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Three-Dimensional Macrocyclic Encapsulation Reactions. II.[1] Synthesis and Properties of Nonoctahedral Clathro Chelates Derived from Tris(2-aldoximo-6-pyridyl)phosphine and Boron Trifluoride or Tetrafluoroborate

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A synthetic procedure has been developed which affords a new series of six-coordinate metal(II) complexes distinguished by a bicyclic ligand framework which encapsulates the metal ions and imposes a trigonal prismatic (TP) or near-TP stereochemistry. The clathro-chelate complexes, fluoroborotris(2-aldoximo-6-pyridyl)phosphinemetal(II) cations, $M(PccBF)^+$ (**7**), containing Fe(II), Co(II), Ni(II), and Zn(II), were synthesized by closure reactions of tris(2-aldoximo-6-pyridyl)phosphinemetal(II) species, $[M(P(Hpox)_3\text{-}H)]^+$, with boron trifluoride etherate or fluoroborate ion and isolated as fluoroborate salts. Preparations of these oxime complexes as their perchlorate salts (M = Co(II), Ni(II), Cu(II), Zn(II)) and the parent ligand tris(2-aldoximo-6-pyridyl)phosphine are described. Evidence is presented which indicates that the Co(II), Ni(II), and Zn(II) oxime complexes exist partially or wholly as structure **6**, which is favorable for subsequent closure reactions. Electronic, nmr, and infrared spectral data, magnetic moments, and conductivities are given for the four $[M(PccBF)](BF_4)$ salts. X-Ray results have shown that the desired TP coordination has been very closely approached in $Ni(PccBF)^+$ and that the Co(II) and Zn(II) salts are isomorphous with the Ni(II) compound. Comparison of this structure with those of analogous metal(II) complexes of open trifurcated sexadentates reveals the greater tendency of the bicyclic PccBF ligand system to stabilize TP stereochemistry.

Introduction

One of the most important classes of metal template reactions is formation of monocyclic ring systems which can function as multidentate ligands.[2,3] In contrast, the intriguing possibility of synthesizing polycyclic ring systems and their derivative complexes by such reactions has been little explored, and only two examples of their formation have been reported.[4,5] Both involve preparation of bicyclic metal-containing species by reaction at specific sites in the coordinated ligands of isolable precursor complexes. The work of Boston and Rose[5] is particularly relevant to the present investigation and other studies under way in this laboratory. By reaction of tris(dimethylglyoximato)cobalt(III) anion with boron trifluoride etherate they obtained the cobalt(III) species $[Co(dmg)_3(BF)_2]^+$, which is the first example of a discrete species containing a metal ion completely encapsulated by a bicyclic ring system. Such species were anticipated by Busch,[3] who coined the general term "clathro chelate" for encapsulated complexes. Subsequent work has led to the isolation of $[Co(dmg)_3(BF)_2]$[6] and X-ray demonstration of the structures of the Co(II) and Co(III) complexes as slightly distorted trigonal prismatic (TP) and intermediate between octahedral and TP,[7] respectively. The torsional or "twist" angle ϕ of the two triangles of donor atoms whose planes are normal to the threefold axis are 8.5 and 45°, respectively, from the TP arrangement ($\phi = 0°$).

The near-TP structure of $[Co(dmg)_3(BF)_2]$ is of particular interest because of the uncommon occurrence of complexes which possess or closely approach this geometry. In other discrete species TP coordination has been established (by X-ray methods) for certain oxidized metal tris(dithiolenes)[8] and tris(selenetenes),[9] the $Co\text{-}O_6$ unit in one diastereomer of $[Co(Co(OCH_2CH_2NH_2)_3)_2]^{2+}$,[10] and *cis,cis*-1,3,5-tris(pyridine-2-carboxaldimino)cyclohexanezinc(II) cation ($\phi = 2.0\text{-}6.6°$).[11] In addition, a number of tris-chelate complexes containing four- and five-membered chelate rings have been structurally characterized and shown to possess twist angles of *ca.* 27-44°.[12] Intermediate coordination geometry has also been found in the zinc(II) complex of the sexadentate ligand 1,1,1-tris(pyridine-2-carboxaldimino)ethane, for which $\phi = 25\text{-}30°$.[13]

The present investigation was undertaken in order to devise a synthetic procedure of sufficient generality that a series of bicyclic clathro chelates containing different metal ions could be obtained. Because none of the above complexes possesses TP or near-TP geometry solely or necessarily as a consequence of ligand structural requirements, a concomitant objective was the design of a ligand system which would constrain the coordination unit to, or close to, TP geometry. This paper reports the design and details of the synthesis and

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the characterization of a series of encapsulation complexes containing iron(II), cobalt(II), nickel(II), and zinc(II). The synthetic procedure has been outlined recently elsewhere.[1] These complexes contain three pyridyl-2-aldimine units, which are also common to less constrained complexes derived from open trifurcated sexadentates, certain physical properties of which will be compared to those of the clathro chelates in a subsequent publication.

Experimental Section

Preparation of Compounds. (a) Precursors for Encapsulation Reactions. 6-Bromopyridine-2-aldehyde (1).—To a slurry of 190 g (0.800 mol) of 2,6-dibromopyridine in 1500 ml of ether, cooled below −60°, 500 ml of 1.6 *N* *n*-butyllithium (0.800 mol) in hexane was added at a rate such that the temperature did not exceed −60° (the use of a pentane slush bath is recommended). After addition was complete, the reaction mixture was allowed to warm to −40° for 15 min; a clear yellow solution resulted. (Warming above −40° results in a green solution and lower yields.) This solution was cooled to −80° and 64 g (0.88 mol) of dry dimethylformamide in 100 ml of ether was added over 20 min as the temperature was allowed to rise to −70°. Stirring was continued for 2 hr at this temperature, producing a gray precipitate. The mixture was then allowed to warm to −10° and hydrolyzed with 300 ml of 6 *N* hydrochloric acid. The aqueous phase was separated and extracted with ether (three 150-ml portions). The extracts and ether phase were combined, washed with water (three 200-ml portions), dried (sodium sulfate), and concentrated on a rotary evaporator until crystallization commenced. Concentration of the mother liquor and addition of *n*-pentane gave a second crop. Recrystallization from ether–*n*-pentane gave 111 g (75%) of pure product as white flakes; mp 80–81.5°; mass spectrum: *m/e* parent ions 185, 187; pmr ($CDCl_3$): multiplet, −7.60 to −7.92 ppm, 3 (ring protons); singlet, −9.93 ppm, 1 (CHO); ir (Kel-F): ν_{CO} 1700 cm^{-1}. *Anal.* Calcd for C_6H_4BrNO: C, 38.74; H, 2.17; N, 7.53. Found: C, 38.52; H, 2.08; N, 7.53.

2-(1,3-Dioxolan-2-yl)-6-bromopyridine (2).—Protection of the aldehyde group in 1 was required for a subsequent transmetalation reaction. A mixture of 111 g (0.60 mol) of 6-bromopyridine-2-carboxaldehyde, 72 ml (*ca.* 1.2 mol) of ethylene glycol, 30 g of *p*-toluenesulfonic acid, 69 g (0.66 mol) of 2,2′-dimethoxypropane, and 300 ml of benzene was slowly distilled over a ~2-hr period until the boiling point exceeded 61°. The undistilled liquid was then added to 750 ml of saturated aqueous sodium carbonate solution, the aqueous and organic layers were separated, and the aqueous layer was extracted with benzene (four 100-ml portions). The combined benzene layer and extracts were washed with two 100-ml portions of water, dried (sodium sulfate), and evaporated to yield a pale yellow oil. The oil was distilled and the fraction with bp 120–122° (1 mm) was collected to give 105 g (76%) of pure product; pmr ($CDCl_3$): multiplet, *ca.* −6.67 ppm, 3 (pyridine ring protons); singlet, −4.85 ppm, 1 (methine H); doublet (J = 2 Hz), −3.17 ppm, 4 (CH_2CH_2). *Anal.* Calcd for $C_8H_8BrNO_2$: C, 41.76; H, 3.50; N, 6.09. Found: C, 41.75; H, 3.82; N, 6.17. The compound should be stored in the dark due to its noticeable darkening when exposed to light.

Tris[2-(1,3-dioxolan-2-yl)-6-pyridyl]phosphine (3).—In an initial experiment designed to assess the extent of lithiation at the pyridine 6 carbon, a solution of 5.8 g (25 mmol) of 2-(1,3-dioxolan-2-yl)-6-bromopyridine in 20 ml of ether was added to 16 ml of 1.6 *N* *n*-butyllithium (25 mmol) in 50 ml of *n*-hexane–ether maintained at −60°. A tan precipitate appeared immediately. After 10 min of stirring 10 ml of methanol was added, causing the precipitate to redissolve. The solution was treated with 10 ml of water. Straightforward work-up of the organic layer afforded 3.20 g (85%) of 2-(1,3-dioxolan-2-yl)pyridine as a pale yellow oil, bp 115° (4 mm) (lit.[14] bp 122° (4 mm)), and further identified by its pmr spectrum.

A solution of 55.5 g (0.242 mol) of 2-(1,3-dioxolan-2-yl)-6-bromopyridine in 450 ml of ether was added during 15 min to a solution of 150 ml of 1.6 *N* *n*-butyllithium (0.240 mol) in 900 ml of ether at −100° (pentane slush bath). This temperature was maintained during the addition, after the completion of which it was allowed to rise to −70°. The resulting orange suspension was stirred for an additional 30 min, its temperature reduced to −100°, and 7 ml (0.080 mol) of freshly distilled phosphorus trichloride added during 45 min while this temperature was maintained. The yellow reaction mixture was stirred at −100° for 1 hr and then was allowed to warm to −10° while stirring was continued for a 6-hr period as the mixture warmed to room temperature. The reaction mixture was then treated with just enough methanol (*ca.* 50 ml) to cause separation of a yellow-orange sludge from a colorless solution. The solution was decanted and discarded, and 250 ml of chloroform was added to the solid residue. The suspension was stirred until all the solid dissolved; the solution was then washed with water (three 50-ml portions) and dried (sodium sulfate), and the solvent was removed. The remaining viscous red oil was quickly dissolved in 75 ml of hot ethanol. Slow cooling of this solution gave 19.2 g of yellow crystals, which were further purified by recrystallization from ethanol and afforded 15.4 g (40%) of colorless crystals, mp 137–138°; pmr ($CDCl_3$): multiplet, *ca.* 7.47 ppm, 3 (pyridine ring protons); singlet, −5.84 ppm, 1 (methine H); singlet, −4.07 ppm, 4 (CH_2CH_2). *Anal.* Calcd for $C_{24}H_{24}N_3O_6P$: C, 59.86; H, 5.02; N, 8.73. Found: C, 60.95; H, 5.04; N, 8.79.

Tris(2-aldoximo-6-pyridyl)phosphine (5).—Tris[2-(1,3-dioxolan-2-yl)-6-pyridyl]phosphine (10.5 g, 22 mmol) was suspended in 200 ml of degassed water at 50° and 15 ml of concentrated hydrochloric acid and 14 g (200 mmol) of hydroxylamine hydrochloride were added. A pale yellow precipitate formed after stirring for 1 hr. The suspension was cooled in an ice bath, treated dropwise with aqueous sodium hydroxide solution until neutral, and filtered. The crude trioxime was washed with water and ethanol and recrystallized twice from dimethylformamide–ethanol. After drying the product at 100° for 24 hr, 6.4 g (75%) of colorless needles was obtained; mp (preheated to 200°) 239–241° dec; ir: ν_{CN} 1490 cm^{-1} (Kel-F); pmr (DMSO-d_6): multiplet, −7.19 to −7.92 ppm, 3 (ring protons); singlet, −8.14 ppm (HC=N), 1; singlet, −11.84 ppm, 1 (NOH). *Anal.* Calcd for $C_{18}H_{15}N_6O_3P$: C, 54.82; H, 3.81; N, 21.32. Found: C, 54.61; H, 4.09; N, 21.08.

(b) Tris(2-aldoximo-6-pyridyl)phosphinemetal(II) Complexes, [M(P(Hpox)$_3$-H)](ClO$_4$) (6).—The following procedure was employed for the preparation of the M = Co(II), Ni(II), Cu(II), and Zn(II) complexes. Filtered solutions of tris(2-aldoximo-6-pyridyl)phosphine (0.39 g, 1.0 mmol) in 100 ml of hot absolute ethanol and $M(H_2O)_6(ClO_4)_2$ (1.0 mmol) in absolute ethanol were mixed and cooled, and the crystalline product was filtered off. In the Co(II) preparation the solutions were degassed before mixing and the mixed solution was filtered before product separation to remove a small amount of insoluble material. Analytically pure products were obtained by recrystallization from the indicated solvents followed by drying to constant weight at 100° *in vacuo* (M, solvent, per cent yield): Co(II), acetone, 59%; Ni(II), acetone, 82%; Cu(II), ethanol, 68%; Zn(II), ethanol, 50%. Attempts were also made to prepare the analogous Mn(II) and Fe(II) complexes by this method and variations thereof but were unsuccessful. Apparent mixtures of compounds or highly insoluble materials were obtained.

(c) Fluoroborotris(2-aldoximo-6-pyridyl)phosphinemetal(II) Complexes, [M(PccBF)](BF$_4$) (7). (i) Reaction with Boron Trifluoride Etherate.—The following procedure was employed for the preparation of the M = Fe(II), Co(II), Ni(II), and Zn(II) complexes. One equivalent of $M(H_2O)_6(BF_4)_2$ and 1 equiv of tris(2-aldoximo-6-pyridyl)phosphine were dissolved in 20 ml of acetonitrile. The solvent was removed *in vacuo* and the material so obtained was dissolved in 20 ml of boron trifluoride etherate (freshly distilled from calcium hydride). After stirring the solution for 12 hr at room temperature, the product was precipitated by the addition of 200 ml of ether, collected by filtration, and washed with 200 ml of ether. This material was dissolved in 20 ml of boron trifluoride etherate and the entire procedure was repeated, yielding the crude product in 50–75% yield. Analytically pure products were isolated by recrystallization from acetonitrile–ethyl acetate (Fe(II), Zn(II)) and acetone–isobutyl alcohol (Co(II), Ni(II)). Attempted recrystallization of the Fe(II) and Zn(II) complexes from hot methanol resulted in partial decomposition. Analytical data are set out in Table I. Magnetic, conductivity, and spectral data are given in Tables II–IV. Use of the Co(II) and Ni(II) complexes [M(P(Hpox)$_3$-H)](ClO$_4$) in this procedure yielded the corresponding clathrochelate cations, identified by their nmr and infrared spectra (*cf.*

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TABLE I

ANALYTICAL DATA FOR [M(P(Hpox)$_3$-H)](ClO$_4$)^a (A) AND [M(PccBF)](BF$_4$)^b (B)

M	Color	% calcd C	% calcd H	% calcd N	% calcd F	% found C	% found H	% found N	% found F
(A) Co	Yellow-brown	39.19	2.56	15.23	...	39.14	2.80	14.75	...
Ni^c	Red	39.21	2.56	15.23	...	38.75	2.38	14.71	...
Cu	Olive	38.86	2.54	15.11	...	38.62	2.65	15.23	...
Zn	Pale yellow	38.73	2.53	15.06	...	38.49	2.44	15.12	...
(B) Fe	Dark red	38.34	2.15	14.91	16.85	38.55	2.27	14.78	16.77
Co	Yellow-brown	38.19	2.12	14.85	16.80	37.50	2.20	14.54	16.98
Ni	Yellow-orange	38.21	2.12	14.85	16.80	37.78	2.06	14.47	16.40
Zn	Pale yellow	37.71	2.10	14.66	16.57	37.50	2.28	14.46	16.38

[a] Stoichiometry $C_{18}H_{14}ClN_6O_7PM$. [b] Stoichiometry $C_{18}H_{12}B_2F_5N_6O_3PM$. [c] Recrystallized from acetone; found for product from ethanol recrystallization: C, 39.58; H, 2.77; N, 14.80.

TABLE II

SPECTRAL, MAGNETIC, AND CONDUCTIVITY DATA FOR [M(P(Hpox)$_3$-H)](ClO$_4$) (A) AND [M(PccBF)](BF$_4$) (B)

M	λ_{max} (ϵ)^a	μ_{eff},^{b} BM	Λ^c
(A) Co	7900 (5.4), 10,500^d (6.0), 12,600^d (5.2), ~20,500 sh (~300), 28,500 sh (3500), 34,000 sh (~11,500)	4.76 (5.0^i)	142
Ni	9500 (19), 10,900 sh (15), 20,500 sh (500), 25,400 (2100), 29,000 sh (3500); 34,000 sh (12,000)	2.29,^{e} 2.51^f (1.6,^{g} 1.9,^{h} 2.4^i)	141
Cu	18,100 (220), 28,200 sh (3900), 34,000 (13,000)	1.81	152
Zn	28,200 sh (2400), 34,200 (15,000), 35,400 (18,000)	Dia	145
(B) Fe	12,000 sh (8.1), 19,200 (12,700), 20,800 sh (9200), 25,300 (2100), 34,000 (14,800), 37,700 sh (39,400)	0.4	154
Co	8130 (3.6), 11,800^d (6.3), 14,250^d (5.7), ~22,000 sh (230), 27,000 (2500), 35,300 (16,000), ~38,000 (24,000)	4.91	145
Ni	9380 (28), 11,000 (27), ~20,500 sh (50), ~22,200 sh (80), ~29,000 sh (3300), 34,500 (14,700), 38,000 (24,000)	3.11	151
Zn	~30,500 sh (2,400), 35,500 (14,700), 39,000 (22,500)	Dia^j	146

[a] In cm^{-1}; acetonitrile solution. [b] Solid state, ~25°; solution values in parentheses. [c] In ohm^{-1} equiv^{-1} cm^2; acetonitrile solution, ~25°; ((n-C$_3$H$_7$)$_4$N)(ClO$_4$), $\Lambda = 158$. [d] Bands possibly due to Co(I) impurity. [e] Product from ethanol recrystallization. [f] Product from acetone recrystallization. [g] DMF. [h] DMSO. [i] Acetonitrile. [j] $\chi_M = -254 \times 10^{-6}$ cgsu.

TABLE III

^{1}H AND ^{19}F NMR DATA FOR [M(P(Hpox)$_3$-H)](ClO$_4$) (A) AND [M(PccBF)](BF$_4$) (B) AT ~30°

M	Solvent	Shifts,^{f} ppm Ring H	HC=N	B—F^a	BF$_4^-$
(A) Ni	DMF-d_7	−9.9, −18.4, −18.7	−51.4	...	...
	DMSO-d_6	−10.6, −28.0, −32.8	d	...	...
Zn^e	DMSO-d_6	−7.9^b	−7.9^c	...	...
(B) Fe	DMSO-d_6	−8.5^b	−9.33	+102.8 (13)	+86.7
Co	DMSO-d_6	−31.4, −96.4, −121.4	d	+69.9	+84.3
Ni	DMSO-d_6	−23.0, −34.0, −65.1	−214	+176.5	+80.5
Zn	DMSO-d_6	−7.9,^{b} −8.3^b	−8.31	+103.2 (12)	+87.0

[a] $J_{^{11}B-F}$(Hz) in parentheses. [b] Center of complex multiplet. [c] Not distinguishable from ring H. [d] Not observed. [e] OH signal at −11.7 ppm. [f] Downfield and upfield shifts relative to internal references (TMS, C$_6$H$_5$CF$_3$) are indicated by − and + signs, respectively.

TABLE IV

INFRARED BANDS OF CRYSTALLINE [M(PccBF)](BF$_4$) IN THE 1650–400-CM^{-1} REGION^a

M	ν, cm^{-1}
Ni	1610 s, 1580 sh, m, 1545 m, 1535 m, 1450–1445^b s, 1410 m, 1390 m, 1350 w, 1290 w, 1262 w, 1240 m, 1228 m, 1220 s, 1185 m, 1150 w, 1112 s, 1090 m, 1062 s, 1018 m, 962 s, 954 w, 901 s, 815 m, 808 m, 749 m, 720 m, 659 s, 592 w, 564 m, 519 m, 493 m, 462 w, 448 w, 420 m
Zn	1615–1605^b s, 1580 m, 1550 m, 1535 m, 1450–1445^b s, 1410 m, 1390 w, 1340 w, 1292 w, 1265 w, 1232 m, 1222 m, 1192 s, 1182 s, 1110 s, 1090 w, 1060 s, 1022 m, 960 s, 943 m, 892 s, 820 m, 808 m, 750 m, 717 m, 654 s, 590 w, 553 m, 519 m, 489 m, 459 m, 411–415^b m
Fe	1590 s, 1565–1560^b m, 1510 s, 1460 m, 1390–1380^b m, s, 1315 w, 1288 w, 1260 m, 1238 m, 1220 w, 1205 m, 1148 m, 1110 s, 1095 w, 1065 s, 1000 w, 968 s, 914 s, 892 w, 808–802^b m, 749 s, 735 w, 725 w, 696 w, 675 m, 662 m, 610 w, 596 w, 570 w, 532 w, 519 m, 498 w, 475 w, 445 w, 417 m

[a] Data obtained using Kel-F and Nujol mulls. [b] Closely spaced doublet.

Tables III and IV), as mixed salts. The four clathro chelates were found to have the same R_f value (~0.4) in tlc on Bakerflex aluminum oxide 1B-F strips using acetonitrile as the solvent.

(ii) **Encapsulation with Tetrafluoroborate.**—The tetrafluoroborate hexahydrate salt of iron(II), cobalt(II), nickel(II), or zinc(II) (1 mmol), 1 mmol (0.39 g) of tris(2-aldoximo-6-pyridyl)phosphine, and 1 mmol (0.12 g) of sodium tetrafluoroborate were refluxed in 50 ml of acetonitrile under a nitrogen atmosphere for 12 hr. The solvent was removed *in vacuo* and the solid was triturated with warm water (two 20-ml portions), filtered, and washed with small volumes of ethanol and ether. Pure products were obtained by recrystallization using the solvents given in the preceding preparation. Identity of these salts with those isolated in the boron trifluoride etherate reactions were established by their nmr and infrared spectra (Tables III and IV). In addition the nickel(II) complex was analyzed. Found: C, 38.21; H, 2.17; N, 14.63; F, 17.24.

The four complexes were also prepared by a somewhat more efficient procedure. A mixture of 0.56 g (1.42 mmol) of tris(2-aldoximo-6-pyridyl)phosphine, 1.5 mmol of metal(II) tetrafluoroborate hexahydrate, and 0.1 g of sodium tetrafluoroborate in 25 ml of acetonitrile was refluxed for 8 hr, cooled, and chromatographed on a 15-mm diameter column containing 25 g of Merck reagent aluminum oxide. Elution with acetonitrile followed by volume reduction of the eluate effected crystallization of the pure complex. After drying *in vacuo* the following yields were obtained: Fe(II), 77%; Co(II), 58%; Ni(II), 59%; Zn(II), 31%.

Attempts to prepare [Mn(PccBF)](BF$_4$) by the tetrafluoroborate encapsulation reaction and [Cu(PccBF)](BF$_4$) by this reaction or by treatment of [Cu(P(Hpox)$_3$-H)](ClO$_4$) with boron trifluoride etherate failed.

(d) **Reaction of Ni(Hdmg)$_2$ with Tetrafluoroborate.**—Bis(dimethylglyoximato)nickel(II) (0.29 g, 1.0 mmol) and 6.65 g

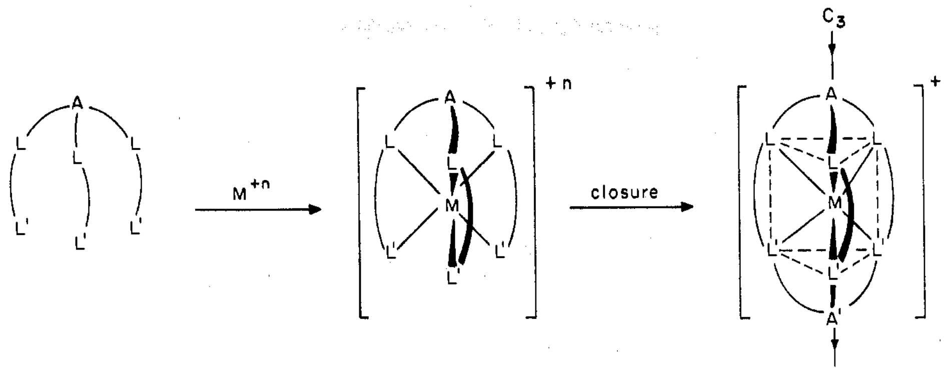


Figure 1.—General scheme for the preparation of a TP clathro chelate by ring closure in an intermediate complex derived from an open trifurcated sexadentate ligand. No specific stereochemistry of the intermediate six-coordinate complex is implied.

(60 mmol) of sodium tetrafluoroborate were refluxed under nitrogen in 175 ml of acetonitrile for 48 hr. The suspension was filtered and solvent completely removed from the red-orange solution. The solid residue was washed thoroughly with water and recrystallized twice from acetone to yield 90 mg (27%) of a red-orange crystalline product which was identified as the half-closed macrocycle Ni(Hdmg)(BF_2dmg) (**12**). *Anal.* Calcd for $C_8H_{13}BF_2N_4O_4Ni$: C, 28.55; H, 3.89; N, 16.64; F, 11.29. Found: C, 29.11; H, 3.97; N, 16.62; F, 10.64.

The compound is diamagnetic. Infrared data (Kel-F mull): ν_{CN} 1610, 1530 cm^{-1}, ν_{OH}, 1710 cm^{-1} (very broad). The mass spectrum (70 eV) showed a principal parent ion peak at *m/e* 336 and peaks corresponding to the loss of F, BF_2, and dmg. The fragments $Hdmg^+$ and $HdmgBF_2^+$ were also identified. Nmr (DMSO-d_6): ^1H signals of equal intensity at -2.07 and -2.14 ppm; ^{19}F signal (quartet, J_{BF} = 6.4 Hz) 13.4 ppm downfield of C_6F_6 internal reference.

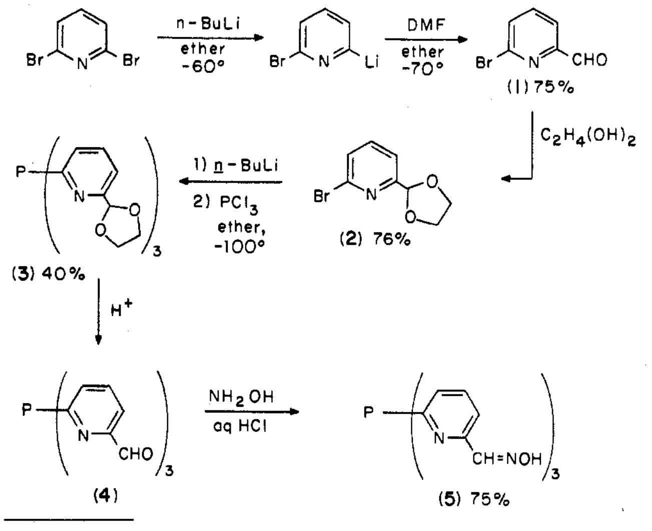
Physical Measurements.—Electronic and infrared spectra were recorded on a Cary Model 14 and a Perkin-Elmer Model 337 grating spectrophotometer, respectively. Conductivities were determined using a Serfass conductivity bridge and $\sim10^{-3}$ *M* acetonitrile solutions. Magnetic moments of solids were determined by the Faraday method ($HgCo(NCS)_4$ calibrant) and solution moments were obtained by the usual nmr method, employing cyclohexane reference signals. Nmr spectra were measured on a Varian HA-100 or Hitachi Perkin-Elmer R-20B spectrometer. Proton and fluorine chemical shifts in Table III are referenced to TMS and $C_6H_5CF_3$ as internal standards, respectively. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-6D spectrometer operating at 70 or 80 eV.

Results and Discussion

In our approach to the design and synthesis of complexes containing encapsulated metal ions with TP or near-TP coordination, a strategy has been employed which has two basic requirements: (a) the presence in the final structure of planar, conjugated five-membered chelate rings attached to two anchoring atoms or groups centered on the C_3 axis by linkages sufficiently inflexible to prevent substantial relative motion of any three donor atoms; (b) the formation, in the last synthetic step, of the macrocyclic cage implied in (a) around the metal ion, thereby encapsulating it. A number of systems which conform to these requirements and are plausible on a synthetic basis can be readily conceived. A general formulation of the procedure used in this work is shown in Figure 1. The open trifurcated sexadentate $A(L-L')_3$, which contains functional groups near L' suitable for a subsequent ring-closure reaction, is treated with a metal ion to form the complex $[M(A(L-L')_3)]^{n+}$. This species is then subjected to a closure reaction to generate the bicyclic clathro chelate $[M(A(L-L')_3A')]^{n'+}$. The stereochemistry of the product is constrained to be TP or nearly so because of the presence of the capping groups A and A', the length and rigidity of the fragments A–L and A'–L', and the nature of the chelate ring as stated in requirement (a). The essential property of the intermediate complex of charge $n+$ is that its stability and spatial arrangement of reactive sites near L' be such that closure can be accomplished. The charge $n'+$ of the encapsulation complex will be dependent upon the nature of the closure reagent.

Preparation of Precursor Ligand and Complexes.—Although a number of sexadentate ligands and their complexes are well known, including several of the open trifurcated types reported prior[15–19] to and during[11,13,20] this investigation, none was suitable for the sequence in Figure 1 because of the lack of functionalities necessary for the closure step. Requirements (a) and (b) are met to a satisfactory degree by complexes derived from the previously unknown ligand tris(2-aldoximo-6-pyridyl)phosphine, $P(Hpox)_3$. When functioning as a sexadentate this molecule can form three unsaturated chelate rings of the pyridyl-2-aldimine type such as are present in open sexadentate[11,13,15–20] and bis- and tris-chelate complexes[21] derived from pyridine-2-carboxaldehyde. As shown in Chart I $P(Hpox)_3$ (**5**) can be obtained in 17% overall yield from 2,6-dibromopyridine

CHART I
SYNTHESIS OF $P(Hpox)_3$



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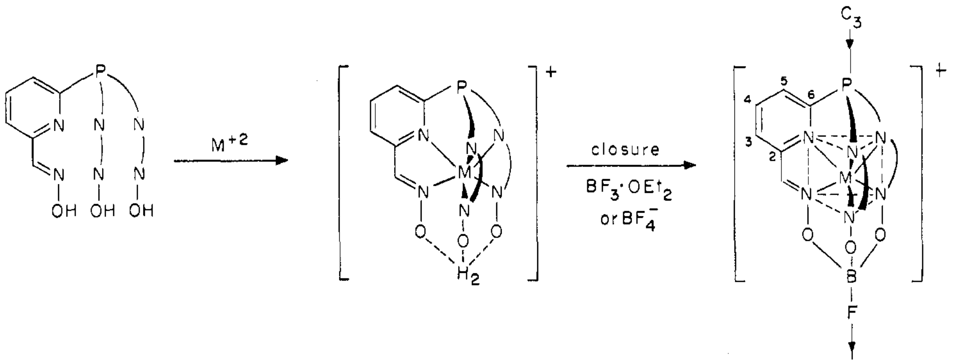

$P(Hpox)_3$ (5) $[M(P(Hpox)_3\text{-}H)]^+$ (6) $[M(PccBF)]^+$ (7)

Figure 2.—Synthesis of $M(PccBF)^+$ complexes from $P(Hpox)_3$ using boron trifluoride etherate or tetrafluoroborate ion as ring-closure reagents. No specific stereochemistry of the intermediate six-coordinate complex **6** is implied. For purposes of clarity only one chelate ring structure is shown in each species.

in a six-step process. The intermediate compounds **1**–**3** were isolated and characterized. Protection of the aldehyde group of **1** was required in the subsequent transmetalation step leading to **3**. Attempts to obtain the trialdehyde **4** by acid hydrolysis of **3** afforded a viscous light yellow oil which could not be crystallized. This material was identified as nearly pure **4** by its pmr and infrared spectra and its mass spectrum, which displayed an intense parent ion peak at *m/e* 349. Acid hydrolysis of **3** for a period of *ca.* 24 hr resulted in carbon–phosphorus bond cleavage and yielded the previously unknown 6,6′-diformyl-2,2′-bipyridyl.[22] The formation of **3** represents the first reported case of the preparation of a 2,6-disubstituted pyridine by transmetalation reactions involving organolithium reagents. A previous attempt to carry out a diinterconversion between 2,6-dibromopyridine and *n*-butyllithium in one step was unsuccessful.[23] Reaction between a 2- or 6-lithiopyridyl species and phosphorus trichloride, as in the conversion **2** → **3**, is readily generalized. Tris(2-pyridyl)phosphine[24] and related compounds, including tris[6-(2,2′-bipyridyl)]phosphine, may be prepared by this route. These and other reactions involving lithiopyridyl species will be described elsewhere.[22]

Reaction of cobalt(II), nickel(II), copper(II), and zinc(II) salts with $P(Hpox)_3$ in acetonitrile yields the cations $[M(P(Hpox)_3\text{-}H)]^+$, which may be isolated as analytically pure perchlorate salts. Physical data are given in Tables II and III. Their composition and behavior as 1:1 electrolytes in acetonitrile are consistent with the ionization of a single proton from the ligand upon complex formation. This behavior finds analogy with the spontaneous ionization of one proton by the iron(II) tris chelates of pyridine-2-carboxaldoxime[25] (Hpox) and methyl 2-pyridyl ketoxime.[26] The detection or isolation of chelate complexes of these ligand and their deprotonated forms further attests to the enhanced acidity of oxime protons upon coordination of ligands closely analogous to $P(Hpox)_3$.[27,28] Infrared spectra of the solid Co(II), Ni(II), Cu(II), and Zn(II) complexes in the 1600–400-cm^{-1} region are quite similar. The strong ν_3 and ν_4 absorptions of uncoordinated perchlorate ions at ~1100 and 620 cm^{-1}, respectively, were readily identified.[29] Bands of medium intensity at 1240–1225 cm^{-1} may be attributed to N–O absorptions if previous assignments[5,30] are accepted. A second N–O band expected near 1100 cm^{-1} [5,28,30] was presumably obscured by perchlorate absorption. Five or six medium to strong bands were found in the 1600–1400-cm^{-1} range. Unlike $Ni(Hpox)_3^{2+}$ [28] and other complexes containing the pyridyl-2-aldimine unit,[11b,13,19,31] no features in the 1660–1600-cm^{-1} interval assignable to perturbed C=N stretches were present. In this sense the complexes are similar to partially deprotonated species such as $Ni(Hdmg)_2$ for which ν_{CN} occurs at 1580 cm^{-1}.[30] The C=N absorption could not be distinguished from the four pyridine ring bands[28] occurring in this range.

In the scheme shown in Figure 2 for the synthesis of the clathro chelates $[M(PccBF)]^+$, $[M(P(Hpox)_3\text{-}H)]^+$ complexes act as intermediates. The indicated structure **6** is intended to represent six-coordination, but without specification of detailed geometry, and attendant interaction of the three oximato oxygens and two protons by hydrogen bonding. Such a structure would appear favorable for the ring-closure reactions described below, and attempts have been made to establish its existence in solution for the three complexes (Co(II), Ni(II), Zn(II)) which undergo closure. The Co(II) complex has a spin-quartet ground state as a solid and in DMSO solution, consistent with the behavior of the six-coordinate sexadentate species $[Co((py)_3tach)]^{2+}$ [11b] (**8**) and $[Co((py)_3tame)]^{2+}$ [13] (**9**) whose schematic structures are given in Figure 3. It exhibits a ligand band at 7900 cm^{-1} (*cf.* Table II) in acetonitrile comparable in energy to near-infrared transitions of these two complexes $[Co(py_3tren)]^{2+}$ (**10**, Figure 3) and $[Co(PccBF)]^+$ in this solvent.[32] Therefore, structure **6** appears to be a

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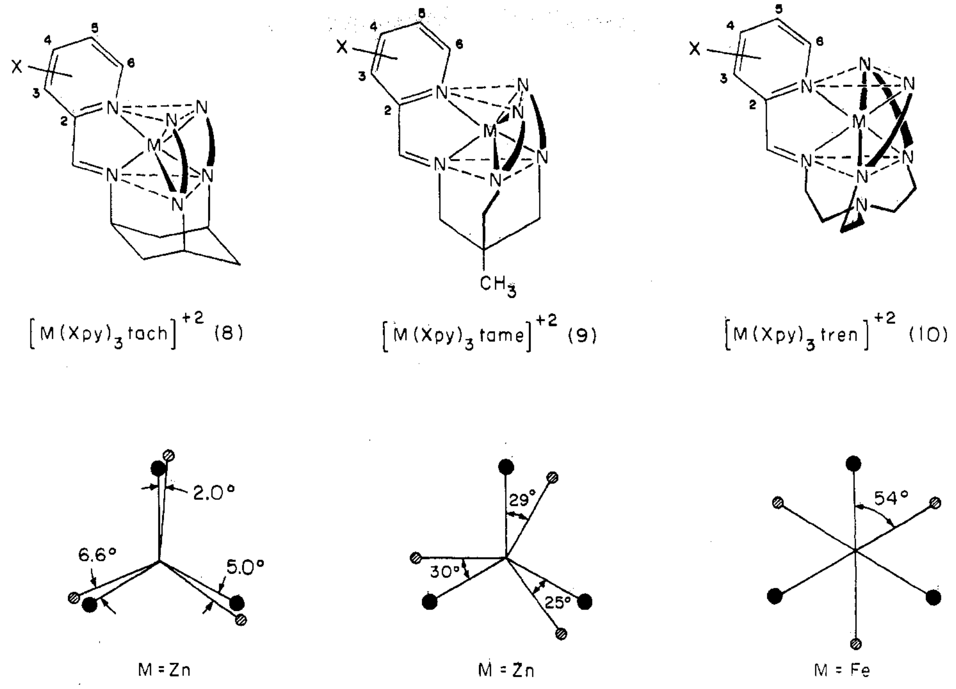
[32] E. Larsen, G. N. La Mar, B. E. Wagner, J. E. Parks, and R. H. Holm, results to be submitted for publication. In citing similarities of ligand field spectra of Co(II) and Ni(II) oxime complexes with those of the corresponding complexes **7**–**10**, it is not implied that within these groups the absorption bands necessarily result from the same transition(s). For present purposes these near-infrared bands are considered merely as diagnostic of a *six*-coordinate structure with an $S = {}^3/_2$ (Co(II)) or $S = 1$ (Ni(II)) ground state.

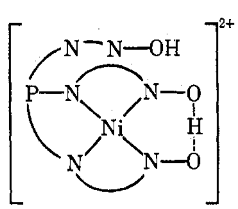


$[M(Xpy)_3tach]^{+2}$ (8) $[M(Xpy)_3tame]^{+2}$ (9) $[M(Xpy)_3tren]^{+2}$ (10)

Figure 3.—Schematic structural formulas of open sexadentate metal(II) complexes (X = H) and twist angles ϕ determined by X-ray studies {$[Zn((py)_3tach)]^{2+}$,[11a] $[Zn((py)_3tame)]^{2+}$,[13] $[Fe((py)_3tren)]^{2+}$ [C. Meali and E. C. Lingafelter, *Chem. Commun.*, 885 (1970)]}. For purposes of clarity only one chelate ring structure is shown in each complex.

reasonable postulate for $[Co(P(Hpox)_3\text{-}H)]^+$. The Zn(II) complex was investigated by pmr (*cf.* Table III). An intensity ratio of 6:1 was found for the complex multiplet centered at *ca.* −7.9 ppm compared to the single feature at −11.7 ppm. Ring and azomethine proton shifts overlap, and the low-field feature can only be assigned to oxime protons. These results are consistent with structure **6** or a dynamic situation in which this structure is in rapid equilibrium with one of lower coordination number produced by dissociation of one arm of the ligand.

The behavior of $[Ni(P(Hpox)_3\text{-}H)]^+$ in solution is interpretable on the basis of such an equilibrium. Recrystallization from several different solvents yielded the pure perchlorate salt with magnetic moments of 2.3–2.5 BM. These values are substantially lower than 3.0–3.1 BM found for the Ni(II) complexes **7**–**10**.[11b,13,18,19] In addition, a diamagnetic modification was obtained by recrystallization from acetonitrile. Each of these samples gave the same nmr and electronic spectra in a given solvent. The band at 9500 cm^{-1} in acetonitrile solution is clearly due to a six-coordinate paramagnetic species since a feature of nearly the same energy is found in the spectrum of $[Ni(PccBF)]^+$. The intensities of this feature and magnetic moments in solution exhibit parallel solvent dependencies and increase in the order DMF $\lesssim$ DMSO < CH_3CN. The same qualitative effect is found in the pmr spectra (Table III). Large downfield shifts of the pyridine ring protons due to paramagnetic interactions are observed, with the shifts smaller in DMF than in DMSO and also smaller than for the fully paramagnetic complexes **7**–**10** under the same conditions. No signals attributable to a diamagnetic complex were observed. These results are consistent with the rapid, solvent-dependent equilibrium diamagnetic $\rightleftharpoons$ paramagnetic ($S = 1$), in which the paramagnetic form may be reasonably represented by structure **6**. The nature of the diamagnetic form is uncertain and it is speculated that it has either the planar structure **11** or possibly a



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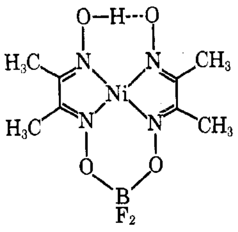
basically square-pyramidal configuration in which only one donor atom of the unique arm is coordinated.

Preparation and Properties of the Clathro Chelates.—The encapsulated cations $[M(PccBF)]^+$ (M = Fe(II), Co(II), Ni(II), Zn(II)) were obtained as their fluoroborate salts by two procedures. The initially developed procedure involved reaction at ambient temperature between boron trifluoride etherate and the material formed from $P(Hpox)_3$ and the tetrafluoroborate hexahydrate salt of Fe(II), Co(II), Ni(II), or Zn(II) in acetonitrile. The use of this closure reagent was suggested by the results of Boston and Rose[5] and by the formation of $Ni[(BF_2)_2(dmg)_2]$ from $Ni(Hdmg)_2$.[30] That the reactive species are $[M(P(Hpox)_3\text{-}H)]^+$ of probable structure **6** was supported by conversion of the preisolated perchlorate salts of Co(II) and Ni(II) to the corresponding clathro-chelate cations under the same conditions. Repeated failure to obtain pure samples of fluoroborate salts of the $[M(P(Hpox)_3\text{-}H)]^+$ cations of these four metal ions led to the supposition that fluoroborate ion could also act as a closure reagent under appropriate conditions. This was confirmed by development of a second procedure in which refluxing of $P(Hpox)_3$, $M(H_2O)_6(BF_4)_2$, and sodium tetrafluoroborate in equimolar ratio in acetonitrile afforded $[M(PccBF)](BF_4)$ in yields comparable to the first procedure. Both procedures failed when applied to the synthesis of the Mn(II) and Cu(II) clathro chelates.

The reactivity of tetrafluoroborate ion toward hydrogen-bonded oxime groups was further investigated. Reaction of $Ni(Hdmg)_2$ with a large excess of sodium tetrafluoroborate in refluxing acetonitrile afforded after purification the previously unknown complex $Ni(Hdmg)(BF_2dmg)$ (**12**) in 27% yield. No evidence was found for formation of the fully closed macrocycle $Ni[(BF_2)_2(dmg)_2]$,[30] which can be prepared in better yield from boron trifluoride etherate under milder conditions. The limited results available suggest that tetrafluoroborate ion is less reactive as a bridging or capping reagent for oxime functionalities than is boron trifluoride etherate.



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Physical data for the four $[M(PccBF)](BF_4)$ salts are given in Tables II–IV. The compounds behave as 1:1 electrolytes in acetonitrile. Like their open sexadentate counterparts **8**–**10**, the Ni(II) and Co(II) complexes are high spin and the Fe(II) complex is essentially diamagnetic. Nmr data are consistent with the encapsulated structure **7**. Two ^{19}F signals of *ca.* 4:1 intensity ratio were observed, corresponding to the fluoroborate ion and the apical B–F group. The infrared spectra of the Co(II), Ni(II), and Zn(II) complexes are essentially identical. In addition to the principal fluoroborate bands at 519 (ν_4) and ~960 cm^{-1} (ν_3),[29] features were observed at *ca.* 820 and 1180 cm^{-1} and *ca.* 1110 and 1230 cm^{-1} which may be tentatively assigned[5,30] to B–O and N–O absorptions, respectively. As with the $[M(P(Hpox)_3\text{-}H)]^+$ complexes, no definite assignment of C=N stretching vibrations could be made.

The structure **7** has been confirmed in detail for $[Ni(PccBF)]^+$ by the X-ray study of Churchill and Reis, and the Co(II) and Zn(II) analogs were determined to be isomorphous and nearly isometric with the Ni(II) compound.[33] The cation very closely approaches the desired TP (C_{3v}) stereochemistry, with all twist angles being less than 2°. Comparison of this structure with those of three open sexadentate complexes[11a,13,34] shown in Figure 3 underscores the desirability of requirement (a) above in the design of TP complexes. The lack of two anchoring atoms or groups allows sufficient structural flexibility that significant distortions from TP stereochemistry are possible. This situation is evident from the structures of the two Zn(II) complexes. Here ligand field factors are absent and, neglecting solid-state effects, the observed structures appear to represent the closest approach to TP geometry inherently possible for the ligands when coordinated to a metal ion of the same charge and approximate size as Zn(II).

$[Fe(PccBF)](BF_4)$ has been found not to be isomorphous with the corresponding Co(II)–Ni(II)–Zn(II) group. Further, the infrared spectrum of this compound differs somewhat from those of this group, most noticeably in the 1600–1400- and 800–400-cm^{-1} regions. Similar differences have been noted for $[Fe((py)_3tach)]^{2+}$ [11b] and $[Fe((py)_3tame)]^{2+}$ [13] compared to their Zn(II) analogs, and it has been suggested that the Fe(II) complexes tend to approach octahedral coordination.[11b,13,35,36] Arguments based on ligand field stabilization energy differences[11b] are consistent with this suggestion. The structure of the Fe(II) clathro chelate is currently under investigation[37] in order to assess the ability of the bicyclic cage structure to impose TP coordination in a case where this stereochemistry is potentially destabilized by the electronic properties of the metal ion.

The presently available structural results, summarized above and in Figure 3, reveal that for a given metal ion the relative tendencies of the sexadentate ligands to approach TP coordination lie in the order

$$(py)_3tren < (py)_3tame < (py)_3tach < PccBF$$

We are currently engaged in developing criteria for TP, octahedral, and intermediate geometries contained in the series **7**–**10**. Ligand field spectra, isotropically shifted nmr spectra of paramagnetic complexes, and polarographic redox potentials are of interest in this connection and the interpretation of these properties will be presented in a subsequent publication.[32]

Acknowledgment.—This research was supported by the National Science Foundation under Grants GP-7576X and GP-18978X and by the National Institutes of Health under Grant GM-15471. We thank Professors M. R. Churchill, E. B. Fleischer, N. J. Rose, and Mr. A. H. Reis, Jr., for communication of results prior to publication.

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[33] M. R. Churchill and A. H. Reis, Jr., *Chem. Commun.*, 879 (1970), and unpublished results.

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[35] This suggestion has been verified in the case of $[Fe((py)_3tame)]^{2+}$, for which twist angles of 39 and 45 (2)° have been found.[36] It is noted, however, that the significant decrease in C=N frequencies of Fe(II) complexes[11b,13] (ν_{CN} <1600 cm^{-1}) compared to the Co(II), Ni(II), and Zn(II) members of the series **8–10** (ν_{CN} ~1660–1620 cm^{-1}) are not necessarily indicative of substantial structural differences. The same behavior is found with $[Fe((py)_3tren)]^{2+}$ (*cf.* Figure 3) and $[Ni((py)_3tren)]^{2+}$, whose structure is described as approximately octahedral,[19] as well as with the tris(*N*-methyl-2-pyridinecarboxaldimino) complexes of Fe(II), Co(II), and Ni(II).[31]

[36] E. B. Fleischer, private communication.

[37] NOTE ADDED IN PROOF.—The structure of $[Fe(PccBF)](BF_4)$ has recently been solved[33] and twist angles of 20, 22, and 22° have been found.