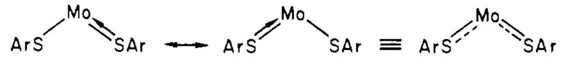
thiolato sulfur in III (Ar = C_6H_4F-*p*) (2.328 (3) and 2.344 (8) Å) are intermediate in length between Mo—SR(thiolato) single bonds (2.45 Å)[18] and the molybdenum–sulfur distance found in the Mo(II) monothiolato complex $HB(Me_2pz)_3Mo(SC_6H_4Cl\text{-}p)(CO)_2$ (2.305 (1) Å).[1] In the latter complex, a full p_π–d_π bond between molybdenum and thiolato sulfur is required if the molybdenum atom is to attain an 18-electron configuration. We interpret this intermediate character of the Mo–S(thiolato) bonds in III as indicating the *both* sulfur atoms participate equally in p_π–d_π interaction with molybdenum so that the latter attains an effective closed valence-shell via a combination of two reasonance structures:



The individual thiolato ligands in III may therefore be regarded as formal 2.5-electron donors. The Mo–S–C angles (111.5 (3) and 113.9 (3)°) are intermediate between those found[19] in (*o*-(phen)Zn($SC_6H_4CH_3$-*p*)$_2$ (104.6 and 95.9 (2)°), where the metal–S bonding is presumably purely σ, and in $HB(Me_2pz)_3Mo(SC_6H_4Cl\text{-}p)(CO)_2$ (116.5 (1)°), where there is strong p_π–d_π bonding.[1]

Analogy with the known chemistry of bis(thiolato) complexes such as (η-C_5H_5)$_2$M(SR)$_2$ (M = Ti, Mo, W)[20] suggested that compounds of type III should behave as chelating (2 + 2)-electron ligand via lone pairs of the thiolato sulfur atoms. However, no evidence for formation of $HB(pz)_3Mo(N_2C_6H_4CH_3\text{-}p)(\mu\text{-}SC_6H_4CH_3\text{-}p)_2Mo(CO)_4$ was observed when complex III (Ar = $C_6H_4CH_3$-*p*) was treated with (norbornadiene)molybdenum tetracarbonyl in benzene and the reactants were recovered unchanged. Reaction did take place between the bis(thiolato) complex and $(C_6H_5CN)_2PdCl_2$ in CH_2Cl_2, but the scarlet product—possibly $HB(pz)_3Mo(N_2C_6H_4CH_3\text{-}p)(\mu\text{-}SC_6H_4CH_3\text{-}p)_2PdCl_2$—decomposed before characterization could be attempted. Neither was it possible to generate seven-coordinate 18-electron anionic species such as $[HB(pz)_3MoCl(SC_6H_4CH_3\text{-}p)_2N_2Ar]^-$ via the reaction of III with halide salts in CH_2Cl_2.

Acknowledgment. This work was supported by a Maintence Award from the Department of Education of the Republic of Ireland (to D.C.) and by the National Research Council of Canada (to G.F.). We are grateful to Dr. N. M. Connelly of the Department of Inorganic Chemistry, Bristol University, for the molecular weight and mass spectroscopic data.

Registry No. $HB(pz)_3Mo(CO)(PPh_3)(N_2C_6H_4CH_3\text{-}p)$, 79329-42-3; $HB(pz)_3Mo(CO)(PPh_3)(N_2C_6H_4F\text{-}p)$, 79329-43-4; $HB(pz)_3W(CO)(PPh_3)(N_2C_6H_4CH_3\text{-}p)$, 79329-44-5; $HB(pz)_3Mo(SC_6H_4CH_3\text{-}p)_2(N_2C_6H_4CH_3\text{-}p)$, 79329-45-6; $HB(pz)_3Mo(SC_6H_4CH_3\text{-}p)_2(N_2C_6H_4F\text{-}p)$, 79357-02-1; $HB(pz)_3Mo(CO)_2(N_2C_6H_4CH_3\text{-}p)$, 53158-54-6; $HB(pz)_3Mo(CO)_2(N_2C_6H_4F\text{-}p)$, 53158-57-9; $HB(pz)_3W(CO)_2(N_2C_6H_4CH_3\text{-}p)$, 79329-46-7.

Supplementary Material Available: Listings of anisotropic thermal parameters, molecular dimensions not included in Table II, calculated hydrogen coordinates, and structure factors (23 pages). Ordering information is given on any current masthead page.

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Preparation, Unusual Spectral Properties, and Structural Characterization of (Terpyridine)(tetrahydroborato-*H*,*H'*)cobalt

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Received August 26, 1980

A new compound of cobalt possessing terpyridine and tetrahydroborato ligands has been prepared by reduction of [Co(terpy)Cl_2] with $NaBH_4$. Single-crystal X-ray and neutron diffraction studies have established the molecular structure of the compound. The coordination sphere of the cobalt can be described as a distorted tetragonal pyramid in which the apex and one basal vertex are occupied by bridging hyrides of the bis-chelate tetrahydroborato ligand. The infrared spectrum of the molecule displays features at variance with those anticipated for a complex with a bis-chelate tetrahydroborato ligand, and we suggest that caution should be exercised in the use of infrared spectroscopy for the structural characterization of tetrahydroborato complexes. Crystallographic details: $C_{15}H_{15}N_3CoB$, space group $P2_1/c$, Z = 4, a = 8.173 (1) Å, b = 15.802 (5) Å, c = 10.708 (4) Å, β = 92.84 (2)° (T = 298 K); a = 8.038 (3) Å, b = 15.701 (5) Å, c = 10.593 (3) Å, β = 94.03 (3)° (T = 50 K). Final $R(F)$ values are 0.047 for 2718 X-ray reflections measured at 298 K and 0.062 for 1497 neutron reflections measured at 50 K.

Introduction

The reactivity of the square-planar cation [Co(*cis*-$Ph_2PCH{=}CHPPh_2)_2]^+$ (**1**) and its congeners toward oxidative addition of H_2 has been reported to decrease in the order Co > Rh > Ir.[2] This suggests that neutral square-planar cobalt(I) complexes, isotypic with Wilkinson's catalyst and Vaska's complex, might be sufficiently reactive oxidative addition substrates to activate sp^3 C–H bonds in a manner reminiscent of the isoelectronic reactive intermediate $[Fe((CH_3)_2PCH_2CH_2P(CH_3)_2)_2]$.[3] Our interest in this area was stimulated by the interest of some of us in the mechanisms of B_{12}-mediated enzymic reactions that led us to suggest the possibility that square-planar cobalt(I) species might be the active species in such reactions.[4] The work reported in this paper represents an attempt to test this hypothesis by the study of appropriate model compounds.

Although the vast majority of four-coordinate cobalt(I) complexes adopt high-spin tetrahedral configurations,[5] both **1** and $[Co(Ph_2PCH_2CH_2PPh_2)_2]^{+}$[6] are known to be low-spin, square-planar complexes. This is presumably a consequence

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(1) (a) Harvard University. (b) Brookhaven National Laboratory.

(2) Vaska, L.; Chen, L. S.; Miller, W. V. *J. Am. Chem. Soc.* **1971**, *93*, 6671.

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of the small bite angles (ca. 85–90°) of the bis chelate phosphine ligands and suggests that the high-spin/low-spin crossover might be accessible with other geometrically constrained ligands. The tris chelate, obligate planar ligand 2,2′:6′2″-terpyridine (terpy) is a promising candidate for such a constrictive ligand, and our experiments were accordingly directed toward the preparation of complexes of stoichiometry [Co(terpy)R] (R = H or alkyl) via reduction of the known cobalt(II) complex [Co(terpy)Cl_2].[7]

Experimental Section

^{1}H NMR spectra were recorded on a Varian A-60 at 60 MHz, a Varian HFT-80 at 80 MHz, or a Varian XL-100 at 100 MHz and calibrated with use of the residual ^{1}H resonances in the deuterated solvents as reference peaks. Mass spectra were recorded on an AEI MS-9 spectrometer. Infrared spectra were recorded from mulls in mineral oil on a Perkin-Elmer 457A spectrometer and calibrated relative to the 1601-cm^{-1} absorption of polystyrene film.

Reactions and manipulations involving air-sensitive organocobalt species were carried out under dry argon with use of standard Schlenk tube and polyethylene glovebag techniques.[8] All glassware used in the experiments was oven-dried or flamed under vacuum before use. Toluene was freshly distilled from calcium hydride before use, and pentane was dried over sodium wire. The ethanol used was absolute grade, dried over 3-Å molecular sieves.

[Co(terpy)Cl_2] was prepared as lime green needles by the literature method,[7] and 2,2′:6′2″-terpyridine (terpy) was used as purchased from the G. F. Smith Chemical Co.

Preparation of (Terpyridine)(tetrahydroborato-*H*,*H*′)cobalt. A solution of vacuum dried $NaBH_4$ (0.9 g, 24 mmole) in dry ethanol (25 mL) was added to a magnetically stirred suspension of [Co(terpy)Cl_2] (0.906 g, 2.50 mmol) in ethanol (25 mL) over a period of 15 min. The solution rapidly acquired an intense red coloration, and crystals began to precipitate. After 2 h at room temperature, all the lime green starting material had disappeared. The mixture was cooled to −20 °C to precipitate the bulk of the product as gray crystals which were collected by filtration, washed with ethanol, and then dried in vacuo for 2 h.

Trituration with toluene (3 × 50 mL) gave an intensely colored red-purple solution, from which the product could be recrystallized by slow concentration under vacuum (6 h, to final volume of 60 mL), giving black crystals. So that the yield could be maximized, the mixture was cooled to −55 °C and kept at that temperature for 12 h before the crystals were collected by filtration and dried in vacuo for 2 h (yield 0.65 g, 2.02 mmol; 80%). Anal. (Dornis and Kolb, Elbach, West Germany.) Calcd for $C_{15}H_{15}N_3CoB$: C, 58.67; H, 4.92. Found: C, 58.78; H, 5.08.

Crystals suitable for single-crystal X-ray and neutron diffraction studies were grown by gently siphoning a layer of pentane on top of a saturated solution of the complex in toluene until the toluene solution was covered by approximately 4 times its own volume of pentane. Crystals of [Co(terpy)BH_4][9] up to 4 mm in length could be grown by slow mixing of the layers over a period of 5 days by diffusion and occasional agitation.

Preparation of (Terpyridine)(tetradeuterioborato-*D*,*D*′)cobalt. A solution of vacuum-dried $NaBD_4$ (0.2 g, 4.8 mmol) in ethanol (15 mL, dried over 3-Å molecular sieves) was added to a vigorously shaken suspension of [Co(terpy)Cl_2] (0.095 g, 0.26 mmol) in dry ethanol (10 mL) to give a purple solution from which dark plates precipitated over a period of 30 min during which all the lime green starting material was consumed. The crystals were collected by filtration, washed with 5 mL of ethanol, and dried under vacuum for 30 min. Trituration with toluene (60 mL) gave an intensely colored red solution which was concentrated under vacuum over a period of 3 h to a volume of 15 mL to precipitate black crystals. The mixture was cooled over a further 3 h to −55 °C and kept at this temperature for 12 h to effect crystallization of the bulk of the product, which was collected by filtration, washed with pentane, and dried under vacuum for 5 h. The mass and infrared spectra of the product[10] showed it to be [Co(terpy)BD_4] (0.046 g, 0.148 mmol; 57%) of reasonable isotopic purity, as indicated by the presence of peaks assigned to [Co(terpy)BD_4]$^+$ and [Co(terpy)D]$^+$. The remainder of the spectrum was identical with that of [Co(terpy)BH_4] without the [Co(terpy)BH_4]$^+$ peak. The weak [Co(terpy)H]$^+$ ion observed (*m*/*e* 293) probably acquired the H atom from a trace of a hydrogen-containing impurity in the spectrometer.

Table I. Crystal Data[17] for (Terpyridine)(tetrahydroborato-*H*,*H*′)cobalt($C_{15}H_{15}N_3CoB$)

	X-ray	neutron
T, K	298	50
a, Å	8.173 (1)	8.038 (3)
b, Å	15.802 (5)	15.701 (5)
c, Å	10.708 (4)	10.593 (3)
β, deg	92.84 (2)	94.03 (3)
V, Å^3	1381.2 (7)	1333.6 (8)
D_c, g/cm^3	1.48	1.53
μ, cm^{-1}	8.6	3.4
space group	$P2_1/c$	$P2_1/c$
Z	4	4

Structural Studies. (A) General Data. The crystals used in these studies were opaque and air sensitive. They were sealed in argon for the X-ray work and helium for the neutron study. X-ray precession photographs showed 2/*m* Laue symmetry and systematic absences indicating space group $P2_1/c$.

(B) X-ray Data. A crystal of dimensions 0.1 × 0.15 × 0.55 mm was chosen for X-ray intensity measurements. With the use of graphite-monochromated Mo K$\bar{\alpha}$ radiation (λ = 0.71069 Å), the cell parameters were determined by a least-squares technique from the setting angles of 25 reflections observed at room temperature. Cell dimensions and other crystal data are listed in Table I. Intensities of reflections with $2\theta < 58°$ were measured on a computer controlled diffractometer using a $\theta/2\theta$ scan, with a 2θ scan range of 1.4°. Background was measured by stationary counts taken at each end of the scans. Intensities of five reflections monitored every 100 measurements showed no systematic variations.

Lorentz and polarization corrections were applied to the data.[11] A semiempirical absorption correction[12] was based on the ψ scans of 20 reflections, and atomic scattering factors were based on literature values.[13,14] Of the 4226 reflections measured, 2718 independent reflections with $I > 2\sigma_{\text{count}}(I)$ were included in the subsequent refinements.

A three-dimensional Patterson synthesis revealed the position of the Co atom, and a subsequent Fourier synthesis using phases derived from the cobalt position revealed all C and N atom positions. A difference synthesis then revealed the position of the B atom. After three cycles of least-squares refinement based on *F* and using isotropic thermal parameters, *R*(*F*) had been reduced to 0.15.[15] Following this refinement the 15 H atoms were located in a difference synthesis.

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(7) Harris, C. N.; Lockyer, T. N.; Stephenson, N. C. *Aust. J. Chem.* **1966**, *19*, 1741.

(8) Shriver, D. F. "The Manipulation of Air Sensitive Compounds"; McGraw-Hill: New York, 1969.

(9) Mass spectrum (^{59}Co 100% natural abundance), *m*/*e* (relative intensity): 307 (23), 303 (6), 293 (63), 292 (71), 291 (100), 264 (13), 244 (60), 243 (33), 233 (89), 232 (31), 205 (20), (principal peaks only). Infrared spectrum (mull) cm^{-1}: 2420 ms, 2403 ms, 2325 m, 2000 w, br, 1985 vw sh, br, 1927 mw, br, 1893 mw, br, 1876 w, 1601 sh, 1588 m, 1543 w, 1517 m, 1470 m, 1453 s, 1432 s, 1381 m, 1350 m, 1320 m, 1307 s, 1286 s, 1277 m, 1252 m, 1190 ms, 1171 w, 1160 w, 1152 m, 1132 s, 1090 w, 1083 w, 1050 vw, 1012 s, 948 w, 888 w, 839 w, 780 m, 760 s, 742 m, 704 w, 670 w. ^{1}H NMR (benzene-d_6; 80 MHz): τ −0.50 (2, d, $J_{H(3'),H(4')}$ = 7.2 Hz, H(3′) + H(5′)), 2.08 (1, t, $J_{H(4'),H(3')}$ = 7.2 Hz, H(4′)), 2.4–3.3 (8, c, H(3)–H(6) and H(3″)–H(6″)), 10.6–16.0 (4, br, BH_4).

(10) Mass spectrum (^{59}Co 100% natural abundance) *m*/*e*: 311, 294, 293, 292, 291, 264, 244, 243, 233, 205 (principal peaks only). Infrared spectrum (mull) cm^{-1}: 1877 w, 1833 w, 1815 ms, 1771 ms, 1721 ms, 1601 sh, 1588 m, 1540 w, 1517 m, 1469 sh, 1454 s, 1432 s, 1398 w, 1382 m, 1350 m, 1321 m, 1307 s, 1286 s, 1276 m, 1270 w, 1253 m, 1173 w, 1162 m, 1154 m, 1132 s, 1090 w, 1083 w, 1050 w, 1011 s, 1004 sh, 948 w, 893 w, 882 w, 861 w, 841 w, 837 w, 798 w, 780 m, 759 s, 741 s, 703 w, 670 w, 657 w.

(11) The polarization term for the monochromator was assumed to be midway between that for a perfect and ideally imperfect crystal.

(12) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *A24*, 351. μ = 8.6 cm^{-1}.

(13) "International Tables for X-ray Crystallography"; Ibers, J., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 72–98.

(14) H atom scattering factors from: Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

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A final refinement included the H atoms with fixed isotropic thermal factors[16] and led to an $R(F)$ value, with anisotropic thermal parameters for all nonhydrogen atoms, of 0.047. Weights were based on a modified Hughes weighting scheme, with $w^{1/2} = 1/F_o$ for $F_o \geq 4F_{o,min}$, $w = 1/[F_o(4F_{o,min})]$ for $F_{o,min} \leq F_o < 4F_{o,min}$, and $w^{1/2} = {}^1/_2F_{o,min}$ for $F_o < F_{o,min}$, using $F_{o,min} = 3$. The goodness-of-fit $S(F) = [\sum w|F_o - F_c|^2/(n_o - n_v)]^{1/2} = 1.05$.

(C) Neutron Data. A crystal of dimensions 0.50 × 0.45 × 1.3 mm was selected and mounted on an aluminum pin oriented approximately along the *a* axis. The sample was sealed in an aluminum container under helium, placed in a closed-cycle helium refrigerator,[18] and mounted on an automated four-circle diffractometer[19,20] at the Brookhaven high-flux beam reactor. A beryllium (002) crystal monochromator was used to select neutrons of wavelength $\lambda = 1.1602$ Å (based on Al_2O_3, hexagonal, $a = 4.7589$ Å, $c = 12.991$ Å at $T = 298$ K). Cell dimensions, refined by a least-squares procedure based on setting angles of 29 reflections, are listed in Table I.

The temperature of the sample was maintained at 50 K throughout data collection. A $\theta/2\theta$ step-scan tecnique was employed with $\Delta 2\theta = 2.8°$ for $0° < 2\theta < 50°$ and $\Delta 2\theta = 3.2°$ for $2\theta > 50°$. Intensities of two reflections were monitored every 100 measurements as a general check of experimental stability. These monitor intensities did not show any systematic variation during the entire period of data collection. The Lorentz correction was applied, and the data were corrected for absorption by means of numerical integration over a Gaussian grid of points.[21] A total of 3416 intensities were recorded, and 1497 independent reflections with intensities greater than 1 esd were used in refinement of the structure. Reflections contaminated by aluminum scattering of the experimental apparatus were discarded.

The X-ray position and thermal parameters for nonhydrogen atoms were used as initial values for the neutron refinement. Neutron scattering lengths were used as follows: $b_C = 0.665$, $b_H = -0.374$, $b_{Co} = 0.308$, $b_N = 0.925$, $b_B = (0.54 + 0.021i) \times 10^{-12}$ cm. After the initial structure factor calculation, all hydrogen atom positions were located in a difference synthesis. Full-matrix least-squares refinement on F^2 of a model with anisotropic thermal parameters for all atoms was continued until the shifts in all parameters were considerably smaller than their associated esd's and resulted in agreement factors of $R(F) = 0.062$ and $R(F^2) = 0.086$. Weights were taken as $w = 1/[\sigma^2{}_{count}(F_o{}^2) + (0.04F_o{}^2)^2]$; an analysis of variance showed no significant variation of $w|F_o{}^2 - F_c{}^2|$ with $F_o{}^2$ or $(\sin\theta)/\lambda$. The goodness-of-fit $S(F)^2 = [\sum w|F_o{}^2 - F_c{}^2|/(n_o - n_v)]^{1/2} = 1.24$. Data were not corrected for extinction, but extinction effects are probably minimal since the sample crystal was small.

Final atomic positional and thermal parameters from both the X-ray and neutron diffraction analyses are presented in Table II.

Results and Discussion

The reduction of $[Co(terpy)Cl_2]$ was attempted with a variety of reagents, although the range of conditions available was severely restricted by the limited solubility of the dichloride. Of the reductants investigated, only $NaBH_4$ gave a tractable product, which was shown to be $[Co(C_{15}H_{11}N_3)BH_4]$ by elemental and mass spectral analysis. It was clear from the volatility of the compound and its solubility in nonpolar solvents that the tetrahydroborato anion was probably coordinated to the cobalt atom, but the coordination mode of the ligand was not immediately obvious. The mass spectrum of the molecule was entirely consistent with a monomeric, covalent formulation in the gas phase, but the limited solubility of the molecule precluded investigation of the solution molecular weight.

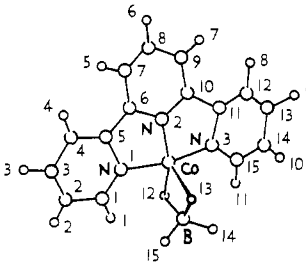

Figure 1. Atom numbering scheme for $[Co(terpy)BH_4]$.

The boron in transition-metal borohydrides is most typically bonded to the metal through two bridging hydrogens,[22] but there are many examples where three hydrogens are involved in the bridging[22] and at least one recent case, that of $[Cu(PPh_2Me)_3BH_4]$, in which only one hydrogen is involved.[23-25] The vibrational spectra of many of these molecules have been extensively studied, and the BH stretching and bending frequencies are usually diagnostic of the bonding mode. The IR spectrum of the compound was accordingly examined with some care. Comparison of the spectrum with that of $[Co(terpy)BD_4]$, prepared by reducing $[Co(terpy)Cl_2]$ with $NaBD_4$, resulted in identification of the features listed in Table III as being associated with H or D derived from the BH_4^- or BD_4^- anion.

The spectrum of $[Co(terpy)BH_4]$ shows a medium-strong intensity doublet with a 17-cm^{-1} splitting and a medium intensity absorption in the terminal boron–hydrogen stretching region (2325–2550 cm^{-1}) and three broad, weak to medium-weak features (one with a shoulder) in the bridging boron–hydrogen stretching region (1900–2050 cm^{-1}). The spectrum of the deuterio complex shows absorptions corresponding to all three terminal B–H stretches with ratios of ν(B–H)/ν(B–D) consistent with those reported in the literature.[26] There is also a weak absorption at 1833 cm^{-1} which is probably a terminal ^{10}B–D stretching frequency. This assignment leads to a value of 1.010 for the $\nu(^{10}\text{B–D})/\nu(^{11}\text{B–D})$ ratio, in good agreement with published values such as 1.009.[27]

Comparison of these absorption frequencies with those recorded in the literature for other tetrahydroborato complexes did not clarify the bonding mode of the anion in this instance, and a single-crystal X-ray diffraction study was undertaken as described above. This showed that $[Co(terpy)BH_4]$ crystallizes as monomeric units. The molecular structure and atomic nomenclature are shown in Figure 1, while the packing of molecules in a unit cell is illustrated in Figure 2.[28] All intermolecular contacts are reasonable: the closest approaches are C⋯H 2.54 and H⋯H 2.23 Å. From the X-ray diffraction studies, it was clear that the tetrahydroborato anion is acting as a bis-chelate ligand. Relevant intramolecular distances and angles are listed in Table IV. As anticipated, the terpyridine ligand remains essentially planar on coordination, as can be seen by examination of the deviations from the terpyridine

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(16) $B = 3.0$ Å^2.

(17) Estimated standard deviations, here and throughout this paper, are given in parentheses in units of the last digit, except where otherwise noted.

(18) Air Products and Chemicals, Inc. Displex® Model CS-202.

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Table II. Atomic Fractional Coordinates and Thermal Parameters for [Co(terpy)BH$_4$][a]

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	0.1855 (1)	0.0531 (1)	0.7492 (1)	0.0096 (1)	0.0018 (1)	0.0047 (1)	0.0004 (1)	0.0014 (1)	−0.0003 (1)
	0.1885 (11)	0.0511 (6)	0.7476 (9)	0.0027 (13)	0.0023 (4)	0.0034 (8)	0.0017 (12)	−0.0057 (18)	−0.0002 (10)
B	0.2573 (7)	−0.0517 (4)	0.6343 (6)	0.0164 (8)	0.0034 (2)	0.0114 (6)	0.0004 (8)	0.0078 (10)	−0.0042 (6)
	0.2539 (6)	−0.0554 (3)	0.6334 (4)	0.0039 (8)	0.0011 (2)	0.0015 (4)	−0.0010 (7)	−0.0006 (10)	−0.0023 (5)
N1	−0.0310 (4)	0.0144 (2)	0.7841 (3)	0.0108 (5)	0.0025 (1)	0.0073 (3)	−0.0002 (4)	0.0010 (6)	−0.0016 (3)
	−0.0325 (3)	0.0128 (2)	0.7840 (3)	0.0018 (4)	0.0010 (1)	0.0030 (3)	0.0003 (4)	0.0007 (6)	0.0002 (3)
N2	0.1401 (4)	0.1302 (2)	0.8676 (3)	0.0106 (5)	0.0022 (1)	0.0052 (2)	0.0000 (4)	0.0017 (5)	−0.0011 (3)
	0.1428 (3)	0.1303 (2)	0.8673 (3)	0.0026 (4)	0.0006 (1)	0.0016 (2)	0.0001 (3)	0.0009 (5)	−0.0005 (3)
N3	0.3824 (4)	0.1194 (2)	0.7422 (3)	0.0114 (5)	0.0021 (1)	0.0059 (3)	0.0012 (4)	0.0018 (6)	0.0013 (3)
	0.3879 (3)	0.1176 (2)	0.7411 (3)	0.0024 (4)	0.0008 (1)	0.0020 (3)	−0.0004 (4)	0.0000 (6)	−0.0005 (3)
C1	−0.1195 (6)	−0.0492 (3)	0.7266 (5)	0.0136 (7)	0.0036 (2)	0.0120 (5)	−0.0032 (6)	0.0002 (10)	−0.0024 (6)
	−0.1235 (5)	−0.0522 (3)	0.7264 (4)	0.0030 (6)	0.0006 (1)	0.0039 (4)	−0.0015 (5)	0.0009 (9)	0.0002 (4)
C2	−0.2701 (6)	−0.0752 (3)	0.7649 (6)	0.0127 (7)	0.0039 (2)	0.0153 (6)	−0.0044 (6)	−0.0020 (11)	−0.0005 (7)
	−0.2750 (5)	−0.0777 (3)	0.7668 (4)	0.0024 (6)	0.0015 (2)	0.0027 (4)	−0.0004 (6)	−0.0005 (8)	0.0001 (4)
C3	−0.3376 (6)	−0.0350 (3)	0.8671 (5)	0.0114 (6)	0.0047 (2)	0.0124 (6)	−0.0015 (6)	0.0009 (9)	0.0043 (5)
	−0.3422 (5)	−0.0371 (3)	0.8688 (4)	0.0023 (7)	0.0009 (2)	0.0032 (4)	−0.0004 (5)	−0.0020 (9)	0.0001 (4)
C4	−0.2522 (5)	0.0303 (3)	0.9251 (4)	0.0108 (6)	0.0044 (2)	0.0086 (4)	0.0003 (6)	0.0021 (8)	0.0027 (5)
	−0.2531 (5)	0.0304 (3)	0.9266 (4)	0.0045 (7)	0.0016 (2)	0.0021 (4)	0.0006 (6)	−0.0003 (9)	0.0006 (4)
C5	−0.1009 (4)	0.0546 (3)	0.8824 (3)	0.0102 (5)	0.0030 (2)	0.0062 (3)	0.0012 (5)	0.0004 (6)	0.0007 (5)
	−0.1010 (5)	0.0541 (2)	0.8814 (4)	0.0033 (6)	0.0008 (1)	0.0012 (3)	−0.0007 (5)	−0.0008 (7)	−0.0011 (4)
C6	−0.0025 (5)	0.1237 (3)	0.9302 (3)	0.0105 (5)	0.0030 (2)	0.0057 (3)	0.0017 (5)	0.0012 (7)	−0.0011 (4)
	0.0019 (5)	0.1247 (2)	0.9292 (3)	0.0028 (6)	0.0011 (2)	0.0009 (3)	0.0002 (5)	−0.0005 (7)	−0.0001 (4)
C7	−0.0362 (6)	0.1808 (3)	1.0238 (4)	0.0137 (6)	0.0045 (2)	0.0077 (4)	0.0025 (7)	0.0044 (8)	0.0027 (5)
	−0.0321 (6)	0.1827 (3)	1.0231 (4)	0.0039 (7)	0.0009 (2)	0.0027 (4)	0.0014 (5)	0.0014 (9)	−0.0012 (4)
C8	0.0755 (6)	0.2447 (3)	1.0556 (5)	0.0182 (8)	0.0046 (2)	0.0093 (4)	0.0020 (8)	0.0056 (10)	−0.0048 (5)
	0.0813 (5)	0.2475 (3)	1.0546 (4)	0.0029 (6)	0.0011 (2)	0.0022 (3)	0.0000 (5)	−0.0006 (8)	−0.0011 (4)
C9	0.2215 (6)	0.2499 (3)	0.9947 (4)	0.0158 (8)	0.0032 (2)	0.0089 (4)	−0.0001 (6)	0.0028 (10)	−0.0032 (4)
	0.2310 (5)	0.2511 (3)	0.9934 (4)	0.0028 (6)	0.0013 (2)	0.0024 (4)	0.0000 (6)	0.0016 (8)	−0.0006 (4)
C10	0.2524 (5)	0.1916 (2)	0.9012 (4)	0.0122 (6)	0.0022 (1)	0.0061 (3)	−0.0004 (5)	−0.0001 (7)	−0.0013 (3)
	0.2597 (5)	0.1917 (2)	0.9007 (4)	0.0028 (6)	0.0007 (1)	0.0020 (3)	0.0002 (5)	0.0012 (8)	−0.0012 (4)
C11	0.3966 (5)	0.1851 (2)	0.8283 (3)	0.0122 (6)	0.0022 (1)	0.0057 (3)	0.0003 (4)	−0.0011 (7)	0.0006 (3)
	0.4027 (5)	0.1832 (2)	0.8265 (4)	0.0032 (6)	0.0008 (1)	0.0013 (3)	0.0007 (5)	−0.0002 (8)	−0.0005 (4)
C12	0.5337 (5)	0.2377 (3)	0.8378 (4)	0.0133 (6)	0.0027 (1)	0.0084 (4)	−0.0011 (6)	0.0003 (8)	0.0014 (4)
	0.5425 (5)	0.2370 (3)	0.8354 (4)	0.0021 (6)	0.0013 (2)	0.0022 (4)	0.0005 (5)	0.0005 (8)	0.0003 (4)
C13	0.6598 (6)	0.2257 (3)	0.7576 (5)	0.0132 (7)	0.0035 (2)	0.0097 (4)	−0.0027 (6)	0.0016 (9)	0.0014 (5)
	0.6690 (5)	0.2240 (3)	0.7562 (4)	0.0023 (6)	0.0008 (2)	0.0025 (4)	−0.0010 (5)	0.0000 (8)	0.0009 (4)
C14	0.6460 (5)	0.1610 (3)	0.6700 (4)	0.0127 (6)	0.0040 (2)	0.0084 (4)	−0.0005 (6)	0.0057 (9)	0.0012 (5)
	0.6521 (5)	0.1582 (3)	0.6662 (4)	0.0016 (6)	0.0011 (2)	0.0033 (4)	−0.0018 (5)	0.0015 (9)	−0.0004 (4)
C15	0.5091 (5)	0.1096 (3)	0.6657 (4)	0.0122 (5)	0.0030 (1)	0.0064 (3)	0.0007 (5)	0.0040 (7)	0.0005 (4)
	0.5115 (5)	0.1063 (3)	0.6624 (4)	0.0025 (6)	0.0010 (2)	0.0022 (4)	0.0004 (5)	0.0029 (8)	0.0013 (4)
H1	−0.079 (6)	−0.069 (3)	0.640 (5)						
	−0.0671 (12)	−0.0812 (6)	0.6485 (9)	0.0078 (15)	0.0024 (4)	0.0054 (9)	−0.0028 (13)	0.0030 (21)	−0.0020 (10)
H2	−0.335 (8)	−0.117 (4)	0.709 (6)						
	−0.3416 (10)	−0.1287 (6)	0.7158 (10)	0.0031 (12)	0.0021 (4)	0.0080 (10)	−0.0015 (12)	−0.0046 (18)	−0.0019 (10)
H3	−0.460 (6)	−0.044 (3)	0.876 (4)						
	−0.4589 (12)	−0.0552 (6)	0.9004 (8)	0.0069 (16)	0.0031 (4)	0.0046 (8)	−0.0011 (13)	−0.0019 (19)	−0.0009 (10)
H4	−0.289 (7)	0.056 (4)	1.004 (5)						
	−0.3008 (10)	0.0646 (6)	1.0054 (9)	0.0042 (13)	0.0028 (4)	0.0046 (8)	−0.0017 (11)	0.0019 (18)	0.0009 (10)
H5	−0.133 (7)	0.173 (4)	1.065 (5)						
	−0.1463 (13)	0.1769 (6)	1.0708 (8)	0.0098 (17)	0.0027 (4)	0.0030 (7)	−0.0026 (12)	0.0041 (19)	−0.0028 (8)
H6	0.062 (7)	0.284 (4)	1.127 (5)						
	0.0587 (12)	0.2939 (6)	1.1288 (9)	0.0089 (15)	0.0028 (4)	0.0057 (8)	−0.0001 (13)	0.0039 (19)	−0.0057 (11)
H7	0.302 (6)	0.294 (3)	1.016 (4)						
	0.3229 (12)	0.3006 (6)	1.0183 (9)	0.0093 (16)	0.0025 (4)	0.0050 (8)	0.0009 (15)	−0.0002 (19)	−0.0011 (9)
H8	0.551 (6)	0.288 (3)	0.912 (4)						
	0.5498 (11)	0.2882 (6)	0.9056 (9)	0.0086 (15)	0.0018 (3)	0.0061 (9)	−0.0041 (12)	0.0042 (19)	−0.0021 (10)
H9	0.775 (6)	0.258 (3)	0.790 (4)						
	0.7800 (12)	0.2654 (6)	0.7626 (10)	0.0058 (15)	0.0031 (4)	0.0073 (10)	−0.0025 (14)	0.0040 (20)	−0.0006 (10)
H10	0.725 (6)	0.147 (4)	0.608 (5)						
	0.7476 (11)	0.1453 (6)	0.6009 (8)	0.0054 (13)	0.0028 (4)	0.0044 (8)	0.0001 (12)	0.0069 (18)	0.0003 (9)
H11	0.502 (6)	0.068 (3)	0.608 (4)						
	0.4955 (11)	0.0543 (5)	0.5958 (8)	0.0075 (14)	0.0020 (4)	0.0034 (8)	0.0001 (12)	0.0000 (16)	−0.0006 (10)
H12	0.164 (7)	0.020 (4)	0.587 (5)						
	0.1814 (11)	0.0141 (6)	0.5958 (7)	0.0100 (15)	0.0027 (4)	0.0021 (7)	−0.0017 (13)	−0.0002 (17)	−0.0016 (9)
H13	0.287 (5)	−0.048 (3)	0.752 (4)						
	0.2781 (11)	−0.0498 (5)	0.7548 (8)	0.0116 (15)	0.0011 (3)	0.0034 (7)	0.0000 (11)	−0.0003 (17)	0.0011 (8)
H14	0.401 (7)	−0.067 (4)	0.599 (5)						
	0.3889 (11)	−0.0598 (6)	0.5891 (9)	0.0057 (15)	0.0034 (4)	0.0067 (9)	−0.0007 (12)	0.0052 (19)	−0.0025 (11)
H15	0.178 (6)	−0.114 (4)	0.611 (5)						
	0.1619 (12)	−0.1154 (6)	0.6077 (10)	0.0092 (15)	0.0016 (3)	0.0078 (10)	−0.0032 (12)	−0.0014 (21)	−0.0031 (9)

[a] X-ray results are given on the first line and neutron results on the second. The form of the anisotropic Debye–Waller factor is $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$.

least-squares plane listed in Table V. A stereoview of the molecule with associated thermal ellipsoids is presented in Figure 3.[28]

In order to be certain of the bonding mode of the tetrahydroborato anion and to obtain accurate positions for the H atoms, we carried out a low-temperature, single-crystal neutron

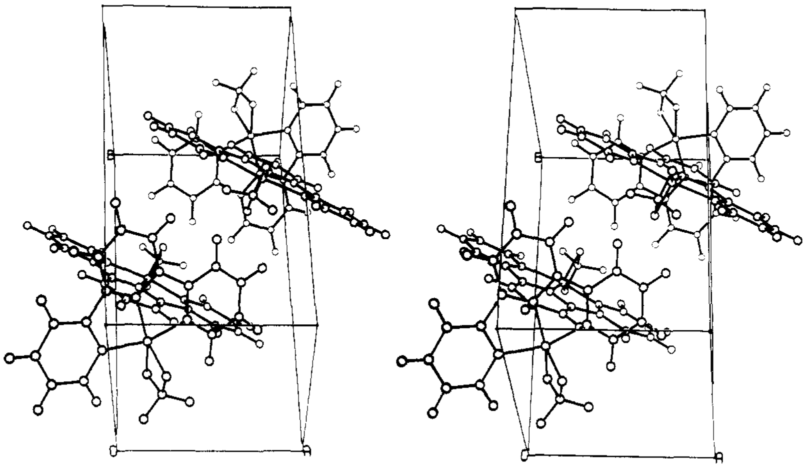

Figure 2. Stereoview of the unit cell of [Co(terpy)BH_4] as determined by neutron diffraction, showing two molecules related by an inversion center.

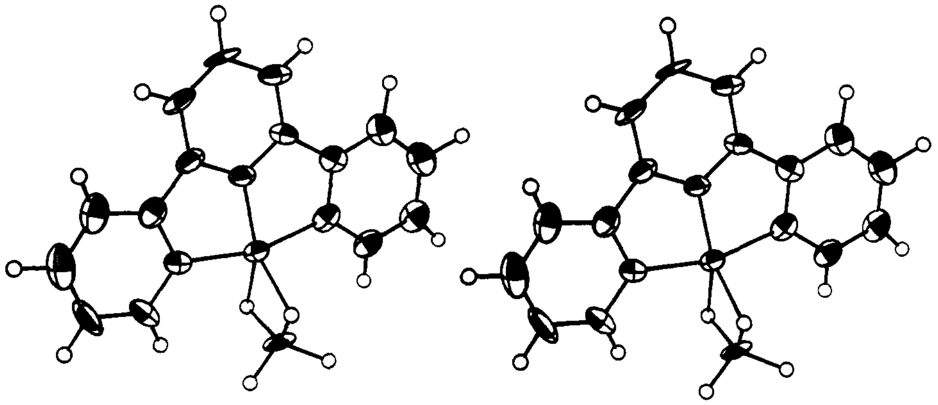

Figure 3. Stereoview of the molecular structure of [Co(terpy)BH_4] as determined by X-ray diffraction (50% probability ellipsoids).

Table III. BH_4^- and BD_4^- Associated Frequencies (cm^{-1}) of the Complexes

	[Co(terpy)BH_4]	[Co(terpy)BD_4]	ν(B-H)/ν(B-D)
terminal B-H stretches		1833 w	
	2420 ms	1815 ms	1.33
	2403 ms	1771 ms	1.36
	2325 m	1721 ms	1.35
bridging B-H stretches	2000 w, br		
	1985 vw sh, br		
	1927 mw, br		
	1893 mw, br		
terminal B-H_2 deformation	1190 ms		
other		1004 sh	

diffraction study of the complex. This confirmed the results of the X-ray study, as can be seen by comparison of the molecular dimensions obtained by the two methods listed in Table IV. The molecular structure as determined by neutron diffraction at 50 K is illustrated in Figure 4. The only significant differences between the two sets of dimensions are those involving the H atoms. The mean C-H bond length in the terpyridine ligand as determined in the X-ray structure is 1.01 (5) Å, while the neutron analysis yields a significantly larger mean bond length of 1.085 (11) Å, with a much smaller esd, as expected. The difference between the X-ray and neutron values of the bond lengths involving the hydrogens on boron are even more marked, but in this case we feel that the positions determined by neutron diffraction are considerably more accurate, and do not attach much significance to the X-ray values. The bond lengths determined by neutron diffraction are very similar to those observed previously by X-ray and neutron methods for bis-chelate tetrahydroborato complexes of d-block transition metals as shown in Table VI.[29] To the best of our knowledge, the present study is the second structural determination of a discrete complex of this type to be carried out with use of neutron diffraction methods.[30,31]

The coordination sphere of the cobalt can be described as a distorted tetragonal pyramid in which the Co atom is slightly above the base of the pyramid, three of the basal vertices are occupied by the N atoms of the terpyridine ligand, and the bridging H atoms occupy the remaining basal vertex and the apex of the pyramid. The major distortion from the idealized geometry involves displacement of the apical bridging H atom toward the B atom (N(2)-Co-H(13) = 133.7 (6)°, H(13)-Co-H(12) = 73.6 (6)°). The structure of [Co(terpy)BH_4] resembles that of [Co(terpy)Cl_2],[39] except that in the latter

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(31) In $U(BH_4)_4$, which has also been studied by neutron diffraction,[32] the coordination about uranium is 14-fold, with four bidentate BH_4^- ions and two tridentate BH_4^- ions surrounding each U^{4+} ion. The bidentate BH_4^- ions are each bonded to two U atoms, with an average U-H distance of 2.41 (3) Å and a B-H distance of 1.25 (4) Å.

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Table IV. Intramolecular Distances (Å) and Angles (Deg) in [Co(terpy)BH_4]

	X-ray	neutron		X-ray	neutron
Co-N(1)	1.926 (3)	1.940 (10)	C(12)-C(13)	1.387 (7)	1.378 (6)
Co-N(2)	1.810 (4)	1.832 (10)	C(13)-C(14)	1.388 (7)	1.406 (6)
Co-N(3)	1.925 (3)	1.918 (10)	C(14)-C(15)	1.382 (6)	1.392 (6)
Co-H(12)	1.81 (5)	1.707 (10)	N(1)-C(1)	1.367 (6)	1.373 (5)
Co-H(13)	1.80 (5)	1.740 (12)	N(1)-C(5)	1.378 (5)	1.367 (5)
B-H(12)	1.44 (6)	1.287 (10)	N(2)-C(6)	1.377 (5)	1.351 (5)
B-H(13)	1.27 (4)	1.290 (9)	N(2)-C(10)	1.371 (5)	1.375 (5)
B-H(14)	1.27 (6)	1.214 (10)	N(3)-C(11)	1.390 (5)	1.370 (5)
B-H(15)	1.20 (6)	1.217 (11)	N(3)-C(15)	1.361 (5)	1.353 (5)
C(1)-C(2)	1.379 (7)	1.378 (6)	C(1)-H(1)	1.05 (5)	1.071 (11)
C(2)-C(3)	1.402 (8)	1.396 (6)	C(2)-H(2)	1.02 (6)	1.086 (10)
C(3)-C(4)	1.377 (7)	1.396 (6)	C(3)-H(3)	1.02 (6)	1.057 (11)
C(4)-C(5)	1.393 (6)	1.395 (6)	C(4)-H(4)	1.00 (6)	1.085 (11)
C(5)-C(6)	1.435 (6)	1.453 (5)	C(7)-H(5)	0.93 (6)	1.082 (11)
C(6)-C(7)	1.386 (6)	1.390 (6)	C(8)-H(6)	1.00 (6)	1.096 (11)
C(7)-C(8)	1.392 (7)	1.391 (6)	C(9)-H(7)	0.98 (5)	1.092 (10)
C(8)-C(9)	1.390 (7)	1.407 (6)	C(12)-H(8)	1.13 (5)	1.094 (11)
C(9)-C(10)	1.393 (6)	1.385 (6)	C(13)-H(9)	1.11 (5)	1.102 (11)
C(10)-C(11)	1.449 (6)	1.444 (6)	C(14)-H(10)	0.97 (5)	1.088 (10)
C(11)-C(12)	1.395 (6)	1.404 (6)	C(15)-H(11)	0.90 (5)	1.081 (9)
N(1)-Co-N(2)	81.7 (1)	80.9 (4)	C(3)-C(4)-C(5)	120 (4)	119.1 (6)
N(1)-Co-N(3)	163.4 (2)	162.8 (6)	C(3)-C(4)-H(4)	121 (3)	121.0 (6)
N(1)-Co-H(12)	93 (2)	96.4 (5)	C(5)-C(4)-H(4)	118 (3)	119.9 (6)
N(1)-Co-H(13)	98 (1)	95.3 (5)	N(1)-C(5)-C(4)	122.1 (4)	122.9 (3)
N(2)-Co-N(3)	82.1 (2)	82.2 (4)	N(1)-C(5)-C(6)	112.2 (3)	112.1 (3)
N(2)-Co-H(12)	148 (2)	152.6 (7)	C(4)-C(5)-C(6)	125.7 (4)	125.1 (4)
N(2)-Co-H(13)	134 (1)	133.7 (6)	N(2)-C(6)-C(5)	110.9 (3)	110.9 (3)
N(3)-Co-H(12)	99 (2)	97.1 (6)	N(2)-C(6)-C(7)	120.4 (4)	121.2 (3)
N(3)-Co-H(13)	96 (1)	98.8 (5)	C(5)-C(6)-C(7)	128.7 (4)	127.9 (4)
H(12)-Co-H(13)	77 (2)	73.6 (6)	C(6)-C(7)-C(8)	119.8 (4)	119.5 (4)
Co-N(1)-C(1)	128.1 (3)	127.5 (4)	C(6)-C(7)-H(5)	117 (4)	119.7 (6)
Co-N(1)-C(5)	114.9 (3)	115.2 (4)	C(8)-C(7)-H(5)	123 (4)	120.8 (6)
C(1)-N(1)-C(5)	116.9 (4)	117.2 (3)	C(7)-C(8)-C(9)	119.7 (5)	119.1 (4)
Co-N(2)-C(6)	119.9 (3)	120.5 (4)	C(7)-C(8)-H(6)	123 (3)	121.3 (6)
Co-N(2)-C(10)	120.1 (3)	119.2 (4)	C(9)-C(8)-H(6)	117 (3)	119.6 (6)
C(6)-N(2)-C(10)	119.8 (3)	120.1 (3)	C(8)-C(9)-C(10)	119.2 (4)	119.3 (4)
Co-N(3)-C(11)	115.0 (3)	114.8 (4)	C(8)-C(9)-H(7)	121 (3)	120.2 (7)
Co-N(3)-C(15)	128.6 (3)	127.0 (4)	C(10)-C(9)-H(7)	120 (3)	120.5 (6)
C(11)-N(3)-C(15)	116.3 (3)	118.2 (3)	N(2)-C(10)-C(9)	120.9 (4)	120.6 (4)
N(1)-C(1)-C(2)	123.0 (5)	122.2 (4)	N(2)-C(10)-C(11)	111.1 (3)	110.5 (3)
N(1)-C(1)-H(1)	116 (3)	114.7 (6)	C(9)-C(10)-C(11)	128.0 (4)	128.8 (3)
C(2)-C(1)-H(1)	120 (3)	123.2 (7)	N(3)-C(11)-C(10)	111.5 (3)	113.2 (3)
C(1)-C(2)-C(3)	119.3 (5)	120.4 (4)	N(3)-C(11)-C(12)	122.3 (4)	121.9 (4)
C(1)-C(2)-H(2)	118 (4)	118.4 (6)	C(10)-C(11)-C(12)	126.2 (3)	124.9 (3)
C(3)-C(2)-H(2)	122 (4)	121.2 (6)	C(11)-C(12)-C(13)	119.5 (4)	119.4 (4)
C(2)-C(3)-C(4)	118.8 (4)	118.1 (4)	C(11)-C(12)-H(8)	123 (3)	119.5 (6)
C(2)-C(3)-H(3)	116 (3)	121.5 (6)	C(13)-C(12)-H(8)	118 (3)	121.1 (6)
C(4)-C(3)-H(3)	123 (3)	120.3 (6)	C(12)-C(13)-C(14)	118.8 (4)	118.8 (4)
C(12)-C(13)-H(9)	113 (2)	120.3 (7)	H(12)-B-H(13)	113 (3)	106.5 (6)
C(14)-C(13)-H(9)	126 (2)	121.0 (7)	H(12)-B-H(14)	122 (4)	109.0 (7)
C(13)-C(14)-C(15)	119.6 (4)	119.3 (4)	H(12)-B-H(15)	108 (3)	109.4 (7)
C(13)-C(14)-H(10)	126 (3)	121.9 (6)	H(13)-B-H(14)	100 (3)	108.2 (7)
C(15)-C(14)-H(10)	114 (3)	118.7 (6)	H(13)-B-H(15)	109 (3)	108.8 (7)
N(3)-C(15)-C(14)	123.5 (4)	122.4 (4)	H(14)-B-H(15)	106 (4)	114.5 (7)
N(3)-C(15)-H(11)	118 (3)	116.3 (6)	Co-H(12)-B	82 (3)	90.8 (6)
C(14)-C(15)-H(11)	118 (3)	121.4 (6)	Co-H(13)-B	88 (2)	89.2 (6)

structure the Co atom is significantly (0.42 Å) above the least-squares plane of the terpyridine ligand and the Cl–Co–Cl angle at 111° is much larger than the H–Co–H angle of 73.6 (6)°. This angle is itself significantly larger than the normal $H_{bridging}$–M–$H_{bridging}$ angles observed for bis-chelate transition-metal tetrahydroborato complexes, which are in the range 56–60°.[22,30] Presumably this widening of the angle represents a compromise between the ideal ligand geometry and the ideal metal geometry in which one hydrogen would be close to the apex of an idealized tetragonal pyramid, although some of the disparity may arise because, with one exception,[30] the previous structure determinations used X-ray methods. The electron distribution in the electron-deficient Co/BH_4^- bonding is likely to lead to $H_{bridging}$–$H_{bridging}$ distances measured by X-ray methods being less than the internuclear separation. A second distortion is the lengthening of the Co–H(13) bond (1.740 (12) Å) relative to the Co–H(12) bond (1.707 (12) Å), although this difference is barely significant at the precision of the present experiment. Note that the two Co–Cl bonds in [Co(terpy)Cl_2] are of equal length.[39]

Distortion from an idealized geometry is common in five-coordinate complexes, which are often best described as lying somewhere along a rearrangement coordinate between a tetragonal-pyramidal and trigonal-bipyramidal geometry.[40] We accordingly also explored a description of the molecule as a distorted trigonal bipyramid, in which nitrogens N(1) and N(3) are taken to define the trigonal axis. The distorting influence of the small bite angle of the tetrahydroborato ligand can be seen particularly clearly in this description: N(2)–

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(40) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748.

(41) Note that the difference between e_2 and e_1 is partly due to the fact that the Co–H(12) and Co–H(13) bonds are shorter than the Co–N(2) bond.

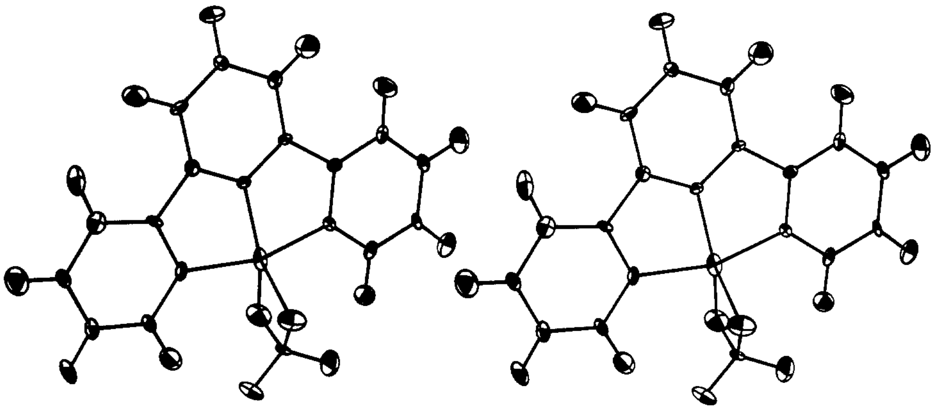

Figure 4. Stereoview of the molecular structure of $[Co(terpy)BH_4]$ as determined by neutron diffraction (50% ellipsoids).

Table V. Deviations (Å) from the Least-Squares Plane Defined by the N and C Atoms of the Terpyridine Ligand

	X-ray	neutron		X-ray	neutron
Co	0.08 (1)	0.08 (1)	C(14)	−0.01 (2)	−0.02 (2)
B	0.55 (1)	0.53 (1)	C(15)	0.01 (2)	0.00 (2)
N(1)	−0.01 (1)	−0.02 (1)	H(1)	−0.35 (7)	−0.15 (2)
N(2)	−0.01 (1)	−0.01 (1)	H(2)	−0.24 (9)	−0.11 (3)
N(3)	0.03 (1)	0.03 (1)	H(3)	−0.22 (7)	0.06 (3)
C(1)	−0.08 (2)	−0.08 (2)	H(4)	0.25 (9)	0.14 (2)
C(2)	−0.05 (2)	−0.04 (2)	H(5)	0.03 (9)	0.00 (2)
C(3)	0.04 (2)	0.05 (2)	H(6)	0.01 (8)	−0.07 (2)
C(4)	0.08 (2)	0.08 (2)	H(7)	−0.06 (7)	−0.04 (2)
C(5)	0.04 (1)	0.03 (1)	H(8)	0.10 (7)	0.04 (2)
C(6)	0.02 (1)	0.01 (1)	H(9)	0.29 (7)	0.02 (3)
C(7)	−0.01 (1)	−0.01 (1)	H(10)	−0.04 (9)	−0.04 (3)
C(8)	−0.05 (1)	−0.06 (1)	H(11)	0.00 (7)	−0.01 (2)
C(9)	−0.04 (1)	−0.03 (1)	H(12)	−0.79 (8)	−0.63 (2)
C(10)	−0.01 (1)	0.00 (1)	H(13)	1.43 (6)	1.39 (2)
C(11)	0.02 (1)	0.03 (1)	H(14)	0.94 (8)	0.71 (2)
C(12)	0.02 (2)	0.02 (2)	H(15)	0.75 (7)	0.64 (2)
C(13)	0.00 (2)	0.01 (2)			

Co–H(13) = 133.7 (6)°, N(2)–Co–H(12) = 152.7 (7)°, H(12)–Co–H(13) = 73.6 (6)°.

Referencing descriptions of real molecules to ideal polyhedra is a convenient way of conveying structural information, but with a low-symmetry molecule such as the title compound such descriptions can be misleadingly precise. Muetterties and Guggenberger[40] have suggested that the description of molecular shapes can conveniently be quantified in terms of the dihedral angles between the faces of the polyhedra whose vertices are defined by the ligating atoms. They have also chosen a suitable shape-determining reference subset of the nine dihedral angles of a polyhedron with five vertices. In the case of $[Co(terpy)BH_4]$, these are the dihedrals which enclose the N(2)–H(13), H(12)–H(13), and N(2)–H(12) edges (e_1, e_2, and e_3, respectively, with use of the nomenclature of ref 40). Table VII gives the observed values for these angles as compared with those for the ideal polyhedra. Comparison of these values indicates that neither description closely matches the geometry of the real molecule.

The mismatch between the observed infrared absorption spectrum of $[Co(terpy)BH_4]$ and that which might be anticipated for a bis chelate tetrahydroborato complex from the study of the spectra of analogous complexes can clearly be seen by comparison of the data in Table III with discussions of such spectra in the literature. An authoritative review,[22] for example, suggests that bis chelate tetrahydroborato complexes should exhibit a strong doublet, 50–80-cm^{-1} splitting, in the B–H$_{\text{terminal}}$ stretching range (2400–2600 cm^{-1}) corresponding to infrared-active A_1 and B_1 modes, and a strong band, possibly with a shoulder, in the B–H$_{\text{bridging}}$ stretching range (1650–2150 cm^{-1}) corresponding to A_1 and B_2 modes. In the case of $[Co(terpy)BH_4]$, there are three bands instead of two in the B–H$_{\text{terminal}}$ stretching region and three weak to medium-weak bands instead of one or two strong bands in the B–H$_{\text{bridging}}$ stretching range.

Generalizations about the characteristic frequencies of vibrating systems with many vibrational degrees of freedom such as the MBH_4 unit with 12 degrees of freedom are often based on the assumption that an analysis of the nature and activity of the normal modes in terms of symmetry theory can be based on the local symmetry of the particular ligand–metal bond (C_{2v} in the case of a bis chelate tetrahydroborato ligand). In the case of $[Co(terpy)BH_4]$, we suggest that the difference between the bonding environments of the two bridging hydride ligands (H(12) and H(13)) is sufficiently marked that this approximation breaks down. The small difference between the two cobalt to hydrogen bond lengths confirms that there is a real difference between the electronic environments of the bridging hydrides in this instance, although such bond length differences would not, of course, be necessary conditions for the observation of anomalous bis chelate tetrahydroborato absorption frequencies. Any departure from local C_{2v} symmetry could, in principle, result in an unusual dipole moment change associated with vibrational excitation. The breakdown of the group frequency approximation in this case implies that it may be a less valid approximation than has been widely assumed, and we would suggest in particular that considerable care should be taken when attempting to apply such generalizations to the determination of the structural features of tetrahydroborato complexes of transition metals.

The ^1H NMR spectrum of the compound also exhibits some unusual features. The protons of the terpyridine ligand have an exceptionally wide range of chemical shifts, covering the range from τ −0.5 to 3.3, and the AA′ and B protons of the

Table VI. Selected Bond Lengths (Å) of Bischelate Tetrahydroborato Complexes

		M–H$_b$	B–H$_b$	B–H$_t$
$[Hf(\eta\text{-}C_5H_4CH_3)_2(BH_4)_2]$[30]	neutron	2.069 (7), 2.120 (8)	1.255 (9), 1.208 (13)	1.186 (16), 1.198 (15)
$[Ti(\eta\text{-}C_5H_5)_2BH_4]$[33]	X-ray	1.75 (8)	1.23 (8)	1.40 (10)
$[Co(P\text{-}(c\text{-}Hx)_3)_2(H)BH_4]$[34]	X-ray	1.84 (9)	1.35 (8)	1.29 (9)
$[Cu(PPh_3)_2BH_4]$[35,36]	X-ray	1.82 (3)	1.07 (3)	1.09 (5)
$[Nb(\eta\text{-}C_5H_5)_2BH_4]$[37]	X-ray	2.0 (1)	1.1 (2)	1.1 (2)
$[Co(terpy)BH_4]$ (this work)	neutron	1.740 (12), 1.707 (12)	1.290 (9), 1.287 (10)	1.214 (10), 1.217 (11)
$[Mo(CO)_4BH_4][N(PPh_2)_3]$[38]	X-ray	2.02 (8)	1.20 (10)	1.11 (11)

Table VII. Shape-Determining Dihedral Angles (Deg) of [Co(terpy)BH_4] (Based on Neutron Results)

	e_1	e_2	e_3
trigonal bipyramid	53.1	53.1	53.1
[Co(terpy)BH_4]	37.2 (3)[41]	82.4 (3)[41]	17.9 (3)
tetragonal pyramid	75.7	75.7	0

middle ring differ sufficiently in shift to show a first-order coupling pattern. This behavior is most readily explained in terms of the magnetic characteristics of the compound, which has a solid-state susceptibility (Guoy method, corrected for diamagnetism) corresponding to an effective magnetic moment of 1.01 μ_B at 299 K and 0.70 μ_B at 78 K.[42] This weak paramagnetism in an essentially low-spin molecule could be responsible for shifting the resonances from their normal positions and could also account for the failure to observe ^{11}B ($I = {}^3/_2$, 81% natural abundance) coupling to the tetrahydroborato protons. This coupling normally results in the observation of these resonances as a quartet which collapses as the rate of quadrupolar spin-lattice relaxation increases, e.g., as the correlation time which characterizes the molecular tumbling is increased by lowering the temperature.[43] The paramagnetism would provide another mechanism for increasing the rate of spin-lattice relaxation of the boron nuclei and would hence decouple them from the protons. The limited solubility of the molecule in inert solvents precluded variable-temperature NMR studies.

The origins of the weak paramagnetism are themselves interesting. The small temperature dependence is consistent with a TIP contribution, but the magnitude and temperature dependence are rather large for that to be the sole origin of the moment. It seems likely that the observed magnetic behavior arises from a combination of factors, e.g., the presence of a ground state which exhibits TIP together with a thermally accessible triplet state, but a definitive interpretation will only be possible after a much more complete study of the magnetic behavior.

Solutions of [Co(terpy)BH_4] are extremely air sensitive and decomposed even when exposed to prepurified argon, possibly by a chain reaction. In contrast, crystalline samples could be handled in air for several minutes without visible evidence of deterioration. The compound reacts readily with a wide variety of reagents, including organolithium compounds, alkyl halides, and donor ligands such as alkyl phosphines. The only tractable product which could be isolated from any of these reactions was the bis(terpyridine)cobalt dication, formed in several instances when an aqueous isolation procedure was used.

Acknowledgment. We thank E. Whitten and W. Reiff of Northeastern University for carrying out the solid-state magnetic susceptibility measurements and for valuable discussions (N.J.C.), and F. Takusagawa for many helpful suggestions (W.M.C.). The technical assistance of J. Henriques in operating the neutron diffractometer is appreciated. We gratefully acknowledge financial support from the National Science Foundation (Grant No. CHE-77-19899 to W.N.L. and Grant No. CHE-75-04124 to E.J.C.). Research at Brookhaven National Laboratory was supported by the Department of Energy, Office of Basic Energy Sciences.

Registry No. Co(terpy)BH_4, 78891-42-6; Co(terpy)BD_4, 78891-41-5; Co(terpy)Cl_2, 14854-50-3.

Supplementary Material Available: Tables of observed and calculated structure factors for the X-ray and neutron analyses (29 pages). Ordering information is given on any current masthead page.

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(Tetramethylporphyrinato)nickel 7,7,8,8-Tetracyanoquinodimethane, Ni(TMP)TCNQ. Synthesis, Structure, and Physical Properties

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Received April 6, 1981

Single crystals of the 1:1 charge-transfer complex (tetramethylporphyrinato)nickel(II) 7,7,8,8-tetracyano-*p*-quinodimethane, Ni(TMP)TCNQ, were afforded by the reaction of Ni(TMP) in benzene with TCNQ in acetonitrile. The compound crystallizes in the space group C_{2h}^5-$P2_1/n$ of the monoclinic system with four formula units in a cell of dimensions a = 17.542 (11) Å, b = 6.868 (5) Å, c = 22.597 (13) Å, and β = 98.42 (2)° at 116 K. Full-matrix least-squares refinement of 407 variables gives a final value of the conventional R index (on F^2) of 0.093 for 5190 observations. The conventional R index on F for 3095 reflections having $F_o^2 > 3\sigma(F_o^2)$ is 0.053. The structure consists of stacks of alternating, parallel Ni(TMP) and TCNQ molecules which are tilted with respect to the stacking axis. The short intrastack interplanar spacing between Ni(TMP) and TCNQ molecules (~3.30 Å) and the presence of two broad charge-transfer bands at 9100 and 11100 cm^{-1} suggest that there is some charge-transfer interaction in the complex. The visible and middle-infrared spectrum of Ni(TMP)TCNQ is essentially a superposition of the spectra of the individual neutral component molecules, so the degree of charge transfer in Ni(TMP)TCNQ is small. An analysis of the bond distances in the TCNQ molecule indicates that the amount of charge transfer is less than 0.2 e. The Ni(TMP)TCNQ complex is diamagnetic, and the conductivity along the single-crystal needle axis is low (<10^{-5} Ω^{-1} cm^{-1}).

Introduction

Charge-transfer complexes composed of various organic and inorganic donors and acceptors have been known for many years and have been the objects of much study.[1,2] Formation of these complexes is assisted if the donors and acceptors are planar, conjugated molecules. Metalloporphyrins have an ideal structure for forming charge-transfer complexes, and there have been several spectroscopic studies of charge-transfer complexes of metalloporphyrins with aromatic organic acceptors.[3-8] However, the main focus of these studies has been

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