be reduced by hydrazine in ethanol to give a species with the empirical formula $MSe_4C_4(CF_3)_4^-$, M = Co or Fe. It was very difficult to obtain crystalline samples of these anions, however. In order to determine the degree of association of $[(C_6H_5)_4As][FeSe_4C_4(CF_3)_4]$ in solution, the equivalent conductivities for acetonitrile solutions were measured as a function of $\sqrt{c}$. The resulting plot was nonlinear. The measured magnetic moments for this complex were μ_{eff} (solid, 22°) 1.11 BM (monomeric formulation) and 1.58 BM (dimeric formulation) and μ_{eff} (acetone, 34°) 2.51 BM (monomeric formulation) and 3.04 BM (dimeric formulation). These results suggest that a monomer $\rightleftarrows$ dimer equilibrium exists here. A polarogram of this material in CH_2Cl_2 using a rotating platinum electrode showed a reversible one-electron wave at $E_{1/2} = +0.58$ V and an irreversible two-electron wave at $E_{1/2} = -0.78$ V.

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Hindered Ligand Systems. IV. Complexes of *cis,cis*-1,3,5-Tris(pyridine-2-carboxaldimino)cyclohexane. Trigonal-Prismatic *vs.* Octahedral Coordination[1]

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Trigonal-prismatic coordination of the metal atom is known to occur in $Zn((py)_3tach)(ClO_4)_2$, where $(py)_3$tach is *cis,cis*-1,3,5-tris(pyridine-2-carboxaldimino)cyclohexane. X-Ray powder patterns of this compound and the corresponding Co(II) and Mn(II) compounds are virtually indistinguishable. However, the patterns of the Ni(II) and Fe(II) compounds differ from each other as well as the others, which suggests that either or both may have a different geometry. No unaccountably large differences occur in any of the vibrational spectra between 400 and 3600 cm^{-1}, but the electronic spectra of the Ni(II) and Fe(II) complexes suggest octahedral or near-octahedral configurations in each case. Ligand field calculations lend some support to this tentative conclusion since the calculations suggest that the tendency toward the octahedral configuration ought to decrease according to: low-spin Fe(II) > Ni(II) > high-spin Co(II) > high-spin Mn(II) = Zn(II). Conformational preferences within the ligand favor trigonal-prismatic coordination. Consequently, a competition between the two geometries may exist. Energy level diagrams for d^7 and d^8 trigonal prismatic complexes have been derived. The spectrum of $Co((py)_3tach)^{2+}$ has been assigned and the magnetic moment (5.0 BM), which is in accord with accepted values for octahedral coordination, has been shown to be also consistent with the predicted ground state of the trigonal prism. On the basis of the d^8 energy level diagram, a remote possibility exists that the spectrum of a trigonal-prismatic complex would be difficult to distinguish from that of an octahedral species.

Lions and Martin[2] have reported the preparation of complexes derived from the Schiff base adduct of pyridine-2-carboxaldehyde and what was thought to be isomerically pure *cis,cis*-1,3,5-triaminocyclohexane (*cis,cis*-tach) with Fe(II), Co(II), and Co(III). Octahedral coordination was assigned to each. Our own interest in this system was derived from our past studies,[3–5] particularly the one that indicated[3] that the synthesis of the triamine results in both possible stereoisomers, research done by others,[6,7] and another important observation. Space-filling molecular models of the *cis,cis*-1,3,5-tris(pyridine-2-carboxaldimino)cyclohexane ligand system ($(py)_3$tach) indicated that, in the absence of a major perturbation caused by the metal ion, metal complexes ought to have a trigonal-prismatic coordination geometry, rather than the octahedral coordination assigned by Lions and Martin. The peculiar nature of this ligand seems to have also been recognized by others[7] but without reference to the possible coordination geometry. Consequently, we deliberately chose to examine the coordination geometry of a complex of this ligand in which the metal ion would have no ligand field preference for either an octahedral or a trigonal-prismatic configuration. The X-ray diffraction study of $Zn((py)_3tach)^{2+}$, using ClO_4^- as the counterion, was described recently.[8] As it was hoped, trigonal-prismatic coordination had been realized.

Other examples of trigonal-prismatic coordination are relatively few. Early structural studies[9] have indicated this geometry exists in MoS_2 and WS_2. More

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[1] Presented in part at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

[2] F. Lions and K. V. Martin, *J. Amer. Chem. Soc.*, **79**, 1572 (1957).

[3] R. A. D. Wentworth and J. J. Felten, *ibid.*, **90**, 621 (1968).

[4] R. A. D. Wentworth, *Inorg. Chem.*, **7**, 1030 (1968).

[5] R. F. Childers and R. A. D. Wentworth, *ibid.*, **8**, 2218 (1969).

[6] F. L. Urbach, J. E. Sarneski, L. J. Turner, and D. H. Busch, *ibid.*, **7**, 2169 (1968).

[7] J. E. Sarneski and F. L. Urbach, *Chem. Commun.*, 1025 (1968).

[8] W. O. Gillum, J. C. Huffman, W. E. Streib, and R. A. D. Wentworth, *ibid.*, 843 (1969). A complete description of the structure will be submitted for publication in a short time.

[9] R. G. Dickinson and L. Pauling, *J. Amer. Chem. Soc.*, **45**, 1466 (1923).

Table I

Analytical[a] Results and Physical Properties

Compound[b]	% C		% H		% N		Color	μ_{eff} (300°K)
	Calcd	Found	Calcd	Found	Calcd	Found		
$MnL(ClO_4)_2$	44.4	43.7	3.7	3.7	12.9	12.8	Light yellow	6.0
$FeL(ClO_4)_2$	44.3	43.5	3.7	3.9	12.9	12.7	Metallic purple	0.6
$CoL(ClO_4)_2$	44.1	43.2	3.7	3.8	12.9	12.9	Orange	5.0
$NiL(ClO_4)_2$	44.1	43.1	3.7	3.7	12.8	13.0	Orange	3.0
$ZnL(ClO_4)_2$	43.6	43.1	3.7	3.8	12.7	12.7	Light yellow	Diamagnetic

[a] Analyses were obtained from Huffman Laboratories, Wheatridge, Colo. [b] L = $(py)_3$tach.

recently, certain Cr, V, Re, W, and Mo derivatives of the dithiolates have been shown to have this configuration.[10-13] The only other authenticated example containing a metal atom from the first transition series is found[14] in a trinuclear cation which is formed from Co and 2-aminoethanol where a Co(II) ion is in trigonal-prismatic coordination with the oxygen atoms of the ligand.

The unusual character of the coordination geometry in $Zn((py)_3tach)^{2+}$ has led to further studies of this ligand system. The number of coordination sites within the ligand suggests that either trigonal-prismatic or octahedral coordination is possible if suitable distortions within the ligand can be achieved. These distortions might include rotation about the carboxaldimino C=N bond or the C—C bond immediately adjacent or distortions within either the cyclohexane or the pyridine ring systems. Furthermore, it would seem reasonable that competition between trigonal-prismatic and octahedral coordination could result. If so, a large octahedral ligand field stabilization energy could overcome ligand conformational energy barriers so that octahedral coordination was achieved at the cost of distortions within the ligand system. We have chosen to study the complexes of Fe(II), Mn(II), Co(II), Ni(II), and Zn(II) because these metal ions can form undistorted octahedral complexes and because, as a group, they provide a broad spectrum of ligand field stabilization energies. However, these studies have pointed to the difficulty of distinguishing octahedral and trigonal-prismatic coordination in general and particularly with this ligand system.

Experimental Section

Preparation of Complexes.—Isomerically pure *cis,cis*-tach·$3HCl \cdot H_2O$ (0.24 g, 0.001 mol), obtained from the acid decomposition[4] of $Ni(cis,cis\text{-tach})_2(NO_3)_2$, was neutralized with 15 ml of 0.2 *M* NaOH. The addition of 0.32 g (0.003 mol) of pyridine-2-carboxaldehyde resulted in a precipitate. The appropriate quantity (0.001 mol) of the hydrated metal perchlorate was added to this mixture, and the volume was adjusted to 50 ml. The mixture was heated and allowed to boil until the precipitate had dissolved. The hot solution was filtered and crystals of the desired compound were obtained when the solution had cooled. These were washed with water and dried in air. The analytical results are given in Table I along with the colors and magnetic moments. Lions and Martin[2] described the Fe(II) compound as glistening red, diamagnetic plates. The Co(II) compound was described as brownish pink with a magnetic moment of 4.73 BM.

Preparation of $(py)_3$tach.—The free ligand was prepared in aqueous solution from stoichiometric quantities of *cis,cis*-tach·$3HCl \cdot H_2O$, pyridine-2-carboxaldehyde, and NaOH. Recrystallization of the precipitate from an ethanol–H_2O mixture gave white needles. The pmr spectrum ($CDCl_3$, TMS) contained peaks at δ 2.1 (multiplet, 6, $>CH_2$), 3.75 (multiplet, 3, $\gtrdot CH$), 7.30 (asymmetric triplet, 3, py ring H), 7.75 (symmetric triplet, 3, py ring H), 8.08 (asymmetric doublet, 3, py ring H), 8.50 (singlet, 3, acyclic –N=CH–), and 8.63 ppm (asymmetric doublet, 3, py ring H).

Instrumentation.—The infrared spectra were obtained using a Perkin-Elmer 621 spectrometer. The electronic spectra were obtained using a Cary Model 14 spectrophotometer. Proton magnetic resonance spectra were obtained with a Varian HA-100 spectrometer. X-Ray powder patterns were obtained using vanadium-filtered chromium Kα radiation. The Faraday apparatus which was used for the magnetic measurements has been previously described.[4]

Results

The Structures.—X-Ray powder patterns of the Mn(II) and Co(II) compounds are virtually identical with that of $Zn((py)_3tach)(ClO_4)_2$, and we presume that these complex ions possess very similar structures. The average coordination geometry within $Zn((py)_3tach)^{2+}$ consists[8] of a slightly tapered trigonal prism whose dimensions are given with Figure 1. On the other hand, the powder patterns of the Fe(II) and Ni(II) compounds differ from each other as well as from those of Zn(II), Mn(II), and Co(II).

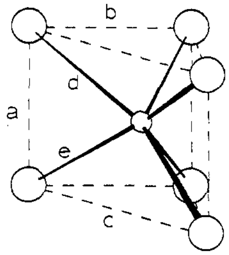

Figure 1.—The trigonal-prismatic coordination in $Zn((py)_3tach)^{2+}$. The upper circles represent the aldimino N atoms while the lower circles belong to the pyridyl N atoms. The average dimensions within the polyhedron are a = 2.70 Å, b = 2.85 Å, c = 3.23 Å, d = 2.15 Å, and e = 2.25 Å. The average aldimino N–Zn–pyridyl N bond angle within the same pyridinecarboxaldimino group is 75.8°. The angle between the threefold axis and any Zn–aldimino N bond is 47.9°, while between that axis and any Zn–pyridyl N bond the angle is 56.3°. All data are taken or calculated from those given in ref 8.

It is also pertinent to note the magnetic moments of each compound given in Table I. None of them differs from accepted values for octahedral coordination, but

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[10] R. Eisenberg and J. A. Ibers, *J. Amer. Chem. Soc.*, **87**, 3776 (1965).

[11] E. I. Steifel and H. B. Gray, *ibid.*, **87**, 4012 (1965).

[12] A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *ibid.*, **87**, 5798 (1965).

[13] R. Eisenberg and H. B. Gray, *Inorg. Chem.*, **6**, 1844 (1967).

[14] J. A. Bertrand, J. A. Kelley, and E. G. Vassian, *J. Amer. Chem. Soc.*, **91**, 2394 (1969).

TABLE II

SELECTED REGIONS OF THE INFRARED SPECTRA OF (py)$_3$tach AND ITS METAL COMPLEXES[a]

Assignment	Free L[b]	MnL(ClO$_4$)$_2$	FeL(ClO$_4$)$_2$	CoL(ClO$_4$)$_2$	NiL(ClO$_4$)$_2$	ZnL(ClO$_4$)$_2$
Combination bands (?)		~3560 w, sh	~3570 w, sh	~3550 w, sh	~3550 w, sh	~3550 w, sh
		3400 w	3400 w	3400 m	3400 w	3400 w
Acyclic C=N	1640 s	1653 m	1545 m	1655 m	1640 m	1665 m
Pyridine	1587 m	1599 s	1607 s	1599 s	1599 s	1599 s
	1567 m	1567 w	1588 w	1568 w	1563 w	1569 w
	1465 s	1483 m	1468 s	1483 m	1475 m	1484 m
	1435 m, sh	1443 s	1440 s	1448 s	1444 m	1447 m
Unassigned		1441 w, sh		1435 m, sh	1435 m, sh	1432 w, sh
		1425 w, sh				
Pyridine ring deformations	570 w					
			516 m			
	501 w	481 m, sh	471 m	488 m, sh	490 m	488 m
	455 w	473 m	450 w	482 m		479 m
		426 w, sh	435 m	430 w, sh	435 w	430 w, sh
		415 m		418 m	420 m	419 m
			390 m			

[a] KBr disks were used between 1400 and 3600 cm^{-1}. CsBr disks were used below 600 cm^{-1}. [b] L = (py)$_3$tach.

it will be shown also that none of them differs markedly from values which would be predicted for trigonal-prismatic coordination.

Vibrational Spectra.—Several principal regions of the infrared spectra of the free ligand and each of its complexes are given in Table II. The stoichiometry of the Ni(II) compound was previously given as a monohydrate on the basis of analytical and infrared results.[7] Our analytical data were too erratic for a reliable judgment about either the presence or the absence of water. The infrared spectrum of each complex contains a band at 3400 cm^{-1} and a shoulder at about 3550 cm^{-1}, which could be assigned to the symmetric and asymmetric stretching modes of H_2O. However, the X-ray study of the Zn(II) compound did not reveal the presence of water of hydration. Furthermore, recrystallization from D_2O did not alter this band structure, nor did it lead to the introduction of additional bands. Consequently, all of the compounds must be anhydrous. An assignment for this band structure is, however, difficult. The frequency is too great for a C–H stretching mode, and the band positions in the remainder of each spectrum rule out the possibility that these are overtone frequencies. Consequently, we believe that both the band and its shoulder are due to combinations which have only gained intensity in the metal complexes. The complexity of the remainder of each spectrum makes it impossible to assign the fundamental frequencies which are involved.

The next region of interest occurs between 1400 and 1700 cm^{-1}. The assignments given in Table I are based on the studies of Busch and coworkers for other α-diimine ligands and their complexes.[15–18] In confirmation of these assignments, the hydrogenation of Ni((py)$_3$tach)$^{2+}$ with NaBH$_4$ led to a spectrum in which $\nu_{C=N}$, the acyclic C=N stretching frequency, was absent but the characteristic pyridine ring bands were present at 1604 (s), 1569 (w), 1483 (m), and 1440 cm^{-1} (m). These results will be described in a subsequent publication. In the spectra of other α-diimine–cobalt(II) and –nickel(II) complexes, a parallel behavior of $\nu_{C=N}$ generally exists; that is, both frequencies can increase or decrease by 15–20 cm^{-1} relative to the same frequency in the free ligand. In complexes of Fe(II), however, it is common that $\nu_{C=N}$ decreases by as much as 100 cm^{-1} due to extensive metal-to-ligand π bonding. Thus, as shown in Table II, except for the fact that $\nu_{C=N}$ remains identical with the free ligand value in the Ni(II) complex while increasing for the Co(II) complex, the general frequency and intensity patterns are very similar to those found with α-diimine complexes with octahedral coordination geometries. There are no bands that might be characteristic of trigonal-prismatic coordination in this region of the spectrum.

The spectra of the complexes are very similar between 600 and 1400 cm^{-1}, but some differences can be discerned between 400 and 600 cm^{-1}, a region which includes out-of-plane ring deformational frequencies. The spectrum of the Fe(II) compound deviates markedly from the others in this region, but an explanation is not available.

Metal–ligand stretching frequencies might be sensitive to the mode of coordination. The metal–ligand stretching frequency in the octahedral M(bipy)$_3{}^{2+}$ complexes is not known but, according to Clark and Williams,[19] they must lie below 200 cm^{-1}. Unfortunately, our spectra were poorly defined below 400 cm^{-1} and we must refrain from conclusions based on this region of the spectrum.

Electronic Spectra and Magnetic Properties.—The electronic spectra in both aqueous and solid phases are presented in Table III. Since only minor shifts in the spectra are observed for Fe((py)$_3$tach)$^{2+}$ and Ni((py)$_3$tach)$^{2+}$, it is safe to assume that no major changes in their coordination geometry have occurred in solution.

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[15] R. C. Stouffer and D. H. Busch, *J. Amer. Chem. Soc.*, **82**, 3491 (1960).

[16] W. J. Stratton and D. H. Busch, *ibid.*, **82**, 4834 (1960).

[17] R. A. Krause, N. B. Colthup, and D. H. Busch, *J. Phys. Chem.*, **65**, 2216 (1961).

[18] P. E. Figgins and D. H. Busch, *ibid.*, **65**, 2236 (1961).

[19] R. J. H. Clark and C. S. Williams, *Spectrochim. Acta*, **23**, 1055 (1967).

TABLE III

ELECTRONIC SPECTRA[a,b]

Phase	$FeL(ClO_4)_2$	$CoL(ClO_4)_2$	$NiL(ClO_4)_2$
Solid[c]	16,800	8,430	11,100
	18,400	19,100	12,100
	27,100	20,200	19,400
Aqueous	17,400 (12.3×10^3)	9,580[d]	11,100 (25)
	18,700 (9.0×10^3)	~20,500[d,e]	12,200 (25)
	27,600 (3.3×10^3)	~21,600[d,e]	19,200 (40)
	36,500 (21.8×10^3)		
	42,100 (14.0×10^3)		

[a] Values are given in wave numbers. Extinction coefficients appear in parentheses with the aqueous spectra. [b] L = $(py)_3$-tach. [c] Measured in Nujol mulls. [d] Saturated solution whose concentration was not measured. [e] Poorly resolved.

On the other hand, the spectrum of $Co((py)_3tach)^{2+}$ in aqueous solution differed somewhat from that obtained from the solid phase. The resolution in the spectrum of the aqueous solution was poor and all bands had moved to higher wave numbers by about 1000–1200 cm^{-1}. Consequently, only the solid-phase spectrum will be discussed in this case. A comparison of each spectrum with the spectrum of the corresponding trisbipyridine derivative is given in Figures 2–4. The latter are in agreement with those given by Palmer and Piper.[20]

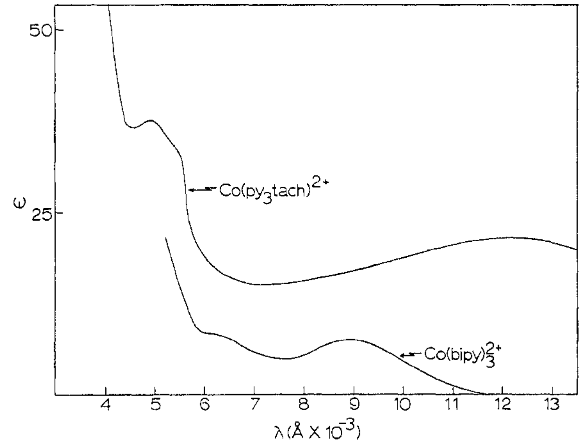

Figure 2.—A comparison of the electronic spectra of $Co((py)_3tach)^{2+}$ and aqueous $Co(bipy)_3^{2+}$. The former was obtained in the solid phase so that the absorption is in arbitrary units. The spectrum was extended to 18,000 Å without the observation of additional bands.

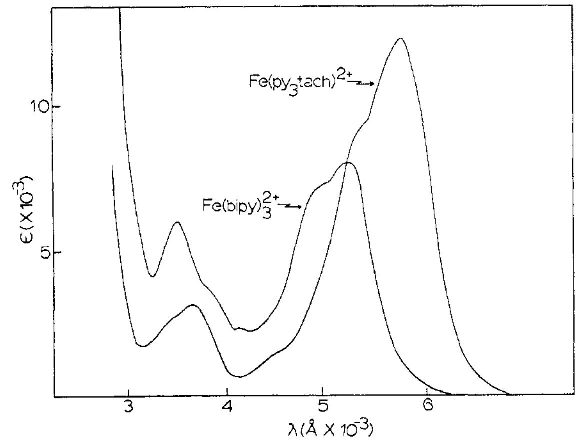

Figure 3.—A comparison of the electronic spectra of aqueous $Fe((py)_3tach)^{2+}$ and aqueous $Fe(bipy)_3^{2+}$.

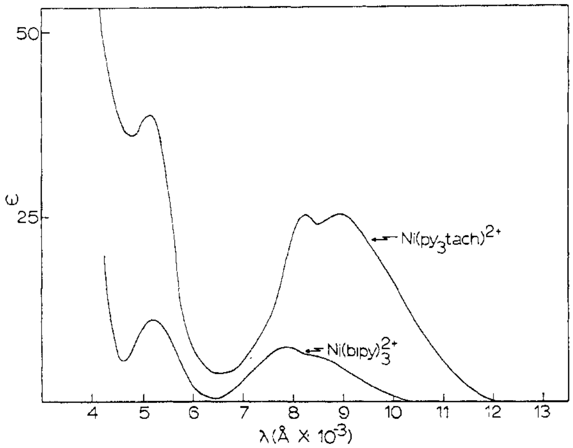

Figure 4.—A comparison of the electronic spectra of aqueous $Ni((py)_3tach)^{2+}$ and aqueous $Ni(bipy)_3^{2+}$.

The spectrum of the $Co((py)_3tach)^{2+}$, which we have assumed to be trigonal prismatic on the basis of its X-ray powder pattern, can be assigned readily using the energy level diagram appearing in Figure 5. This diagram, which is based on the ligand field potential given in the Appendix and the matrix elements in Table IV, is only partially complete in that it contains only the states of highest spin multiplicity. The observed bands in the spectrum are then assigned as $^4E'' \rightarrow {}^4E' + {}^4A_2'' + {}^4A_1', {}^4A_2'$ (unresolved) at 8430 cm^{-1}, $^4E'' \rightarrow {}^4E'(P)$ at 19,000 cm^{-1}, and $^4E'' \rightarrow {}^4A_2''(P)$ at 20,200 cm^{-1}. The true symmetry of $Co((py)_3tach)^{2+}$ is not D_{3h} but approximately C_{3v}. However, only the notation will be affected and no new splitting would result in the correct symmetry. It is also possible to obtain approximate values for *Dq* and *B* from the diagram. If the midpoint of the lower manifold of states is taken as 8430 cm^{-1} above the ground state, then on the basis of this energy and the band energy at 19,000 cm^{-1} *Dq* is about 1340 cm^{-1} and *B* is close to

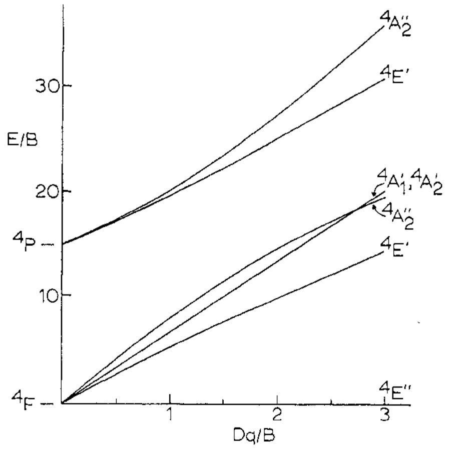

Figure 5.—Energy level diagram for a d^7 trigonal-prismatic complex. Only the states of highest spin multiplicity were included in the calculation.

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(20) R. A. Palmer and T. S. Piper, *Inorg. Chem.*, **5**, 864 (1966).

TABLE IV

LIGAND FIELD MATRICES FOR d^8 (AND d^7)[a] ELECTRON CONFIGURATION WITH $\varphi = 0°$ (IN UNITS OF Dq)

$$\overbrace{\begin{array}{lll} (3,\pm1) & -2/3 & -\sqrt{8/3} \\ (1,\pm1) & & 0 \end{array}}^{{}^3E'({}^3F,{}^3P)} \qquad \overbrace{\begin{array}{lll} (3,0) & -4 & -8/3 \\ (1,0) & & 0 \end{array}}^{{}^3A_2''({}^3F,\ {}^3P)} \qquad \begin{array}{l} {}^3A_1',\ {}^3A_2'({}^3F)\ (3,\pm3):\ \ -2 \\ \\ {}^3E''({}^3F)\ (3,\pm2):\ \ 14/3 \end{array}$$

$$\overbrace{\begin{array}{llll} (4,\pm4) & 4/3 & 0 & 0 \\ (4,\pm2) & & -22/21 & \sqrt{1200/49} \\ (2,\pm2) & & & 8/21 \end{array}}^{{}^1E'({}^1G,\ {}^1D,\ {}^1S)} \qquad \overbrace{\begin{array}{llll} (4,0) & 12/7 & -\sqrt{8000/441} & \sqrt{224/9} \\ (2,0) & & 16/7 & 0 \\ (0,0) & & & 0 \end{array}}^{{}^1A_2''({}^1G,\ {}^1D,\ {}^1S)} \qquad \overbrace{\begin{array}{lll} (4,\pm1) & 6/7 & -\sqrt{200/147} \\ (2,\pm1) & & -32/21 \end{array}}^{{}^1E''({}^1G,\ {}^1D)}$$

A_1'', $A_2''({}^1G)$ $(4, \pm3)$: -2

[a] The matrix elements for the states of highest spin multiplicity for the d^7 electron configuration may be obtained by reversing the sign of the matrix elements for the states of highest spin multiplicity which are given above.

820 cm^{-1} ($Dq/B = 1.64$). These values were obtained directly from the diagram and not from the solutions of a secular equation. Nevertheless, the worth of this procedure can be tested. According to the diagram, E/B for the highest energy transition is 24.7 at $Dq/B = 1.64$. With $B = 820$ cm^{-1}, the predicted energy of this transition should be about 20,300 cm^{-1} in close agreement to the observed value. These values can be compared to those previously given[20] for the octahedral Co(bipy)$_3^{2+}$, *e.g.*, $Dq = 1267$ cm^{-1} and $B = 791$ cm^{-1}. The similarities in the ligands as well as the mathematical development would suggest that the spectrochemical parameters in each case ought to be close in value.

Although the observed magnetic moment of 5.0 BM is in the range normally associated with a d^7 octahedral complex, this value is also explicable in terms of a trigonal-prismatic complex. An expression for the parallel and perpendicular susceptibilities is given in the Appendix. Magnetic moments derived from the average susceptibility have been calculated at values of kT/λ between 0 and -3. The results never differed by more than 0.2 BM from a value of 5.1 BM. At 25° with λ -170 cm^{-1}, a typical value for Co(II) compounds, the predicted magnetic moment is 5.28 BM.

A comparison of the spectra of Fe((py)$_3$tach)$^{2+}$ and Fe(bipy)$_3^{2+}$ is shown in Figure 3. Clear similarities exist but the spectrum of the former is more intense and it appears at somewhat longer wavelengths. The band at 19,200 cm^{-1}, with the shoulder at about 20,300 cm^{-1}, in the spectrum of Fe(bipy)$_3^{2+}$ is particularly characteristic of octahedral Fe(α-diimine)$_3^{2+}$ systems. Consequently, it is of interest to see a band system of similar shape, but at somewhat lower wave numbers, in the spectrum of Fe((py)$_3$tach)$^{2+}$. It is known,[21] however, that the band position of octahedral Fe(α-diimine)$_3^{2+}$ systems is a sensitive function of the nature of the ligand. The intensity differences shown in Figure 3 do not necessarily indicate a departure from octahedral symmetry, since similar differences occur when the spectrum of Fe(bipy)$_3^{2+}$ is compared to that of the corresponding *o*-phenanthroline derivative.[21] Thus, the electronic spectrum of Fe((py)$_3$tach)$^{2+}$ suggests that the coordination geometry could be octahedral. We do not have in hand any energy level calculations which would affirm or deny this possibility. The magnetic moment is consistent with either the t_{2g}^6 configuration of the octahedron or the $(a_1')^2$-$(e')^4$ configuration of the trigonal prism (see Figure 8).

The similarities in the spectra of Ni((py)$_3$tach)$^{2+}$ and Ni(bipy)$_3^{2+}$ (Figure 4) are at least as striking as those found in the spectra of their Fe(II) counterparts. However, the differences that do exist lead to a considerable disparity in the spectroscopic parameters for the two complexes if Ni((py)$_3$tach)$^{2+}$ is octahedral. For the bipyridine derivative, Dq is 1280 cm^{-1} while B is 710 cm^{-1}.[20] For octahedral Ni((py)$_3$tach)$^{2+}$, Dq would be 1210 cm^{-1} while B would be 980 cm^{-1}, a remarkably high and unusual value.

Alternatively, it is possible that Ni((py)$_3$tach)$^{2+}$ is trigonal prismatic and that the spectrum of such a complex would be very similar to, and possibly virtually indistinguishable from, its octahedral counterpart. A complete energy level calculation, based on the matrix elements in Table IV, is given in Figure 6.

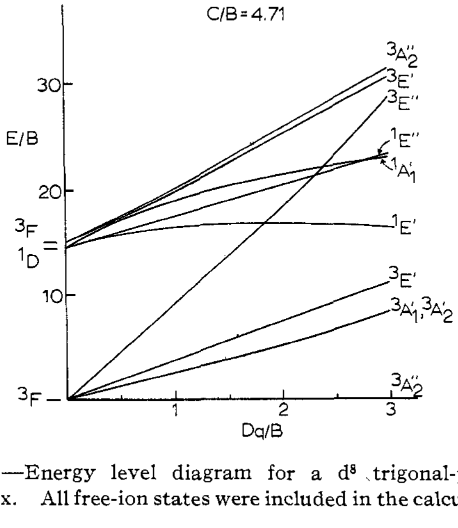

Figure 6.—Energy level diagram for a d^8 trigonal-prismatic complex. All free-ion states were included in the calculation.

If the band at 11,100 cm^{-1} is assigned to the transition ${}^3A_2'' \rightarrow {}^1E'$ and the band at 12,200 cm^{-1} is due to the transition ${}^3A_2'' \rightarrow {}^3E''$, then the approximate value of Dq/B is 2.0 and B is about 670 cm^{-1}. This choice predicts that the transition ${}^3A_2'' \rightarrow {}^3A_2''(P) + {}^3E'(P)$ should occur at about 16,800 cm^{-1}. By reversing the assignments the approximate value of Dq/B becomes 1.7 while B is about 740 cm^{-1}. The transition ${}^3A_2'' \rightarrow$

(21) P. Krumholtz, *J. Amer. Chem. Soc.*, **75**, 2163 (1953).

$^3A_2''(P) + {}^3E'(P)$ is predicted at about 17,300 cm^{-1}. The first assignment results in a Dq value which is identical with that found for Co((py)$_3$tach)$^{2+}$. This is also very nearly the case for the corresponding octahedral tris-bipyridine derivatives. Thus, the first assignment could be the correct one. However, both of these assignments lead to a poor estimate for the energy of the highest lying transition. It is conceivable that the inaccurate prediction for this transition is a result of the assumed angles in the trigonal prism (see the Appendix). In addition, two spin-allowed transitions should also be present between 3000 and 5000 cm^{-1} while two spin-forbidden transitions should occur in the neighborhood of 14,000 cm^{-1}. A careful search of the spectrum did not reveal any additional bands. However, the bands at long wavelengths might be difficult to find due to their expected width while the spin-forbidden bands might lack sufficient intensity to be seen.

Since the ground state in either coordination geometry is an orbital singlet, the magnetic moment is not expected to serve as a signal for either geometry. This condition holds true for Mn((py)$_3$tach)$^{2+}$ as well.

Discussion

A comparison of the ligand field stabilization energies associated with the octahedral and trigonal-prismatic coordination geometries for the various d^n electron configurations shows that the overall tendency toward octahedral geometry ought to decrease according to: low-spin Fe(II) > Ni(II) > high-spin Co(II) > high-spin Mn(II) = Zn(II), as shown in Figure 7. Although ligand field stabilization energies will make only a relatively small contribution to the total bonding energy, it is clear that a partial explanation may be found in these terms. A definite electronic preference for octahedral coordination should exist in Fe((py)$_3$tach)$^{2+}$, and perhaps in Ni((py)$_3$tach)$^{2+}$. This preference should be lessened in Co((py)$_3$tach)$^{2+}$ and cease to exist in the Mn(II) and Zn(II) derivatives. The experimental data indicate that the Co(II) and Mn(II) complexes, as well as Zn((py)$_3$tach)$^{2+}$, are trigonal prismatic. Thus, the complexes with the least octahedral preference in terms of ligand field stabilization energies are believed to have a trigonal-prismatic coordination environment. The electronic spectra of Fe((py)$_3$tach)$^{2+}$ and Ni((py)$_3$tach)$^{2+}$ suggest that either or both could have an octahedral configuration. However, the unusually large value for B (980 cm^{-1}) obtained from the spectrum of Ni((py)$_3$tach)$^{2+}$ suggests that some distortion from a strict octahedron has occurred.[22]

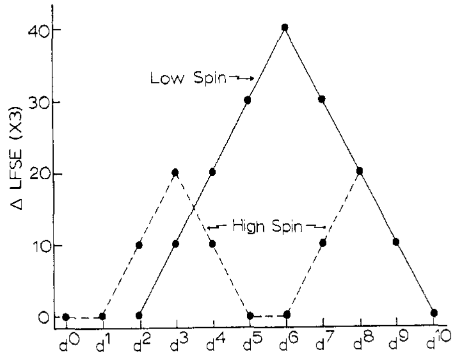

Figure 7.—The variation of ΔLFSE with atomic number, where ΔLFSE = LFSE(octahedron) − LFSE(trigonal prism). LFSE (trigonal prism) values were obtained from one-electron orbital energies which were calculated from the matrix elements of V_{LF}, the ligand field potential given in the Appendix, with $\varphi = 0°$.

Conformational preferences within the ligand, however, favor trigonal-prismatic coordination for all complexes. Consequently, a competition between the two coordination geometries can result if suitable distortions can be introduced within the ligand. It is possible that electronic preferences have outweighed ligand conformational preferences in the case of either Fe((py)$_3$tach)$^{2+}$ or Ni((py)$_3$tach)$^{2+}$. Evidence for or against this possibility might be found in the vibrational spectra. Distortions within the pyridine rings can probably be ruled out because the basic four-band pattern between 1400 and 1600 cm^{-1} due to the pyridine ring is virtually the same in the spectra of all of the complexes. (Note, however, the differences in the Fe(II) spectrum between 400 and 600 cm^{-1}.) Furthermore, the overall similarity of all of the spectra, with the exclusion of their differences in the carboxaldimino C═N stretching frequency, would rule out the possibility that distortions in the cyclohexane ring of any of the complexes were not also present in all of the complexes. Finally, rotations about either the carboxaldimino C═N bond or the C—C bond which is immediately adjacent are also possible distortions. In the free ligand the first of these rotations would be energetically less feasible[23] than the second possibility. Metal-to-ligand π bonding in the complex will lower the bond order of the CN bond and decrease the rotational energy barrier. The decrease in the bond order will be signaled by a decrease in $\nu_{C=N}$ regardless of whether rotation has occurred or not. Nevertheless, since $\nu_{C=N}$ in the infrared spectrum of Fe((py)$_3$tach)$^{2+}$ has decreased by slightly over 100 cm^{-1} relative to $\nu_{C=N}$ in the Zn(II) complex, it is possible that rotation has occurred. Simultaneous rotation about the C═N bond as well as the adjacent C—C bond is also a possibility that cannot be excluded by the data. In the spectrum of the Ni(II) complex, $\nu_{C=N}$ has decreased by only 15–25 cm^{-1} relative to that stretching frequency found for the trigonal-prismatic complexes. The majority of the rotation, if it has occurred, must have taken place in the C—C bond. In the free ligand this

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[22] We have also calculated the variation of the energy levels of a d^8 complex as one face of a trigonal prism is continuously rotated with respect to the other trigonal face (*cf.* V_{LF} in the Appendix). This calculation suggests that a rotation of about 40–50° from the trigonal prism toward the octahedron could result in a good fit to the electronic spectrum while allowing B to assume a value close to that found in Ni(bipy)$_3^{2+}$. Additional splitting of the energy levels would be too small, presumably, to be observed in the spectrum. Clearly, a structural characterization is necessary.

[23] The lower limit of the barrier to rotation about an imine C═N is probably 20 kcal/mol.

rotation would have caused an increase in $\nu_{C=N}$, but the presence of any metal-to-ligand π bonding in the complex could easily offset this increase so that a net decrease in $\nu_{C=N}$ is observed.

It is also important to note that the similarity of the X-ray powder patterns of the Co(II) and Zn(II) compounds is the most striking evidence for the stereochemistry of $Co((py)_3tach)^{2+}$. In the absence of this similarity conclusions from either the magnetic properties or the electronic spectrum would not have been firmly based. Calculations have indicated that the magnetic moments of either octahedral or trigonal-prismatic d^7 complexes will be very similar. Similarly, it appears that the electronic spectrum, which has been successfully assigned on the basis of trigonal-prismatic coordination, could be handled using an octahedral assignment. Thus, the band at 8430 cm^{-1} becomes the $^4T_1 \rightarrow {}^4T_2$ transition, while the $^4T_1 \rightarrow {}^4A_2$ transition could be the band at either 19,100 or 20,200 cm^{-1}, and the $^4T_1 \rightarrow {}^4T_1(P)$ transition would then be found at either 20,200 or 19,100 cm^{-1}.

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Appendix

The ligand field calculations were based on a trigonal prism with equal metal–ligand bond distances and a polar angle of half the tetrahedral angle, *e.g.*, 54° 44′, which is very close to the observed average polar angle of 52° in $Zn((py)_3tach)^{2+}$. Furthermore, a ready comparison of the energy levels of a trigonal-prismatic complex with this polar angle and a regular octahedral complex is possible since the polar angle in the latter is also 54° 44′. This comparison is readily achieved by deriving the ligand field potential in terms of an angle, φ, which describes the rotation of one triangular face of the prism with respect to the other. The trigonal prism exists at $\varphi = 0°$ while the octahedron then exists at $\varphi = 60°$. The potential is

$$V_{LF} = 14eq\sqrt{\pi}\{-Y_4{}^0 + \sqrt{5/14}[(1 - e^{-i3\varphi})\,Y_4{}^3 - (1 - e^{i3\varphi})\,Y_4{}^{-3}]\} \times (r^4/R^5)/9$$

where e and r are the electronic charge and radius while q and R are the effective ligand charge and metal–ligand distance, respectively, and the $Y_l{}^m$ are the angularly dependent spherical harmonics.[24] This potential reduces to that of an undistorted octahedron with $\varphi = 60°$. Furthermore, it is easily verified that it will depend only upon $Y_4{}^0$ when $\varphi = 0°$, *i.e.*, the trigonal prism. It is clear also that the matrix elements of this potential with the d orbitals will contain only fourth-order radial integrals. Consequently, it is convenient to define for any value of φ

$$Dq = {}^1/_6 eq\langle r^4/R^5\rangle$$

where the symbols have their usual meaning. This is, of course, the definition customarily used only for the octahedron. The nonvanishing matrix elements are $\langle d_{\pm2}|V_{LF}|d_{\pm2}\rangle = -{}^2/_3Dq$, $\langle d_{\pm1}|V_{LF}|d_{\pm1}\rangle = {}^8/_3Dq$, $\langle d_0|V_{LF}|d_0\rangle = -4Dq$, $\langle d_{\pm2}|V_{LF}|d_{\mp1}\rangle = \mp\sqrt{50/9}\cdot(1 - e^{\pm i3\varphi})Dq$, and $\langle d_{\mp1}|V_{LF}|d_{\pm2}\rangle = \pm\sqrt{50/9}(1 - e^{\mp i3\varphi})Dq$. The results are plotted as a function of φ in Figure 8. The pattern of orbital energies in the trigonal prism is then similar to that of an octahedron with a strong axial distortion.

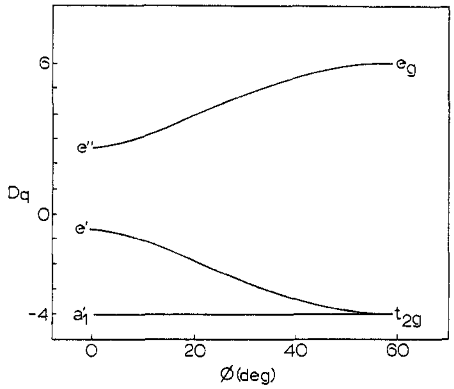

Figure 8.—The variation of the energies of the d orbitals as a function of φ, the angle between the trigonal faces of the polyhedron. The undistorted trigonal prism has $\varphi = 0°$, while the undistorted octahedron has $\varphi = 60°$.

A complete set of matrix elements for a d^8 electron configuration with $\varphi = 0°$ is given in Table IV. In addition, those which pertain to the quartet states of a d^7 electron configuration can also be obtained from Table IV. Free ion angular wave functions were the bases for each calculation.

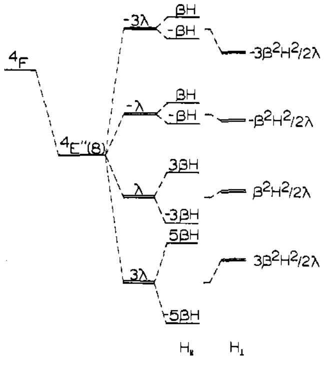

Figure 9.—Schematic representation of the successive influences of the ligand field, spin–orbit coupling, and magnetic field on the ^4F state from a d^7 electron configuration. Note that λ is negative so that the spin–orbit state with an energy of 3λ lies lowest.

The calculation of the magnetic moment for a d^7, trigonal-prismatic D_{3h} complex was of considerable importance. The ground state is $^4E''$ (see Figure 5) with its eightfold degeneracy derived from the $(a_1')^2(e')^3(e'')^2$ electronic configuration. No other states of the same symmetry exist. Consequently, the ligand field is not capable of causing an admixture of an excited state with the ground state, and the free ion wave func-

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[24] A complementary ligand field potential to account for the trigonal twist in $Ti(urea)_6{}^{3+}$ has been given by P. H. Davis and J. S Wood, *Chem. Phys. Lett.*, **4**, 466 (1969).

tions with $L = 3$ and $M_l = 2$ are a completely suitable basis for the calculation. Inclusion of spin–orbit coupling removes the eightfold degeneracy and gives four doubly degenerate levels at 3λ, λ, $-\lambda$, and -3λ. To simplify the calculation, the admixture of excited states with the ground state through spin–orbit coupling was neglected. The application of the Zeeman operators for the two unique directions yields the results given in Figure 9. The parallel and perpendicular susceptibilities, according to the Van Vleck equation, are

$$\chi_{\parallel} = \left(\frac{N\beta^2}{kT}\right)\frac{25 + 9e^{2x} + e^{4x} + e^{6x}}{1 + e^{2x} + e^{4x} + e^{6x}}$$

$$\chi_{\perp} = \left(\frac{N\beta^2}{kT}\right)\left(\frac{1}{x}\right)\frac{-3 - e^{2x} + e^{4x} + 3e^{6x}}{1 + e^{2x} + e^{4x} + e^{6x}}$$

with $x = \lambda/kT$. Magnetic moments were calculated according to $\mu_{\text{eff}} = (3kT/N\beta^2)^{1/2}(^1/_3\chi_{\parallel} + {}^2/_3\chi_{\perp})^{1/2}$.

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Halogenated Symmetrical Dipyrromethene Chelates[1,2]

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A series of new chloro- and bromodipyrromethene chelates, synthesized by a novel metal ion exchange reaction, is described. These compounds were studied by nuclear magnetic resonance spectrometry and by infrared and electronic spectrophotometry. Physical and spectroscopic evidence are interpreted and correlated to deduce the microscopic structures of the Ca(II), Cu(II), Ni(II), Zn(II), and Mn(II) chelates with 3,3′,4,4′-tetrachloro- and 3,3′,4,4′-tetrabromo-5,5′-dicarbethoxy-2,2′-dipyrromethene ligands.

Dipyrromethenes have been known for many years and have been widely used as intermediates in porphyrin synthesis.[4] Their ability to form stable chelates with bivalent metal ions has also been described.[4] Since the initial work on these interesting chelate compounds comparatively few structural investigations have been reported. Porter[5] was the first to call attention to the exciting stereochemical problem caused by bulky substituents in the adjacent α positions of different ligands coordinated to the same metal ion. Mellor and Lockwood[6] measured the magnetic moment of a Ni(II) chelate. West[7] investigated the exchange of radioactive Co(II) with a cobalt(II) dipyrromethenato chelate in pyridine solution. Corwin and Melville[8] studied the relative stabilities of metal chelates of porphyrins and dipyrromethenes. Eley and Spivey[9] measured the semiconductivities of several dipyrromethene chelates and concluded that there is some interaction between the π systems of ligands coordinated to the same metal ion. Ferguson, *et al.*,[10,11] studied several bivalent metal chelates and on the basis of ligand field spectra, magnetic data, and X-ray powder photographs made conclusions favoring a general tendency toward tetrahedral configuration irrespective of the presence of α substituents on the ligand. Murakami and Sakata[12] complemented this study with the inclusion of both near- and far-infrared spectral data as well as the calculation of Racah interelectronic repulsion integrals for these and similar systems.

The purpose of this work is to extend the relatively limited body of information available on dipyrromethene chelates. For the first time nuclear magnetic resonance (pmr) evidence is used in the elucidation of the structure of dipyrromethene chelates. This information is correlated with infrared and electronic spectra, followed by a discussion of heretofore unreported effects of the electronegative halo substituents on the ligands. Novel dipyrromethene chelates of a nontransition element ion, the Ca(II) ion, are described for the first time.

Experimental Section

General Data.—Melting points were obtained with a Fisher-Johns melting point apparatus and are uncorrected. The microanalytical determinations were made by Alfred Bernhardt, Hohenweg, Germany. The proton magnetic resonance spectra were measured with a Varian Model A-60 spectrometer (tetramethylsilane internal standard; τ units[13]). The solution infrared spectra were recorded with Spectrograde carbon tetrachloride as solvent in 0.10-mm sodium chloride cells on a Beckman Model IR-8 spectrophotometer calibrated with polystyrene film. The ultra-

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[2] Abstracted in part from a thesis submitted by R. J. Motekaitis to the faculty of the Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June 1967.

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