Structural Studies on Clathro-chelate Complexes. Part III.[1,2] Trigonal Prismatic Co-ordination of d^7 Cobalt(II) in Orthorhombic Crystalline $[\{FB(ONCHC_5H_3N)_3P\}Co^{II+}][BF_4^-]$,MeCN and a Single-crystal Transformation of Unsolvated Monoclinic $[\{FB(ONCHC_5H_3N)_3P\}Co^{II+}][BF_4^-]$

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{Fluoro-[6,6′,6″-phosphinidynetris-(pyridine-2-carbaldehyde oximato)(3−)]borato(1−)}cobalt(1+)† tetrafluoroborate–acetonitrile (I) crystallizes in the noncentrosymmetric space group *Aba*2 with a = 23·408(19), b = 17·494(15), c = 12·090(8) Å, and Z = 8. A single-crystal X-ray diffraction study by Patterson and Fourier methods from diffractometer data has led to the location of all non-hydrogen atoms, with R 10·5% for 1126 independent non-zero reflections. The cation has approximate C_{3v} symmetry, with the central Co^{II} atom co-ordinated to six nitrogen atoms, mean Co–N(aldoximo) 2·063(18) and Co–N(pyridyl) 2·118(38) Å. The co-ordination sphere of the cobalt(II) atom defines a slightly tapered trigonal prism, with N(aldoximo) · · · N(aldoximo) 2·738(25)—2·822(29), N(pyridyl) · · · N(pyridyl) 2·917(30)—3·050(29) Å, and the N(aldoximo) · · · N(pyridyl) 'bite' 2·512(30)—2·598(29) Å. The triangle defined by the three aldoximo-nitrogen atoms is rotated by only 0·89° relative to that defined by the three pyridyl nitrogens.

The unsolvated species $[\{FB(ONCHC_5H_3N)_3P\}Co^{II+}][BF_4^-]$ (II) crystallizes in the monoclinic space group $P2_1/c$ with a = 13·262(12), b = 17·967(4), c = 10·656(16) Å, β = 108·87(12)°, and Z = 4. An attempted X-ray crystallographic study of this complex was thwarted by an apparently hydrolytic single-crystal transformation to an unknown species.

HOLM and his co-workers have reported the synthesis and properties of Fe^{II}, Co^{II}, Ni^{II}, and Zn^{II} complexes [d^6, d^7, d^8, d^{10} electronic configuration, respectively] of the bicyclic clathrochelate [or 'encapsulation'] ligand $[FB(O\dot{N}CHC_5H_3\dot{N})_3P^-]$.[3-5] We have shown previously that the d^8 Ni^{II} derivative adopts a conformation such that the metal atom is in essentially trigonal prismatic co-ordination[1] and that the d^6 Fe^{II} derivative differs in that its co-ordination geometry is intermediate between trigonal prismatic and octahedral with a 'twist angle' of 21·7° between the triangle defined by the pyridyl nitrogen atoms and that defined by the aldoximo-nitrogen atoms.

We now report the results of X-ray diffraction studies on $[\{FB(ONCHC_5H_3N)_3P\}Co^{II+}][BF_4^-]$,MeCN, (I) and $[\{FB(ONCHC_5H_3N)_3P\}Co^{II+}][BF_4^-]$, the unsolvated species (II).

Structural information on these Co^{II} species is of considerable interest since the central metal atom is expected[2] to be too large to fit into the encapsulation cavity without causing significant strain elsewhere in the system.

EXPERIMENTAL

Crystal Data.—(*a*) $C_{20}H_{15}B_2CoF_5N_7O_3P$ [*i.e.* the MeCN solvate (I)], M = 607·907, Orthorhombic, a = 23·408(19), b = 17·494(15), c = 12·090(8) Å, U = 4950·8 Å^3, D_m = 1·631(5), Z = 8, D_c = 1·632, $F(000)$ = 2440. Space group *Aba*2 (C_{2v}^{17}, No. 41) or *Abam* (D_{2h}^{18}, No. 64) from systematic absences: hkl, $k + l = 2n + 1$; $0kl$, $k = 2n + 1$; and $h0l$, $h = 2n + 1$; space group *Aba*2 by subsequent successful refinement. Cu-K_α radiation, λ = 1·5418 Å; μ(Cu-K_α) = 69·3 cm^{-1}.

(*b*) $C_{18}H_{12}B_2CoF_5N_6O_3P$ [unsolvated species (II)], M = 566·858, Monoclinic, a = 13·262(12), b = 17·967(4), c = 10·656(16) Å, β = 108·87(12)°, U = 2402·7 Å^3, D_m = 1·65, Z = 4, D_c = 1·56, $F(000)$ = 1132. Space group $P2_1/c$. Mo-K_α radiation, λ = 0·7107 Å; μ(Mo-K_α) = 8·86 cm^{-1}.

Collection and Reduction of Data for Monoclinic (II).—Crystals of (II) were prepared as described in ref. 4. Diffraction data were collected, but a study of Weissenberg photographs of the $0kl$ level taken at the beginning and end of data collection revealed that the crystal, while still a single crystal, was undergoing a transformation, and that the original and final intensities were grossly different [see Appendix].

However, the initial Co^{II} species is isomorphous (and, presumably, isostructural) with the known species $[\{FB(ONCHC_5H_3N)_3P\}Ni^{II+}][BF_4^-]$[1] and $[\{FB(ONCHC_5H_3N)_3P\}Zn^{II+}][BF_4^-]$[6] (see Table 1).

TABLE 1

Unit-cell parameters of some $[\{FB(ONCHC_5H_3N)_3P\}M^{II+}][BF_4^-]$ species

	M		
	Co	Ni[a]	Zn[b]
a/Å	13·262	13·296	13·340
b/Å	17·967	17·857	17·921
c/Å	10·656	10·580	10·662
β/°	108·87	108·68	108·60
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$

[a] See ref. 1. [b] See ref. 6.

Attempts to recrystallize all the existing Co^{II} complex

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† Also known as [fluoroborotris-(2-aldoximo-6-pyridyl)phosphine]cobalt (1+).

[1] Part I, M. R. Churchill and A. H. Reis, *Inorg. Chem.*, 1972, **11**, 1811.

[2] Part II, M. R. Churchill and A. H. Reis, *Inorg. Chem.*, 1972, **11**, 2299.

[3] J. E. Parks, B. E. Wagner, and R. H. Holm, *J. Amer. Chem. Soc.*, 1970, **92**, 3500.

[4] J. E. Parks, B. E. Wagner, and R. H. Holm, *Inorg. Chem.*, 1971, **10**, 2472.

[5] E. Larsen, G. N. LaMar, B. E. Wagner, J. E. Parks, and R. H. Holm, *Inorg. Chem.*, 1972, **11**, 2652.

[6] A. H. Reis, Ph.D. Thesis, Department of Chemistry, Harvard University, 1972; M. R. Churchill and A. H. Reis, *Inorg. Chem.*, in press.

from spectral-grade acetonitrile under anhydrous conditions produced only crystals of $[\{FB(ONCHC_5H_3N)_3P\}Co^{II+}][BF_4^-],MeCN$. We therefore attempted an *X*-ray structural analysis of this new crystalline species.

Collection and Reduction of Diffraction Data for the Solvated Crystals, (I).—Diffraction data for levels 0—$9kl$ and $h0$—$13l$ were collected to $\sin\theta$ 0·80 with a Supper–Pace diffractometer, as described in ref. 7. Data were corrected for Lorentz, polarization, and absorption [8] effects and placed on a common scale *via* a least-squares procedure.[9] R for scaling was 8·8%, based on F^2. The resulting 1126 reflections for which $I(hkl) > 3{\cdot}0[\sigma\{I(hkl)\}]$ were used in a Wilson plot,[10] from which were determined the approximate absolute scale factor and the overall isotropic thermal parameter ($\bar{B} = 1{\cdot}77$ Å^2).

All calculations were performed by use of CRYSIS (a locally modified version of Marsh's CRYM system of crystallographic subroutines) on the MIT/Harvard IBM 370 computer. Scattering curves for neutral hydrogen, boron, carbon, nitrogen, oxygen, and fluorine were used; [11] the Hartree–Fock–Slater values for cobalt and phosphorus were corrected for dispersion ($\Delta f'$ and $\Delta f''$).[11,12]

The function minimized in the least-squares process was $\Sigma w(|F_o|^2 - |F_c|^2)^2$.

Solution and Refinement of the Structure.—The positions of the cobalt and phosphorus atoms were determined from a three-dimensional Patterson map. Their different z coordinates indicated that the true space group was the non-centro-symmetric *Aba*2. A series of three-dimensional Fourier syntheses revealed all non-hydrogen atom positions; refinement of positional and isotropic thermal parameters converged at R 13·5%. Refinement was continued with anisotropic thermal parameters for the heavier atoms (*i.e.* Co, P, F, and O) and isotropic thermal parameters for the lighter atoms (N, C, and B) [this being the only acceptable compromise between isotropic refinement (for which the ratio of observations to parameters is 7·27 : 1) and full anisotropic refinement (for which this ratio is an unacceptably low 3·21 : 1); the compromise leads to the 1126 observations being used to refine 236 parameters (ratio 4·77 : 1).]. Nine cycles of refinement led to convergence at R 10·9%. Finally, all twelve hydrogen atoms of the cation were included in calculated positions (assuming C–H 1·00 Å and the appropriate trigonal geometry) but were not refined. Two final cycles of refinement led to convergence at R 10·5%, at which stage $(\Delta/\sigma)_{\max.} < 0{\cdot}1$ and the structural analysis was adjudged to be complete. A final difference-Fourier synthesis showed no unaccountable regions of electron density.

Final observed and calculated structure factor amplitudes are listed in Supplementary Publication No. SUP 20723 (3 pp., 1 microfiche).*

Atomic positional and thermal parameters, with their estimated standard deviations are listed in Table 2.

TABLE 2

(*a*) Final positional parameters [a]

Atom	*x*	*y*	*z*	*B*/Å^2
Atoms within the clathro-chelate cation				
Co	0·33965(16)	0·48287(21)	0	
P	0·41783(28)	0·57365(43)	0·20061(74)	
N(1)	0·2530(7)	0·4927(9)	−0·0366(13)	0·93(32)
N(1′)	0·3495(12)	0·4840(11)	−0·1682(17)	2·24(38)
N(1″)	0·3226(8)	0·3678(11)	−0·1480(19)	3·11(46)
N(2)	0·3062(10)	0·5645(14)	0·1111(22)	3·94(53)
N(2′)	0·4154(7)	0·5512(10)	−0·0253(14)	1·54(37)
N(2″)	0·3806(9)	0·4317(11)	0·1337(18)	2·52(41)
C(1)	0·2221(10)	0·5365(14)	0·0148(28)	3·84(58)
C(2)	0·2509(8)	0·5814(10)	0·1032(17)	0·38(34)
C(3)	0·2279(13)	0·6318(18)	0·1761(29)	4·74(71)
C(4)	0·2553(14)	0·6683(15)	0·2586(30)	4·71(59)
C(5)	0·3145(14)	0·6503(20)	0·2525(30)	5·46(79)
C(6)	0·3435(9)	0·6009(13)	0·1865(21)	2·04(45)
C(1′)	0·3914(11)	0·5167(16)	−0·2116(22)	3·20(55)
C(2′)	0·4295(11)	0·5546(15)	−0·1308(23)	2·96(56)
C(3′)	0·4704(12)	0·5998(17)	−0·1565(28)	4·37(68)
C(4′)	0·5039(15)	0·6471(19)	−0·0804(31)	5·29(72)
C(5′)	0·4873(8)	0·6371(13)	0·0353(19)	1·94(47)
C(6′)	0·4383(10)	0·5822(14)	0·0558(21)	2·88(56)
C(1″)	0·3425(11)	0·3224(14)	0·0472(22)	3·25(54)
C(2″)	0·3762(10)	0·3520(13)	0·1352(20)	1·80(45)
C(3″)	0·4001(12)	0·3152(16)	0·2267(27)	4·21(65)
C(4″)	0·4288(11)	0·3575(15)	0·3031(23)	2·96(54)
C(5″)	0·4359(11)	0·4329(16)	0·2967(23)	3·02(55)
C(6″)	0·4126(11)	0·4639(13)	0·2104(25)	3·08(52)
O(1)	0·2269(8)	0·4557(11)	−0·1270(17)	
O(1′)	0·3164(8)	0·4416(13)	−0·2439(17)	
O(1″)	0·2911(8)	0·3385(11)	−0·1038(17)	
B(1)	0·2673(13)	0·3946(19)	−0·1842(31)	3·11(71)
F(1)	0·2417(7)	0·3613(8)	−0·2648(13)	
Atoms within the BF_4^- anion				
B(2)	0·4374(14)	0·1417(18)	0·0185(34)	3·93(68)
F(2)	0·4056(9)	0·1475(14)	0·1107(18)	
F(3)	0·4940(9)	0·1378(15)	0·0462(20)	
F(4)	0·4256(12)	0·0640(14)	−0·0141(22)	
F(5)	0·4284(9)	0·1936(12)	−0·0572(21)	
Atoms within the acetonitrile molecule				
Me(1)	0·3478(18)	0·8214(24)	0·0574(34)	7·39(108)
C(7)	0·3483(15)	0·7588(16)	−0·0057(32)	4·53(66)
N(3)	0·3438(12)	0·7060(16)	−0·0541(23)	5·30(61)
Calculated hydrogen atom positions [b]				
H(1)	0·1804	0·5418	−0·0014	
H(3)	0·1862	0·6424	0·1691	
H(4)	0·2376	0·7030	0·3139	
H(5)	0·3391	0·6782	0·3064	
H(1′)	0·3984	0·5174	−0·2932	
H(3′)	0·4810	0·6029	−0·2346	
H(4′)	0·5347	0·6828	−0·1049	
H(5′)	0·5068	0·6648	0·0967	
H(1″)	0·3356	0·2662	0·0379	
H(3″)	0·3966	0·2585	0·2356	
H(4″)	0·4454	0·3303	0·3685	
H(5″)	0·4575	0·4630	0·3537	

(*b*) Anisotropic thermal parameters ($\times 10^4$) [a,c]

Atom	β_{11}	β_{22}	β_{33}
Co	10·2(7)	20·9(13)	65·9(33)
P	12·1(13)	35·6(30)	55·2(58)
O(1)	16(4)	38(8)	76(18)
O(1′)	17(3)	46(8)	62(16)
O(1″)	15(4)	34(7)	55(15)
F(1)	23(3)	29(6)	69(15)
F(2)	35(5)	84(10)	98(19)
F(3)	28(4)	104(13)	163(28)
F(4)	61(7)	58(9)	148(24)
F(5)	39(5)	51(9)	151(23)

* See note concerning Supplementary Publications in Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue (items less than 10 pp. will be supplied as full-sized copies).

[7] M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 1968, **7**, 1123.

[8] C. W. Burnham, *Amer. Mineral.*, 1966, **51**, 159.

[9] A. D. Rae, *Acta Cryst.*, 1965, **19**, 683.

[10] A. J. C. Wilson, *Nature*, 1942, **150**, 152.

[11] 'International Tables for *X*-Ray Crystallography,' vol. 3, Kynoch Press, Birmingham, 1962, pp. 202—203, 214.

[12] H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Cryst.*, 1964, **17**, 1040.

TABLE 2 (*Continued*)

Atom	β_{12}	β_{13}	β_{23}
Co	1·7(20)	−3·7(35)	−9·2(54)
P	−7·7(35)	−21·4(58)	−20·4(80)
O(1)	2(9)	−26(15)	−18(18)
O(1′)	−7(10)	−4(14)	28(21)
O(1″)	−6(8)	−8(15)	−27(19)
F(1)	−13(8)	−35(12)	4(18)
F(2)	27(13)	24(18)	18(28)
F(3)	13(13)	12(13)	60(35)
F(4)	−5(16)	56(26)	19(29)
F(5)	3(12)	−37(22)	20(24)

(*c*) Principal axes of atomic vibration ellipsoids [d]

Atom	$B_{\mathrm{min.}}/\mathrm{\AA}^2$ (*dc* Minor axis)	$B_{\mathrm{med.}}/\mathrm{\AA}^2$ (*dc* Median axis)	$B_{\mathrm{max.}}/\mathrm{\AA}^2$ (*dc* Major axis)
Co	2·17 (0·953, −0·299, 0·050)	2·47 (0·271, 0·915, 0·300)	3·99 (−0·136, −0·272, 0·952)
P	1·34 (−0·721, −0·326, −0·611)	4·07 (0·693, −0·358, −0·626)	4·82 (−0·015, −0·874, 0·484)
O(1)	2·44 (−0·770, −0·145, −0·621)	4·31 (0·405, −0·863, −0·300)	6·00 (−0·493, −0·482, 0·723)
O(1′)	3·10 (0·687, 0·426, −0·902)	3·68 (−0·967, −0·192, −0·164)	6·43 (0·243, −0·884, −0·398)
O(1″)	2·08 (−0·464, −0·515, −0·721)	3·77 (0·874, −0·133, −0·468)	5·03 (0·145, −0·847, 0·512)
F(1)	2·31 (−0·621, −0·423, −0·661)	3·55 (0·050, −0·862, 0·504)	7·02 (0·783, −0·280, −0·556)
F(2)	5·03 (−0·501, 0·082, 0·861)	6·92 (0·691, −0·056, 0·455)	11·94 (−0·520, −0·820, −0·224)
F(3)	5·96 (0·986, −0·118, −0·115)	8·17 (−0·043, 0·491, −0·870)	14·41 (−0·160, −0·863, −0·479)
F(4)	6·17 (−0·323, −0·699, 0·638)	8·04 (−0·304, 0·715, 0·629)	15·08 (−0·896, 0·010, −0·443)
F(5)	5·61 (−0·379, 0·803, −0·460)	7·27 (−0·632, 0·588, −0·505)	10·94 (0·676, −0·099, −0·730)

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit in the preceding number.
[b] Hydrogen atoms are numbered similarly to their attached carbon atoms.
[c] In the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.
[d] Direction cosines (dc) of the principal axes of the ellipsoids are referred to the natural orthorhombic crystal axes. The length of an axis is defined in terms of B, the normal isotropic thermal parameter. The transformation to root-mean-square displacement is $(\overline{U^2})^{\frac{1}{2}} = [B/8\pi^2]^{\frac{1}{2}}$.

RESULTS AND DISCUSSION

Description of the Structure.—The crystal consists of discrete [{FB(ONCHC$_5$H$_3$N)$_3$P}Co$^{\mathrm{II}+}$] cations, BF$_4^-$ anions, and MeCN molecules which are mutually separated by normal van der Waals' distances. The packing of these species in the unit cell is shown in Figure 1.

Individual intramolecular distances are in Table 3, and bond angles in Table 4, both with estimated standard deviations. Figure 2 shows the cation projected on (010) and illustrates the scheme used in numbering non-hydrogen atoms. The three aldoximo-pyridyl arms of the clathro-chelate ligand are designated as non-, singly- and doubly-primed. Hydrogen atoms, which have been omitted from this diagram for the sake of clarity, are numbered similarly to their attached carbon atoms.

The d^7 Co$^{\mathrm{II}}$ ion is totally encapsulated by the [FB(O$\dot{\mathrm{N}}$CHC$_5$H$_3\ddot{\mathrm{N}}$)$_3$P$^-$] ligand, resulting in an approximate C_3 axis defined by P · · · Co · · · B(1)–F(1). The phosphorus and boron atoms act as ' caps ' in the formation of this clathro-chelate complex. The cation possesses approximate, but not exact (*vide infra*) C_{3v} symmetry.

TABLE 3

Interatomic distances (Å)

(*a*) Distances from cobalt atom

Co–N(1)	2·083(17)	Co–N(2)	2·111(25)
Co–N(1′)	2·047(20)	Co–N(2′)	2·160(17)
Co–N(1″)	2·059(20)	Co–N(2″)	2·082(21)

(*b*) Distances within non-primed aldoximo-pyridyl ligand

B(1)–O(1)	1·588(38)	C(4)–C(5)	1·422(47)
O(1)–N(1)	1·409(25)	C(5)–C(6)	1·359(42)
N(1)–C(1)	1·224(32)	C(6)–N(2)	1·414(34)
C(1)–C(2)	1·488(36)	C(6)–P	1·811(23)
C(2)–C(3)	1·357(38)	N(2)–C(2)	1·332(29)
C(3)–C(4)	1·347(47)		

(*c*) Distances within singly-primed ligand

B(1)–O(1′)	1·586(38)	C(4′)–C(5′)	1·462(43)
O(1′)–N(1′)	1·409(31)	C(5′)–C(6′)	1·516(32)
N(1′)–C(1′)	1·251(36)	C(6′)–N(2′)	1·242(30)
C(1′)–C(2′)	1·480(38)	C(6′)–P	1·823(26)
C(2′)–C(3′)	1·281(39)	N(2′)–C(2′)	1·319(32)
C(3′)–C(4′)	1·465(48)		

(*d*) Distances within doubly-primed ligand

B(1)–O(1″)	1·489(39)	C(4″)–C(5″)	1·332(38)
O(1″)–N(1″)	1·402(29)	C(5″)–C(6″)	1·296(39)
N(1″)–C(1″)	1·188(33)	C(6″)–N(2″)	1·319(34)
C(1″)–C(2″)	1·422(35)	C(6″)–P	1·928(25)
C(2″)–C(3″)	1·396(39)	N(2″)–C(2″)	1·399(30)
C(3″)–C(4″)	1·362(41)		

(*e*) Boron–fluorine distance within cation

B(1)–F(1)	1·284(38)

(*f*) Boron–fluorine distances within anion

B(2)–F(2)	1·343(44)	B(2)–F(4)	1·442(41)
B(2)–F(3)	1·368(40)	B(2)–F(5)	1·306(44)

(*g*) Distances within the acetonitrile

Me(1)–C(7)	1·376(52)	C(7)–N(3)	1·098(42)

(*h*) Non-bonded contacts within cobalt co-ordination environment

N(1) · · · N(1′)	2·766(30)	N(1) · · · N(2)	3·513(29)
N(1′) · · · N(1″)	2·822(29)	N(1′) · · · N(2′)	2·598(29)
N(1″) · · · N(1)	2·738(25)	N(1″) · · · N(2″)	2·512(30)
N(2) · · · N(2′)	3·050(29)	Co · · · P	3·428(8)
N(2′) · · · N(2″)	2·955(27)	Co · · · B(1)	3·196(34)
N(2″) · · · N(2)	2·917(30)		

(*i*) Interionic contacts

F(2) · · · H(1″)	2·787	F(4) · · · H(1″)	2·767
F(2) · · · H(3″)	2·469	F(4) · · · H(3″)	3·792
F(3) · · · H(3″)	3·850	Me(1) · · · H(4)	3·952

The Co$^{\mathrm{II}}$ Co-ordination Sphere.—The co-ordination sphere of the central d^7 Co$^{\mathrm{II}}$ atom consists of six nitrogen atoms, each of which donates two electrons, yielding an outer electronic configuration of nineteen electrons. The observed magnetic moment of 4·91 B.M.,[4] consistent with three unpaired electrons, is indicative of a high-spin situation. The six nitrogen atoms define a slightly tapered trigonal prism with little distortion towards an octahedral geometry. As shown in Figure 3 and Table 5, the twist angles N(1)–⟨N(1)⟩–⟨N(2)⟩–N(2), N(1′)–⟨N(1)⟩–⟨N(2)⟩–N(2′), and N(1″)–⟨N(1)⟩–⟨N(2)⟩–N(2″) are 0·44, 3·24, and –0·96°. [Here, ⟨N(1)⟩ is the centre of the N(1)–N(1′)–N(1″) triangular face and ⟨N(2)⟩ is the centre of the N(2)–N(2′)–N(2″) face.] The mean twist angle is 0·89° [*cf.*, mean twist angle in the analogous d^8 Ni^{II} species [1] is *ca.* 1·6°, and in the d^6 Fe^{II} complex [2] *ca.* 21·7°]. It should be emphasized that one of the twist angles in the present Co^{II} complex is in the opposite sense to the other two.

TABLE 4

Individual interatomic angles (deg.)

(*a*) Angles about cobalt atom

N(1)–Co–N(2)	73·6(0·8)	N(2″)–Co–N(2)	88·2(0·9)
N(1)–Co–N(2′)	76·2(0·8)	N(1)–Co–N(2″)	130·5(0·7)
N(1″)–Co–N(2″)	74·7(0·8)	N(1)–Co–N(2′)	136·3(0·6)
N(1)–Co–N(1′)	84·1(0·9)	N(1′)–Co–N(2″)	136·3(0·9)
N(1′)–Co–N(1″)	86·8(0·8)	N(1′)–Co–N(2)	131·9(0·9)
N(1″)–Co–N(1)	82·8(0·7)	N(1″)–Co–N(2)	130·1(0·9)
N(2)–Co–N(2′)	91·1(0·8)	N(1″)–Co–N(2′)	133·4(0·7)
N(2′)–Co–N(2″)	88·3(0·7)		

(*b*) Angles about the boron atom of the cation

O(1)–B(1)–F(1)	110·9(2·2)	O(1)–B(1)–O(1′)	106·3(2·2)
O(1′)–B(1)–F(1)	103·2(2·5)	O(1′)–B(1)–O(1″)	111·6(2·1)
O(1″)–B(1)–F(1)	111·8(2·5)	O(1″)–B(1)–O(1)	112·5(2·5)

(*c*) Angles about the phosphorus atom

C(6)–P–C(6′)	98·1(1·2)	C(6″)–P–C(6)	101·9(1·1)
C(6′)–P–C(6″)	99·1(1·2)		

(*d*) Angles within the non-primed aldoximo-pyridyl ligand

B(1)–O(1)–N(1)	112·8(1·8)	C(3)–C(4)–C(5)	108·6(2·9)
O(1)–N(1)–C(1)	115·0(1·0)	C(4)–C(5)–C(6)	131·2(3·1)
N(1)–C(1)–C(2)	115·3(2·1)	C(5)–C(6)–N(2)	110·8(2·3)
C(1)–C(2)–N(2)	112·0(1·9)	C(6)–N(2)–C(2)	123·2(2·2)
C(1)–C(2)–C(3)	129·1(2·1)	N(2)–C(6)–P	122·4(1·7)
N(2)–C(2)–C(3)	118·8(2·2)	C(5)–C(6)–P	126·4(2·1)
C(2)–C(3)–C(4)	126·9(2·8)		

(*e*) Angles within the singly-primed ligand

B(1)–O(1′)–N(1′)	112·1(2·0)	C(3′)–C(4′)–C(5′)	113·0(2·7)
O(1′)–N(1′)–C(1′)	113·6(2·1)	C(4′)–C(5′)–C(6′)	115·7(2·2)
N(1′)–C(1′)–C(2′)	113·6(2·4)	C(5′)–C(6′)–N(2′)	118·3(2·1)
C(1′)–C(2′)–N(2′)	117·9(2·2)	C(6′)–N(2′)–C(2′)	129·4(2·1)
C(1′)–C(2′)–C(3′)	124·6(2·7)	N(2′)–C(6′)–P	127·5(1·8)
N(2′)–C(2′)–C(3′)	116·7(2·6)	C(5′)–C(6′)–P	114·1(1·7)
C(2′)–C(3′)–C(4′)	126·6(3·2)		

(*f*) Angles within the doubly-primed ligand

B(1)–O(1″)–N(1″)	117·2(2·0)	C(3″)–C(4″)–C(5″)	124·1(2·6)
O(1″)–N(1″)–C(1″)	116·4(2·1)	C(4″)–C(5″)–C(6″)	114·1(2·5)
N(1″)–C(1″)–C(2″)	116·5(2·3)	C(5″)–C(6″)–N(2″)	128·8(2·4)
C(1″)–C(2″)–N(2″)	113·2(2·1)	C(6″)–N(2″)–C(2″)	117·2(2·1)
C(1″)–C(2″)–C(3″)	130·3(2·2)	N(2″)–C(6″)–P	114·7(1·9)
N(2″)–C(2″)–C(3″)	116·2(2·2)	C(5″)–C(6″)–P	116·0(2·1)
C(2″)–C(3″)–C(4″)	119·0(2·5)		

(*g*) Angles in the BF_4^- anion

F(2)–B(2)–F(3)	109·7(21)	F(3)–B(2)–F(4)	101·9(25)
F(2)–B(2)–F(4)	101·1(26)	F(3)–B(2)–F(5)	111·2(28)
F(2)–B(2)–F(5)	116·0(28)	F(4)–B(2)–F(5)	115·6(31)

(*h*) Angles within the acetonitrile

Me(1)–C(7)–N(3)	173·8(3·9)

The mean Co–N(aldoximo) and Co–N(pyridyl) bond

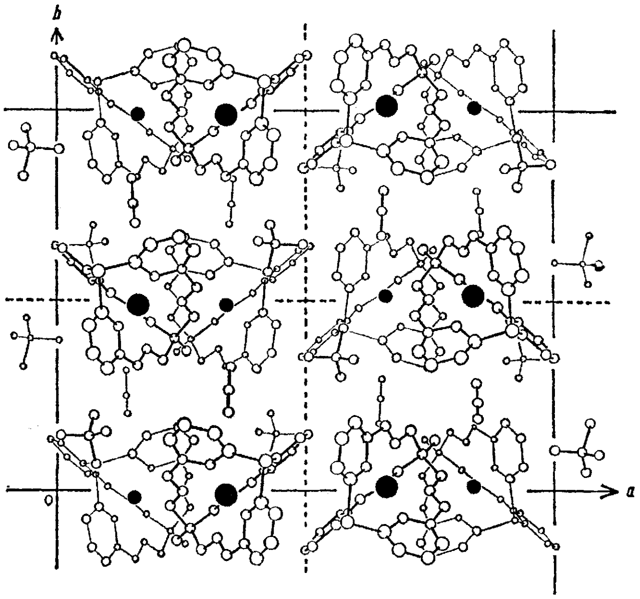

FIGURE 1 Packing of ions and solvent molecules, viewed down *c*

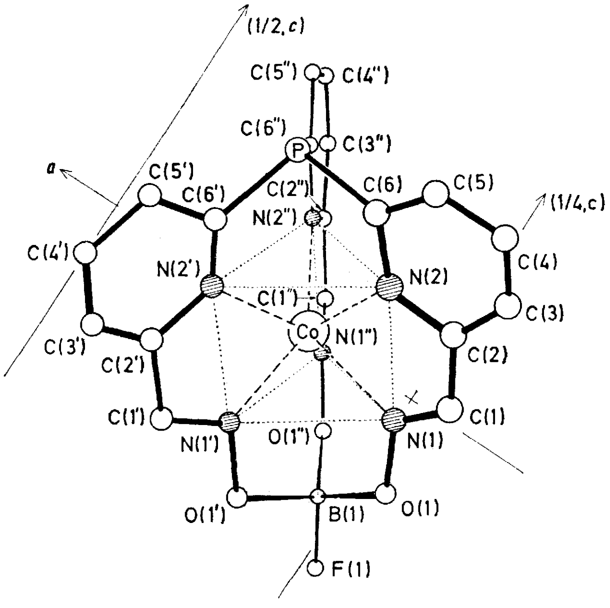

FIGURE 2 The cation viewed down *b*

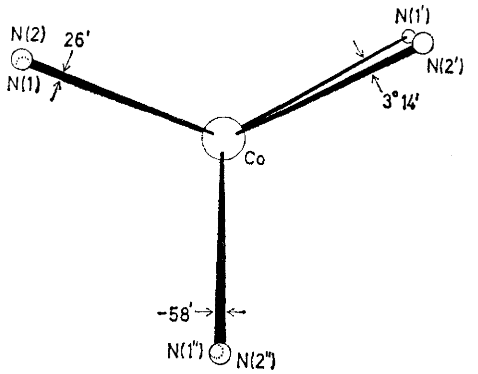

FIGURE 3 The CoN_6 core, showing ' twist angles '

lengths are 2·063(18) * and 2·118(38) Å. Mean distances within the N(1) · · · N(1′) · · · N(1″) triangle are 2·775(43), and in the N(2) · · · N(2′) · · · N(2″) system 2·974(68) Å. The ' bites ' of the aldoximo-pyridyl chelate systems average 2·541(49) Å.

The cobalt–phosphorus and –boron distances of 3·428(8) and 3·196(34) Å, are outside normal bonding range.

Angles subtended at the cobalt(II) atom by pairs of adjacent nitrogen atoms define three sets: those of the type N(1)–Co–N(1′) average 84·6(2·0)°, those of the type N(2)–Co–N(2′) average 89·2(1·6)°, and the aldoximo-pyridyl chelate ' bite ' angles average 74·8(1·3)°. The ' non-*cis* ' or ' pseudo-*trans* ' angles of the type N(1)–Co–N(2″) range from 130·1(0·9)—136·3(0·9)°.

Table 5

Dihedral angles within the molecule (deg.)

O(1)–B(1) · · · P–C(6)	1·7
O(1′)–B(1) · · · P–C(6′)	1·9
O(1″)–B(1) · · · P–C(6″)	0·2
B(1)–O(1)–N(1)–C(1)	175·1
B(1)–O(1′)–N(1′)–C(1′)	174·4
B(1)–O(1″)–N(1″)–C(1″)	178·2
O(1)–N(1)–C(1)–C(2)	174·2
O(1′)–N(1′)–C(1′)–C(2′)	174·1
O(1″)–N(1″)–C(1″)–C(2″)	177·8
N(1)–C(1)–C(2)–N(2)	0·8
N(1′)–C(1′)–C(2′)–N(2′)	1·0
N(1″)–C(1″)–C(2″)–N(2″)	0·3
N(1)–⟨N(1)⟩–⟨N(2)⟩–N(2)	0·44 [a]
N(1′)–⟨N(1)⟩–⟨N(2)⟩–N(2′)	3·24 [a]
N(1″)–⟨N(1)⟩–⟨N(2)⟩–N(2″)	−0·96 [a]

[a] ⟨N(1)⟩ and ⟨N(2)⟩ are defined as the centres of the triangles N(1), N(1′), N(1″) and N(2), N(2′), N(2″).

Geometry of the Clathro-chelate Ligand.—The least-squares planes passing through the individual pyridyl rings and the three separate aldoximo-pyridyl systems are defined in Table 6.

The root-mean-square deviations of the constituent atoms from the planes of their pyridyl rings are 0·026, 0·017, and 0·028 Å. Although the deviations are small, they do seem to show a systematic pattern, with the nitrogen atom and the *para*-carbon atom being displaced to one side of the least-squares plane, while the remaining atoms are displaced to the other side. (The single exception is atom C(3″) in plane (*C*), which is displaced by an insignificant 0·003 Å in the ' wrong ' direction).

Thus, for plane (*A*), N(2) and C(4) are displaced by −0·033 and −0·034 Å from the least-squares plane, while C(2), C(3), C(5), and C(6) are displaced by 0·019, 0·015, 0·023, and 0·010 Å, respectively.

A rather more well-defined distortion of a pyridyl ring from a planar, towards a ' boat ', conformation has been documented in our previous structural investigation of $[\{\mathrm{FB(ONCHC_5H_3N)_3P}\}\mathrm{Fe^{II}}^{+}][\mathrm{BF_4}^{-}],\mathrm{CH_2Cl_2}$.[2]

As might be expected, the aldoximo-pyridyl systems also show slight deviations from planarity [see planes (*D*), (*E*), (*F*) of Table 6]. In calculating these planes the C–N–O atoms of the aldoximo-functions (which are the most flexible portions of the ligands) have been given zero weight. The root-mean-square deviations of the constituent atoms from these three P–($\mathrm{C_5H_3N}$) · · · B–F planes are 0·043, 0·056, and 0·037 Å.

Table 6

Equations of least-squares planes, within the cation, in the form $lx + mY + nZ = p$, where X, Y, and Z are Cartesian co-ordinates related to the cell co-ordinates by $X = xa$, $Y = yb$, $Z = zc$. Deviation (Å) of atoms from the planes are listed in square brackets

Plane (*A*): C(2)—(6), N(2)

$$0{\cdot}177X + 0{\cdot}746Y - 0{\cdot}642Z = 7{\cdot}807$$

[C(2) 0·019, C(3) 0·015, C(4) −0·034, C(5) 0·023, C(6) 0·010, N(2) −0·033]

Plane (*B*): C(2′)—(6′), N(2′)

$$-0{\cdot}649X + 0{\cdot}754Y - 0{\cdot}102Z = 0{\cdot}972$$

[C(2′) −0·014, C(3′) −0·007, C(4′) 0·015, C(5′) −0·007, C(6′) −0·014, N(2′) 0·026]

Plane (*C*): C(2″)—(6″), N(2″)

$$0{\cdot}841X - 0{\cdot}122Y - 0{\cdot}527Z = 5{\cdot}762$$

[C(2″) 0·031, C(3″) −0·003, C(4″) −0·015, C(5″) 0·003, C(6″) 0·028, N(2″) −0·044]

Plane (*D*): P, C(2)—(6), N(2), B(1), F(1)

$$0{\cdot}204X + 0{\cdot}734Y - 0{\cdot}648Z = 7{\cdot}833$$

[P −0·045, C(2) 0·022, C(3) −0·012, C(4) −0·058, C(5) 0·040, C(6) 0·061, N(2) 0·007, C(1) −0·001, N(1) −0·012, O(1) 0·096, B(1) −0·049, F(1) 0·033]

Plane (*E*): P, C(2′)—(6′), N(2′), B(1), F(1)

$$-0{\cdot}605X + 0{\cdot}792Y - 0{\cdot}083Z = 1{\cdot}828$$

[P −0·001, C(2′) −0·097, C(3′) −0·024, C(4′) 0·080, C(5′) 0·062, C(6′) −0·027, N(2′) −0·049, C(1′) −0·002, N(1′) 0·095, O(1′) 0·053, B(1) 0·036, F(1) 0·020]

Plane (*F*): P, C(2″)—(6″), N(2″), B(1), F(1)

$$0{\cdot}832X - 0{\cdot}113Y - 0{\cdot}543Z = 5{\cdot}694$$

[P −0·007, C(2″) 0·051, C(3″) −0·010, C(4″) −0·037, C(5″) −0·006, C(6″) 0·044, N(2″) −0·012, C(1″) 0·031, N(1″) −0·041, O(1″) −0·013, B(1) −0·060, F(1) 0·036]

The principal distortions of the ligand from C_{3v} symmetry, may be identified from Table 5. Thus the dihedral angles O(1)–B(1) · · · P–C(6), O(1′)–B(1) · · · P–C(6′), and O(1″)–B(1) · · · P–C(6″) are 1·70, 1·87, and 0·20°; these should be zero for a ligand of true C_{3v} symmetry. Twists about bonds of the type N(1)–C(1) average 4·64°, and about O(1)–N(1) 4·09°. There is little torsion in C(1)–C(2) bonds.

Mean bond lengths within the aldoxime frameworks are O–N 1·407(4), N–C 1·221(30), and C(aldoximo)–C(pyridyl) 1·463(41) Å. The N–C distances are shorter than in the other clathro-chelate complexes, *cf.* mean values of 1·291(11) for the $\mathrm{Fe^{II}}$ species [2] and 1·303(44) Å for the $\mathrm{Ni^{II}}$ complex.[1]

Interionic Contacts.—Both the tetrafluoroborate anion [mean B–F 1·365(56) Å] and the acetonitrile molecule

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* Estimated standard deviations for mean distances or angles are calculated by use of the ' scatter ' equation: $\sigma = \left[\sum_{i=l}^{i=N} (\chi_i - \bar{\chi})^2/(N - 1)\right]^{\frac{1}{2}}$, where χ_i is the ith value and $\bar{\chi}$ is the mean of N equivalent values.

[Me(1)–C(7) 1·376(52), C(7)–N(3) 1·098(42) Å] have the expected geometry. Interionic contacts are listed in section (*i*) of Table 3. The shortest is F(2) · · · H(3″) 2·469 Å.

Conclusions.—The principal effects which may influence when a metal atom will attain a trigonal prismatic, rather than octahedral, co-ordination environment in a clathro-chelate complex are the following: (i) relative sizes of the metal atom and the cavity within the clathro-chelate ligand,[5,13,14] and (ii) ligand-field stabilization energy (LFSE).[15]

The accepted ionic radii for Fe^{2+}, Co^{2+}, and Ni^{2+} (0·61, 0·74, and 0·70 Å) are, indeed, closely paralleled by the M–N(aldoximo) and M–N(pyridyl) distances in the $[\{FB(ONCHC_5H_3N)_3P\}M^{II+}]$ (M = Fe, Co, Ni) cations (see Table 7). Thus, the overall geometry of the clathro-chelate ligand does change in such a way as to allow ' normal ' metal–nitrogen distances.

TABLE 7

Data for $[\{FB(ONCHC_5H_3N)_3P\}M^{II+}]$ ions

M	Fe [a]	Co	Ni [b]
$r(M^{2+})$	0·61	0·74	0·70
M–N(aldoximo)	1·931(11)	2·063(18)	2·030(21)
M–N(pyridyl)	1·978(06)	2·118(38)	2·043(20)
M · · · P	3·445(03)	3·428(08)	3·452(03)
M · · · B(1)	3·035(12)	3·196(34)	3·089(11)
N(1) · · · N(1′)	2·584(11)	2·775(43)	2·678(12)
N(2) · · · N(2′)	2·740(21)	2·974(69)	2·848(11)
N(1) · · · N(2)	2·483(11)	2·541(54)	2·531(11)
$\phi_{av.}$ [c]	21·7°	0·9°	1·6°

[a] See ref. 2. [b] See ref. 1. [c] This is the average of the three dihedral angles of the type N(1)–⟨N(1)⟩–⟨N(2)⟩–N(2); see Table 5.

Unfortunately, LFSE considerations lead to precisely the same order, since an octahedral geometry is favoured over a trigonal prismatic in the order d^6(low-spin) > d^8 > d^7 (see ref. 15).

The two effects cannot, therefore, be separated on the basis of these crystallographic results alone.

The ionic radius for Ni^{2+} is 0·70 Å and the Ni^{II} derivative already has a trigonal prismatic geometry. It would appear, then, that the metal ion in the Co^{II} complex [$r(Co^{2+})$ 0·74 Å] is ' too large ' to fit symmetrically into the cavity of the hexadentate encapsulation ligand. There is substantial evidence that this is, in fact, the case: (*a*) Co–N(pyridyl) distances vary from 2·082(21)—2·160(17) Å; (*b*) N(pyridyl) · · · N(pyridyl) contacts range from 2·917(30) to 3·050(29) Å; and (*c*) at a lower level of significance, N(aldoximo) · · · N(aldoximo) and N(aldoximo) · · · N(pyridyl) distances also show some variations.

APPENDIX

Single-crystal Transformation of Monoclinic $[\{FB(ONCHC_5H_3N)_3P\}Co^{II+}][BF_4^-]$.—As outlined earlier, X-ray diffraction data were first collected from monoclinic crystals of the unsolvated Co^{II} complex (II). Since we had no evidence that the complex was air- or moisture-sensitive, the crystals were exposed to the atmosphere during data collection.

We subsequently noticed that some diffraction peaks appeared to have shoulders (as monitored on a chart recorder), so zero-level 0*kl* Weissenberg photographs of the crystal were retaken. However, we found no sign of the (expected) elongated diffraction spots that might be caused by crystal deterioration but, rather, observed the development of a totally new diffraction pattern.

The new diffraction pattern, which was monitored for *ca.* 15 months *via* 0*kl* Weissenberg photographs, shows definite twinning characteristics, with certain reflections close together and at irregular intervals.

Upon being viewed through a microscope, the modified crystals appear opaque with small cracks on their surfaces. (The original crystals were clear orange plates.)

Possible reactions that the Co^{II} complex (II) might undergo include the following: (i) a simple phase-transition with no chemical changes; (ii) simple hydration of the crystal lattice; (iii) hydrolysis of a B–F bond to give B–OH; (iv) hydrolysis of one or more aldoxime C=N bonds; and (v) formation of a Co^{II}–O_2 complex.

The experimental information is meagre. An i.r. spectrum of a sample of the complex which had been exposed to the atmosphere for 18 months showed only two new absorptions, relative to that of the authentic complex (*cf.* ref. 4). These were a broad weak band at 3615 and a weak band at 3530 cm^{-1}. These could be O–H and N–H stretching frequencies, which might have resulted from addition of H_2O to a C=N bond without cleavage, *i.e.* formation of an α-hydroxyamine. No C=O stretch is observed, so cleavage of a C=N bond can probably be ruled out.

Thus, possibility (iv) seems to be the most likely process; it is also consistent with crystallographic information on the relative stabilities of the various $[\{FB(ONCHC_5H_3N)_3P\}M^{II+}]$ cations. Thus the Co^{II} and Zn^{II} (ref. 6) complexes have longer M–N and N · · · N distances than do the Ni^{II} (ref. 1) and Fe^{II} (ref. 2) derivatives. While the Ni^{II} and Fe^{II} species seem fairly stable, the Co^{II} complex undergoes a slow solid-state reaction (*vide supra*) and the Zn^{II} complex also appears to be susceptible to hydrolysis. [It decomposes slowly (*ca.* 10 min) in water. Crystals also become opaque and show surface cracks upon exposure to the atmosphere.]

These observations seem to correlate with the amount of strain in the ligand system. The Mn^{II} complex cannot be made,[4] probably because the ionic radius of Mn^{2+} (0·80 Å) renders it too large to fit into the cavity within the clathro-chelate ligand. Thus the series $Mn^{II} > Zn^{II} \sim Co^{II} > Ni^{II} > Fe^{II}$ represents the change in ionic radius, the strain in the cation, and the readiness of the ligand to undergo a hydrolysis reaction.

The addition of H_2O across a C=N bond would give rise to an increase in the size of the cage (since the carbon–nitrogen distance will increase) and the strain in the cation would also be reduced by the resultant flexibility of the sp^3 hybridized carbon and nitrogen atoms, allowing a rotation of the N(1)–N(1′)–N(1″) relative to the N(2)–N(2′)–N(2″) triangular face and leading to a more stable stereochemical configuration. Such an effect has previously been

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reported by Wentworth,[16] who found that the reaction of the trigonal prismatic complexes [*cis,cis*-1,3,5-C_6H_9(-$\ddot{N}$=CH-$C_5H_4\ddot{N}$)$_3M^{II2+}$] (M = Mn^{II}, Zn^{II}, Co^{II}) with BH_4^- gave rise to the octahedral hydrogenation products [*cis,cis*-1,3,5-C_6H_9(-$\ddot{N}$H-CH_2-$C_5H_4\ddot{N}$)$_3M^{II2+}$].

A gross rearrangement of the cation is consistent with the abrupt changes observed in the diffraction pattern of our present Co^{II} complex.

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