2)	0.050 (1)	2.6 (6)
CC6	−0.4122 (2)	0.4084 (3)	0.1327 (2)		HD3	−0.179 (2)	0.331 (3)	−0.059 (1)	4.8 (9)
CD1	−0.2875 (2)	0.2538 (3)	0.0551 (1)		HD4	−0.311 (2)	0.297 (3)	−0.120 (2)	6 (1)
CD2	−0.2171 (2)	0.2904 (3)	0.0241 (2)		HD5	−0.438 (2)	0.222 (3)	−0.078 (2)	6.3 (9)
CD3	−0.2260 (3)	0.3071 (4)	−0.0426 (2)		HD6	−0.417 (2)	0.203 (3)	0.031 (1)	4.9 (9)
CD4	−0.3083 (3)	0.2854 (4)	−0.0807 (2)						

Final Anistropic Thermal Parameters for the Tetraphenylborate Anion[e]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
B2	3.1 (2)	7.7 (4)	1.81 (8)	0.1 (2)	0.31 (9)	0.4 (1)	CC1	3.3 (1)	7.5 (3)	1.84 (8)	−0.4 (2)	0.15 (8)	−0.4 (1)
CA1	3.9 (2)	7.6 (3)	1.42 (7)	0.2 (2)	0.29 (8)	−0.0 (1)	CC2	4.1 (2)	9.5 (4)	2.36 (9)	0.4 (2)	0.7 (1)	−0.1 (2)
CA2	4.3 (2)	9.4 (4)	2.7 (1)	0.1 (2)	0.8 (1)	−0.1 (2)	CC3	5.4 (2)	14.0 (5)	2.8 (1)	−0.2 (3)	1.6 (1)	−0.7 (2)
CA3	6.5 (3)	10.0 (4)	3.0 (1)	−2.7 (3)	1.0 (1)	−0.5 (2)	CC4	4.3 (2)	13.0 (5)	4.1 (1)	−0.0 (3)	1.5 (1)	−1.7 (2)
CA4	8.4 (3)	7.9 (4)	2.7 (1)	0.5 (3)	0.6 (1)	−0.2 (2)	CC5	4.7 (2)	8.6 (4)	4.2 (1)	1.5 (3)	0.2 (1)	−0.3 (2)
CA5	6.1 (2)	10.8 (5)	2.3 (1)	2.3 (3)	0.6 (1)	−0.1 (2)	CC6	4.4 (2)	8.8 (4)	2.7 (1)	0.4 (2)	0.5 (1)	0.2 (2)
CA6	4.4 (2)	8.6 (4)	1.97 (9)	0.5 (2)	0.3 (1)	−0.1 (1)	CD1	3.8 (2)	7.5 (3)	1.87 (7)	0.7 (2)	0.30 (9)	0.2 (1)
CB1	3.1 (1)	8.3 (3)	1.98 (8)	0.8 (2)	0.58 (9)	−0.7 (1)	CD2	4.6 (2)	9.8 (4)	2.10 (9)	0.4 (2)	0.4 (1)	0.1 (2)
CB2	4.1 (2)	9.3 (4)	2.7 (1)	−0.4 (2)	0.6 (1)	−0.7 (2)	CD3	7.2 (3)	11.0 (5)	2.5 (1)	0.9 (3)	1.5 (1)	1.2 (2)
CB3	4.9 (2)	11.5 (5)	4.0 (1)	−1.9 (3)	1.0 (1)	−2.1 (2)	CD4	10.0 (4)	14.0 (5)	1.7 (1)	2.0 (3)	0.4 (2)	1.2 (2)
CB4	3.7 (2)	16.5 (7)	4.1 (1)	0.4 (3)	−0.2 (1)	−4.4 (3)	CD5	6.6 (3)	16.1 (6)	2.4 (1)	1.0 (3)	−0.6 (1)	0.5 (2)
CB5	5.2 (2)	15.6 (6)	2.5 (1)	3.2 (3)	−0.9 (1)	−1.8 (2)	CD6	4.9 (2)	13.7 (5)	2.2 (1)	0.2 (3)	0.1 (1)	0.3 (2)
CB6	4.7 (2)	9.8 (4)	2.20 (9)	1.4 (2)	0.0 (1)	−0.8 (2)							

[a] Atoms are labeled as indicated in Figure 1. [b] Standard deviations, in parentheses, occur in the last significant figure for each parameter. [c] In this table, H21 and H22, for example, refer to the first and second hydrogens on carbon atom 2. [d] In this table, H33 and H34, for example, refer to the two hydrogen atoms on nitrogen atom 3. [e] β's are defined in footnote 21; values reported here are $\times 10^3$. [f] Carbon atom labeling proceeds in order around each ring; CR1 is the carbon atom of ring R bonded to the boron atom.

Table III. Molecular Geometry of $[(\text{tren})\text{Ni}(\text{NCBH}_3)]_2(\text{BPh}_4)_2$[a]

Selected Intramolecular Bond Distances, Å			
The Dimeric Cation $[(\text{tren})\text{Ni}(\text{NCBH}_3)]_2^{2+}$			
(i) Coordination sphere			
Ni-N1	2.006 (3)	Ni-N3	2.112 (4)
Ni-H2	2.145 (26)	Ni-N4	2.074 (3)
Ni-N2	2.093 (3)	Ni-N5	2.062 (3)
(ii) The $-\text{NCBH}_3$ Bridge			
N1-Cl	1.122 (4)	B1-H2	0.99 (2)
C1-B1	1.604 (6)	B1-H3	1.31 (4)
B1-H1	1.03 (4)	Ni· · ·Ni	5.933 (2)
(iii) The tren Ligand			
N2-C2	1.480 (5)	C6-C7	1.514 (5)
N2-C4	1.485 (4)	N3-H33	0.67 (4)
N2-C6	1.495 (5)	N3-H34	0.98 (4)
N3-C3	1.467 (6)	N4-H43	0.87 (3)
N4-C5	1.462 (5)	N4-H44	0.75 (3)
N5-C7	1.455 (5)	N5-H53	0.71 (4)
C2-C3	1.490 (6)	N5-H54	0.91 (4)
C4-C5	1.498 (6)		
The Tetraphenylborate Anion			
B2-CA1	1.643 (4)	B2-CC1	1.643 (4)
B2-CB1	1.641 (4)	B2-CD1	1.642 (4)
CA1-CA2	1.390 (4)	CC1-CC2	1.398 (4)
CA2-CA3	1.386 (5)	CC2-CC3	1.384 (4)
CA3-CA4	1.364 (5)	CC3-CC4	1.372 (5)
CA4-CA5	1.361 (5)	CC4-CC5	1.361 (5)
CA5-CA6	1.380 (5)	CC5-CC6	1.392 (5)
CA6-CA1	1.396 (4)	CC6-CC1	1.394 (4)
CB1-CB2	1.406 (4)	CD1-CD2	1.383 (4)
CB2-CB3	1.382 (4)	CD2-CD3	1.388 (4)
CB3-CB4	1.362 (5)	CD3-CD4	1.364 (5)
CB4-CB5	1.366 (6)	CD4-CD5	1.364 (5)
CB5-CB6	1.395 (5)	CD5-CD6	1.380 (5)
CB6-CB1	1.395 (4)	CD6-CD1	1.398 (4)
Selected Bond Angles, Deg			
The Dimeric Cation $[(\text{tren})\text{Ni}(\text{NCBH}_3)]_2^{2+}$			
N1-Ni-N2	179.1 (7)	N2-Ni-H2	94.5 (7)
N1-Ni-N3	98.0 (1)	N3-Ni-N4	157.8 (1)
N1-Ni-N4	96.8 (1)	N3-Ni-N5	98.4 (1)
N1-Ni-N5	95.3 (1)	N3-Ni-H2	82.5 (7)
N1-Ni-H2	86.4 (7)	N4-Ni-N5	96.5 (1)
N2-Ni-N3	82.4 (1)	N4-Ni-H2	82.1 (6)
N2-Ni-N4	83.0 (1)	N5-Ni-H2	177.9 (6)
N2-Ni-N5	83.8 (1)	Ni-N2-C2	105.6 (2)
Ni-N1-C1	169.7 (3)	Ni-N2-C4	106.1 (2)
N1-C1-B1	176.9 (5)	Ni-N2-C6	108.3 (2)
C1-B1-H2	102 (2)	Ni-N3-C3	110.3 (3)
Ni-H2-B1	159 (2)	Ni-N4-C5	110.4 (2)
N2-C2-C3	111.1 (3)	Ni-N5-C7	108.4 (2)
N2-C4-C5	110.0 (3)	C2-N2-C4	111.8 (3)
N2-C6-C7	113.3 (3)	C2-N2-C6	113.2 (3)
N3-C3-C2	110.4 (3)	C4-N2-C6	111.3 (3)
N4-C5-C4	109.0 (4)	N5-C7-C6	109.4 (3)
The Tetraphenylborate Anion			
CA1-B2-CB1	111.5 (2)	CB1-B2-CC1	103.9 (2)
CA1-B2-CC1	112.9 (2)	CB1-B2-CD1	113.6 (2)
CA1-B2-CD1	103.8 (2)	CC1-B2-CD1	111.5 (2)
CA6-CA1-CA2	114.2 (3)	CC6-CC1-CC2	114.8 (3)
CA1-CA2-CA3	122.5 (3)	CC1-CC2-CC3	123.0 (3)
CA2-CA3-CA4	120.8 (4)	CC2-CC3-CC4	119.9 (3)
CA3-CA4-CA5	119.0 (3)	CC3-CC4-CC5	119.3 (3)
CA4-CA5-CA6	119.8 (4)	CC4-CC5-CC6	120.5 (3)
CA5-CA6-CA1	123.7 (3)	CC5-CC6-CC1	122.4 (3)
CB6-CB1-CB2	114.9 (3)	CD6-CD1-CD2	114.3 (3)
CB1-CB2-CB3	122.3 (3)	CD1-CD2-CD3	123.8 (3)
CB2-CB3-CB4	121.1 (4)	CD2-CD3-CD4	119.0 (4)
CB3-CB4-CB5	118.8 (3)	CD3-CD4-CD5	120.0 (3)
CB4-CB5-CB6	120.7 (4)	CD4-CD5-CD6	119.9 (4)
CB5-CB6-CB1	122.2 (3)	CD5-CD6-CD1	123.0 (4)
B2-CA1-CA2	124.4 (3)	B2-CC1-CC2	121.0 (3)
B2-CA1-CA6	121.1 (3)	B2-CC1-CC6	124.0 (3)
B2-CB1-CB2	121.5 (3)	B2-CD1-CD2	125.6 (3)
B2-CB1-CB6	123.1 (3)	B2-CD1-CD6	119.9 (3)

[a] See footnotes *a* and *b*, Table II.

The nickel atoms in $[(\text{tren})\text{Ni}(\text{NCBH}_3)]_2^{2+}$ are octahedrally coordinated, just as in the cyanate-, thiocyanate-, and azide-bridged dimers. Four of the coordination sites are occupied by nitrogen atoms of the ligand tren. The tren Ni–N distances range from 2.062 to 2.112 Å whereas in the $[(\text{tren})\text{Ni}(\text{OCN})]_2^{2+}$ cation they vary from 2.047 to 2.130 Å[11] and in $[(\text{tren})\text{Ni}(\text{N}_3)]_2^{2+}$ they range from 2.067 to 2.117 Å.[13] The average Ni–N(tren) distances are 2.085 ± 0.017 Å in the cyanotrihydroborate-bridged dimer, 2.085 ± 0.016 Å in the azide-bridged dimer, and 2.082 ± 0.031 Å in the cyanate-bridged dimer. It has been noted[12] that in the dimeric cations $[(\text{tren})\text{Cu}(\text{OCN})]_2^{2+}$ and $[(\text{tren})\text{Cu}(\text{CN})]_2^{2+}$ the shortest Cu–N(tren) distance is that to the tertiary tren nitrogen atom, whereas in $[(\text{tren})\text{Ni}(\text{OCN})]_2^{2+}$ the Ni–N(tren) bond to the tertiary nitrogen atom is the longest. This result was rationalized on the basis that the copper atom is five-coordinate while the nickel atom is six-coordinate. In the present compound and in the azide-bridged dimer[13] the Ni–N(tren) bond to the tertiary nitrogen atom is neither the longest nor the shortest. In $[(\text{tren})\text{Ni}(\text{NCS})]_2$[26] the differences between the four Ni–N(tren) distances are statistically insignificant but the bond to the tertiary nitrogen atom is actually the shortest (2.11 (2) Å as compared with 2.11 (2), 2.15 (2), and 2.16 (2) Å for the other three distances). The variations in the Ni–N(tren) distances thus appear to depend on specific and individual steric considerations and no general conclusions about the effect of five- vs. six-coordination can be drawn.

The Ni–NCBH_3 distance is 2.006 Å, considerably shorter than the tren Ni–N distances, just as the Ni–NCO distance is shorter (2.018 Å) in the cyanate-bridged structure.[11] The Ni–H bond at 2.145 (26) Å is the longest of the six bonds to nickel and is one of the longest transition metal M–H bonds observed to date (see below, however). Published tabulations[10,27] of metal–hydrogen bond lengths in transition metal hydrides show them to range from 1.4 to 1.9 Å, centering around a value of 1.7 Å. The only Ni–H distance listed in these tabulations is 1.4 Å for a terminal Ni–H bond in $\text{NiHCl}[\text{P}(i\text{-C}_3\text{H}_7)_3]_2$.[27] The long Ni–H distance observed here is consistent with the finding that one of the Ni–N bonds to the azide ligand in the azide-bridged dimer is unusually long (2.195 (7) Å)[13] and that the Ni–O bond in the cyanate-bridged dimer is considerably longer than typical Ni–O bond lengths. The Ni–O bond distance is 1.90 Å in bis(acetylacetonato)nickel(II)[28] and 1.84 Å in bis(salicylideniminato)nickel(II)[29] and ~2.0 Å when H_2O is coordinated to nickel.[30] In the dimeric $[(\text{tren})\text{Ni}(\text{OCN})]_2^{2+}$ cation the Ni–O distance is 2.336 (5) Å,[11] about 0.4 Å longer than expected. Similarly, the Ni–H bond in $[(\text{tren})\text{Ni}(\text{NCBH}_3)]_2^{2+}$ is about 0.4 Å longer than expected. There is some evidence that bridging metal–hydrogen bond distances tend to be longer than terminal metal–hydrogen bond distances. In dodecacarbonyltrihydrotrimanganese,[31] for example, the hydrogen atoms bridge manganese atoms and the average Mn–H distance is 1.72 (3) Å, slightly longer than the terminal Mn–H distance of 1.60 (1) Å found in $\text{HMn}(\text{CO})_5$.[32] The Ni–H distance observed in the cyanotrihydroborate-bridged dimer is unusually long, even for a bridging metal–hydrogen bond; nevertheless it seems clear that there is a bonding interaction between the nickel and hydrogen atoms. The Ni···B distance is 3.088 (6) Å, much too long for a bond between the nickel and boron atoms, and the hydrogen atom does occupy the sixth coordination site of the octahedral geometry. The trans N–Ni–H bond angle is 177.9°. The H–Ni–NCBH_3 bond angle, 86.4 (7)°, deviates less from the expected 90° for pure octahedral geometry than any of the corresponding angles involving a nitrogen atom of the tren ligand.

The average B–H distance of 1.11 (13) Å compares favorably with the 1.13 (10) Å value reported for

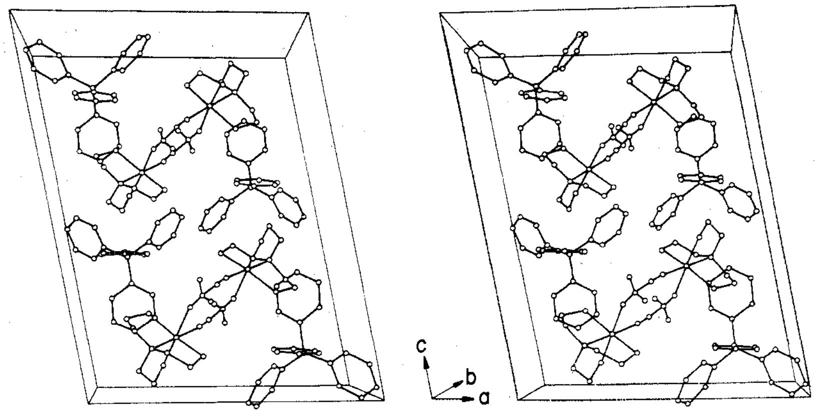

Figure 2. Stereoscopic view of one unit cell showing the packing of the two dimeric cations and four tetraphenylborate anions. Hydrogen atoms other than those in the $-NCBH_3$ group are not shown.

$[(Ph_3P)_2Cu(NCBH_3)]_2$,[9] the 1.07 (4) Å value found in monomeric $(Me_5dien)Cu(NCBH_3)_2$[8] and the 1.11 (8) Å value observed in $[(Ph_3P)_2Cu]_2B_{10}H_{10}$. The bridging B–H distance at 0.99 (2) Å seems short but does not deviate significantly from values reported for the other two cyanotrihydroborate complexes. These B–H distances as determined by x-ray diffraction are known to be artificially short, and the extent of the shortening has been calculated to be 0.1 Å.[33] It should be noted that increasing the bridging B–H bond distance by 0.1 Å (to 1.09 Å) along the B–H bond axis, that is, keeping the C–B–H bond angle fixed, would result in a Ni–H length of 2.05 Å. Increasing the B–H bond length by 0.2 Å (to 1.19 Å) would result in an Ni–H distance of 1.95 Å. We therefore consider the standard deviation to be greater than that determined in the refinement of the structure and prefer to report the Ni–H bond length as 2.1 (1) Å.

Bond distances and angles within the tren ligand appear normal. The six N–C distances have a mean value of 1.474 (6) Å.[34] The three N–C distances to the tertiary nitrogen atom of tren are all longer than this value, while the other three N–C distances are all shorter. The three C–C distances have a mean value of 1.501 (7) Å. None of the six Ni–N–C bond angles, the six N–C–C bond angles, or the three C–N–C bond angles deviates by more than 4° from the tetrahedral value of 109.5° indicating very little strain in the chelate rings. The twelve methylene C–H distances have a mean value of 1.00 (2) Å[34] while the six N–H distances are considerably shorter, as expected, with a mean value of 0.82 (5) Å.

The ten-membered ring consisting of the two cyanotrihydroborate bridges and the two nickel atoms is almost planar. The six N–C–B atoms lie on a plane from which the nickel atoms deviate by ±0.3670 (4) Å and the hydrogen atoms deviate by ±0.35 (3) Å.

The N≡C bond length found for this compound is 1.122 (4) Å which is in reasonable agreement with the values of 1.137 (5) and 1.126 (4) Å reported for the monomer $(Me_5dien)Cu(NCBH_3)_2$[8] and the average value of 1.14 (1) Å found in dimeric $[(Ph_3P)_2Cu(NCBH_3)]_2$.[9] The short bond distance is consistent with the observation of the N≡C stretch in the infrared spectrum at a high frequency, 2221 cm^{-1} (vide infra). The C–B bond distance of 1.606 (6) Å is slightly longer than the C–B bond distances of 1.547 (6) and 1.591 (6) Å observed in $(Me_5dien)Cu(NCBH_3)_2$[8] and of 1.53 (2) and 1.59 (2) Å found in $[(Ph_3P)_2Cu(NCBH_3)]_2$.[9] In all three of these cyanotrihydroborate complexes, the shorter and stronger N≡C bond is associated with the longer and weaker C—B bond.

The structure and conformation of the tetraphenylborate anion have been discussed in detail.[11,35] The four B–C distances observed in the cyanotrihydroborate-bridged dimer are identical within one standard deviation and the mean value of 1.642 (1) Å agrees very well with the mean value of 1.643 (4) Å reported in ref 35. The values reported in ref 11 vary from 1.635 to 1.687 Å. The mean C–C distance in the phenyl rings is 1.382 (3) Å,[34] which should be compared with the 1.383 (4) Å value reported in ref 35. The mean C–H distance is 0.91 (1) Å. The distortion of the rings from a regular hexagonal structure described in ref 35 is also observed in this compound. The C–C–C bond angles at the carbon atoms bonded to boron (denoted α by Di Vaira) are all less than 120° and have a mean value of 114.6 (2)°. The eight C–C–C bond angles adjacent to these (denoted β by Di Vaira) are all larger than 120°, have a mean value of 122.9 (2)°, and range from 122.2 to 123.8°. The other twelve C–C–C bond angles are close to 120° and range from 118.8 (3) to 121.1 (4)° with a mean value of 119.9 (2)°. The principal difference between the structure of the tetraphenylborate anion observed here and that reported by Di Vaira and Orlandini[35] is the deviation of the B–C bond from coplanarity with the phenyl rings. The average distance of the boron atom from the plane of the phenyl rings is 0.05 Å for Di Vaira's structure but is considerably larger, 0.12 (2) Å, for the present compound. In $[(tren)Ni(OCN)]_2(BPh_4)_2$[11] the boron atom lies, on the average, 0.12 Å out of the plane of the rings. Table IV gives the least-squares planes for the four phenyl rings of the tetraphenylborate anion and the dihedral angles between those planes. Di Vaira and Orlandini[35] calculated the inter-ring interaction energy assuming that the B–C bond (the rotation axis of the phenyl rings) is coplanar with the rings. They found the energy to be fairly sensitive to a change in the angle of rotation of a phenyl ring and concluded that the anion is not as flexible as had been assumed and that the rotation of the rings is rather hindered. Di Vaira proposed that the limited flexibility of the bulky tetraphenylborate anion could contribute to stabilize particular conformations of complex cations in the solid phase. There is some indication that the tetraphenylborate anion does contribute to the stability of the present compound in its packing arrangement with the dimeric $[(tren)Ni(NCBH_3)]_2^{2+}$ cation because several attempts to synthesize $[(tren)Ni(NCBH_3)]_2(PF_6)_2$ by replacing $NaBPh_4$ with KPF_6, in the preparation described previously, failed.

Infrared Spectrum. The infrared spectrum of a Nujol mull of $[(tren)Ni(NCBH_3)]_2(BPh_4)_2$ and of the deuterated compound $[(tren)Ni(NCBD_3)]_2(BPh_4)_2$ were compared so that the B–H frequencies could be assigned unambiguously. Figure 3 shows the infrared spectra of these two complexes and, for comparison, those of $[(Ph_3P)_2Cu(NCBH_3)]_2$ and $[(Ph_3P)_2Cu(NCBD_3)]_2$. Table V lists the IR bands and their assignments for these compounds.

The C≡N stretching frequency in the nickel cyanotrihydroborate-bridged dimer occurs at 2221 cm^{-1}, a higher frequency than the peaks in the copper-bridged dimer[6] (2190 and 2207 cm^{-1}) or in $(Me_5dien)Cu(NCBH_3)_2$[8] (2192 and 2210

Table IV. Equations of Planes of Best Fit for the Four Phenyl Rings in Fractional Coordinates[a]

Ring	Equation	Ring	Equation
A	$-0.057x + 0.022y - 0.998z + 2.578 = 0$	C	$0.630x + 0.632y + 0.451z + 0.433 = 0$
B	$0.737x - 0.415y - 0.533z + 5.706 = 0$	D	$0.263x - 0.961y - 0.880z + 3.692 = 0$

	Distances of atoms from planes, A						
Ring	C1	C2	C3	C4	C5	C6	B[b]
A	0.001 (3)	0.002 (3)	−0.004 (4)	−0.000 (4)	0.006 (3)	−0.005 (3)	0.154 (3)
B	0.004 (3)	−0.007 (3)	0.002 (4)	0.006 (4)	−0.006 (4)	−0.001 (3)	−0.145 (3)
C	0.000 (3)	0.001 (3)	−0.002 (4)	−0.001 (4)	0.003 (4)	−0.002 (3)	−0.128 (3)
D	−0.008 (3)	0.009 (3)	0.001 (4)	−0.013 (4)	0.008 (4)	0.005 (4)	0.067 (4)

Rings	Dihedral angle, deg	Rings	Dihedral angle, deg	Rings	Dihedral angle, deg	Rings	Dihedral angle, deg
A–B	61.2	B–C	87.8	A–D	87.0	C–D	61.3
A–C	61.8	B–D	50.2				

[a] Calculations performed using the program MEANPLANE by M. E. Pippy and F. R. Ahmed. [b] Atom not included in best plane calculations.

Table V. Summary of Selected Infrared Spectral Bands for Cyanotrihydroborate-Bridged Dimers and Their Deuterated Analogues[a,b]

ν, cm^{-1}				
$[(\text{tren})\text{Ni}(\text{NCBH}_3)]_2^{2+}$	$[(\text{tren})\text{Ni}(\text{NCBD}_3)]_2^{2+}$	$[(\text{Ph}_3\text{P})_2\text{Cu}(\text{NCBH}_3)]_2$	$[(\text{Ph}_3\text{P})_2\text{Cu}(\text{NCBD}_3)]_2$	Assignment
		2408 sh	. . .	
		2388 sh	. . .	
2380 s	. . .	2376 s	. . .	ν_{BH}
2372 sh	2374 w, br			
2350 sh	2340 sh			
2276 m	. . .			$\nu_{\text{Ni-H-B}}$
2241 m	. . .			$\nu_{\text{Ni-H-B}}$
2221 s	2221 s	2207 s	2206 s	ν_{CN}
2200 m	. . .	2200 br	. . .	$\nu_{\text{M-H-B}}$
		2190 s	2189 s	ν_{CN}
. . .	1815 w, sh	. . .	1799 w, sh	$(^{10}\text{B})\nu_{\text{BD}}$
. . .	1798 s	. . .	1784 m	$(^{11}\text{B})\nu_{\text{BD}}$
. . .	1751 w, sh			$(^{10}\text{B})\nu_{\text{Ni-D-B}}$
. . .	1739 s			$(^{11}\text{B})\nu_{\text{Ni-D-B}}$
		. . .	1731 w	$(^{10}\text{B})\nu_{\text{Cu-D-B}}$
		. . .	1717 m	$(^{11}\text{B})\nu_{\text{Cu-D-B}}$
. . .	1675 w, sh			$(^{10}\text{B})\nu_{\text{Ni-D-B}}$
. . .	1660 m, br			$(^{11}\text{B})\nu_{\text{Ni-D-B}}$
. . .	1630 w	. . .	1616 m, br	
1130 w, sh	. . .			$(^{10}\text{B})\delta_{\text{BH}}$
1114 m	. . .	1100 vs[c]		$(^{11}\text{B})\delta_{\text{BH}}$

[a] Solid samples were mulled in Nujol. [b] Abbreviations: s, strong; m, medium; w, weak; br, broad; sh, shoulder; . . . means no band observed. [c] Triphenylphosphine also absorbs at this frequency.

cm^{-1}), both of which have two C≡N frequencies owing to the nonequivalence of the two $-\text{NCBH}_3$ ligands. The sharp band at 2207 cm^{-1} in the spectrum of the dimeric $[(\text{Ph}_3\text{P})_2\text{Cu}(\text{NCBH}_3)]_2$ has been attributed to a bridging $\nu_{\text{B-H}}$.[36] This assignment is not correct because the band at 2207 cm^{-1} is still present in the spectrum of the deuterated compound $[(\text{Ph}_3\text{P})_2\text{Cu}(\text{NCBD}_3)]_2$ (see Figure 3). The shift to higher frequencies for coordinated nitriles has been attributed to increased σ bonding between carbon and nitrogen when the nitrogen atom is complexed to a metal atom.[37,38] The short C—N distance observed (1.122 (4) Å) is consistent with the high C≡N stretching frequency of 2221 cm^{-1}.

The terminal B—H stretching mode ($\nu^{\text{c}}_{\text{BH}}$) appears at 2320–2350 cm^{-1} when the cyanotrihydroborate group is monodentate.[6,8] When the $-\text{NCBH}_3$ group is a bridging ligand, a strong ν_{BH} band appears at a higher frequency, 2376 cm^{-1} in $[(\text{Ph}_3\text{P})_2\text{Cu}(\text{NCBH}_3)]_2$ and 2380 cm^{-1} in the $[(\text{tren})\text{Ni}(\text{NCBH}_3)]_2^{2+}$ cation. These bands are absent in the spectra of the corresponding deuterated compounds; new bands appear at 1784 cm^{-1} ($\nu_{\text{B-D}}/\nu_{\text{B-H}} = 0.751$) and 1798 cm^{-1} ($\nu_{\text{B-D}}/\nu_{\text{B-H}} = 0.755$), respectively. The calculated ratio of $\nu_{\text{B-D}}/\nu_{\text{B-H}}$ based on the reduced masses of the atom pairs is 0.736 for ^{11}B. Each of the $\nu_{\text{B-D}}$ bands in the spectra of the deuterated compounds has a weak, higher frequency shoulder attributable to ^{10}B. The breadth of the band at 2380 cm^{-1} in the cyanotrihydroborate-bridged nickel dimer is caused by an underlying weaker peak at 2374 cm^{-1} which remains in the spectrum of the deuterated compound. By way of comparison, the strong peak at 2376 cm^{-1} in the $[(\text{Ph}_3\text{P})_2\text{Cu}(\text{NCBH}_3)]_2$ dimer is almost completely missing in the deuterated analogue which was prepared from a fresh sample of NaNCBD_3. The weak peak at 2374 cm^{-1} is due simply to the presence of some undeuterated material in the NaNCBD_3 which appeared upon aging.

In dimeric $[(\text{Ph}_3\text{P})_2\text{Cu}(\text{NCBH}_3)]_2$ there is a broad band at 2200 cm^{-1}, underlying the two sharp C≡N stretching frequencies, which has been attributed to a Cu–H–B stretching vibration.[6] This band is shifted in the deuterated analogue; new bands appear at 1717 and 1616 cm^{-1}. In the spectrum of the cyanotrihydroborate-bridged nickel dimer there are three somewhat overlapped peaks at 2276, 2241, and 2200 cm^{-1}, all of which are shifted in the deuterated compound. These three peaks constitute a broad band which underlies the strong sharp C≡N stretch at 2221 cm^{-1}.

In the deuterated nickel compound new peaks appear at 1739 and 1660 cm^{-1}. Each has a high-frequency shoulder attributable to the presence of ^{10}B. There is also a weak peak at 1630 cm^{-1} (and at 1616 cm^{-1} in the deuterated copper compound) which overlaps a strong somewhat broad peak at 1588 cm^{-1} which appears in the spectrum of all four species. The monodentate cyanotrihydroborate group has C_{3v} symmetry, but the three B–H bonds are not equivalent when the

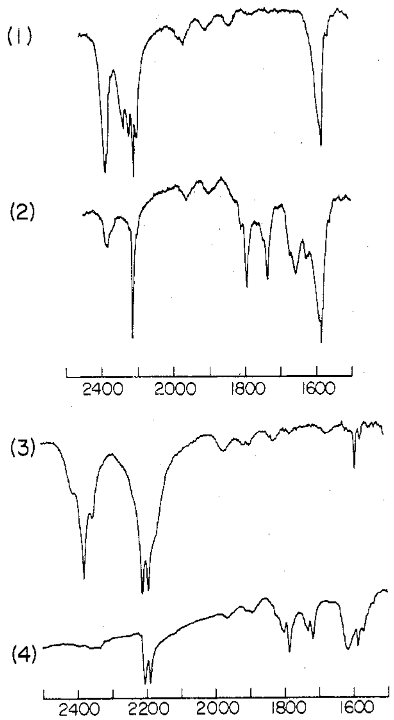

Figure 3. Comparison of infrared spectra for (1) $[(\mathrm{tren})\mathrm{Ni}(\mathrm{NCBH_3})]_2(\mathrm{BPh_4})_2$ and (2) $[(\mathrm{tren})\mathrm{Ni}(\mathrm{NCBD_3})]_2(\mathrm{BPh_4})_2$; (3) $[(\mathrm{Ph_3P})_2\mathrm{Cu}(\mathrm{NCBH_3})]_2$ and (4) $[(\mathrm{Ph_3P})_2\mathrm{Cu}(\mathrm{NCBD_3})]_2$ all mulled in Nujol.

$-\mathrm{NCBH_3}$ group serves as a bridging ligand. Four different frequencies, two terminal B–H stretches, a bridging B–H and an M–H stretching frequency, are expected. The very broad band (width at half-height ~70 cm^{-1}) centered at 2200 cm^{-1} in the spectrum of $[(\mathrm{Ph_3P})_2\mathrm{Cu}(\mathrm{NCBH_3})]_2$ is attributed to the Cu–H–B stretching vibrations, but it is also possible that one of the two terminal B–H stretching frequencies is included in this band. One of the three peaks in $[(\mathrm{tren})\mathrm{Ni}(\mathrm{NCBH_3})]_2^{2+}$ assigned to the Ni–H–B stretching vibration may also be terminal ν_{BH}.

The terminal H–B–H deformation modes (δ_{BH}) in the cyanotrihydroborate-bridged nickel dimer appear as a band at 1114 cm^{-1} with a broad shoulder from 1129 to 1135 cm^{-1}. These peaks are shifted to ~845 and 820 cm^{-1} in the spectrum of the deuterated compound, but there is a fairly strong broad peak at 848 cm^{-1} in the undeuterated bridged nickel dimer which overlaps the shifted peaks. The H–B–H deformation mode in $[(\mathrm{Ph_3P})_2\mathrm{Cu}(\mathrm{NCBH_3})]_2$ is hidden under an intense triphenylphosphine absorption.

It is of use to summarize the infrared spectral differences between the cyanotrihydroborate group as a bridging ligand and as a monodentate ligand: (1) The terminal B–H stretching mode ($\nu^{\mathrm{e}}_{\mathrm{BH}}$) in the monodentate ligand appears at 2320–2350 cm^{-1}. A terminal ν_{BH} stretching mode, shifted to a higher frequency (~2380 cm^{-1}), is observed when the cyanotrihydroborate group is a bridging ligand. (2) A very broad band, or a band consisting of three somewhat overlapped peaks, appears in the dimers at a frequency of ~2200–2280 cm^{-1}. This band is absent in the monodentate complexes and is shifted to lower frequencies in the deuterated complexes. It is attributed to the M–H–B stretching vibrations and possibly to a second ν_{BH} since the two terminal B–H groups are not equivalent in the dimeric complexes. (3) The terminal H–B–H modes (δ_{BH}) appear at ~1115 cm^{-1} when the cyanotrihydroborate group is a monodentate ligand[6] and also in the bridged nickel dimer. This bending mode is hidden under an intense triphenylphosphine absorption at 1100 cm^{-1} in the copper-bridged dimer.

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Registry No. $[(\mathrm{tren})\mathrm{Ni}(\mathrm{NCBH_3})]_2(\mathrm{BPh_4})_2$, 62431-09-8; $[(\mathrm{tren})\mathrm{Ni}(\mathrm{NCBD_3})]_2(\mathrm{BPh_4})_2$, 62431-07-6; $[(\mathrm{Ph_3P})_2\mathrm{Cu}(\mathrm{NCBH_3})]_2$, 51321-47-2; $[(\mathrm{Ph_3P})_2\mathrm{Cu}(\mathrm{NCBD_3})]_2$, 62431-05-4.

Supplementary Material Available: Tables S1 and S2, listing structure factor amplitudes and root-mean-square thermal amplitudes (27 pages). Ordering information is given on any current masthead page.

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(21) Anisotropic thermal parameters are of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.
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