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Structural Studies on Clathro Chelate Complexes. IV.[1-3] Trigonal-Prismatic Coordination of d^{10} Zinc(II) in Crystalline [{FB(ONCHC$_5$H$_3$N)$_3$P}Zn$^+$][BF$_4^-$]

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[Fluoroborotris(2-aldoximo-6-pyridyl)phosphine]zinc(II) tetrafluoroborate, [{FB(ONCHC$_5$H$_3$N)$_3$P}Zn$^+$][BF$_4^-$], crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5; No. 14) with $a = 13.340$ (22), $b = 17.921$ (13), $c = 10.662$ (14) Å; $\beta = 108.60$ (7)°; $Z = 4$; $\rho_{\text{obsd}} = 1.60$ (5) and $\rho_{\text{calcd}} = 1.58$ g cm^{-3}. The crystals are isomorphous with the corresponding (unsolvated) Co(II) and Ni(II) species. Three-dimensional X-ray diffraction data ($\sin\theta_{\max} = 0.86$; Cu Kα radiation) were collected with a Supper-Pace diffractometer. All nonhydrogen atoms have been accurately located, the final discrepancy index being $R_F = 8.2\%$ for the 2728 independent nonzero [*i.e.*, $I > 3\sigma(I)$] reflections. The zinc(II) atom is in approximate trigonal-prismatic coordination to six nitrogen atoms, with Zn–N(aldoximo) = 2.078 (8)–2.110 (8) Å (average = 2.099 ± 0.018 Å) and Zn–N(pyridyl) = 2.057 (6)–2.097 (6) Å (average = 2.071 ± 0.022 Å). The six nitrogen atoms define a slightly tapered trigonal prism in which N(aldoximo)· · ·N(aldoximo) = 2.697 (12)–2.766 (11) Å, N(pyridyl)· · ·N(pyridyl) = 2.892 (11)–2.976 (10) Å, and N(aldoximo)· · ·N(pyridyl) = 2.557 (10)–2.617 (13) Å.

Introduction

Holm and his coworkers have reported the synthesis and properties of the d^6 Fe(II), d^7 Co(II), d^8 Ni(II), and d^{10} Zn(II) derivatives of the bicyclic clathro chelate ("encapsulation") ligand [FB(ONCHC$_5$H$_3$N)$_3$P$^-$].[4-6] Attempts to prepare the d^5 Mn(II) and d^9 Cu(II) derivatives have so far been unsuccessful.[7]

We have previously reported the results of crystallographic studies on [{FB(ONCHC$_5$H$_3$N)$_3$P}Ni$^+$][BF$_4^-$],[1] [{FB(ONCHC$_5$H$_3$N)$_3$P}Fe$^+$][BF$_4^-$]·CH$_2$Cl$_2$,[2] and [{FB(ONCHC$_5$H$_3$N)$_3$P}Co$^+$][BF$_4^-$]·CH$_3$CN and have noted[8] that [{FB(ONCHC$_5$H$_3$N)$_3$P}Zn$^+$][BF$_4^-$] is isomorphous with the analogous unsolvated Ni(II) and Co(II) species. The detailed geometry of the d^{10} Zn(II) derivative is of considerable interest for two reasons: (i) there are no ligand field effects, since a d^{10} electronic configuration is spherically symmetric, and (ii) the Zn(II) ion is believed to be larger than the cavity within the idealized free encapusulation ligand, indicating that distortions should be observed. Since *isomorphous species need not be precisely isostructural*, and because of the interest in the precise geometry of the Zn(II)-containing cation, we have undertaken a single-crystal X-ray structural analysis of [{FB(ONCHC$_5$H$_3$N)$_3$P}Zn$^+$][BF$_4^-$]; our results are reported below.

Experimental Section

A sample of the complex was supplied by Professor R. H. Holm of the Massachusetts Institute of Technology. Recrystallization from acetonitrile yielded transparent white plates, most (but not all) of which were hexagonal in shape. The crystals do not appear to be X-ray sensitive but do become opaque upon exposure to the atmosphere, probably due to hydrolysis of the bicyclic ligand (*cf.* ref 3).

Optical examination and the observed Laue symmetry (C_{2h}; $2/m$) indicated that the crystals belonged to the monoclinic system. A careful study of $(0\text{–}2)kl$, $h(0\text{–}2)l$, and $hk(0\text{–}2)$ photographs revealed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, consistent only with the centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14].

Unit cell parameters, obtained from calibrated [Pb(NO$_3$)$_2$; $a_{25°} = 7.8571$ Å] zero-level precession photographs, taken at 25°, are $a = 13.340$ (22) Å, $b = 17.921$ (13) Å, $c = 10.662$ (14) Å, and $\beta = 108.60$ (7)°. The unit cell volume is 2416 Å^3. The measured density (1.60 ± 0.05 g cm^{-3} by neutral buoyancy in CCl$_4$-CHBr$_3$) is consistent with the value of 1.58 g cm^{-3} calculated for $M = 573.30$ and $Z = 4$. No crystallographic symmetry is imposed upon either the cation or the anion.

Only one crystal was used during the course of data collection. It was initially sealed into a Lindemann glass capillary and was aligned along its c axis. Later it was removed from the capillary, reorientated, and sealed into another capillary, now mounted along its a axis. Principal dimensions were $(100) \rightarrow (\bar{1}00) = 0.65$ mm, $(010) \rightarrow (0\bar{1}0) = 0.64$ mm, and $(001) \rightarrow (00\bar{1}) = 0.48$ mm.

Intensity data were collected with a Supper-Pace diffractometer using equiinclination Weissenberg geometry and an ω-scan technique with stationary-crystal, stationary-counter backgrounds collected at the beginning and end of the ω scan. The apparatus and experimental method have been described in a previous publication.[9] Details of the present analysis are as follows. (1) Cu Kα radiation ($\bar{\lambda} = 1.5418$ Å) was used. (2) $d\omega/dt = 2°$ min^{-1}. (3) The scan angle was $\omega(hkl) = [1.8 + 0.6/L(hkl)]°$, where the Lorentz factor, $L(hkl)$, is given by $\cos^2\bar{\mu}\sin\Upsilon$; $\bar{\mu}$ is the equiinclination angle and Υ is the usual vertical Weissenberg coordinate. (The term involving $L^{-1}(hkl)$ allows for the extension of low angle reflections on upper levels, caused by divergence of the X-ray beam.[10]) The count associated with the ω scan was $C(hkl)$. (4) Initial and final backgrounds $B_\text{i}(hkl)$ and $B_\text{f}(hkl)$ were each measured for one-fourth of the time of the ω scan. (5) The stability of the system (*i.e.*, crystal and counter) was monitored by remeasuring a preselected strong reflection (within a given Weissenberg level) after each 40 reflections had been collected; no significant (*i.e.*, >2%) deviations were detected. (6) $I(hkl)$, the net intensity of the reflection hkl, was calculated from the expression $I(hkl) = C(hkl) - 2[B_\text{i}(hkl) + B_\text{f}(hkl)]$.

Data (to $\sin\theta = 0.86$) for quadrants hkl and $\bar{h}kl$ of levels $hk(0\text{–}8)$ were collected from the crystal mounted on its c axis. Of 2791 reflections collected, 2198 were more than 3σ above background and were retained. With the crystal mounted on its a axis, data (to $\sin\theta = 86$) were collected from quadrants hkl and $hk\bar{l}$ of levels $(0\text{–}12)kl$; of 3391 recorded reflections, 2868 were $>3\sigma$ above background.

All data were corrected for absorption;[11] with $\mu = 27.22$ cm^{-1}, transmission factors ranged from 0.29 to 0.46. Common or symmetry-related data within a given level were averaged and all data were merged to a common scale using a least-squares method which minimizes a set of residuals linear in the logarithms of the individual scale factors;[12] the "R factor" for interlevel scaling was 4.9%. The

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(2) Part II: M. R. Churchill and A. H. Reis, *Inorg. Chem.*, **11**, 2299 (1972).

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(approximate) absolute scale was determined from a Wilson plot[13] based on the 2728 independent nonzero reflections.

Solution and Refinement of the Structure. All subsequent calculations were performed using a Harvard-modified version of R. E. Marsh's CRYM system of crystallographic routines for the IBM 360 computer. The scattering factors for neutral H, B, C, N, O, and F were taken from ref 14a; the Hartree-Foch-Slater values[15] for neutral Zn and P were corrected for both the real and the imaginary components of anomalous dispersion [$\Delta f'(\mathrm{Zn}) = -1.7$, $\Delta f''(\mathrm{Zn}) = +0.8$, $\Delta f'(\mathrm{P}) = +0.2$, $\Delta f''(\mathrm{P}) = +0.5$ e$^-$].[14b] The discrepancy index used below is defined as $R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. The function minimized in least-squares refinement processes was $\Sigma w(|F_o|^2 - |F_c|^2)^2$.

Since the present Zn(II) complex is isomorphous with the previously examined Ni(II) species,[1] the atomic coordinates for the Ni(II) complex were used to begin the phasing of the Zn(II) structure, resulting in an initial discrepancy index of $R_F = 18.9\%$. A three-dimensional Fourier synthesis yielded more accurate positions for the nonhydrogen atoms (leading to $R_F = 16.9\%$). Seven cycles of "six matrix"[16] least-squares refinement of positional and isotropic thermal parameters led to convergence with $R_F = 12.3\%$. Refinement was continued using anisotropic thermal parameters for all nonhydrogen atoms and with hydrogen atoms included in calculated positions (with the appropriate trigonal geometry, with d(C–H) = 1.00 Å, and with each hydrogen atom being assigned an isotropic thermal parameter equal to that of its attached carbon atom). Seven cycles of anisotropic "six matrix"[16] least-squares refinement led to final convergence [$(\Delta/\sigma)_{\max} < 0.2$] with $R_F = 8.2\%$. A final difference-Fourier synthesis showed no unexpected features. A table of observed and calculated structure factor amplitudes is available.[17] Final atomic positional parameters are listed in Table I. Anisotropic thermal parameters are collected in Table II; the associated atomic vibration ellipsoids are illustrated in Figure 1 and defined in Table III.

Description of the Molecular Structure. Intramolecular distances and their estimated standard deviations (esd's) are shown in Table IV; bond angles and their esd's are collected in Table V. Figure 2 shows the molecule projected on (010) and illustrates the scheme used in numbering all nonhydrogen atoms. The 12 hydrogen atoms, which have been omitted from the diagram for the sake of clarity, are numbered similarly to their attached carbon atoms. Figure 3 shows the central $\mathrm{ZnN_6}$ "core" of the molecule, indicating the angles of twist from a perfect tapered trigonal prism (*i.e.*, C_{3v} symmetry). Other torsional angles are collected in Table VI; important least-squares planes are shown in Table VII.

As expected, the d^{10} zinc(II) atom is totally encapsulated by the bicyclic hexadentate fluoroborotris(2-aldoximo-6-pyridyl)phosphine monoanion.

Zinc(II) Coordination Environment. As in the analogous d^7 cobalt(II)[3] and d^8 nickel(II)[1] complexes, the clathro chelate zinc(II) cation possesses approximate (but not exact) C_{3v} symmetry, with atoms F(1), B(1), Zn, and P defining the threefold axis. The immediate coordination environment of the zinc(II) atom consists of six nitrogen atoms which define a slightly tapered trigonal prism with very little rotational distortion. The individual twist angles (ϕ) are: N(1)-⟨N(1)⟩-⟨N(2)⟩-N(2) = +2.26°, N(1′)-⟨N(1)⟩-⟨N(2)⟩-N(2′) = −1.06°, and N(1″)-⟨N(1)⟩-⟨N(2)⟩-N(2″) = +2.33°. [Here, ⟨N(1)⟩ is the midpoint of the triangle defined by N(1), N(1′), and N(1″); ⟨N(2)⟩ is the midpoint of the triangle defined by N(2), N(2′), and N(2″).] We may note that in the iron(II) ($\phi_{\mathrm{av}} = 21.7°$)[2] and nickel(II) ($\phi_{\mathrm{av}} = 1.6°$)[1] complexes the twist angles all have the same sense. In the present zinc(II) case ($\phi_{\mathrm{av}} = 1.18°$) and in the cobalt(II) species ($\phi_{\mathrm{av}} = 0.89°$) one twist angle is in the opposite sense to the remaining two. The distortion of the ligand from threefold symmetry is probably caused by the encapsulated metal ion's being larger than the cavity within the free unperturbed fluoroborotris(2-aldoximo-6-pyridyl)-

Table I. Final Positional Parameters for Atoms in the $[\{\mathrm{FB(ONCHC_5H_3N)_3P}\}\mathrm{Zn^+}][\mathrm{BF_4^-}]$ Molecule, with Estimated Standard Deviations

Atom	x	y	z
	(A) Atoms within the Clathro Chelate Cation		
Zn	0.82969 (9)	0.10325 (5)	0.12139 (10)
P	0.70845 (20)	0.03181 (13)	0.33097 (21)
N(1)	0.9780 (5)	0.1517 (6)	0.1605 (6)
N(1′)	0.8699 (6)	0.0526 (5)	−0.0347 (6)
N(1″)	0.7914 (9)	0.1918 (4)	−0.0163 (8)
N(2)	0.8964 (6)	0.0975 (4)	0.3278 (6)
N(2′)	0.7774 (6)	−0.0049 (3)	0.1185 (6)
N(2″)	0.6949 (6)	0.1461 (5)	0.1483 (6)
C(1)	1.0391 (7)	0.1578 (5)	0.2813 (8)
C(2)	0.9900 (6)	0.1274 (4)	0.3788 (8)
C(3)	1.0408 (8)	0.1300 (5)	0.5166 (8)
C(4)	0.9879 (8)	0.1012 (6)	0.5958 (9)
C(5)	0.8909 (8)	0.0693 (7)	0.5465 (10)
C(6)	0.8437 (7)	0.0697 (6)	0.4062 (8)
C(1′)	0.8473 (8)	−0.0154 (6)	−0.0605 (9)
C(2′)	0.7950 (6)	−0.0522 (5)	0.0265 (9)
C(3′)	0.7668 (9)	−0.1243 (5)	0.0201 (9)
C(4′)	0.7200 (10)	−0.1517 (5)	0.1083 (10)
C(5′)	0.7023 (7)	−0.1072 (5)	0.2036 (8)
C(6′)	0.7303 (7)	−0.0307 (4)	0.2056 (8)
C(1″)	0.7110 (11)	0.2375 (9)	−0.0066 (12)
C(2″)	0.6522 (8)	0.2073 (6)	0.0781 (11)
C(3″)	0.5612 (1)	0.2378 (7)	0.0879 (12)
C(4″)	0.5085 (8)	0.2026 (7)	0.1633 (11)
C(5″)	0.5527 (7)	0.1397 (6)	0.2343 (9)
C(6″)	0.6479 (7)	0.1121 (5)	0.2262 (8)
O(1)	1.0150 (5)	0.1781 (4)	0.0614 (6)
O(1′)	0.9163 (5)	0.0897 (4)	−0.1126 (6)
O(1″)	0.8474 (9)	0.2180 (6)	−0.0860 (8)
B(1)	0.9412 (13)	0.1674 (7)	−0.0671 (11)
F(1)	0.9842 (6)	0.1991 (4)	−0.1566 (5)
	(B) Atoms within the $\mathrm{BF_4^-}$ Anion		
B(2)	0.3266 (10)	0.1268 (7)	0.4102 (13)
F(1)	0.3001 (7)	0.1692 (4)	0.5037 (6)
F(2)	0.4262 (6)	0.1009 (5)	0.4654 (9)
F(3)	0.2522 (6)	0.0727 (4)	0.3697 (8)
F(4)	0.3190 (9)	0.1738 (4)	0.3053 (6)
	(C) Calculated Hydrogen Atom Position[a]		
H(1)	1.1113	0.1804	0.3070
H(3)	1.1130	0.1520	0.5548
H(4)	1.0217	0.1037	0.6939
H(5)	0.8543	0.0466	0.6057
H(1′)	0.8635	−0.0422	−0.1340
H(3′)	0.7796	−0.1578	−0.0483
H(4′)	0.6985	−0.2054	0.1028
H(5′)	0.6707	−0.1280	0.2696
H(1″)	0.6941	0.2867	−0.0529
H(3″)	0.5331	0.2853	0.0408
H(4″)	0.4392	0.2223	0.1664
H(5″)	0.5163	0.1141	0.2912

[a] Hydrogen atoms are numbered similarly to their attached carbon atoms.

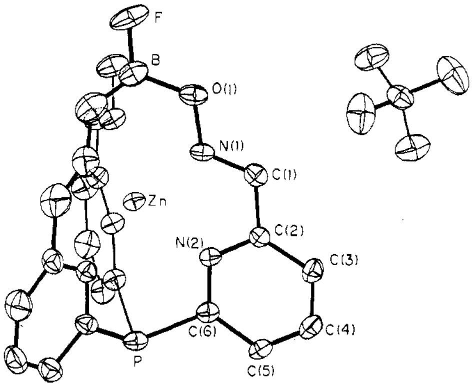

Figure 1. Atomic vibration ellipsoids for nonhydrogen atoms in $[\{\mathrm{FB(ONCHC_5H_3N)_3P}\}\mathrm{Zn^{II+}}][\mathrm{BF_4^-}]$.

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(16) Due to a limitation in available storage space the 325 variables could not be refined in a single matrix. Refined parameters were thus blocked into six submatrices as follows: matrix 1, parameters for Ni, P, six N's, and the scale factor; matrix 2, parameters for F(1), B(1), three O's; matrices 3-5, parameters for C(1)-C(6), C(1′)-C(6′), C(1″)-C(6″), respectively; matrix 6, parameters for atoms of the $\mathrm{BF_4^-}$ ion.

(17) See paragraph at end of paper regarding supplementary material.

Table II. Anisotropic Thermal Parameters ($\times 10^4$)[a,b]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zn	74.4 (7)	23.2 (3)	89.9 (9)	4.5 (8)	73.1 (10)	5.8 (11)
P	86.2 (17)	43.8 (8)	117.5 (27)	−8.8 (24)	106.5 (25)	3.4 (22)
N(1)	81 (4)	27 (2)	127 (7)	−10 (5)	123 (11)	−3 (7)
N(1′)	112 (6)	35 (3)	102 (3)	−2 (6)	96 (13)	5 (8)
N(1″)	122 (11)	43 (3)	189 (11)	−23 (7)	54 (13)	88 (8)
N(2)	72 (5)	24 (2)	98 (5)	3 (5)	78 (11)	−0 (7)
N(2′)	86 (4)	22 (2)	105 (7)	−0 (6)	72 (10)	−4 (6)
N(2″)	67 (5)	30 (2)	105 (6)	7 (6)	48 (8)	2 (6)
C(1)	78 (5)	30 (3)	143 (6)	11 (7)	81 (12)	−16 (11)
C(2)	65 (5)	27 (2)	104 (9)	18 (6)	55 (11)	−2 (8)
C(3)	83 (6)	41 (3)	105 (8)	11 (7)	27 (13)	−15 (10)
C(4)	111 (8)	47 (3)	91 (8)	26 (9)	49 (12)	−5 (12)
C(5)	97 (6)	41 (3)	86 (7)	11 (8)	75 (10)	5 (9)
C(6)	81 (5)	24 (2)	111 (8)	−6 (6)	80 (9)	−19 (8)
C(1′)	116 (8)	31 (2)	127 (8)	−8 (7)	111 (11)	−23 (9)
C(2′)	78 (5)	28 (2)	113 (8)	0 (6)	60 (11)	−13 (8)
C(3′)	115 (8)	25 (3)	144 (9)	−12 (8)	94 (13)	−27 (9)
C(4′)	113 (10)	24 (3)	160 (11)	−15 (9)	49 (16)	−35 (9)
C(5′)	91 (6)	29 (2)	146 (9)	−11 (7)	68 (11)	22 (9)
C(6′)	81 (5)	28 (2)	109 (10)	−7 (8)	72 (11)	−0 (8)
C(1″)	169 (11)	75 (5)	212 (16)	109 (14)	79 (25)	134 (16)
C(2″)	68 (6)	42 (3)	142 (12)	27 (8)	31 (16)	30 (12)
C(3″)	116 (9)	48 (4)	195 (15)	42 (10)	53 (22)	32 (15)
C(4″)	63 (6)	63 (4)	198 (13)	20 (10)	45 (15)	−26 (15)
C(5″)	74 (6)	47 (4)	157 (13)	−2 (7)	82 (13)	−34 (11)
C(6″)	72 (5)	35 (3)	124 (7)	−10 (8)	80 (9)	−23 (8)
O(1)	108 (4)	36 (2)	163 (5)	−22 (4)	159 (6)	−7 (6)
O(1′)	162 (4)	36 (2)	136 (5)	−10 (7)	165 (8)	11 (7)
O(1″)	185 (9)	66 (4)	178 (9)	6 (9)	124 (16)	73 (11)
B(1)	136 (10)	41 (6)	142 (12)	−0 (12)	112 (15)	3 (11)
F(1)	271 (7)	60 (3)	154 (7)	−77 (7)	275 (9)	−3 (7)
B(2)	85 (8)	38 (4)	189 (15)	4 (9)	112 (16)	32 (14)
F(2)	192 (6)	68 (3)	198 (6)	−21 (7)	202 (10)	−2 (8)
F(3)	109 (5)	81 (5)	412 (15)	26 (8)	107 (14)	78 (13)
F(4)	164 (7)	46 (2)	283 (12)	−48 (6)	−16 (15)	21 (7)
F(5)	207 (6)	57 (2)	202 (7)	−3 (7)	233 (10)	33 (8)

[a] The anisotropic thermal parameter is defined as $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Estimated standard deviations (shown in parentheses) are right adjusted to the least significant digit of the preceding number.

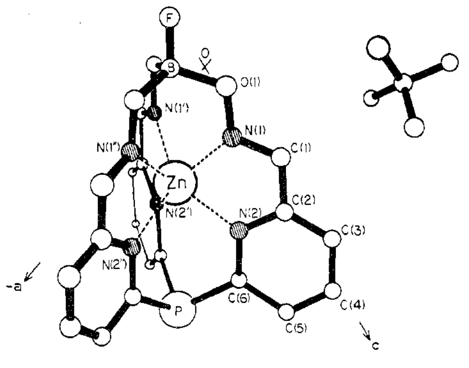

Figure 2. The labeling of atoms and molecular stereochemistry of $[\{FB(ONCHC_5H_3N)_3P\}Zn^{II+}][BF_4^-]$.

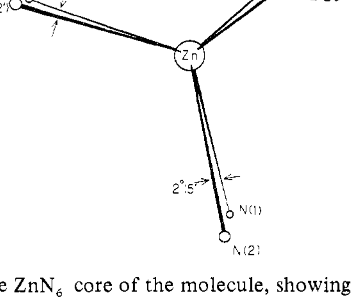

Figure 3. The ZnN_6 core of the molecule, showing the observed derivations from a truly trigonal-prismatic geometry.

phosphine cage. The possibility of intermolecular forces also being involved cannot, however, be entirely ruled out.

Individual Zn-N(aldoximo) distances are 2.078 (8), 2.110 (7), and 2.110 (8) Å (average 2.099 ± 0.018 Å),[18] while Zn-N(pyridyl) distances are 2.097 (6), 2.057 (6), and 2.058 (8) Å (average 2.071 ± 0.022 Å). The N(aldoximo)· · ·N(aldoximo) contacts are 2.766 (11), 2.737 (12), and 2.697 (12) Å (average 2.732 ± 0.037 Å), while the N(pyridyl)· · ·N(pyridyl) contacts of 2.934 (9), 2.976 (10), and 2.892 (11) Å (average 2.934 ± 0.034 Å) are appreciably longer, as the net result of the longer P-C(6) *vis-a-vis* B-O(1) distances, and angular requirements about the boron and phosphorus atoms. (The mean O-B-O angle is 114.2 ± 3.9°, while the average C-P-C angle is 99.7 ± 0.8°.)

The N(aldoximo)· · ·N(pyridyl) "bite" distances are 2.561 (10), 2.557 (10), and 2.617 (13) Å (average 2.587 ± 0.033 Å).

Average bond angles within the ZnN_6 core of the present cation are N(aldoximo)-Zn-N(aldoximo) = 81.2 ± 1.3°, N(pyridyl)-Zn-N(pyridyl) = 90.2 ± 2.2°, and N(aldoximo)-Zn-N(pyridyl) = 76.4 ± 1.3° (for the cis "bite" angles) and 133.4 ± 2.3° (for the pseudo-trans or non-cis angles).

[Fluoroborotris(2-aldoximo-6-pyridyl)phosphine] Cage. The three aldoximo-pyridyl portions of the clathro chelate ligand are designated as nonprimed, singly primed, and doubly primed. As may be ascertained from Table VII, the three pyridyl systems are each essentially planar, with root-mean-square (rms) deviations from planarity of 0.008, 0.008, and 0.012 Å, respectively. The entire aldoximo-pyridyl ligands show rather greater deviations from planarity, with rms values of 0.023, 0.026, and 0.052 Å. [Atoms O(1), N(1), and C(1) in each ligand, which define the flexible aldoximo system of the ligand, were assigned zero weight in these calculations.

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(18) Throughout the text esd's on individual bond lengths and bond angles are given in parentheses, while esd's on average bond lengths and angles are given as ±X.XXX Å or ±X.X°. These latter values are "root-mean-square scatters" calculated from the expression $\sigma = [\{\Sigma_{i=1}^{i=N}(\chi_i - \bar{\chi})^2\}/(N-1)]^{1/2}$. Here χ_i is the *i*th value and $\bar{\chi}$ is the mean of the *N* (usually three) equivalent values.

Table III. Principal Axes of Atomic Vibration Ellipsoids[a-c]

Atom	$B_{\min}$ (dc's minor axis)	B_{med} (dc's median axis)	$B_{\max}$ (dc's major axis)
Zn	1.29 (−71, −941, 335)	3.25 (542, −314, −911)	4.88 (−837, −122, −237)
P	3.36 (688, 359, −816)	4.59 (150, −920, −390)	6.06 (−709, 154, −425)
N(1)	2.88 (757, 431, −707)	3.56 (281, −893, −422)	6.38 (−590, 128, −567)
N(1′)	3.66 (−363, −254, 965)	4.68 (−63, 967, 255)	7.20 (929, −32, 52)
N(1″)	3.06 (−226, −829, 557)	7.21 (767, 172, 341)	11.71 (−600, 532, 758)
N(2)	3.03 (304, −920, −330)	3.38 (593, 385, −859)	4.90 (745, 68, 390)
N(2′)	2.82 (44, −991, −132)	4.11 (389, 132, −988)	5.53 (−920, 8, −77)
N(2″)	3.70 (457, −855, 85)	4.32 (−142, −341, −835)	4.60 (−878, −390, 542)
C(1)	3.35 (470, −849, −379)	5.21 (−883, −454, 167)	6.02 (−7, 271, −910)
C(2)	2.87 (572, −816, −260)	4.27 (−59, 58, −925)	4.81 (−818, −575, 275)
C(3)	3.95 (239, 259, 810)	4.84 (−570, 817, 105)	6.73 (785, 514, −576)
C(4)	3.69 (−61, 118, 959)	5.37 (−523, 841, 41)	8.29 (850, 526, −280)
C(5)	3.26 (299, 14, −999)	5.10 (406, −906, −21)	6.46 (−863, −422, 13)
C(6)	2.88 (107, −903, −429)	4.26 (691, 369, −809)	5.47 (−715, 221, −400)
C(1′)	3.49 (−174, 826, 563)	4.98 (−491, −544, 801)	7.60 (853, −145, 202)
C(2′)	3.38 (115, −921, −389)	4.81 (−7, 373, −876)	5.04 (−993, −109, 282)
C(3′)	2.92 (11, 947, 299)	5.94 (−432, −283, 949)	7.48 (901, −148, 98)
C(4′)	2.66 (111, 937, 279)	6.62 (−455, 345, −633)	8.36 (−883, −59, 722)
C(5′)	3.26 (279, 922, −342)	5.80 (716, −14, 432)	6.59 (−639, 385, 834)
C(6′)	3.53 (267, 957, −191)	4.28 (−404, 216, 971)	5.34 (874, −192, 143)
C(1″)	3.19 (349, −676, 502)	11.29 (752, −210, −832)	15.41 (−558, −705, −234)
C(2″)	3.28 (653, −551, 283)	6.10 (−709, −684, 384)	6.80 (263, −477, −878)
C(3″)	4.54 (479, −760, 263)	8.45 (−290, −609, −606)	9.46 (828, 226, −750)
C(4″)	3.82 (934, −221, −32)	7.17 (−31, 730, 656)	9.77 (−355, −646, 753)
C(5″)	4.41 (−922, 315, 504)	5.12 (−382, −678, −472)	7.52 (48, 664, −723)
C(6″)	3.87 (−375, 687, 709)	4.11 (876, 482, −282)	5.87 (302, −543, 646)
O(1)	3.59 (709, 565, −624)	4.91 (−336, 796, 584)	8.44 (618, −216, 518)
O(1′)	3.74 (−404, −584, 795)	5.12 (−217, 808, 588)	10.58 (888, −68, 147)
O(1″)	5.05 (−154, −609, 786)	10.65 (86, −792, −600)	11.92 (−984, 26, 148)
B(1)	5.18 (178, 863, −504)	5.52 (−298, 505, 862)	8.72 (937, −3, 30)
F(1)	3.25 (−473, −361, 912)	7.31 (−103, −883, −400)	18.58 (−874, 300, −82)
B(2)	4.34 (−504, −795, 479)	5.04 (−857, 508, 194)	8.21 (−104, −329, −856)
F(2)	6.33 (−534, −187, 951)	8.64 (86, 958, 232)	12.78 (841, −217, 201)
F(3)	6.63 (889, −316, 28)	9.92 (395, 895, −322)	18.48 (−229, 315, 946)
F(4)	5.09 (359, 924, 8)	8.34 (526, −315, 581)	17.42 (771, −215, 814)
F(5)	5.19 (455, 517, −831)	8.18 (301, −855, −496)	13.71 (−837, −26, 250)

[a] Direction cosines (dc's) are referred to the monoclinic axis system; they are multiplied by 10^3. [b] The minor, median, and major axes of the ellipsoids are defined in terms of B (the isotropic thermal parameter, having units of Å^2). The transformation to root-mean-square displacement is $(\overline{U^2})^{1/2} = [B/8\pi^2]^{1/2}$. [c] The vibration ellipsoids are illustrated in Figure 1.

Mean deviations are 0.068 Å for oxygen, 0.019 Å for N(aldoximo), and 0.023 Å for C(aldoximo). It should be noted that, within the analogous Fe(II) complex,[3] distortions of the aldoximo moiety are much greater, with atoms being displaced from the P-$C_5H_5N\cdots$BF plane by as much as 0.67 Å.]

Torsional angles of the type O(1)-B(1)· · ·P-C(6) provide a measure of the distortion of the overall clathro chelate ligand from true C_{3v} symmetry. As shown in Table VI, individual values are 1.2, 2.3, and 2.5°.

There are no appreciable "twists" within the nonprimed aldoximo ligand [B(1)-O(1)-N(1)-C(1) = 179.3°, O(1)-N(1)-C(1)-C(2) = 179.9°, N(1)-C(1)-C(2)-N(2) = 2.3°] or in the singly primed ligand [B(1)-O(1′)-N(1′)-C(1′) = 177.9°, O(1′)-N(1′)-C(1′)-C(2′) = 178.8°, N(1′)-C(1′)-C(2′)-N(2′) = 1.7°], but there are significant twists about bonds in the doubly primed aldoximo-pyridyl moiety [B(1)-O(1″)-N(1″)-C(1″) = 170.7°, O(1″)-N(1″)-C(1″)-C(2″) = 177.5°, N(1″)-C(1″)-C(2″)-N(2″) = 9.5°]. Since the overall distortion of the doubly primed ligand is only 2.5° [as measured by the O(1″)-B(1)-P-C(6″) torsional angle], the two large twists about the O(1″)-N(1″) and C(1″)-C(2″) bonds are mutually compensatory. This pattern of distortions probably results from the relatively large size of the zinc(II) ion, which is really too large to fit comfortably into the clathro chelate cage. Other data are consistent with the proposal that the strain in the cation is taken up principally by means of distortions in the doubly primed aldoximo-pyridyl arm.

Thus, the N(1″)-C(1″) distance of 1.380 (19) Å is significantly greater than the values of 1.291 (11) Å for N(1)-C(1) and 1.263 (14) for N(1′)-C(1′). This appears to be compensated, in part, by opposing changes in the oxygen-nitrogen bond lengths, *viz.*, O(1″)-N(1″) = 1.298 (15) Å, whereas O(1)-N(1) = 1.383 (10) Å and O(1′)-N(1′) = 1.358 (10) Å. It should be noted that atoms O(1″), N(1″), and C(1″) all have abnormally high thermal parameters (see Table III), indicating the possibility of slight disorder in this part of the molecule. We interpret this in terms of some loss of rigidity of the cage at this point.

A reaction (probably hydrolysis) is observed in the solid state upon leaving the crystals exposed to air. No new lattice reflections appear, but total amorphism results. The crystals (which initially have well-defined mirror-like faces) appear opaque after prolonged exposure to air and tiny cracks appear on each face. The lengthening of the N(1″)-C(1″) bond, the high thermal motion of the atoms O(1″), N(1″), and C(1″), and the two large twists about the O(1″)-N(1″) and C(1″)-C(2″) bonds suggest significant weakness in the N(1″)-C(1″) bond, providing a convenient location for hydrolysis to occur. If hydrolysis occurs as an addition reaction to the N(1″)-C(1″) bond, both atoms will become sp^3 hybridized and strain within the ligand system can be released.[19] Hydrolysis appears to take place in the Zn(II) case faster than in the Co(II) case where the reaction was monitored by recording the diffraction pattern every few months (*cf.* ref 3). Exposure of the Fe(II) and Ni(II) complexes (in which the encapsulated metal ions are smaller than Zn(II) or Co(II)) to atmospheric moisture does not lead to any solid state reaction. We may note here that the Zn(II) complex has been shown to decompose in water in approximately 10 min.[20]

Discussion

The present structural study completes our set of crystallographic studies on the currently known $[\{FB(ONCHC_5H_3N)_3P\}(M^{II})^+]$ ions (M = Fe, Co, Ni, Zn). Relevant data from these four determinations are listed in Table VIII. The ionic radii used herewithin are the Shannon and Prewitt values for octahedral coordination based on $r(^{VI}O^{2-})$ =

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(19) R. A. D. Wentworth, *Inorg. Chem.*, 10, 2615 (1971). In this article Wentworth reports that the *trigonal*-prismatic species *cis,cis*-1,3,5-$C_6H_9(\text{-N=CH-}C_5H_4N)_3(M^{II})^{2+}$ (M = Mn, Zn) can be hydrogenated to yield the *octahedral* products *cis,cis*-1,3,5-$C_6H_9(\text{-NH-CH}_2\text{-}C_5H_4N)_3(M^{II})^{2+}$. Clearly, in this case, change in hybridization of the nitrogen and carbon atoms results in a drastic change of geometry of the hexadentate ligand system.

(20) B. E. Wagner, Ph.D. Thesis, Department of Chemistry, Massachusetts Institute of Technology, 1971.

Table IV. Interatomic Distances (Å)

Atom	Distance	Atom	Distance
(A) Distances from Zinc Atom			
Zn–N(1)	2.078 (8)	Zn–N(2)	2.097 (6)
Zn–N(1′)	2.110 (7)	Zn–N(2′)	2.057 (6)
Zn–N(1″)	2.110 (8)	Zn–N(2″)	2.058 (8)
Zn· · ·P	3.399 (3)	Zn· · ·B(1)	3.078 (15)
(B) Distances within Nonprimed Aldoximo–Pyridyl Ligand			
B(1)–O(1)	1.422 (14)	C(4)–C(5)	1.358 (15)
O(1)–N(1)	1.383 (10)	C(5)–C(6)	1.426 (13)
N(1)–C(1)	1.291 (11)	C(6)–N(2)	1.346 (12)
C(1)–C(2)	1.496 (12)	C(6)–P	1.854 (10)
C(2)–C(3)	1.409 (12)	N(2)–C(2)	1.308 (11)
C(3)–C(4)	1.363 (15)		
(C) Distances within Singly Primed Ligand			
B(1)–O(1′)	1.476 (15)	C(4′)–C(5′)	1.371 (14)
O(1′)–N(1′)	1.358 (10)	C(5′)–C(6′)	1.421 (12)
N(1′)–C(1′)	1.263 (14)	C(6′)–N(2′)	1.357 (12)
C(1′)–C(2′)	1.483 (14)	C(6′)–P	1.837 (9)
C(2′)–C(3′)	1.342 (13)	N(2′)–C(2′)	1.371 (11)
C(3′)–C(4′)	1.374 (15)		
(D) Distances within Doubly Primed Ligand			
B(1)–O(1″)	1.506 (20)	C(4″)–C(5″)	1.381 (15)
O(1″)–N(1″)	1.298 (15)	C(5″)–C(6″)	1.392 (14)
N(1″)–C(1″)	1.380 (19)	C(6″)–N(2″)	1.336 (12)
C(1″)–C(2″)	1.476 (18)	C(6″)–P	1.842 (9)
C(2″)–C(3″)	1.365 (17)	N(2″)–C(2″)	1.347 (13)
C(3″)–C(4″)	1.377 (17)		
(E) Boron–Fluorine Distance within Cation			
B(1)–F(1)	1.383 (16)		
(F) Boron–Fluorine Distances within Anion			
B(2)–F(2)	1.386 (15)	B(2)–F(4)	1.356 (15)
B(2)–F(3)	1.386 (15)	B(2)–F(5)	1.377 (14)
(G) Nonbonded Contacts within Zinc Coordination Environment			
N(1)· · ·N(1′)	2.766 (11)	N(1)· · ·N(2)	2.561 (10)
N(1′)· · ·N(1″)	2.737 (12)	N(1′)· · ·N(2′)	2.557 (10)
N(1″)· · ·N(1)	2.697 (12)	N(1″)· · ·N(2″)	2.617 (13)
N(2)· · ·N(2′)	2.934 (9)		
N(2′)· · ·N(2″)	2.976 (10)		
N(2″)· · ·N(2)	2.892 (11)		
Interatomic Contacts			
C(5″)· · ·F(3)	3.471 (13)	C(4″)· · ·F(5)	3.375 (15)
C(5″)· · ·F(5)	3.487 (15)		
H(5″)· · ·F(3)	2.522	H(4″)· · ·F(5)	2.649
H(5″)· · ·F(5)	2.893		

1.40 Å.[21] We make the following observations.

(1) The M–N(aldoximo) distances vary in the order Fe << Ni < Co < Zn, values being 1.931 (11), 2.030 (21), 2.063 (18), and 2.099 (18) Å, respectively. However, the differences between these bond distances and the appropriate $^{\mathrm{VI}}\mathrm{M}^{2+}$ ionic radii are very similar, individual values being 1.32 (1), 1.33 (2), 1.33 (2), and 1.35 (2) Å.

(2) The M–N(pyridyl) distances vary in the order Fe << Ni < Zn < Co, values being 1.978 (6), 2.043 (20), 2.071 (22), and 2.118 (38) Å; the differences between bond distance and metal ionic radius are, again, identical within the limits of experimental error, individual values being 1.37 (1), 1.34 (2), 1.33 (2), and 1.38 (4) Å (respectively).

(3) The average M–N(pyridyl) distance is slightly longer than the average M–N(aldoximo) distance for all except the Zn(II) derivative. Values for [M–N(pyridyl)–M–N-(aldoximo)] are +0.047 (13) Å for Fe(II), +0.055 (42) Å for Co(II), +0.013 (29) Å for Ni(II), and −0.028 (28) Å for Zn(II).

(4) The *overall* average M–N distances vary in the order Fe << Ni < Zn ~ Co (1.954, 2.037, 2.085, and 2.090 Å, respectively). The differences between average M–N distance and $^{\mathrm{VI}}\mathrm{M}^{2+}$ radii are 1.344 Å for Fe(II), 1.337 Å for Ni(II), 1.340 Å for Zn(II), and 1.355 Å for Co(II); *i.e.*, this remains

Table V. Individual Interatomic Angles (deg)

Atoms	Angle	Atoms	Angle
(A) Angles about Zinc Atom			
N(1)–Zn–N(2)	75.7 (3)	N(2″)–Zn–N(2)	88.2 (3)
N(1′)–Zn–N(2′)	75.7 (3)	N(1)–Zn–N(2″)	129.4 (3)
N(1″)–Zn–N(2″)	77.8 (4)	N(1)–Zn–N(2′)	133.9 (3)
N(1)–Zn–N(1′)	82.7 (3)	N(1′)–Zn–N(2″)	136.4 (3)
N(1′)–Zn–N(1″)	80.3 (3)	N(1′)–Zn–N(2)	132.6 (3)
N(1″)–Zn–N(1)	80.2 (4)	N(1″)–Zn–N(2)	134.0 (3)
N(2)–Zn–N(2′)	89.9 (3)	N(1″)–Zn–N(2′)	133.8 (3)
N(2′)–Zn–N(2″)	92.6 (3)		
(B) Angles about the Boron Atom of the Cation			
O(1)–B(1)–F(1)	107.3 (11)	O(1)–B(1)–O(1′)	117.3 (9)
O(1′)–B(1)–F(1)	105.1 (9)	O(1′)–B(1)–O(1″)	115.6 (12)
O(1″)–B(1)–F(1)	99.8 (9)	O(1″)–B(1)–O(1)	109.7 (9)
(C) Angles about the Phosphorus Atom			
C(6)–P–C(6′)	100.3 (4)	C(6″)–P–C(6)	98.8 (4)
C(6′)–P–C(6″)	100.1 (4)		
(D) Angles within the Nonprimed Aldoximo–Pyridyl Ligand			
B(1)–O(1)–N(1)	112.6 (8)	C(3)–C(4)–C(5)	122.5 (9)
O(1)–N(1)–C(1)	117.9 (8)	C(4)–C(5)–C(6)	116.8 (9)
N(1)–C(1)–C(2)	112.7 (8)	C(5)–C(6)–N(2)	120.6 (9)
C(1)–C(2)–N(2)	115.6 (7)	C(6)–N(2)–C(2)	120.8 (7)
C(1)–C(2)–C(3)	122.8 (8)	N(2)–C(6)–P	119.7 (6)
N(2)–C(2)–C(3)	121.6 (8)	C(5)–C(6)–P	119.7 (7)
C(2)–C(3)–C(4)	117.5 (9)		
(E) Angles within the Singly Primed Ligand			
B(1)–O(1′)–N(1′)	111.1 (8)	C(3′)–C(4′)–C(5′)	121.5 (9)
O(1′)–N(1′)–C(1′)	117.6 (8)	C(4′)–C(5′)–C(6′)	117.8 (9)
N(1′)–C(1′)–C(2′)	114.8 (8)	C(5′)–C(6′)–N(2′)	119.7 (8)
C(1′)–C(2′)–N(2′)	113.3 (8)	C(6′)–N(2′)–C(2′)	120.1 (7)
C(1′)–C(2′)–C(3′)	125.2 (9)	N(2′)–C(6′)–P	120.4 (6)
N(2′)–C(2′)–C(3′)	121.5 (8)	C(5′)–C(6′)–P	119.9 (7)
C(2′)–C(3)–C(4′)	119.4 (9)		
(F) Angles within the Doubly Primed Ligand			
B(1)–O(1″)–N(1″)	108.1 (9)	C(3″)–C(4″)–C(5″)	119.1 (10)
O(1″)–N(1″)–C(1″)	115.5 (10)	C(4″)–C(5″)–C(6″)	119.6 (9)
N(1″)–C(1″)–C(2″)	113.9 (11)	C(5″)–C(6″)–N(2″)	119.7 (8)
C(1″)–C(2″)–N(2″)	115.2 (10)	C(6″)–N(2″)–C(2″)	121.2 (9)
C(1″)–C(2″)–C(3″)	124.0 (11)	N(2″)–C(6″)–P	122.1 (7)
N(2″)–C(2″)–C(3″)	120.8 (10)	C(5″)–C(6″)–P	118.2 (7)
C(2″)–C(3″)–C(4″)	119.5 (11)		
(G) Angles in the BF_4^- Anion			
F(2)–B(2)–F(3)	108.4 (10)	F(3)–B(2)–F(4)	114.3 (10)
F(2)–B(2)–F(4)	106.9 (11)	F(3)–B(2)–F(5)	111.8 (12)
F(2)–B(2)–F(5)	106.2 (9)	F(4)–B(2)–F(5)	108.8 (10)

Table VI. Torsional Angles within the Molecule (deg)

Atoms	Angles
O(1)–B(1)· · ·P–C(6)	1.2
O(1′)–B(1)· · ·P–C(6′)	2.3
O(1″)–B(1)· · ·P–C(6″)	2.5
B(1)–O(1)–N(1)–C(1)	179.3
B(1)–O(1′)–N(1′)–C(1′)	177.9
B(1)–O(1″)–N(1″)–C(1″)	170.7
O(1)–N(1)–C(1)–C(2)	179.9
O(1′)–N(1′)–C(1′)–C(2′)	178.8
O(1″)–N(1″)–C(1″)–C(2″)	177.5
N(1)–C(1)–C(2)–N(2)	2.3
N(1′)–C(1′)–C(2′)–N(2′)	1.7
N(1″)–C(1″)–C(2″)–N(2″)	9.5
N(1)–⟨N(1)⟩–⟨N(2)⟩–N(2)[a]	+2.26
N(1′)–⟨N(1)⟩–⟨N(2)⟩–N(2′)[a]	−1.06
N(1″)–⟨N(1)⟩–⟨N(2)⟩–N(2″)[a]	+2.33

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

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[21] R. D. Shannon and C. T. Prewitt, *Acta Crystallogr., Sect. B*, **25**, 925 (1969).

Table VII. Least-Squares Planes[a,b] within the $[\{FB(ONCHC_5H_3N)_3P\}Zn^+]$ Cation

Atom	Dev, Å	Atom	Dev, Å
(A) Unprimed Pyridyl Group:			
	$0.4514X - 0.8916Y - 0.1775Z = 3.211$		
C(2)	−0.003	C(5)	0.012
C(3)	0.002	C(6)	−0.013
C(4)	−0.007	N(2)	0.009
(B) Singly Primed Pyridyl Group:			
	$0.7371X - 0.2261Y + 0.3585Z = 8.126$		
C(2′)	0.006	C(5′)	0.014
C(3′)	−0.004	C(6′)	−0.013
C(4′)	−0.006	N(2′)	0.003
(C) Doubly Primed Pyridyl Group:			
	$0.2782X + 0.5699Y + 0.6441Z = 5.091$		
C(2″)	−0.017	C(5″)	−0.005
C(3″)	0.024	C(6″)	0.012
C(4″)	−0.013	N(2″)	−0.002
(D) $0.4467X - 0.8928Y - 0.1973Z = 3.046$			
P(1)	−0.030	N(2)	0.047
C(2)	+0.018	C(1)*	0.030
C(3)	−0.010	N(1)*	0.018
C(4)	−0.032	O(1)*	0.024
C(5)	0.005	B(1)	0.026
C(6)	0.012	F(1)	−0.037
(E) $0.7200X - 0.2444Y + 0.3777Z = 8.057$			
P(1)	−0.002	N(2′)	−0.029
C(2′)	−0.022	C(1′)*	−0.027
C(3′)	−0.005	N(1′)*	−0.002
C(4′)	0.018	O(1′)*	−0.029
C(5′)	0.035	B(1)	0.056
C(6′)	−0.021	F(1)	−0.028
(F) $0.3270X + 0.5952Y + 0.5914Z = 5.473$			
P(1)	0.043	N(2″)	0.051
C(2″)	0.075	C(1″)*	0.120
C(3″)	0.066	N(1″)*	−0.078
C(4″)	−0.065	O(1″)*	0.006
C(5″)	−0.096	B(1)	−0.005
C(6″)	−0.025	F(1)	−0.044

[a] Equations to planes are given in Cartesian coordinates (X,Y,Z) which are related to the fractional cell coordinates (x,y,z) by the transformation $[X,Y,Z] = [xa + zc\cos\beta, yb, zc\sin\beta]$. [b] Atoms marked with an asterisk were given zero weight in the least-squares plane calculation; all other atoms entered below the equation to a specific plane were given unit weight.

Table VIII. Intramolecular Distances (Å) and Angles (deg) for $[\{FB(ONCHC_5H_3N)_3P\}M(II)^+]$ Ions

M(II)	Fe(II) (low spin)	Co(II) (high spin)	Ni(II)	Zn(II)
Electronic configuration	d^6	d^7	d^8	d^{10}
Ionic radius[a]	0.61	0.735	0.700	0.745
M–N(aldoximo)	1.931 (11)	2.063 (18)	2.030 (21)	2.099 (18)
M–N(pyridyl)	1.978 (06)	2.118 (38)	2.043 (20)	2.071 (22)
M–N(average)	1.954	2.090	2.037	2.085
N(aldoximo)· · ·N-(aldoximo)	2.584 (09)	2.774 (43)	2.678 (35)	2.732 (12)
N(pyridyl)· · ·N-(pyridyl)	2.740 (22)	2.974 (69)	2.848 (18)	2.934 (10)
N(aldoximo)· · ·N-(pyridyl)	2.483 (20)	2.541 (54)	2.531 (12)	2.578 (11)
N(aldoximo)–M–N-(pyridyl)	78.9 (5)	74.8 (13)	76.8 (6)	76.4 (13)
ϕ_{av}[b]	21.7	0.9	1.6	1.2
C(6)–P· · ·B–O	32.3	1.3	3.8	2.0

[a] See ref 21. [b] ϕ_{av} is the average of the three torsional 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″).

essentially constant (within the limits of experimental error) from one metal to another.

(5) The N(aldoximo)· · ·N(aldoximo) distances vary in the order Fe < Ni < Zn < Co [2.584 (9), 2.678 (35), 2.732 (12), 2.774 (43) Å], and the N(pyridyl)· · ·N(pyridyl) distances vary in the same order [2.740 (22), 2.848 (18), 2.934 (10), 2.974 (69) Å]. However, the difference between N(aldoximo)· · ·N(aldoximo) and N(pyridyl)· · ·N(pyridyl) distances remains essentially constant [0.156 (24) Å for Fe(II), 0.170 (39) Å for Ni(II), 0.200 (81) Å for Co(II), 0.202 (16) Å for Zn(II)].

(6) The N(aldoximo)· · ·N(pyridyl) "bite" within an aldoximo-pyridyl moiety varies in the order Fe < Ni < Co < Zn.

(7) The N(aldoximo)-M-N(pyridyl) "bite" angle decreases with the size (as judged by $^{VI}M^{2+}$ radii) of the encapsulated metal atom with values of 78.9 (5)° for Fe(II), 76.8 (6)° for Ni(II), 76.4 (13)° for Zn(II), and 74.8 (13)° for the Co(II) derivative.

(8) The angle ϕ_{av}, given by N(aldoximo)-⟨N(aldoximo)⟩-⟨N(pyridyl)⟩-N(pyridyl), is one of the most significant indicators of distortions from true trigonal-prismatic (or, to be precise, from C_{3v}) symmetry. This angle has the value 21.7° for the Fe(II), 1.6° for the Ni(II), 1.2° for the Zn(II), and 0.9° for the Co(II) derivative. We should note that for both the Zn(II) and Co(II) complexes one ligand is displaced in the opposite direction to the other two (*vide supra*).

(9) Another measure of the distortion of the ligand from C_{3v} symmetry is the torsional angle C(6)-P· · ·B-O, for which appropriate values are 32.3° for Fe(II), 3.8° for Ni(II), 2.0° for Zn(II), and 1.3° for Co(II). Differences between these values and those in (8) result from torsion in the O(1)-N(1), C(1)-C(2), and C(1)-N(1) bonds.

All of the above data are consistent with the geometry of the metal coordination sphere being determined simply by the relative sizes of the metal atom and the cavity within the bicyclic encapsulation ligand. The Fe(II) atom is clearly too small to fit into the cavity without causing a severe distortion toward an octahedral geometry, the Ni(II) atom is close to the ideal size and forms a complex in which the $[\{FB(ONCHC_5H_3N)_3P\}(M^{II})^+]$ ion is very close to the ideal C_{3v} symmetry, but both the Co(II) and Zn(II) atoms appear to be slightly too large for the cavity and significant deviations from threefold symmetry are observed. The nonoccurrence of a Mn(II) derivative can also be understood as a size effect since the radius of (high spin) $^{VI}Mn^{2+}$ is 0.820 Å.[20]

Finally, we may note that Gillum, Wentworth, and Childers[22] have considered the relative stabilities of octahedral and trigonal-prismatic geometries as a function of ligand field stabilization energy (LFSE). Their order of stability for trigonal-prismatic geometry is Fe(II) < Ni(II) < high spin Co(II) < Zn(II) = Mn(II). While this order is in agreement with the order that we find for $FB(ONCHC_5H_3N)_3P^-$ derivatives, it is clear that LFSE effects are more important to ligand systems with a flexible geometry than to the present rather rigid cage structures.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× *reduction, negatives) containing all of the supplementary material for*

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the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-2280.

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Structure of Sodium Nitrilotriacetatocopper(II) Monohydrate

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The crystal and molecular structure of sodium nitrilotriacetatocopper(II) monohydrate, $NaCuN(CH_2COO)_3 \cdot H_2O$, has been determined by single-crystal X-ray analysis. The compound is formed when Cu^{2+} ions are leached from copper tubing by an aqueous solution of $Na_3N(CH_2COO)_3$. The crystals are orthorhombic, with $a = 9.899$ (5), $b = 12.565$ (5), and $c = 7.548$ (5) Å, and belong to the space group $P2_12_12_1$. There are four formula units in the unit cell. The atomic coordinates and anisotropic thermal parameters have been refined by full-matrix least-squares methods from diffractometer data to a final R value of 0.032 for 947 independent observed reflections. Each copper atom in the structure is effectively chelated by an enveloping nitrilotriacetate (NTA) group by means of four connecting bonds (three O-Cu, one N-Cu). Additional contacts between neighboring NTA groups and the copper complete a distorted octahedral coordination which is nevertheless characterized by the usual two long-four short arrangement of bonds. The Cu-O bond lengths range between 1.950 (4) and 2.351 (4) Å. The sodium atoms are bonded to four adjacent NTA groups and a water molecule with Na-O distances from 2.282 (5) to 2.372 (5) Å. Evidence for a 1:2 Cu-NTA complex and speculation about the Cu-NTA structure in solution are presented.

Introduction

For ecological reasons limits have recently been imposed on the maximum phosphate content of detergents. These restrictions have prompted the use of other solubilizing agents, the best known (and most controversial) of which is the trisodium salt of nitrilotriacetic acid (Na_3NTA). Considerable research has been carried out on nitrilotriacetic acid (H_3NTA) and its derivatives including several crystallographic studies: $K_2Zr(NTA)_2 \cdot H_2O$,[1] H_3NTA,[2] $Na_3NTA \cdot H_2O$,[3] and $CaHNTA \cdot 2H_2O$.[4] In addition, preliminary reports have appeared for $LiCuNTA \cdot 3H_2O$[5] and $K_4Ni(NTA)_2 \cdot 8H_2O$.[6] In general, these investigations have shown the NTA group to be multidentate, but shared among several cations in the crystal structure. In $CaHNTA \cdot 2H_2O$, for example, although five Ca-NTA bonds exist, only one bond is formed between an NTA group and a particular calcium atom. A test in our laboratory, however, has suggested that the interaction between Cu^{2+} and the NTA^{3-} ion could be considerably stronger and more specific.

In our experiment, an aqueous solution of 0.1 M Na_3NTA (pH ~11) was circulated continuously through a coil of copper tubing. During a period of several days the initially colorless solution became blue suggesting a complex had been formed between the NTA group and copper ions leached from the inside of the tubing walls. This effect is somewhat alarming since much modern plumbing is made of copper and could conceivably be damaged by the presence of NTA in washing solutions. The present X-ray analysis was undertaken to investigate the chemical structure of the complex formed.

Experimental Section

When an aqueous solution of H_3NTA and $Cu(NO_3)_2$ (made basic with Na_2CO_3) is evaporated to dryness, crystals of sodium nitrilotriacetatocopper(II) monohydrate, $NaCuN(CH_2COO)_3 \cdot H_2O$ (hereafter $NaCuNTA \cdot H_2O$), precipitate as pale blue prisms. Infrared spectra and X-ray powder patterns confirm that these are identical with crystals formed from solutions obtained by passing aqueous Na_3NTA through copper pipes. The crystals precipitate together with a darker polycrystalline form which is thought to be a 1:2 Cu-NTA complex from atomic absorption analysis (for Na and Cu) and preliminary X-ray work.

$Cu(H_2NTA)_2 \cdot 2H_2O$. X-Ray investigation of this dark blue compound was limited to a photographic determination of the unit cell parameters and space group. The cell constants determined are $a = 6.86$ (3), $b = 14.05$ (3), $c = 9.42$ (3) Å, and $\beta = 91° \; 45 \; (10)'$, with the monoclinic space group $P2_1/c$ ($C_{2h}{}^5$) indicated by the systematic absences $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$. The density measured by flotation, 1.72 (2) g cm^{-3}, and the unit cell dimensions suggest the tentative formula $Cu(H_2NTA)_2 \cdot 2H_2O$. For this formula the calculated density is 1.76 g cm^{-3} assuming two formula units per unit cell.[7]

$NaCuNTA \cdot H_2O$. The remainder of the paper refers to the pale blue $NaCuNTA \cdot H_2O$ compound for which a complete structure determination has been carried out. The crystal selected for the X-ray measurements was mounted on an arcless goniometer head with a approximately parallel to the ϕ axis of the diffractometer. The {011} faces were prominent and the crystal measured 0.17 × 0.13 mm in the [011] and [01$\bar{1}$] directions, respectively. The overall length was 0.26 mm with the top capped by four faces. The unit cell parameters were derived by a least-squares technique from the optimum settings of 22 reflections aligned on an automatic four-circle diffractometer using a takeoff angle of 1.5° and a graphite monochromator with Mo Kα_1 radiation (λ 0.70926 Å). The cell dimensions were determined to be $a = 9.899$ (5), $b = 12.565$ (5), and $c = 7.548$ (5) Å at 22°. The crystal is orthorhombic and belongs to the space group $P2_12_12_1$

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(7) Some structural deductions about this compound can be made because the presence of only two formula units in the unit cell would position the Cu atoms at crystallographic centers of symmetry. This would allow a maximum of three bonds between copper and each NTA group for the coordination number not to exceed 6. Peaks at 1695 and 1725 cm^{-1} in the infrared spectrum of the solid (measured in Nujol) can be assigned to uncoordinated -COOH stretching vibrations and suggest that two carboxylate groups are not bonded directly to the metal atom. The remaining Cu-N and Cu-O bonds between Cu and each NTA group must be arranged so as to preserve centrosymmetry, and two water molecules probably bond to Cu to complete an octahedral configuration.