Structure of the Cobalt(III) and Cobalt(II) Complexes of the Cage Ligand 1,8-Bis(fluoroboro)-2,7,9,14,15,20-hexaoxa-3,6,10,13,16,19-hexaaza-4,5,11,12,17,18-hexamethylbicyclo-[6.6.6]eicosa-3,5,10,12,16,18-hexaene

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Abstract: The crystal structures of the two clathro chelate compounds, $CoLBF_4$ and CoL, of the cage ligand $C_{12}H_{18}N_6O_6B_2F_2^{2-}$ have been determined and refined by full-matrix least squares using Mo Kα X-ray data collected by the θ–2θ scan technique on a four-circle diffractometer, out to $2\theta = 55°$. The final values of R are 0.061 and 0.043, respectively. $CoLBF_4$ crystallizes in space group *Fdd*2 with eight molecules in a cell of dimensions a = 16.582 (1), b = 20.844 (3), c = 12.191 (1) Å; CoL crystallizes in space group $R\bar{3}c$ with six molecules in a cell of hexagonal dimensions a = 11.543 (1), c = 22.849 (5) Å. Bond distances and bond angles within the ligand are the same in the two compounds. Mean Co–N distances are 1.893 (4) Å in CoL^+ and 1.973 (2) Å in CoL. The CoN_6 coordination polyhedron in CoL^+ is slightly distorted from D_3 symmetry (actual symmetry C_2) and is midway between octahedral and trigonal prismatic. The polyhedron in CoL has D_3 symmetry and is only slightly (8.6°) distorted from trigonal prismatic.

Boston and Rose[1] have recently reported the synthesis of the clathro chelate 1,8-bis(fluoroboro)-2,7,9,14,15,20-hexaoxa-3,6,10,13,16,19-hexaaza-4,5,11,-12,17,18-hexamethylbicyclo[6.6.6]eicosa-3,5,10,12,16,18-hexaenecobalt(III) tetrafluoroborate. Reaction of this compound with sodium iodide in acetonitrile solution gives crystals of the neutral cobalt(II) compound.[2] In order to confirm the cage structure of the ligand and to compare its conformation with the two cobalt ions, we have determined the crystal structures of both compounds.

Experimental Section

Crystals of both compounds were provided by Mr. Boston and Professor Rose. Oscillation and Weissenberg photographs showed the dark violet crystals of $CoL(BF_4)$ to be orthorhombic. Systematic absence of hkl for $h + k$, $k + l$, or $h + l = 2n + 1$, of $h0l$ for $h + 1 \neq 4n$, and of $0kl$ for $k + l = 4n$ identified the space group as *Fdd*2. The dark red crystals of CoL were initially thought to be monoclinic, space group $C2/c$, but, after the structure was solved they were recognized to be rhombohedral. Systematic absence of (hexagonal indices) hkl for $-h + k + l \neq 3n$ and of $h\bar{h}l$ for $l \neq 2n$ indicated the space group $R3c$ or $R\bar{3}c$. The latter was initially assumed and later confirmed by the successful refinement of the structure.

Cell dimensions were determined at 25° from least-squares treatment of several *(15 for $CoLBF_4$, 20 for CoL)* 2θ values measured by the $+2\theta$, -2θ technique with Mo $K\alpha$ radiation (λ 0.71069 Å) on a Picker four-angle diffractometer.

The results for $CoLBF_4$ are a = 16.582 (1), b = 20.844 (3), c = 12.191 (1) Å, V = 4213.6 Å^3. Assuming eight molecules per cell, d_{calcd} = 1.725 g cm^{-3} and the density measured by flotation is 1.722 g cm^{-3}. For CoL, a = 11.543 (1), c = 22.849 (5) Å, V = 2636.6 Å^3. Assuming six molecules per cell, d_{calcd} = 1.74 g cm^{-3} and the density measured by flotation is 1.72 g cm^{-3}.

Intensity data were collected with niobium-filtered Mo Kα radiation on a Picker automated four-circle diffractometer equipped with a scintillation counter and a pulse-height discriminator. Diffractometer settings for the θ–2θ scan method were calculated using the formula of Alexander and Smith:[3] scan range = $A + B \tan \theta$, with A = 0.90° and B = 1.0°. Background counts were measured at each end of the scan range for preset times. Data were collected out to $2\theta = 60°$ for $CoLBF_4$ and to $2\theta = 55°$ for CoL. In each case, a set of four standard reflections was remeasured about every 2 hr, and these measurements were used to correct all measured intensities to a common scale. The intensity of each reflection and its standard deviation were calculated by the formulas

$$I = S - \frac{t_s}{2t_B}(B_1 + B_2) - 0.45\left(2\frac{t_s}{2t_B} - 1\right)$$

$$\sigma^2(I) = \frac{1}{10}\left[S + \left(\frac{t_s}{2t_B}\right)^2(B_1 + B_2)\right] + k^2\left[S + \frac{t_s}{2t_B}(B_1 + B_2)\right]^2 + 0.25$$

where S = the truncated dekacounts recorded during scan time t_s, B_i = the truncated dekacounts recorded during background time t_B, and k = the empirical stability constant, set at 0.004 for $CoLBF_4$ and 0.01 for CoL. The terms 0.45 $(2(t_s/2t_B) - 1)$ and 0.25 are corrections for the truncation of counts to dekacounts

Of the 1582 reflections measured for $CoLBF_4$, 264 had intensity less than twice the estimated standard deviation. These were coded as unobserved and assigned intensities equal to $I + 2\sigma$ for special treatment during least-squares refinement. The intensities of 2107 reflections were measured for CoL under the assumption that it was monoclinic. These were later combined and averaged to give 664 independent reflections in the space group $R\bar{3}c$. Lorentz and polarization factors were applied and the structure factor and its standard deviation were calculated for each reflection. For both crystals, maximum and minimum transmission factors differed by less than 10%, and no absorption corrections were made. Examination of both sets of data near the end of the refinement showed no evidence of secondary extinction effects.

All calculations were carried out on an IBM 7040-7094 direct coupled system using the set of programs written or adapted by Stewart.[4] The atomic scattering factors were from Cromer and

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(1) D. Boston and N. J. Rose, *J. Amer. Chem. Soc.*, **90**, 6859 (1968).

(2) D. Boston and N. J. Rose, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. INOR 096.

(3) L. E. Alexander and G. S. Smith, *Acta Crystallogr.*, **17**, 1195 (1964).

(4) J. M. Stewart, Technical Report No. TR-64-6, Crystal Structure Calculation System for IBM 709, 7090, 7094, Computer Science Center, University of Maryland, College Park, Md., 1964.

Table I. $CoLBF_4$ Final Parameters

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Positions Multiplied by 10^4, Thermal Parameters by 10^2									
Co	1/4	1/4	1/4	258 (3)	177 (3)	306 (3)	25 (3)	0	0
N1	1795 (2)	2652 (2)	1313 (4)	264 (19)	132 (14)	410 (22)	−12 (12)	−26 (16)	−23 (14)
N2	2429 (2)	3392 (2)	2834 (3)	277 (15)	175 (11)	356 (22)	52 (13)	35 (17)	−24 (12)
N3	1582 (2)	2404 (2)	3401 (3)	266 (18)	182 (15)	383 (21)	51 (13)	19 (16)	−11 (15)
O1	1060 (2)	2929 (1)	1463 (3)	293 (16)	308 (15)	501 (20)	51 (12)	−69 (14)	−2 (14)
O2	1750 (2)	3731 (1)	2603 (3)	335 (13)	194 (11)	546 (18)	77 (9)	−77 (16)	33 (15)
O3	998 (2)	2861 (2)	3474 (3)	296 (15)	301 (14)	471 (19)	102 (12)	40 (13)	−10 (14)
B1	1039 (3)	3300 (2)	2496 (6)	272 (21)	255 (19)	430 (27)	76 (17)	−42 (26)	−41 (27)
B2	0	0	3653 (8)	525 (51)	569 (51)	389 (48)	−106 (47)	0	0
F1	358 (1)	3668 (1)	2498 (3)	301 (11)	303 (10)	744 (17)	126 (9)	−18 (15)	−30 (16)
F21	364 (2)	452 (2)	3000 (3)	825 (22)	546 (18)	518 (19)	−201 (16)	70 (17)	23 (14)
F22	−556 (2)	288 (2)	316 (3)	849 (26)	935 (28)	748 (25)	−78 (19)	265 (21)	−256 (21)
C11	2084 (2)	2623 (2)	332 (4)	330 (20)	172 (17)	294 (22)	−68 (14)	3 (17)	13 (15)
C12	1636 (3)	2805 (3)	−659 (5)	489 (30)	436 (25)	437 (30)	−70 (23)	−140 (25)	62 (23)
C21	2912 (3)	3610 (2)	3569 (4)	298 (20)	199 (16)	282 (22)	−2 (15)	−14 (18)	3 (15)
C22	2816 (3)	4242 (2)	4126 (5)	484 (27)	266 (20)	566 (32)	44 (19)	−6 (25)	128 (22)
C31	1449 (3)	1847 (2)	3842 (4)	298 (20)	298 (19)	291 (22)	5 (17)	0 (18)	−4 (18)
C32	744 (3)	1707 (2)	4571 (4)	389 (23)	354 (22)	471 (29)	−18 (19)	111 (21)	37 (20)
Positions Multiplied by 10^3, Thermal Parameters by 1									
			x/a		y/b		z/c		B
H11			151		242		−111		6
H12			108		296		−46		6
H13			187		312		−111		6
H21			228		443		393		6
H22			319		456		380		6
H23			287		425		487		6
H31			31		203		441		6
H32			43		134		425		6
H33			81		165		539		6

Waber[5] for the cobalt ions and the boron, carbon, nitrogen, oxygen, and fluorine atoms, and from Stewart, Davidson, and Simpson[6] for the hydrogen atom.

$CoLBF_4$ Structure Determination

Since there are 8 molecules in the unit cell and the general set in the space group *Fdd*2 contains 16 independent positions, the cobalt ion must lie in a special position and can be placed at ($^1/_4$, $^1/_4$, $^1/_4$) without loss of generality. A structure factor calculation was performed with the cobalt ion in this position and resulted in an R value of 0.47. R is defined throughout as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. In the following Fourier syntheses all of the nonhydrogen atoms in the asymmetric unit were found. The R value at this point was 0.36. A difference synthesis with these atoms in their assigned positions showed no peaks higher than 1.4 e/Å^3. Further refinement was performed using full-matrix least squares. The function minimized was $\Sigma w(|F_o - |F_c|)^2$, and w was set equal to 0 for each unobserved reflection for each cycle in which its $F_c < F_o$. In the initial cycles, all other $w = 1$. Isotropic temperature factors were used in the form $\exp(-B \sin^2 \theta/\lambda^2)$ and anisotropic temperature factors in the form $\exp(-{}^1/_4\Sigma\Sigma h_ih_ja_i^*a_j^*B_{ij})$. Four cycles of isotropic refinement reduced R to 0.094, and two cycles of anisotropic refinement then reduced R to 0.048. At this point weights of $1/\sigma^2$ were introduced, where $\sigma_F = (F_o^2 + \sigma_I/Lp)^{1/2} - F_o$. Two cycles of anisotropic refinement resulted in an R value of 0.054 and a weighted R value of 0.047. Weighted R_w is defined as $R_w = [\Sigma w(F_o - F_c)^2/\Sigma wF_o^2]^{1/2}$. At this point the hydrogen atoms were located from a difference synthesis and were used as a fixed-atom contribution with $B = 6.0$; two cycles of anisotropic refinement on the heavy atoms resulted in $R = 0.049$ and $R_w = 0.037$. The average shift/error in the last of these cycles was 0.157, with the maximum being less than 0.8. Finally, three cycles of isotropic least squares were performed using the nonhydrogen atoms as a fixed-atom contribution and refining the hydrogen parameters, leading to $R = 0.048$ and $R_w = 0.033$. The average shift/error in the final hydrogen refinement cycle was equal to 0.423, with the maximum being 1.47. At this point the least-squares program, CRYLSQ, became available, which permitted minimization of the function $\Sigma w(I_o - I_c)^2$ with inclusion of anomalous dispersion corrections. The values used for Co^{3+} were $\Delta f' = 0.38, \Delta f'' = 1.05$. After two cycles of refinement of the nonhydrogen atoms, the hydrogen atoms were located from a new ΔF synthesis. An attempt was made to refine the positions of the hydrogen atoms, but convergence was slow and the refinement was terminated after two cycles. Isotropic thermal parameters of the hydrogen atoms were set to $B = 6.0$ Å^{-2}, and two cycles of refinement of all parameters except those of the hydrogen atoms gave final values of $R = 0.061$ and $R_w = 0.033$. During the final cycle, the mean parameter change was 0.07σ and the maximum was 0.4σ. Refinement of the inverted structure gave $R_w = 0.037$. Applying Hamilton's[7] R factor ratio test, $R = 1.120$ and $R_{154,1428,0.005} = 1.072$. Therefore, the

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[5] D. Cromer and J. Waber, *Acta Crystallogr.*, 18, 104 (1965).

[6] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

[7] W. C. Hamilton, *Acta Crystallogr.*, 18, 502 (1965).

Table II. CoL Final Parameters

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
			Positions Multiplied by 10^4, Thermal Parameters by 10^2						
Co	0	0	1/4	385 (2)	385 (2)	280 (3)	192 (1)	0	0
F	0	0	4413 (1)	688 (9)	688 (9)	295 (9)	344 (5)	0	0
B	0	0	3819 (2)	396 (11)	396 (11)	311 (15)	198 (6)	0	0
O	1193 (1)	1267 (1)	3630 (1)	399 (7)	386 (7)	344 (6)	169 (6)	−57 (5)	−57 (5)
N	1285 (2)	1401 (2)	3032 (1)	313 (7)	290 (7)	348 (7)	155 (6)	−25 (6)	−22 (5)
C1	2382 (2)	2376 (2)	2819 (1)	276 (8)	254 (7)	455 (10)	146 (7)	−34 (7)	−34 (7)
C2	3539 (3)	3350 (3)	3176 (1)	363 (10)	314 (10)	632 (16)	114 (8)	−128 (9)	−83 (10)
			Positions Multiplied by 10^3, Thermal Parameters by 1						
H1	340 (3)	323 (4)	359 (2)	9 (1)					
H2	388 (4)	419 (4)	306 (1)	7 (1)					
H3	430 (4)	315 (3)	312 (1)	8 (1)					

hypothesis that the inverted structure is correct can be rejected at the 0.5% significance level. This conclusion is also indicated by the observation that the bond distances are much more reasonable in the reported structure than in the "refined" inverted structure. Final values of the parameters and their standard deviations are given in Table I.[8]

CoL Structure Determination

Assuming the crystal to belong to $C2/c$ with four molecules per cell, the position of the cobalt ion was found from a three-dimensional Patterson synthesis and all other nonhydrogen atoms were found in a series of Fourier syntheses. After a few cycles of least-squares refinement, the structure was found to conform to the symmetry of the rhombohedral space group, $R\bar{3}c$. Appropriate transformations of the reflections and of the parameters of the trial structure were applied and the refinement was continued.

Hydrogen atom positions were found in a three-dimensional difference Fourier synthesis, and a final set of three cycles of full-matrix least squares refinement was carried out. The function minimized was $w(F_o^2 - F_c^2)^2$, with $w = 1/\sigma^2(F_o^2)$. Anisotropic thermal parameters for the nonhydrogen atoms were of the form $\exp(-{}^1/_4\Sigma_{j=1}{}^3\Sigma_{j=1}{}^3 h_i h_j a_i^* a_j^* B_{ij})$, and isotropic thermal parameters for the hydrogen atoms were of the form $\exp(-B \sin^2 \theta/\lambda^2)$. In the final cycle of refinement, the average parameter shift was 0.055 and the maximum was 0.275. The final values of $R(F^2) = \Sigma(F_o^2 - F_c^2)/\Sigma(F_o^2)$, $R_w(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^4]^{1/2}$, and $R(F) = \Sigma||F_o| - |F_o||/\Sigma|F_o|$ were 0.054, 0.078, and 0.043, respectively.[8] The final values of the parameters and their standard deviations are given in Table II.

Discussion

Both compounds contain the same cage ligand, L^{2-}, formed by condensation of two BF_3 molecules with three dimethylglyoximate ions, with a metal ion at the center. The neutral molecule CoL lies at a site of D_3 symmetry. The cation CoL^+ in the compound $CoLBF_4$ lies at a site of C_2 symmetry, with the twofold axis passing through the cobalt(III) ion and the midpoint of the central bond, C11–C11′, of one of the DMG arms of the cage. Figure 1 shows the cation and a neighboring BF_4^- ion. Bond distances and angles for CoL and the corresponding mean values for CoL^+ are given in Table III. Individual bond lengths and angles for $CoLBF_4$ are given in Table IV. Comparing the bond lengths and angles within the ligand, there seem to be no significant differences between the two independent arms of CoL^+ or between CoL^+ and CoL, except the O–B–O angles.

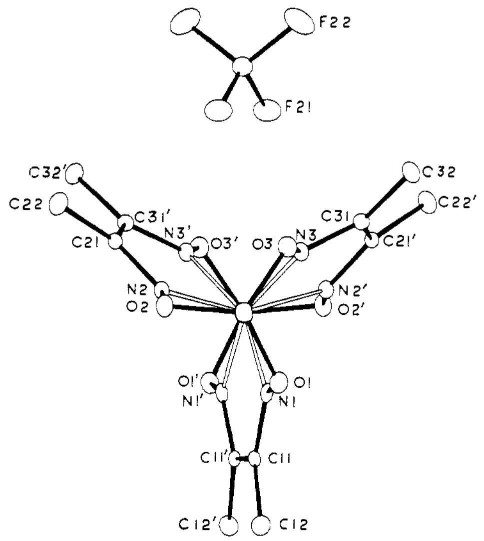

Figure 1. One CoL^+ cation and one neighboring BF_4^- anion in projection down the pseudothreefold axis of the cation. The twofold axis lies in the plane of the projection and passes through the centers of the cation and the anion. Only the fluorine atom, F1, is visible in the center of the cation; the atoms B1, Co, B1′, and F1′ are eclipsed by F1.

To discuss the details of the ligand conformation in the two clathro chelates, it seems reasonable to assume that the "natural" conformation of the "empty" ligand would be the eclipsed D_{3h} (trigonal prismatic) conformation with exactly planar dimethylglyoximate groups.

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(8) Observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche.

Table III. Interatomic Distances (Å) and Angles (Deg) in CoL and Mean Values in CoL^+ [a]

	CoL	CoL^+
Co–N	1.973 (2)	1.893 (4)
F–B	1.357 (5)	1.369 (5)
B–O	1.486 (2)	1.489 (7)
O–N	1.373 (2)	1.361 (5)
N–C1	1.296 (2)	1.291 (6)
C1–C2	1.487 (3)	1.486 (7)
C1–C1′	1.459 (3)	1.467 (6)
N–N′	2.441 (2)	2.426 (6)
N–N″	2.693 (2)	2.613 (6)
N–N‴	3.536 (2)	3.101 (6)
N–N⁗	3.709 (2)	3.714 (6)
N–Co–N′	76.4 (1)	79.8 (2)
N–Co–N″	86.1 (1)	87.3 (2)
N–Co–N‴	127.3 (1)	110.1 (2)
F–B–O	106.9 (2)	108.0 (4)
B–O–N	112.5 (2)	110.6 (3)
O–N–C1	117.2 (2)	118.5 (4)
N–C1–C1′	111.9 (2)	111.7 (4)
N–C1–C2	124.8 (2)	124.0 (4)
C2–C1–C1′	123.3 (2)	124.2 (4)
O–B–O″	111.9 (2)	110.9 (4)
O–N–Co	122.4 (1)	121.6 (3)
C1–N–Co	119.2 (1)	117.9 (3)

[a] N and N′ are in the same arm, related by a twofold axis (N–N′ is the dimethylglyoxime chelate bite distance). N and N″ are related by the threefold axis. N and N‴ are in different arms, related by a twofold axis, and move closer together as the polyhedron twists away from trigonal prismatic. N and N⁗ are in different arms, related by a twofold axis, and move farther apart as the polyhedron twists away from trigonal prismatic.

Table IV. Interatomic Distances (Å) and Angles (Deg) in $CoLBF_4$

Co–N1	1.886 (4)	N1–Co–N2	87.9 (2)
Co–N2	1.906 (3)	N2–Co–N3	86.0 (2)
Co–N3	1.888 (4)	N3–Co–N1	88.0 (2)
F–B	1.369 (5)	N1–Co–N1′	79.8 (2)
B–O1	1.475 (8)	N2–Co–N3′	79.7 (2)
B–O2	1.492 (5)	N1–Co–N2′	111.4 (2)
B–O3	1.500 (7)	N3–Co–N3′	108.8 (2)
O1–N1	1.362 (5)	F–B–O1	108.4 (5)
O2–N2	1.360 (4)	F–B–O2	108.0 (3)
O3–N3	1.362 (5)	F–B–O3	107.6 (4)
N1–C11	1.290 (6)	B–O1–N1	110.9 (4)
N2–C21	1.285 (5)	B–O2–N2	110.9 (3)
N3–C31	1.298 (6)	B–O3–N3	109.9 (3)
C11–C12	1.469 (7)	O1–N1–C11	118.5 (4)
C21–C22	1.491 (6)	O2–N2–C21	118.5 (3)
C31–C32	1.497 (7)	O3–N3–C31	118.5 (4)
C11–C11′	1.471 (6)	N1–C11–C11′	111.4 (4)
C21–C31′	1.463 (6)	N2–C21–C31′	112.3 (4)
N1–N1′	2.420 (6)	N3–C31–C21′	111.4 (4)
N2–N3′	2.432 (5)	N1–C11–C12	124.2 (4)
N1–N2	2.631 (6)	N2–C21–C22	124.3 (4)
N2–N3	2.587 (6)	N3–C31–C32	123.6 (4)
N3–N1	2.621 (6)	C12–C11–C11′	124.4 (4)
N1–N2′	3.133 (6)	C22–C21–C31′	123.3 (4)
N3–N3′	3.069 (6)	C32–C31–C21′	125.0 (4)
N1–N3′	3.705 (6)	O1–B–O2	111.8 (4)
N2–N2′	3.724 (6)	O2–B–O3	109.5 (4)
B2–F21	1.373 (7)	O3–B–O1	111.4 (3)
B2–F22	1.365 (7)	O1–N1–Co	121.5 (3)
		O2–N2–Co	120.9 (2)
		O3–N3–Co	122.5 (3)
		C11–N1–Co	118.3 (3)
		C21–N2–Co	117.1 (3)
		C31–N3–Co	118.3 (3)
		F21–B2–F21′	109.2 (7)
		F22–B2–F22′	107.4 (7)
		F21–B2–F22	109.8 (2)
		F21–B2–F22′	110.3 (2)

Calculations on such a model, assuming F–B–O angles and B–O distances as the mean values from CoL and CoL^+ and other bond lengths and angles as the mean values from published crystal structures of glyoxime and dimethylglyoxime complexes, give a trigonal prism of nitrogen atoms, each at a distance of 1.995 Å from the center. Assuming all bond distances and angles in the model to be those found in CoL^+ gives a center-to-nitrogen distance of 1.988 Å, and assuming the values from CoL gives 1.966 Å. The only experimental value available for a low-spin cobalt(II)–nitrogen bond distance in sixfold coordination is 1.98 (2) Å in $K_2BaCo(NO_2)_6$.[9] Thus, one would predict the ligand cage to be undistorted in CoL. In fact, the Co–N distance is found to be 1.973 (2) Å and the ligand is only slightly distorted from the D_{3h} conformation. The ligand retains D_3 symmetry, and the distortion may be described as a twisting about the threefold axis from the D_{3h} conformation by the following amounts: C1, −0.1°; C2, −2.7°; N, 4.3°; O, 3.0°. This is clearly not a simple twisting with retention of the planarity of the dimethylglyoximate group, since this would require all four atoms to move in the same direction. Calculations on the model show that for a 3.0° twist of the oxygen atom (as observed in CoL) with retention of planarity, the twist angle for the other atoms would be: C1, 0.4°; C2, 0.6°; N, 1.3°. Thus the twisting about the threefold axis has been accompanied by a significant distortion of the dimethylglyoximate group from planarity. The twisting and distortion may be described in several ways. We have selected a description in terms of twisting about the several bonds in the ligand. Thus, starting with the D_{3h} conformation, we can arrive at the observed conformation by twisting about the bonds in the following manner: B–O, +1.6°; O–N, +9.4°; N–C1, −2.1°; C1–C1′, −12.1° (defined in terms of the nitrogen atoms) or −16.2° (defined in terms of the methyl carbon atoms, C2). The signs are appropriate for the molecule with the cobalt atom at 0, 0, $^1/_4$, and are, of course, of opposite sign for the molecule with the cobalt atom at 0, 0, $^3/_4$. Alternatively, the conformation may be described in terms of the distances of the several atoms from the plane defined by the fluorine, boron, and cobalt atoms and the midpoint of the C1–C1′ bond. These distances (Å) are: O, +.074; N, +0.144; C1, −0.006; C2, −0.188. These distortions from the D_{3h} conformation may be due to any one or a combination of the following: (i) crystal packing effects, *i.e.*, specific attractions and/or repulsions between atoms of different molecules; (ii) intramolecular steric effects, *i.e.*, specific attractions and/or repulsions between nonbonded atoms within the molecule; (iii) coordination effects, *i.e.*, an adjustment of the coordination polyhedron to give optimum Co–N distances and CoN_6 symmetry. It does not appear possible at this point to ascertain the relative importance of these several effects.

Two crystal structures have been reported containing oxime nitrogen atoms coordinated to low-spin cobalt(III). The Co–N distance is 1.88 (2) Å in *O*-methylcarboxymethylbis(dimethylglyoximato)pyridinatocobalt-

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(9) J. A. Bertrand and D. A. Carpenter, *Inorg. Chem.*, 5, 514 (1966).

(III)[10] and 1.890 (10) Å in dichlorobis(2-amino-2-methyl-3-butanonoximato)cobalt(III).[11] Therefore, we might expect that the Co–N distance (1.99 Å) in the D_{3h} conformation of CoL$^+$ would be considerably longer than optimum. The Co–N distance may be decreased by twisting the ligand about the threefold axis. Calculations made assuming retention of D_3 symmetry and planarity of the dimethylglyoximate groups show that a twist of 50° of one BO$_3$ group with respect to the other would decrease the Co–N distance to 1.89 Å. This corresponds to a twist of the CoN$_6$ coordination polyhedron of 22° from trigonal prismatic toward trigonal antiprismatic (pseudooctahedral). In fact, the CoL$^+$ cation is found to deviate only slightly from a D_3 conformation, with a twist of 51.5° between the two BO$_3$ groups. However, as in CoL, there is a significant deviation of the dimethylglyoximate groups from planarity. The mean angles of twist about the pseudo-threefold axis (the F–B–Co–B–F axis) are C1, 4.1°; C2, 4.4°; N, 15.6°; and O, 25.8°, while twist angles calculated from the model with retention of planarity are C1, 3.8°; C2, 5.6°; N, 11.8°; and O, 25.8°. The observation that the mean angle of twist of the nitrogen atom, 15.6°, is so much greater than the angle, 11.8°, calculated from the model may be due to the well-known preference of Co^{3+} for octahedral coordination. As in the case of the CoL molecule, we may describe the conformation of the CoL$^+$ cation in terms of the twisting about the several bonds which are required to go from the D_{3h} conformation to the observed conformation. The bond twists (with signs appropriate for the cation with the cobalt atom at $^1/_4$, $^1/_4$, $^1/_4$) are: B1–O1, −12.2°; O1–N1, +37.2°; N1–C11, −6.4°; C11–C11′, −10.7° (defined in terms of the nitrogen atoms) or 9.1° (defined in terms of the methyl carbon atoms, C12) and B1–O3, −11.1°; O3–N3, +30.0°; N3–C31, −7.4°; C31–C21′, −9.5° (defined in terms of the nitrogen atoms) or −10.0 (defined in terms of the methyl carbon atoms, C32 and C22′); C21–N2′, −8.3°; N2′–O2′, +43.3°; O2′–B1′, −12.7°. The loss of the threefold symmetry in CoL$^+$ is most conveniently illustrated by the X$_2$–Co–X$_3$ angles (in projection as viewed down the threefold axis) between pairs of atoms, one from each of the two dimethylglyoximate groups related by the twofold symmetry axis of the cation. These angles are: O2–Co–O3, 118.3°; N2–Co–N3, 117.4°; C21–Co–C31, 112.5°; C22–Co–C32, 108.9°. Thus, the two "arms" of the cage which are related by the twofold axis have been drawn toward another and away from the third arm. We suggest that this has been caused by an attractive interaction between these two arms and the two fluorine atoms, F21 and F21′, from the adjacent BF$_4^-$ ion, as shown in Figure 1. This is indicated by the fact that the distances of each of these fluorine atoms from the closest atoms of one of the arms are O3, 3.12; N3, 2.95; C31, 3.27 Å and from those of the other arm are N3′, 3.41; C31′, 3.13; C21, 3.01; C22, 3.36; N2, 3.41 Å.

The B–F bond distances in the BF$_4^-$ anion are normal, mean value 1.369 (7) Å, and the ion shows a small but significant distortion from regular tetrahedral symmetry.

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Structural Effects on Lithium-7 Relaxation Times of Organometallic Compounds in Solution[1]

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Abstract: The lithium-7 spin–lattice relaxation times in a series of organolithium compounds of known aggregation have been measured in various solvents. These measurements provide lower limits for the ^{7}Li line widths, which range from 0.05 Hz for symmetrical tetrahedral species to 30 Hz for some larger or smaller aggregates at low temperatures. The measurements suggest that the tetramer of (CH$_3$)$_3$SiCH$_2$Li is distorted away from a tetrahedral structure, and that tetrameric CH$_3$Li also loses its high symmetry above 0°. Quadrupolar broadening becomes a dominant factor in low-temperature lithium-7 high-resolution nmr studies of nontetrahedral organolithium species. This broadening is partly responsible for the difficulties encountered in studies of spin–spin coupling and exchange processes in such species.

High-resolution lithium-7 nmr has been of great value in the study of organolithium compounds in solution. Although the quadrupole moment of the ^{7}Li nucleus is large, the "natural" line widths are often sufficiently narrow for the study of inter- and intra-

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