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Transition Metal Hydroborate Complexes. 10.[1] Crystal and Molecular Structure of Tris(tetrahydroborato)tris(tetrahydrofuran)yttrium(III)

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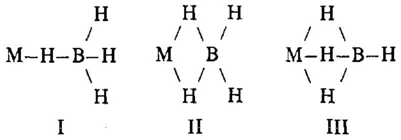
The molecular structure of $Y(BH_4)_3(THF)_3$ has been determined by a single-crystal x-ray diffraction study. The complex crystallizes in the space group *Pbcn* of the orthorhombic system, with four molecules per unit cell. Lattice parameters are $a = 9.314$ (6), $b = 14.597$ (8), and $c = 14.540$ (9) Å. The gadolinium analogue $Gd(BH_4)_3(THF)_3$ forms isomorphous crystals. The structure was solved and refined on F to a final value for the discrepancy index R_1 of 0.053, using 804 unique observed reflections collected by diffractometer. The molecular symmetry is crystallographically required to be C_2. The three boron atoms and three oxygen atoms of the THF rings are at the corners of a distorted octahedron centered about the yttrium atom. One of the three tetrahydroborate groups is bidentate and the other two are tridentate. The yttrium atom therefore has a formal coordination number of 11. In the tridentate $Y-BH_4$ attachment, the tetrahydroborate ligand is slightly tilted from local C_{3v} symmetry, resulting in inequivalent Y–H bond lengths. The Y–B distance of 2.68 (2) Å for the bidentate tetrahydroborate ligand is significantly longer than the value of 2.58 (1) Å found for the two tridentate groups. Metal–hydrogen distances are compared with metal–boron distances in 17 tetrahydroborate complexes for which structural data are available. Good agreement is obtained between observed metal–hydrogen distances and values calculated assuming the BH_4^- anion to be a regular tetrahedron bonded to the metal ion with the appropriate bidentate or tridentate coordination.

Introduction

The tetrahydroborate anion, BH_4^-, forms a large variety of covalent complexes with transition metal, lanthanide, and actinide ions. A recent review article[3] summarizes the many reasons for interest in these compounds, which often have properties typical of organic, molecular crystals: low melting points, high vapor pressure, and solubility in nonpolar solvents. The optical, vibrational, and magnetic properties of metal tetrahydroborate complexes have been extensively investigated, and a complete knowledge of their crystal and molecular structures is often necessary to interpret the data. Coordination of the tetrahydroborate anion to the metal ion occurs through bridging hydrogen atoms and can be mono-, bi-, or tridentate (structures I, II, and III). A number of structural investigations of tetrahydroborate complexes have appeared recently,[4–6] and the first example of monodentate coordination of the BH_4^- group has just been reported.[7,8]


I mono-dentate
II bidentate
III tridentate

Most of the tetrahydroborate complexes that have been structurally characterized contain main-group, transition metal, or actinide ions. Recently, several tetrahydroborate complexes with lanthanide or pseudolanthanide ions have been prepared,[9,10] and the optical spectra of mixed crystals of $Er(BH_4)_3(THF)_3/Y(BH_4)_3(THF)_3$, $Er(BH_4)_3(THF)_3/Gd(BH_4)_3(THF)_3$, and $Er(BH_4)_3(THF)_3/La(BH_4)_3(THF)_3$ have been investigated,[10] where THF represents tetrahydrofuran. Knowledge of the crystal structures of $Y(BH_4)_3(THF)_3$, $Gd(BH_4)_3(THF)_3$, and $La(BH_4)_3(THF)_3$ will aid in the interpretation of the optical spectra. To provide this information and to probe further the factors that govern bidentate vs. tridentate coordination of the small, anionic BH_4^- ligand to metals, an x-ray diffraction study of one of these lanthanide or pseudolanthanide tetrahydroborate complexes was undertaken. The yttrium complex was chosen because its significantly smaller electron density compared with that of the lanthanides facilitates location of hydrogen atom positions.

Nuclear magnetic resonance studies have shown that for both bidentate and tridentate coordination, in almost all known tetrahydroborate complexes, there is a dynamic intramolecular rearrangement process that rapidly interchanges bridging and terminal hydrogens. One mechanism proposed[11,12] for this

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rearrangement is a bidentate $\rightleftharpoons$ tridentate equilibrium, suggesting that the potential energy barrier between these two modes of coordination is not large. There are many more compounds in which the mode of attachment of the BH_4^- to the metal ion involves two rather than three bridging hydrogen atoms. Tridentate coordination has been observed only for the larger metal ions, i.e., those with an ionic radius[13] about 0.7 Å or greater: U(IV) in $U(BH_4)_4$,[14] Hf(IV) in $Hf(BH_4)_4$,[15] Zr(IV) in $Zr(BH_4)_4$,[16,17] Sc(III) in $Sc(BH_4)_3(THF)_2$,[4] and Ti(III) in $[CpTiCl(BH_4)]_2$.[5] Information about the nature of the coordination of the BH_4^- group to another large metal ion, Y(III), adds to our knowledge of how the chemical and structural properties of these complexes respond to variations in the metal ion.

Experimental Section

Collection and Reduction of the X-Ray Data. A colorless crystal of approximate dimensions 0.1 × 0.27 × 0.43 mm, sealed in a 0.3-mm × 4-cm quartz capillary under a dry THF atmosphere because of the air sensitivity of $Y(BH_4)_3(THF)_3$, was supplied by Drs. K.-M. Chen and E. R. Bernstein. The synthesis and properties of $Y(BH_4)_3(THF)_3$ and the analogous lanthanide complexes are described in ref 10.

Preliminary precession photographs using Cu Kα radiation (λ 1.5418 Å) showed the lattice to have *mmm* Laue symmetry. The systematic absences $h0l$, $l \neq 2n$, $0kl$, $k \neq 2n$, and $hk0$, $h + k \neq 2n$, uniquely indicate the space group to be *Pbcn* (D_{2h}^{14}).[18] The mounting axis was a^*. Precession photographs also showed that $Gd(BH_4)_3(THF)_3$ is isomorphous with $Y(BH_4)_3(THF)_3$ with very similar lattice parameters (a = 9.26 (3), b = 14.49 (5), c = 14.43 (5) Å; uncalibrated film data) but that $La(BH_4)_3(THF)_3$ is triclinic (reduced cell parameters a = 7.92 (3) Å, b = 8.80 (3) Å, c = 5.41 (3) Å, α = 94.0 (5)°, β = 99.5 (5)°, γ = 86.5 (5)°; uncalibrated film data). The density of $Y(BH_4)_3(THF)_3$ was not measured but the density of $Gd(BH_4)_3(THF)_3$ was measured by flotation in *o*-bromotoluene and found to be 1.42 g/cm^3.[10a] The calculated density of $Gd(BH_4)_3(THF)_3$ for four molecules per unit cell is 1.43 g/cm^3, in very good agreement with the experimental value. Details of the data collection and reduction for $Y(BH_4)_3(THF)_3$ 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 B, C, O, and Y atoms and corrections for the anomalous dispersion effects for the yttrium atom were obtained from ref 19. Scattering factors for neutral hydrogen atoms were taken from Stewart et al.[20] With phasing based only on the yttrium atom in the asymmetric unit, the discrepancy factors were R_1 = 0.291 and R_2 = 0.396.[21] Two cycles of unit weight and individual isotropic refinement of the 11 nonhydrogen atoms in the asymmetric unit decreased the discrepancy factors to R_1 = 0.095 and R_2 = 0.106. All atoms other than hydrogen were then assigned anisotropic temperature factors.[22] Hydrogen atoms were located on a difference Fourier map, but refinement of some of these atoms was not possible because of the large thermal motion of the atoms to which they are bonded. Correlation coefficients between the x, y, and z coordinates and the isotropic temperature factors of the hydrogen atoms and the respective parameters of the atoms to which they are attached were quite large (>0.6 in many cases). As a consequence, refinement produced abnormally short C–H or B–H distances and negative temperature factors for some of the hydrogen atoms. Any methylene hydrogen atom on a THF ligand that could not be refined was held fixed at the idealized position calculated with a C–H distance of 0.95 Å and H–C–H bond angles of 109° 28′. The BH_4^- ligands were then treated as rigid tetrahedral groups, with refinement at first only of the boron atom isotropic temperature factor and an overall group temperature factor. The B–H distance was fixed at 1.10 Å. In the final refinement with rigid tetrahedral BH_4^- groups, all five atoms were allowed individual isotropic temperature factors. No parameter varied by more than 0.25 of its estimated standard deviation. The discrepancy indices R_1 and R_2 converged at 0.054 and 0.050, respectively. A final refinement with each atom of the BH_4^- ligands varied individually converged at R_1 = 0.053 and R_2 = 0.048. Since there were only 804 unique reflections for which $F_o^2 > 2\sigma(F_o^2)$ to refine 139 variables, the last refinement was repeated using 1078 unique reflections for which $F_o^2 > \sigma(F_o^2)$. While the discrepancy factors increased to R_1 = 0.090 and R_2 = 0.060, all atomic positions remained the same to within one standard deviation.

Table I. Experimental Details of the X-Ray Diffraction Study of $Y(BH_4)_3(THF)_3$

(A) Crystal Parameters[a] at 23 °C

a = 9.314 (6) A
b = 14.597 (8) A
c = 14.540 (9) A
Z = 4
V = 1977 (4) A^3
Mol wt 349.8
Space group *Pbcn*
ρ(calcd) = 1.175 g/cm^3

(B) Collection of Intensity Data

Instrument: Picker FACS-I-DOS diffractometer
Radiation: Mo Kα (λ_{α_1} = 0.709 30 A), graphite monochromatized
Takeoff angle: 1.9°
Detector aperture: 4 mm × 4 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 [(402), ($\bar{1}\bar{5}1$), ($\bar{2}2\bar{3}$)] measured every 77 data reflections; correction later made for ca. 8% linear crystal decomposition
No. of reflections collected: 3613

(C) Treatment of Intensity Data[b]

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;[c,d] ϵ[e] = 0.04
Absorption correction: μ = 29.67 cm^{-1}; because faces were not clearly visible in the capillary, not applied
Averaging: 999 equivalent pairs in the inner sphere ($2\theta \leqslant 35°$); 33 reflections with 3 observations; R_{av}[f] = 0.040
Scaling: Wilson's method;[g] $\bar{B}$ = 4.45 A^2
Observed data: 804 unique reflections for which $F_o^2 > 2\sigma(F_o^2)$

[a] From a least-squares fit to the setting angles of 12 reflections using the logic of the FACS-I-DOS system. [b] Programs for an IBM 360/91 computer used in this work include the following: AVSORT, which computes a weighted average of equivalent reflections and which was written by J. T. Gill; XDATA, the Brookhaven Wilson plot and scaling 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 ORLFS; 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. [c] Reference 26. [d] Reference 27. [e] P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967). [f] $R_{av} = \Sigma_{i=1}^{N}\Sigma_{j=1}^{n}|\bar{F}_i^2 - F_{ij}^2|/\Sigma_{i=1}^{N}\bar{F}_i^2$, where N is the number of reflections measured more than once and n is the number of observations of the Nth reflection. [g] A. J. C. Wilson, *Nature (London)*, 150, 151 (1942).

The $|F_o| - |F_c|$ differences 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 with respect both 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 1.37.[23] A final difference Fourier map showed a residual electron density of 0.98 e/Å^3 exactly at the position of the yttrium atom and slight residual electron density of 0.46 e/Å^3 along the twofold axis between the yttrium and oxygen atoms and ~0.4 e/Å^3 near some of the methylene hydrogen atoms of the THF rings.

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.[24] The C–H bond distances and bond angles involving H atoms on the THF ligands are reported in Table S3.[24] The sizes and orientations of the anisotropic ellipsoids are shown along with the

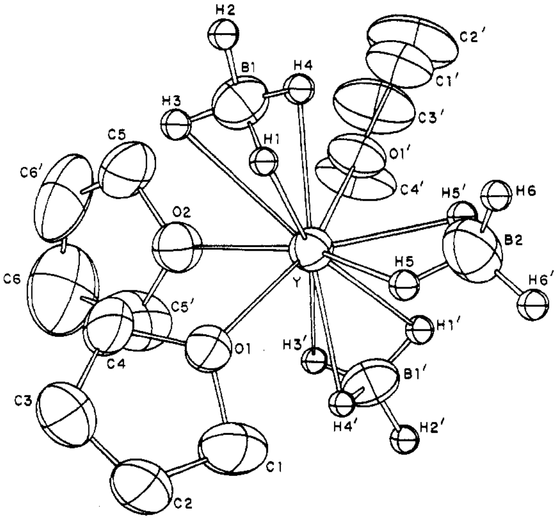

Figure 1. Structure and atom-labeling scheme of $Y(BH_4)_3(THF)_3$. Hydrogen atoms on the THF rings are not shown. Primed atoms are related to unprimed atoms by the symmetry operation ($\bar{x}$, y, $^1/_2 - z$). The thermal ellipsoids are scaled at the 35% probability level. The hydrogen atoms are represented as arbitrary spheres with root-mean-square amplitudes of vibration set at 0.15 Å.

atom-labeling scheme in Figure 1.

Results and Discussion

Crystal and Molecular Structure. In the solid state, $Y(BH_4)_3(THF)_3$ exists in discrete molecular units. The yttrium atom, one oxygen atom of a tetrahydrofuran ring, and one of the three boron atoms are situated on a crystallographically required twofold symmetry axis. All intermolecular contacts are greater than the sum of the van der Waals radii of the atoms. Figure 2 shows the packing of molecules in the unit cell.

The most striking feature of the molecular structure of $Y(BH_4)_3(THF)_3$ is the inequivalence of the three tetrahydroborate groups, of which one is attached to yttrium by a two-hydrogen-atom bridge and the other two are attached by three-hydrogen-atom bridges. The resulting yttrium atom coordination number is 11. Alternatively, yttrium can be considered to be pseudooctahedrally coordinated, as the three oxygen and three boron atoms are at the corners of a distorted octahedron centered about the yttrium atom. The four B–Y–O bond angles are 89.4 (4), 90.1 (4), 100.7 (2), and 88.7 (4)° (see Table III). Two Y–B distances are 2.58 (1) Å, significantly shorter than the third, which is 2.68 (2) Å. The tetrahydroborate groups for which the Y–B distance is shorter are tridentate; the BH_4^- group with the longer Y–B distance is bidentate. The significant shortening of the metal–boron separation on tridentate compared to bidentate bonding of a tetrahydroborate group has been observed and discussed previously.[4,14]

Large thermal motion of the boron and hydrogen atoms was apparent during the least-squares refinement of the positions of the hydrogen atoms in $Y(BH_4)_3(THF)_3$, and there are corresponding large uncertainties in the positional parameters of the tetrahydroborate hydrogen atoms (see Table II). Nevertheless, the inequivalence in the coordination of the three BH_4^- ligands was quite apparent during the refinement. Since one of the three boron atoms sits on a twofold symmetry axis in the unit cell, that tetrahydroborate group must be bidentate (barring disorder). The two bridging hydrogen atoms, H5 and H5', were located on a difference Fourier synthesis and refined without difficulty. The hydrogen atom positions of the other two tetrahydroborate groups (also located on a difference Fourier map) did not refine well, however, and the BH_4^- moieties were therefore refined as rigid tetrahedral groups with the B–H distance fixed at 1.10 Å. The true value of the B–H distance is undoubtedly larger than 1.10 Å. The average length of the B–H bond in $U(BH_4)_4$[14] is 1.24 (5) Å and in $Hf(BH_4)_4$[15] it is 1.26 (6) Å. Both of these values have been determined by neutron diffraction studies. It is well-known that B–H distances as determined by x-ray diffraction are artificially short.[25] Recent x-ray diffraction studies of a number of diverse compounds have obtained B–H distances close to 1.10 Å: the average value is 1.10 (5) Å in $[CpTiCl(BH_4)]_2$,[5] 1.11 (13) Å in $[(tren)Ni(NCBH_3)]_2(BPh_4)_2$,[1] 1.11 (8) Å in $[(Ph_3P)_2Cu]_2B_{10}H_{10}$,[26] 1.08 (4) Å in $[(Ph_3P)_2Cu(BH_4)]$,[26] 1.08 (5) Å in $Sc(BH_4)_3(THF)_2$,[4] and 1.07 (4) Å in $(Me_5dien)Cu(NCBH_3)_2$.[27] Initially all three tetrahydroborate groups were assigned a bidentate coordination to the yttrium atom during the rigid-body refinement. The two equivalent tetrahydroborate groups moved to a tridentate configuration as refinement progressed. The positions of the hydrogen atoms when each atom in the molecule is refined individually are not identical with the positions determined when the BH_4^- ligands are refined as rigid tetrahedral groups, but the nature of the coordination to the yttrium atom does not change. On individual atom refinement, three of the hydrogen atoms, H2, H3, and H6, refine to locations closer to the boron atoms than 1.10 Å (see Table III). These abnormally short distances are not considered to be significant. Despite the fact that some of the B–H distances refine to values much too short to be correct (particularly for the two terminal H atoms H2 and H6), the distinction between the tridentate and the bidentate coordination remains clear.

The Y–H bond distances also contain large uncertainties and depend on the method of refinement. Semenenko et al.[5] suggested that tridentate coordination, which leads to a shortening of the metal–boron bond, also results in a lengthening of the metal–hydrogen bond. They found the Ti–H distance to be 1.94 (7) Å in contrast to the Ti–H distance of 1.75 (8) Å found in $Cp_2Ti(BH_4)$[28] in which the BH_4^- groups are bidentate. In view of the large uncertainties in these distances, the difference is not statistically meaningful ($\Delta/\sigma = 2.4$). It should be noted that in the neutron diffraction study

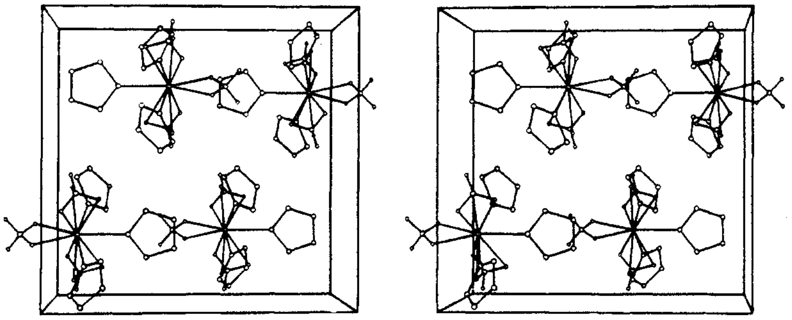

Figure 2. Stereoscopic view of one unit cell showing the packing of four molecules of $Y(BH_4)_3(THF)_3$. Hydrogen atoms on the THF rings are not shown.

Table II

Final Positional and Isotropic Thermal Parameters for $Y(BH_4)_3(THF)_3$[a,b]

Atoms Refined Anisotropically

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Y	0	0.14838 (7)	0.25	O2	0	−0.0169 (5)	0.25
O1	0.1941 (7)	0.1186 (4)	0.1512 (4)	C5	0.015 (3)	−0.0773 (8)	0.328 (1)
C1	0.216 (2)	0.159 (1)	0.0587 (9)	C6	0.000 (4)	−0.1684 (9)	0.202 (1)
C2	0.352 (2)	0.120 (2)	0.027 (1)	B1	0.173 (2)	0.144 (1)	0.388 (1)
C3	0.397 (1)	0.054 (1)	0.0914 (9)	B2	0	0.332 (1)	0.25
C4	0.319 (1)	0.063 (1)	0.1717 (8)				

Tetrahydroborate Hydrogens

	Rigid-body refinement of BH_4^-				Individual atom refinement			
Atom	*x*	*y*	*z*	*B*, Å^2	*x*	*y*	*z*	*B*, Å^2
H1	0.209 (6)	0.189 (4)	0.332 (3)	9 (2)	0.189 (12)	0.191 (7)	0.330 (7)	13^c
H2	0.244 (7)	0.158 (5)	0.450 (3)	35 (10)	0.241 (18)	0.152 (9)	0.418 (9)	13^c
H3	0.184 (8)	0.073 (1)	0.369 (5)	13 (4)	0.154 (14)	0.089 (7)	0.375 (8)	13^c
H4	0.063 (3)	0.161 (5)	0.407 (4)	8 (2)	0.071 (12)	0.165 (8)	0.408 (9)	13^c
H5^b	0.081	0.290	0.217	12 (3)	0.074 (9)	0.293 (6)	0.218 (5)	9 (3)
H6^b	0.052	0.377	0.302	13 (4)	0.025 (16)	0.374 (6)	0.290 (7)	12 (4)

Rigid Groups[d]

Group	X_0	Y_0	Z_0	ϕ	θ	ρ
$BH_4$1	0.175 (1)	0.1452 (8)	0.3896 (9)	3.00 (6)	3.45 (6)	1.20 (7)
$BH_4$2	0	0.333 (1)	0.25	$-\pi/2$	2.57 (7)	π

Methylene Hydrogen Atoms on THF Rings

Atom	*x*	*y*	*z*	*B*, Å^2
H11^e	0.240 (12)	0.221 (5)	0.079 (6)	10 (3)
H12	0.145 (17)	0.110 (8)	0.033 (9)	15 (6)
H21	0.371 (10)	0.115 (5)	−0.027 (5)	6 (2)
H22	0.435 (19)	0.159 (12)	0.044 (12)	18 (4)
H31	0.382^c	−0.005^c	0.067^c	9^c
H32	0.496^c	0.063^c	0.005^c	9^c
H41	0.376^c	0.093^c	0.217^c	12^c
H42	0.276 (8)	0.014 (5)	0.215 (5)	6 (2)
H51	−0.033 (8)	−0.054 (5)	0.373 (4)	4 (3)
H52	0.130 (14)	−0.081 (10)	0.331 (10)	16 (6)
H61	0.088 (9)	−0.151 (7)	0.195 (5)	4 (2)
H62	−0.076^c	−0.205^c	0.179^c	9^c

Final Anisotropic Thermal Parameters for $Y(BH_4)_3(THF)_3$[f]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Y	14.5 (1)	5.22 (5)	5.65 (6)	0	0.8 (2)	0
O1	16 (1)	8.5 (4)	5.6 (3)	2.0 (5)	1.7 (5)	1.0 (3)
O2	27 (1)	5.4 (4)	7.5 (5)	0	−0.7 (16)	0
C1	26 (3)	12 (1)	7.8 (8)	3 (2)	4 (1)	1.6 (9)
C2	32 (4)	19 (2)	8.2 (9)	11 (2)	7 (2)	2 (1)
C3	29 (2)	18 (1)	9.9 (9)	12 (2)	6 (1)	1.4 (9)
C4	25 (2)	17 (1)	8.7 (8)	14 (1)	3 (1)	3.8 (8)
C5	49 (4)	6.9 (7)	10.1 (9)	2 (3)	1 (3)	2.5 (7)
C6	49 (4)	8.3 (9)	27 (3)	−5 (3)	−9 (5)	−4.2 (9)
B1	17 (2)	9 (1)	6.8 (8)	2 (2)	−3 (1)	−0.7 (9)
B2	33 (5)	6 (1)	11 (2)	0	6 (4)	0

[a] Atoms are labeled as indicated in Figure 1. [b] Standard deviations, in parentheses, occur in the last significant figure for each parameter. Positional coordinate errors for atoms H5 and H6 were not computed for rigid-body refinement owing to a program malfunction. [c] Not refined. [d] X_0, Y_0, and Z_0 are the fractional coordinates of the boron atoms which are the center of gravity of the rigid-body-constrained tetrahedral BH_4^- groups, and ϕ, θ, and ρ are the orientation angles given in radians. For definitions of these coordinates see R. J. Doedens in "Crystallographic Computing", F. R. Ahmed, S. R. Hall, and C. P. Huber, Ed., Munskgaard, Copenhagen, 1970, pp 198–200. [e] In this table, H11 and H12, for example, refer to the two hydrogens on carbon atom 1. [f] β's are defined in footnote 22; values reported here are ×10^3.

of $U(BH_4)_4$[14] no correlation was found between the length of the U–H bond and the nature of the coordination of the tetrahydroborate group. In the present compound, the Y–H distances are somewhat longer for the tridentate BH_4^- groups than for the bidentate ligand, but the differences are not significant.

Simple relations exist between the ratios $R = r_{\text{M-H}}/r_{\text{B-H}}$ and $S = r_{\text{M-B}}/r_{\text{B-H}}$ for a regular tetrahedron bonded to a metal ion. The nature of the relationship depends on whether the attachment to the metal is bidentate or tridentate. These relations, derived from elementary geometrical considerations, have been given previously.[14] We can use these equations to test whether or not it is possible, in the present case, for the BH_4^- group which is considered to be tridentate to be, in fact, bidentate. For $r_{\text{Y-B}} = 2.58$ Å and $r_{\text{B-H}} = 1.10$ Å, $r_{\text{Y-H}}$ is calculated to be 2.44 Å for a three-point attachment and 2.14 Å for a two-point attachment. Calculated values of $r_{\text{Y-H}}$ are not sensitive to the value chosen for $r_{\text{B-H}}$ (vide infra). Values of the Y–H distances obtained for H1, H3, and H4 range from 2.20 to 2.68 Å and depend on whether the tetrahydroborate group is refined as a rigid body or as individual atoms, but the calculated Y–H distance of 2.44 Å is in reasonable

Table III. Molecular Geometry of $Y(BH_4)_3(THF)_3$[a]

Selected Intramolecular Bond Distances, Å

Coordination Sphere			THF Rings		BH_4^- Groups[b]	
Y–O1	2.350 (6)		O1–C1	1.48 (1)	B1–H1	1.09 (10)
Y–O2	2.412 (7)		C1–C2	1.46 (2)	B1–H2	0.77 (8)
Y···B1	2.58 (1)[b]	2.60 (1)[c]	C2–C3	1.41 (2)	B1–H3	0.86 (11)
Y···B2	2.68 (2)[b]	2.70 (1)[c]	C3–C4	1.38 (1)	B1–H4	1.04 (11)
Y–H1	2.20 (11)[b]	2.36 (5)[c]	O1–C4	1.45 (1)	B2–H5	1.01 (8)
Y–H3	2.48 (12)[b]	2.68 (7)[c]	O2–C5	1.45 (1)	B2–H6	0.88 (10)
Y–H4	2.41 (12)[b]	2.37 (6)[c]	C5–C6′[d]	1.41 (2)		
Y–H5	2.27 (9)[b]	2.25[c]	C6–C6′	1.40 (4)		

Selected Bond Angles, Deg

O1–Y–O2	79.3 (2)		O1–Y–O1′	158.6 (3)	
O1–Y–B1	89.4 (4)[b]	89.6 (3)[c]	B1–Y–B1′	177.5 (8)[b]	177.9 (4)[c]
O1–Y–B1′	90.1 (4)[b]	90.0 (3)[c]	O1–Y–B2	100.7 (2)[b]	100.7 (2)[c]
B1–Y–O2	88.7 (4)[b]	89.0 (3)[c]	B1–Y–B2	91.3 (4)[b]	91.0 (3)[c]
H1–Y–H3	41 (4)[b]	41 (2)[c]	H1–Y–B1	25 (3)[b]	25 (1)[c]
H1–Y–H4	41 (3)[b]	45 (2)[c]	H3–Y–B1	19 (2)[b]	24 (1)[c]
H3–Y–H4	34 (3)[b]	41 (2)[c]	H4–Y–B1	24 (3)[b]	25 (1)[c]
H5–Y–H5′	43 (4)[b]	47 (2)[c]	H5–Y–B2	22 (2)[b]	24 (1)[c]
Y–B1–H2	161 (10)[b]	169 (3)[c]	Y–B2–H6	134 (6)[b]	125 (3)[c]
Y–O1–C1	126.1 (7)		Y–O2–C5	127.5 (6)	
Y–O1–C4	126.6 (6)		C5–O2–C5′	105 (1)	
C1–O1–C4	107.1 (8)		O2–C5–C6′	109 (1)	
O1–C1–C2	105 (1)		C5–C6′–C6	108 (1)	
C1–C2–C3	108 (1)		C3–C4–O1	107.6 (9)	
C2–C3–C4	110 (1)		H1–B1–H2	104 (11)	
H1–B1–H3	117 (10)		H1–B1–H4	99 (8)	
H2–B1–H3	116 (13)		H2–B1–H4	123 (10)	
H3–B1–H4	98 (10)		H5–B2–H5′	111 (10)	
H5–B2–H6′	106 (9)		H5–B2–H6	121 (11)	
			H6–B2–H6′	91 (13)	

[a] See footnotes *a* and *b*, Table II; values reported here have not been corrected for thermal motion. [b] Individual atom refinement. [c] Rigid tetrahedral BH_4^- groups; B–H distance fixed at 1.10 Å. [d] Primed atoms are related to unprimed atoms by the symmetry operation ($\bar{x}, y, {}^1/_2 - z$).

agreement with the values obtained (see Table III), whereas 2.14 Å is significantly shorter. Similarly, for the ligand with the B atom on the twofold axis, if r_{Y-B} = 2.69 Å and r_{B-H} = 1.10 Å, r_{Y-H} is calculated to be 2.24 Å for a two-point attachment and 2.54 Å for a three-point attachment. The observed value is 2.27 Å. We consider, therefore, that there is a real difference between the coordination of the tetrahydroborate ligands.

Both bidentate and tridentate coordination of BH_4^- ligands within the same molecule has now been observed in three complexes: $U(BH_4)_4$,[14] $Sc(BH_4)_3(THF)_2$,[4] and $Y(BH_4)_3(THF)_3$. In addition, the tetrahydroborate ligand is coordinated to Ti(III) by a two-hydrogen bridge in $Cp_2Ti(BH_4)$[28] and by a three-hydrogen bridge in $[CpTiCl(BH_4)]_2$,[5] and the coordination to Hf(IV) is bidentate in $(CH_3C_5H_4)_2Hf(BH_4)_2$[6] and tridentate in $Hf(BH_4)_4$.[15] In all of these cases the M–B bond is significantly shorter for tridentate coordination than for bidentate coordination. It is particularly striking that in both $Y(BH_4)_3(THF)_3$ and $Sc(BH_4)_3(THF)_2$[4] there are one bidentate and two tridentate BH_4^- ligands, despite the difference in the number of THF ligands. The larger radius of Y(III) (0.89 Å for coordination number 6[13]) compared to that of Sc(III) (0.73 Å for coordination number 6[13]) is consistent with the presence of an extra THF ligand in the yttrium complex. It has been proposed[5] that in the absence of steric hindrances the BH_4^- coordination will always be tridentate and that bidentate coordination will occur only when there are other bulky ligands which force the BH_4^- tetrahedron to present an edge, rather than a face, to the metal atom. The presence of both types of coordination in $Y(BH_4)_3(THF)_3$ and in $Sc(BH_4)_3(THF)_2$ seems to indicate that the difference between the potential energy well minima for bidentate and tridentate coordination is quite small. In fact, coordination which is partially bidentate and partially tridentate is also possible. We note that the three M–H distances are not equal for the tridentate BH_4^- groups in either of these two compounds and that the Y–B–H_t bond angle in $Y(BH_4)_3(THF)_3$ is 161 (10)°, compared with the value of 180° expected for pure tridentate coordination. The coordination of the tetrahydroborate ligands observed in these two compounds supports the mechanism proposed[11,12] for the intramolecular rearrangement that interchanges bridging and terminal hydrogen atoms in solution.

The geometry of the THF rings is typical for x-ray structure determinations. The THF rings are almost planar and have short C–C and O–C bonds, which is observed when the molecule is in dynamic disorder. As can be seen from Figure 1 and Table S2, there is large thermal motion of the carbon atoms, the direction of maximum amplitude of which is perpendicular to the plane of the THF rings. This feature results in short C–C and O–C bond distances if no corrections are made for thermal motion (see Table III). Using the thermal parameters listed in Table S2, a "riding" correction for thermal motion was found to increase the observed bond distances by 0.04–0.05 Å. If an absorption correction (the transmission coefficients are estimated to be ~0.50–0.55) could have been made, an even larger increase in the bond distances would be expected. The average O–C distance observed[29] is 1.46 (1) Å and the average C–C distance is 1.41 (2) Å. These thermally uncorrected values may be compared with the corresponding values of 1.47 (1) and 1.48 (1) Å for $ScCl_3(THF)_3$.[30] The C–C–C, O–C–C, and C–O–C bond angles range from 105 (1) to 110 (1)°, whereas in $ScCl_3(THF)_3$[30] they range from 103 (1) to 111 (1)°. The distorted octahedral geometry of the yttrium complex can be compared with the distorted trigonal-bipyramidal geometry of $Sc(BH_4)_3(THF)_2$.[4] In the latter compound the two THF rings are axial, the O–Sc–O bond angle is 160.0 (1)°, and the O–Sc bond distances are 2.170 (2) and 2.163 (3) Å. In $Y(BH_4)_3(THF)_3$, two THF rings are trans to one another with

Table IV. Metal-Hydrogen and Metal-Boron Distances (Å) in Complex Tetrahydroborates

Compd	$(M-B)_{obsd}$	$(M-H)_{obsd}$[a]	$(M-H)_{calcd}$	$r_{M(ion)}$[b]
	Bidentate Coordination			
$U(BH_4)_4$[c]	2.86 (4)[a]	2.40 (3)	2.37[d]	1.05
$Y(BH_4)_3(THF)_3$	2.68 (2)	2.27 (9)	2.23[e]	1.02
$(CH_3C_5H_4)_2Hf(BH_4)_2$[f]	2.553 (6)	2.10 (2)	2.10[d]	0.71
$Sc(BH_4)_3(THF)_2$[g]	2.551 (5)	2.09 (5)	2.12[e]	0.73
$(Ph_3P)_2N^+[Mo(CO)_4(BH_4)]^-$[h]	2.41 (2)	2.02 (8)	1.99[e]	0.67
$Cp_2Ti(BH_4)$[i]	2.37 (1)	1.75 (8)	1.94[d]	0.67
$Cp_2Nb(BH_4)$[j]	2.26 (6)	2.0 (1)	1.9[e]	0.70
$Al(BH_4)_3(NH_3)$[k]	2.229 (8)	1.77 (7)	1.83[e]	0.53
$Al(BH_4)_3 \cdot N(CH_3)_3$[l]	2.22 (2)	1.85 (6)	1.81[d]	0.53
$Al(BH_4)_2N(CH_2)_2$[m]	2.19 (1)	1.74 (6)	1.79[e]	0.53
$(Ph_3P)_2Cu(BH_4)$[n]	2.185 (6)	1.82 (3)	1.79[e]	0.46
$Al(BH_4)_3$[o]	2.143 (3)	1.80 (1)	1.75[d]	0.53
$(Cy_3P)_2CoH(BH_4)$[p]	2.13 (1)	1.84 (9)	1.74[d]	0.65
$Be(BH_4)_2$[q]	1.96 (4)[a]	1.59 (2)	1.60[d]	0.27
	Tridentate Coordination			
$Y(BH_4)_3(THF)_3$	2.58 (1)	2.36 (11)	2.44[e]	1.02
$U(BH_4)_4$[c]	2.52 (1)	2.34 (2)	2.41[d]	1.05
$Zr(BH_4)_4$[r]	2.31 (1)	2.21 (4)	2.23[d]	0.84
$Sc(BH_4)_3(THF)_2$[g]	2.33 (1) 2.23 (1)	2.09 (5)	2.22[e] 2.13[e]	0.73
$Hf(BH_4)_4$[s]	2.25 (3)	2.06 (2)	2.18[d]	0.71
$[CpTiCl(BH_4)]_2$[t]	2.17 (1)	1.95 (7)	2.08[e]	0.67

[a] Averaged value. [b] Ionic radii were taken from ref 13 for appropriate ions of similar oxidation state and coordination number. Values given are "effective ionic radii" determined from metal oxides. [c] Reference 14. [d] Calculated using B–H = 1.24 Å. [e] Calculated using B–H = 1.10 Å. [f] Reference 6. [g] Reference 4. [h] S. W. Kirtley, M. A. Andrews, R. Bau, G. W. Grynkewich, T. J. Marks, D. L. Tipton, and B. R. Whittlesey, *J. Am. Chem. Soc.*, 99, 7154 (1977). [i] Reference 28. [j] N. I. Kirilova, A. I. Gusev, and Yu. T. Struchkov, *Zh. Strukt. Khim.*, 15, 662 (1974). [k] E. B. Lobkovskii, V. B. Polyakova, S. P. Shilkin, and K. N. Semenenko, *ibid.*, 16, 77 (1975); E. B. Lobkovskii, K. N. Semenenko, and A. L. Dorosinskii, *ibid.*, **15**, 70 (1974). [l] N. A. Bailey, P. H. Bird, and M. G. H. Wallbridge, *Chem. Commun.*, 438 (1965); *Chem. Commun.*, 286 (1966); *Inorg. Chem.*, 7, 1575 (1968). [m] K. N. Semenenko, E. B. Lobkovskii, B. L. Tarnopolskii, and M. A. Simonov, *Zh. Strukt. Khim.*, 17, 1076 (1976). [n] S. J. Lippard and K. M. Melmed, *Inorg. Chem.*, 6, 2223 (1967), and ref 26. [o] A. Almenningen, G. Gundersen, and A. Haaland, *Acta Chem. Scand.*, 22, 328 (1968). [p] M. Nakajima, H. Moriyama, A. Kobayashi, T. Saito, and Y. Sasaki, *J. Chem. Soc., Chem. Commun.*, 80 (1975). [q] D. S. Marynick and W. N. Lipscomb, *J. Am. Chem. Soc.*, 93, 2322 (1971); *Inorg. Chem.*, 11, 820 (1972). [r] References 16 and 17. [s] Reference 15. [t] Reference 5.

an O–Y–O bond angle of 158.6 (3)°. The Y–O bond distance is 2.350 (6) Å, consistent with the 0.16-Å increase in the metal ion radius when Y(III) replaces Sc(III).[13] The larger size of Y(III) allows more room in the equatorial plane and a third THF ring bonds to the metal. This ligand is trans to the bidentate BH_4^- group, with the B, O, and Y atoms all situated on the twofold symmetry axis. The Y–O distance for this tetrahydrofuran ring, 2.412 (7) Å, is slightly larger than the 2.350 (6) Å distance for the other two rings, most likely because steric crowding prevents the third THF ligand from moving in more closely.

Correlation between Metal–Boron and Metal–Hydrogen Distances. There are now 14 complexes in which bidentate coordination of the BH_4^- group to the metal ion has been demonstrated by a structural determination and six in which the coordination is tridentate. A tabulation of the observed metal–boron and metal–hydrogen distances in these 20 examples is given in Table IV. Included in this table are values of the metal–hydrogen distance calculated using eq 1 and 2 of ref 14 assuming that the BH_4^- group is a regular tetrahedron. In making this calculation a value must be assigned to the B–H distance. Calculations were performed using both 1.24 and 1.10 Å for the B–H distance. The resulting values of r_{M-H} were remarkably insensitive to the value used for r_{B-H}. Except for the three largest metal ions, r_{M-H} was never more than 0.01 Å larger when a value of 1.10 Å instead of 1.24 Å was used for r_{B-H}. For the three largest metal ions r_{M-H} was 0.02 Å larger when the smaller value of the B–H distance was employed. In preparing Table IV, the B–H distance used was either 1.10 or 1.24 Å, whichever was closer to the observed B–H distances for that compound. The table shows that there is excellent agreement between the calculated and observed values of the M–H distance. The large M–B distances correspond to the large M–H distances. The most anomalous of the 20 entries in the table is that for $Cp_2Ti(BH_4)$. Both the Patterson and the difference Fourier maps for that compound revealed substantial disorder[28] in the orientation of the cyclopentadienyl rings and the Ti–H distance reported is not considered to be reliable to better than 0.2 Å. It should be noted that the unrefined Ti–H distance, calculated from the Fourier map, was 1.83 Å. It would be useful to collect a low-temperature neutron diffraction data set on $Cp_2Ti(BH_4)$ or, even better, on $(MeCp)_2Ti(BH_4)$ since methylation of the cyclopentadienyl rings would probably lock them into a fixed position in the structure.

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Registry No. $Y(BH_4)_3(THF)_3$, 65415-37-4.

Supplementary Material Available: Listings of structure factor amplitudes and root-mean-square thermal amplitudes and bond distances and angles involving the H atoms on the THF ligands (7 pages). Ordering information is given on any current masthead page.

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Structure of a Dioxygen Adduct of (1-Methylimidazole)-*meso*-tetrakis($\alpha,\alpha,\alpha,\alpha$-*o*-pivalamidophenyl)porphinatoiron(II). An Iron Dioxygen Model for the Heme Component of Oxymyoglobin[1a]

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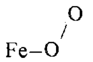
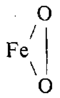
The structure of a solvate of mono(1-methylimidazole)(dioxygen)-*meso*-tetrakis($\alpha,\alpha,\alpha,\alpha$-*o*-pivalamidophenyl)porphinatoiron(II), $[\mathrm{Fe(TpivPP)(1\text{-}Me\text{-}imid)(O_2)}]\cdot{}^1/_2(C_6H_6)\cdot{}^1/_2(N_2C_4H_6)$, has been determined using three-dimensional x-ray diffraction data collected by counter methods. Crystal symmetry is consistent with the monoclinic space groups $C2/c$ or Cc. The unit cell parameters are a = 18.690 (3) Å, b = 19.154 (3) Å, c = 18.638 (3) Å, β = 91.00 (1)°, and Z = 4. Least-squares refinement of the structure in space group $C2/c$ has led to a conventional R factor (on F) of 0.109 using 1784 reflections with $I > \sigma_I$. The crystal structure consists of monomeric units of Fe(TpivPP)(1-Me-imid)(O_2) with benzene or 1-methylimidazole molecules occupying one solvate site in the asymmetric unit. Dioxygen is coordinated to the iron atom in the end-on bent bond mode. The Fe–O separation is 1.75 (2) Å. As a consequence of the twofold symmetry imposed on the molecule, the 1-methylimidazole group and the terminal oxygen atom are disordered. Additional disorder is found for the *tert*-butyl groups and for the terminal oxygen atom which can also occupy either of two crystallographically independent sites and which thus exhibits overall fourfold disorder. The two crystallographically independent O–O separations are 1.15 (4) and 1.17 (4) Å and the respective Fe–O–O bond angles are 133 (2) and 129 (2)°. The O–O separations may be underestimated by as much as 0.15 Å. The Fe–N_{porph} separations are 1.99 (1) and 1.97 (1) Å and the iron atom is displaced 0.03 Å from the mean plane of the porphinato nitrogen atoms toward the dioxygen ligand. The Fe–N_{imid} separation is 2.07 (2) Å. Precise structure analysis is prevented by limited data of poor quality and by the disorder and high thermal motion of many parts of the structure.

Introduction

For many years there has been considerable interest in the geometry of the iron–dioxygen bond in oxyhemoglobin and oxymyoglobin.[2–4] Pauling[2] originally proposed an angular, end-on



geometry and Griffith[3] a side-on, π-bonded



structure. Both models could account for the apparent diamagnetism of oxygenated hemes.[5] Both structural types have been characterized by single-crystal x-ray diffraction techniques.[6] The side-on mode has been observed for complexes of many transition metals but it has yet to be observed for an iron–dioxygen complex;[6d] the O–O separations are almost invariably in the range 1.4–1.5 Å. The end-on mode has been associated with dioxygen adducts of d^7 cobalt(II) complexes,[7–13] and O–O separations in the range 1.27 (1)[10] to 1.302 (3) Å[11] and Co–O–O bond angles of approximately 120° have been determined, except for the anionic complex $[\mathrm{Co(CN)_5(O_2)}]^{3-}$, where the respective parameters were found to be 1.24 (2) Å and 153 (2)°.[13] These separations are slightly less than that observed for the superoxide ion (1.32–1.35 Å[14,15]).

The results from a large number of other studies including ESR,[16] infrared,[17] and x-ray photoelectron (ESCA) spectroscopy,[18] and linear-free-energy relationships[17,19] may be used to support the formulation of these complexes as $\mathrm{Co^{III}\text{–}O_2^-}$ species. Recent ESR studies[20] indicated that this formulation may be inappropriate for some Co–O_2 complexes of quadridentate, dianionic, conjugated ligand systems. That the unpaired electron resides in a molecular orbital which is predominantly $\pi^*(O_2)$ in character is well established.[16,20]

In view of the additional valence electron which these Co–O_2 complexes possess compared to a dioxygen adduct of an iron(II) complex, the applicability of these cobalt models to oxyhemoglobin and oxymyoglobin may be questioned. However, both hemoglobin and cobalt-substituted hemoglobin possess similar cooperativity in their binding of dioxygen.[21,22] A bent bond configuration is also exhibited by cobalt–nitrosyl complexes,[23] which are formally isoelectronic with Fe–O_2 systems. The relationship between Co–NO and Fe–O_2 systems has been discussed.[24] The recent report that the triplet state of oxyhemoglobin is only 146 cm⁻¹ above the ground state[25] is of interest since the triplet state is consistent with an $\mathrm{Fe^{III}}$(S