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Transition Metal Complexes with Schiff Base Derivatives of 1,1,1-Tris(aminomethyl)ethane

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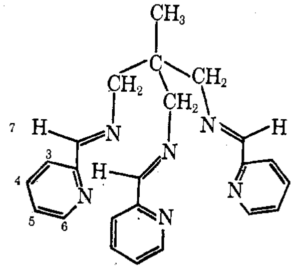
Complexes of Schiff base condensates derived from pyridine-2-carboxaldehyde and 1,1,1-tris(aminomethyl)ethane have been prepared with Mn(II), Fe(II), Co(III), Ni(II), Cu(II), and Zn(II) ions *via* a template reaction. Analytical data reveal that the Mn(II) and Cu(II) complexes contain a potentially pentadentate ligand, ($(py)_2$ tame), in which only 2 mol of pyridine-2-carboxaldehyde has condensed with the triamine. Complexes containing the sexadentate ligand 1,1,1-tris(pyridine-2-carboxaldiminomethyl)ethane ($(py)_3$tame) were obtained for the remaining metal ions as shown by analytical, infrared, and ^{1}H nmr spectral data. The ^{1}H nmr spectra of diamagnetic Fe($(py)_3$tame)$^{2+}$ and Co($(py)_3$tame)$^{3+}$ reveal that these complexes are pseudooctahedral on the basis of the observed diastereotopic behavior of the methylene protons. In aqueous solution, the methylene AB pattern of the Fe(II) chelate collapses to a singlet at 95°, indicating racemization of the pseudooctahedral structure. ^{1}H nmr evidence also indicates that racemization of the Co(III) chelate in DMSO solution occurs at ~145°. The ^{1}H nmr spectrum of the paramagnetic Ni(II) complex provided proof for the sexadentate coordination of the ligand but no conclusive evidence for the stereochemistry of this complex was obtained. The spectral and magnetic properties of the complexes in which $(py)_3$tame functions as a sexadentate ligand are assigned on the basis of pseudooctahedral structures.

Introduction

Sexadentate ligands which produce metal ion complexes having a characteristic trigonal symmetry were originally designed[1] and synthesized[2] by Lions and coworkers. Recently there has been renewed interest[3–9] in trigonal sexadentate ligands arising from their potential capabilities to produce complexes with coordination geometries distorted from typical octahedral arrangements. The nickel(II) complex of *cis,cis*-1,3,5-tris(pyridine-2-carboxaldimino)cyclohexane, Ni($(py)_3$tach)$^{2+}$, exhibits an unusual ligand field spectrum which suggests that this complex has a trigonally distorted stereochemistry.[3,5] Recently, a totally encapsulated Ni(II) complex has been synthesized[6] where the metal ion is constrained in a trigonal-prismatic environment and displays an electronic spectrum similar to that of Ni($(py)_3$tach)$^{2+}$. In the absence of ligand field stabilization of octahedral geometry the less rigid ligand $(py)_3$tach also produces trigonal-prismatic complexes, *i.e.*, with Zn(II), Mn(II), and Co(II).[4,5]

We have extended our studies to a similar trigonal sexadentate ligand, 1,1,1-tris(pyridine-2-carboxaldiminomethyl)ethane ($(py)_3$tame), **1**, and report here the preparation and characterization of a series of transition metal complexes with this ligand. Unlike $(py)_3$tach, the ligand $(py)_3$tame offers a potential probe of the stereochemistry adopted by a metal ion upon complexation. For a chiral, pseudooctahedral complex of $(py)_3$tame the methylene protons will be magnetically nonequivalent and may exhibit a pair of AB doublets in the ^{1}H nmr spectrum.



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Complexes of $(py)_3$tame which possess pseudooctahedral coordination geometries provide simplified systems for the study of metal chelate racemization mechanisms. Tris-bidentate chelates[10–14] can undergo racemization by several different twisting (no bond rupture) pathways or by bond-rupture mechanisms involving five-coordinate intermediates. In comparison to this complicated situation existing for tris-bidentate complexes, the steric constraints imposed by the sexadentate ligand $(py)_3$tame greatly restrict the possible pathways for racemization. Two of the complexes described here, Fe($(py)_3$tame)$^{2+}$ and Co($(py)_3$tame)$^{3+}$, undergo facile racemization and a preliminary investigation of the mechanistic details of these processes is reported. Preliminary reports of crystallographic[7] and nmr[7,8] studies of $(py)_3$tame chelates have appeared.

Experimental Section

Syntheses.—1,1,1-Tris(aminomethyl)ethane (tame) was prepared by a modification of the Gabriel synthesis reported[15] previously. Pyridine-2-carboxaldehyde (Aldrich Chemical Co.) was distilled prior to use. All solvents and materials employed in this study were reagent grade or equivalent.

Preparation of the Metal Complexes.—To a warm solution containing 0.01 mol of tame and 0.01 mol of an appropriate metal salt in dry ethanol was slowly added 0.03 mol of pyridine-2-carboxaldehyde. After gentle reflux for 5–10 min, the solution was allowed to cool whereupon the complex usually precipitated. The crystals were collected, washed with ethanol, and dried *in vacuo*. The yields were approximately 30% based on the triamine. All of the complexes were recrystallized from methanol and all were stable toward air after drying.

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(1) F. Lions, *Rec. Chem. Progr.*, **22**, 69 (1961).

(2) F. P. Dwyer, N. S. Gill, E. C. Gyarfas, and F. Lions, *J. Amer. Chem. Soc.*, **79**, 1269 (1957).

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

(4) W. O. Gillum, J. C. Huffman, W. E. Streib, and R. A. D. Wentworth, *ibid.*, 843 (1969).

(5) W. O. Gillum, R. A. D. Wentworth, and R. F. Childers, *Inorg. Chem.*, **9**, 1825 (1970).

(6) J. E. Parks, B. E. Wagner, and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 3500 (1970).

(7) E. B. Fleischer, A. E. Gebala, and P. A. Tasker, *ibid.*, **92**, 6365 (1970).

(8) F. L. Urbach and S. O. Wandiga, *J. Chem. Soc. D*, 1572 (1970).

(9) J. E. Sarneski and F. L. Urbach, *J. Amer. Chem. Soc.*, **93**, 884 (1971).

(10) R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964).

(11) C. S. Springer, Jr., and R. E. Sievers, *ibid.*, **6**, 852 (1967).

(12) J. G. Gordon, II, and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 5319 (1970).

(13) A. Y. Girgis and R. C. Fay, *ibid.*, **92**, 7061 (1970).

(14) J. R. Hutchison, J. G. Gordon, II, and R. H. Holm, *Inorg. Chem.*, **10**, 1004 (1971).

(15) H. Stetter and W. Bockmann, *Chem. Ber.*, **84**, 834 (1951).

1,1-Bis(pyridine-2-carboxaldiminomethyl)-1-(aminomethyl)-ethanemanganese(II) chloride, Mn((py)$_2$tame)Cl$_2$, was obtained as white crystals by the above method. The synthesis was performed under a nitrogen atmosphere; however, the dried solid complex was nonhygroscopic and stable toward air. Moist samples of this complex rapidly turn brown upon exposure to air. *Anal.* Calcd for $MnC_{17}H_{21}N_5Cl_2$: C, 47.35; H, 5.15; N, 16.24. Found: C, 47.75; H, 5.01; N, 16.21. **1,1-Bis(pyridine-2-carboxaldiminomethyl)-1-(aminomethyl)ethanecopper(II) chloride monohydrate, Cu((py)$_2$tame)Cl$_2\cdot$H$_2$O,** was obtained as blue-green crystals by the above method followed by recrystallization from a water–ethanol mixture. *Anal.* Calcd for $CuC_{17}H_{23}N_5OCl_2$: C, 45.59; H, 5.18; N, 15.83. Found: C, 45.45; H, 4.98; N, 15.53. **1,1,1-Tris(pyridine-2-carboxaldiminomethyl)-ethanezinc(II) perchlorate, Zn((py$_3$)tame)(ClO$_4$)$_2$,** was obtained as light yellow needles. Zinc acetate tetrahydrate was employed in the reaction; sodium perchlorate was added to precipitate the perchlorate salt. *Anal.* Calcd for $ZnC_{23}H_{24}N_6O_8Cl_2$: C, 42.65; H, 3.73; N, 12.95. Found: C, 42.43; H, 3.78; N, 12.86.

1,1,1-Tris(pyridine-2-carboxaldiminomethyl)ethanenickel(II) perchlorate, Ni((py)$_3$tame)(ClO$_4$)$_2$, was obtained as deep red crystals. Nickel chloride hexahydrate was employed for the synthesis; sodium perchlorate was added to precipitate the perchlorate salt. *Anal.* Calcd for $NiC_{23}H_{24}N_6O_8Cl_2$: C, 43.02; H, 3.77; N, 13.09. Found: C, 42.90; H, 3.76; N, 13.01.

1,1,1-Tris(pyridine-2-carboxaldiminomethyl)ethanecobalt(III) iodide trihydrate, Co((py)$_3$tame)I$_3\cdot$3H$_2$O, was obtained by oxidizing the cobalt(II) complex with 3% hydrogen peroxide and adding tetra-*n*-hexylammonium iodide to precipitate the complex. The dark red crystalline complex decomposes above 100° and is very hygroscopic. *Anal.* Calcd for $CoC_{23}H_{30}N_6O_3I_3$: C, 31.42; H, 3.43; N, 9.56. Found: C, 31.61; H, 2.88; N, 9.67.

1,1,1-Tris(pyridine-2-carboxaldiminomethyl)ethaneiron(II) chloride dihydrate, Fe((py)$_3$tame)Cl$_2\cdot$2H$_2$O, was obtained as red-purple crystals by the literature method.[2] *Anal.* Calcd for $FeC_{23}H_{28}N_6O_2Cl_2$: C, 49.55; H, 5.21; N, 15.08. Found: C, 49.77; H, 5.34; N, 15.30.

Physical Measurements.—Infrared spectra were obtained for Nujol mulls with a Beckman IR-8 spectrophotometer. A Cary Model 14 recording spectrophotometer equipped with a high-intensity tungsten source was used to measure electronic spectra. Magnetic susceptibilities were measured by the Faraday method. Hg[Co(NCS)$_4$] was employed as a calibrant; diamagnetic corrections for the ligands were calculated from tables[16] of Pascal's constants. Galbraith Laboratories, Knoxville, Tenn., provided the microanalytical data.

Proton nmr measurements were obtained with Varian A-60A or HA-100 spectrometers equipped with variable-temperature units. Frequencies were measured by the usual side-band technique relative to tetramethylsilane (TMS) or 3-(trimethylsilyl)-1-propanesulfonate (DSS) as internal references. Sample concentration ranged between 0.05 and 0.1 *M*. Spectral data for each complex were taken at least five times on different samples. The spectra of the paramagnetic nickel(II) chelates were obtained with the HA-100 instrument using a modulation frequency of 30 kHz produced by an external signal generator and calibrated by the frequency counter (V-4315) on the instrument. The compensated driver amplifier circuit was replaced with a modified circuit, Varian 910884-01, to enhance the signal to noise ratio. Spectra were obtained without an internal lock signal by sweeping the magnetic field, carefully minimizing field drift. Signal saturation was generally not observed although high power levels were employed. Planimetric integration of resonance areas was performed where possible.

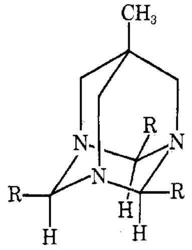
For the acid-dependence racemization studies, the pH of the solutions was adjusted with D_2SO_4 or NaOD solutions. The concentration of complex ion in these solutions was 0.03–0.05 *M*. The **pH measurements** were made with a Sargent-Welch Model LS pH meter, using a Sargent combination glass electrode. Nmr spectra were measured immediately after the pH adjustment and after a period of 48 hr. A correction of 0.40 unit was added to all pH readings to compensate for the differential glass electrode response in H_2O and D_2O.[17]

Conductivity measurements were made at 25.0 ± 0.2° with an Industrial Instruments Model RC 16B2 conductivity bridge. The cell constant ($\theta = 1.434 \pm 0.007$ cm^{-1}) was determined using 0.100 *M* KCl solutions. The absolute methanol used as a solvent gave a specific conductivity of 1.0×10^{-6} ohm^{-1} cm^{-1}.

Kinetic Analysis.—The kinetics of the racemization of Co((py)$_3$tame)$^{3+}$ in DMSO-d_6 and Fe((py)$_3$tame)$^{2+}$ in D_2O were determined from the temperature dependence of the resonance positions of the methylene protons. Each dynamic process was treated as a simple two-site exchange between environments A and B which have identical populations and relaxation times. The separation of the AB protons at 32° was taken as the frozen state for both systems since lowering the temperature did not result in a further spread of the peak positions. The measured separations ($\Delta\nu$) were corrected for solvent and temperature effects from a plot of $\Delta\nu$ *vs.* T. The peak separations used in calculating the rate constants were then read from this plot.

Results and Discussion

The condensation of pyridine-2-carboxaldehyde with tris(aminomethyl)ethane (tame) in the absence of a metal salt leads to the cross-condensed product **2**.[18]



2, R = 2-pyridyl

Ferrous ion is capable of producing a rearrangement of this cross-condensed hexamine to the Schiff base form **1**, presumably *via* stabilization of the α-diimine grouping.[18] Since other metal ions do not effect this transformation, it is necessary to employ a template reaction in order to prepare complexes containing the Schiff base form of the ligand. This template reaction is accomplished by combining aqueous or alcoholic solutions of an appropriate metal salt and tame in a 1:1 mole ratio and then adding pyridine-2-carboxaldehyde. Since the condensation reaction occurs near or within the coordination sphere of the metal ion, the Schiff base form of the ligand is immediately complexed and cross condensation is precluded. For those reactions where a color change is produced, *i.e.*, Ni(II) and Cu(II), the condensation appears to be instantaneous. Complexes which did not crystallize spontaneously were precipitated in crystalline form by the addition of sodium perchlorate.

Complexes of (py)$_2$tame.—For two metal ions, Mn(II) and Cu(II), the above preparative method yielded products in which only 2 mol of pyridine-2-carboxaldehyde condensed with the triamine. The composition of these chelates as deduced from analytical data was supported by their infrared spectra which indicated the presence of a primary amine group.

An attempt was made to determine the nature of the coordination of the potentially pentadentate ligand, (py)$_2$tame, with Mn(II) and Cu(II). The magnetic moment (Table I) of Mn((py)$_2$tame)Cl$_2$ is typical[19] for a high-spin Mn(II) complex. No absorption bands for the d–d transitions of Mn((py)$_2$tame)$^{2+}$ were observed, presumably because of the low extinction coefficients of these spin-forbidden transitions.[20] The position of the amine stretching frequency (3358 cm^{-1})

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(16) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960, Chapter 6.

(17) P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 188 (1960).

(18) D. A. Durham, F. A. Hart, and D. Shaw, *J. Inorg. Nucl. Chem.*, **29**, 509 (1967).

(19) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 154 (1964).

(20) C. K. Jørgensen, *Inorg. Chim. Acta*, **3**, 313 (1969).

TABLE I

MAGNETIC MOMENTS FOR THE COMPLEXES[a]

Complex	μ'_{eff},[b] BM
Mn((py)$_2$tame)Cl$_2$	5.85
Cu((py)$_2$tame)Cl$_2$	1.81
Ni((py)$_3$tame)(ClO$_4$)$_2$	2.97

[a] Measured by the Faraday method. [b] Bohr magnetons.

in the solid-state infrared spectrum of Mn((py)$_2$tame)$^{2+}$ is close to those observed for the free amine tame (3390, 3300, and 3200 (sh) cm^{-1}) and suggests only a weak coordination of the primary amine group.[21] A molar conductance value of 76 ohm^{-1} cm^2 mol^{-1} in methanol indicates a 1:1 electrolyte behavior for this complex in this solvent.

For the complex Cu((py)$_2$tame)Cl$_2$·H$_2$O, the solid-state magnetic moment of 1.81 BM is consistent with a d^9 configuration. Cu((py)$_2$tame)Cl$_2$·H$_2$O is formulated as a 1:1 electrolyte in methanol, presumably with a coordinated chloride ion, on the basis of a molar conductance value of 69.5 ohm^{-1} cm^2 mol^{-1}. The electronic spectrum of [Cu((py)$_2$tame)Cl]$^+$ in methanol (Table II) is significantly different from that reported[22] for the analogous tetradentate complex [*N*,*N*′-bis(pyridyl-2-methylene)-1,3-diaminopropane]copper(II) perchlorate in nitromethane ($\nu_{\max}$ 16,500 cm^{-1}, ϵ 90) where no axial coordination is expected to occur. In methanol solution, where conductance data suggest the axial coordination of a chloride ion, the band maxima for this complex shifts to 12,900 cm^{-1} (ϵ 195), characteristic of a five-coordinate [Cu$^{\text{II}}$N$_4$X]$^+$ chromophore.[22] [Cu((py)$_2$tame)Cl]$^+$ exhibits a band maximum in methanol at higher energy than [Cu$^{\text{II}}$N$_4$X]$^+$ which suggests some additional axial perturbation by the primary amine group. This axial amine coordination, which is invoked to rationalize the electronic spectral data, is supported by the observed solid-state amine stretching frequency (ν_{NH} 3330 cm^{-1}) which is lowered compared to that of the free amine tame.

TABLE II

ELECTRONIC SPECTRAL DATA FOR THE COMPLEXES

Complex	Phase (solvent)	$\tilde{\nu}_{\max}$[a] ($\epsilon_{\max}$)
Cu((py)$_2$tame)Cl$_2$	Solid	15,000
	Methanol	15,000 (103)
Ni((py)$_3$tame)(ClO$_4$)$_2$	Water	11,800 (22) sh,[b] 12,500 (27), 20,600 (70) sh[b]
Ni((pic)$_3$tach)(PF$_6$)$_2$	Water	12,000 (11) sh,[b] 12,600 (16), 19,600 (13)
Co((py)$_3$tame)I$_3$·3H$_2$O	Water	22,875 (260), 32,790 (14,300), 35,250 (14,400), 44,450 (80,400)
Fe((py)$_3$tame)Cl$_2$·2H$_2$O	Methanol	17,610 (14,400), 19,230 (9000) sh,[b] 28,170 (4950), 36,500 sh,[b] 42,000 (26,800)

[a] Reported in cm^{-1}. [b] Shoulder.

Complexes of the Sexadentate Ligand (py)$_3$tame.—For Fe(II), Co(III), Ni(II), and Zn(II), it was possible to obtain crystalline salts with a stoichiometry corresponding to the presence of the intact ligand (py)$_3$tame. The coordination stereochemistry and electronic structure of each of these derivatives will now be discussed in detail.

Zn((py)$_3$tame)(ClO$_4$)$_2$.—A trigonal-prismatic coordination geometry has been established for a similar Zn(II) complex[4,5] with the ligand *cis,cis*-1,3,5-tris(pyridine-2-carboxaldimino)cyclohexane, Zn((py)$_3$tach)$^{2+}$. In view of this result an attempt was made to determine the stereochemistry of the less rigidly constrained chelate Zn((py)$_3$tame)$^{2+}$. The 100-MHz ^{1}H nmr spectrum for Zn((py)$_3$tame)$^{2+}$ (Figure 1) indicates that the ligand functions in a sexadentate manner in DMSO-d_6 solution. This conclusion is based on the observed simplicity of the pyridine aromatic resonances and the single azomethine proton resonance. (See Table III.)

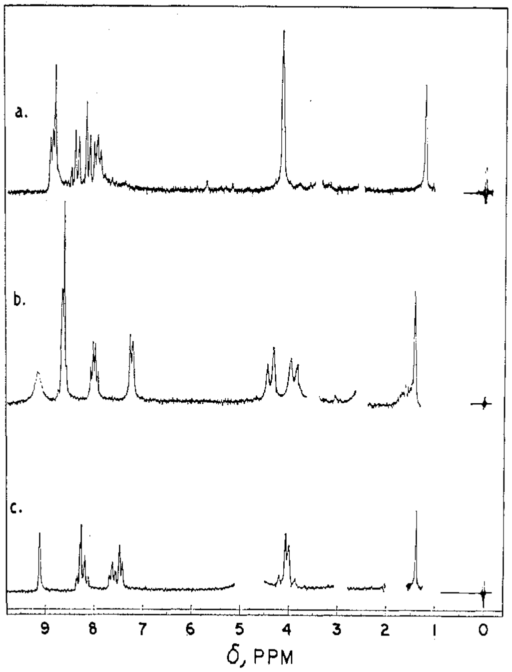

Figure 1.—The ^{1}H nmr spectra of the diamagnetic M((py)$_3$tame)$^{n+}$ complexes: (a) Zn((py)$_3$tame)$^{2+}$ in DMSO-d_6, TMS as internal standard; (b) Co((py)$_3$tame)$^{3+}$ in DMSO-d_6, DSS (sodium 3-(trimethylsilyl)propane-1-sulfonate) as internal standard; (c) Fe((py)$_3$tame)$^{2+}$ in D$_2$O, DSS as internal standard. Solvent and reference signals have been deleted for simplicity.

TABLE III

^{1}H NMR DATA FOR THE DIAMAGNETIC COMPLEXES[a]

Complex	δ_i (*vs.* DSS), ppm CH$_3$	CH$_2$	3	4	5	6	7
Zn((py)$_3$tame)(ClO$_4$)$_2$[b,c]	1.31	4.29	8.21	8.42	8.00	9.04	8.92
Co((py)$_3$tame)I$_3$·3H$_2$O[b]	1.42	3.90[d] 4.38	7.24	8.00	8.00	8.65	9.16
Fe((py)$_3$tame)Cl$_2$·2H$_2$O[e]	1.40	3.99[f] 4.12	8.41	8.24	7.70	7.50	9.26

[a] The pyridine proton resonances were assigned by reference to the coupling constant data reported by F. A. Kramer and R. West, *J. Phys. Chem.*, **69**, 673 (1965). [b] In DMSO-d_6 solution at 298°K. [c] TMS as internal standard. [d] J_{AB} = 13 Hz. [e] In D$_2$O solution at 298°K. [f] J_{AB} = 14 Hz.

The methylene protons in Zn((py)$_3$tame)$^{2+}$ offer a potential probe for the stereochemistry of this chelate. If the ligand adopts a chiral, pseudooctahedral geometry, the two methylene protons will be magnetically nonequivalent and may exhibit an AB pattern. At room temperature in DMSO-d_6 solution, the methylene protons exhibit a sharp singlet (half-bandwidth 3 Hz). Fleischer, *et al.*,[7] have reported that in acetonitrile-d_3 the methylene proton resonance is split with a coupling constant of 2 Hz and have concluded from this observa-

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[21] J. Chatt, L. A. Duncanson, and L. M. Venanzi, *J. Chem. Soc.*, 4461 (1955); 2712 (1956).

[22] C. M. Harris and E. D. McKenzie, *J. Chem. Soc. A*, 746 (1969).

TABLE IV

^{1}H NMR DATA FOR THE PARAMAGNETIC NICKEL(II) COMPLEXES[a]

Complex[c]	δ_i (*vs.* TMA[b]), ppm CH$_3$	α-CH	β-CH$_2$	3	4	5	6	7
$Ni((py)_3tame)^{2+}$	+1.2	*d*	...	−46	−12	−46	*d*	*d*
$Ni((py)_3tach)^{2+}$	...	−300	+8.6 +7.4	−44	−11	−43	−120	−270
$Ni((pic)_3tach)^{2+}$	...	*d*	+18 +14	−41	−11	−41	−120	*d*

[a] Assignments of the resonances were made by comparison with the spectra of the diaquo[*N,N'*-bis(pyridyl-2-methylene)-1,3-diaminopropane]nickel(II) cation and substituted derivatives.[24] [b] TMA = tetramethylammonium ion. [c] In D_2O solution at 298°K. [d] Not observed.

tion that $Zn((py)_3tame)^{2+}$ is distorted away from a trigonal-prismatic geometry in solution. We have examined the source of this observed splitting and have found that it arises from allylic coupling between the methylene protons and the azomethine proton. Upon double irradiation at 860 Hz, the position of the azomethine signal, the methylene doublet collapses to a sharp singlet. The lack of observable magnetic nonequivalence of the methylene protons rules out a static pseudooctahedral structure provided that the chemical shift difference between the A and B protons is sufficient to be observed. As shown below an observable chemical shift difference for the methylene protons is obtained for the Fe(II) and Co(III) complexes. It is concluded therefore that $Zn((py)_3tame)^{2+}$ either (1) possesses a trigonal-prismatic stereochemistry or (2) is undergoing rapid racemization which averages the environments of the methylene protons. Although a singlet was observed for the methylene protons down to −47° (in acetone-d_6:DMSO-d_6 = 10:1), a choice cannot be made between these two possible explanations. The less rigid ligand $(py)_3tame$ should not impose a trigonal-prismatic geometry on the Zn(II) to the same extent as $(py)_3tach$; however, the trigonal-prismatic structure cannot be ruled out or be confirmed from the present data since a facile racemization process involving pseudooctahedral enantiomers could also produce the observed pmr behavior.

$Ni((py)_3tame)(ClO_4)_2$.—The red-brown complex $Ni((py)_3tame)(ClO_4)_2$ is similar in appearance and spectral properties (*vide infra*) to the closely analogous complex $Ni((py)_3tach)(ClO_4)_2$.[3,5] In view of the difficulty encountered in assigning the stereochemistry of $Ni((py)_3tach)^{2+}$ on the basis of its electronic absorption spectrum,[3,5] an attempt was made to determine the coordination geometry of $Ni((py)_3tame)^{2+}$ by means of ^{1}H nmr spectroscopy. The chemical shift data for $Ni((py)_3tame)^{2+}$ are summarized in Table IV, along with the corresponding data for the related complexes $Ni((py)_3tach)^{2+}$ and $Ni((pic)_3tach)^{2+}$ for comparison. $Ni((pic)_3tach)^{2+}$ represents the complex obtained upon the hydrogenation of the three azomethine linkages in $Ni((py)_3tach)^{2+}$.

The three fully paramagnetic nickel(II) complexes give rise to contact-shifted[23] resonances ranging from +20 to −300 ppm relative to $(CH_3)_4N^+$. Assignments of the resonances are made by comparison with the extensive contact shift data for coordinated pyridine[24-26] and by comparison with the contact-shift spectra of diaquo[*N,N'*-bis(pyridyl-2-methylene)-1,3-diaminopropane]nickel(II) cation, $Ni((pya)_2tn)(D_2O)_2^{2+}$, and substituted derivatives.[27]

The most strongly shifted resonances for $Ni((py)_3tach)^{2+}$ were difficult to locate because of their large bandwidths. In the case of $Ni((py)_3tame)^{2+}$ and $Ni((pic)_3tach)^{2+}$ several of the resonances which are most influenced by the unpaired spin could not be detected. Similar broadening was observed for the 6-H, 7-H (azomethine), and α-CH_2 resonances of $Ni((pya)_2tn)^{2+}$ in the presence of pyridine and was suggested[27] to arise from an unfavorable electronic relaxation time for the nickel(II) ion coordinated with six imine donors. The failure to observe the α-CH_2 resonances of $Ni((py)_3tame)^{2+}$ ruled out the possibility of using these protons as a probe of the stereochemistry of the complex. For the observed resonances, the presence of only one signal for each unique proton confirms the sexadentate nature of the ligands in the three nickel(II) complexes.

The contact shifts observed for the pyridine protons are similar to those reported[24-27] for various substituted pyridines and the same electron delocalization mechanism undoubtedly prevails. This mechanism involves primarily the direct delocalization of unpaired electrons *via* the ligand σ-bonding system. All of the proton shifts are predicted to occur at lower fields and attenuate with increasing distance from the metal ion. This mechanism, however, cannot explain the upfield shifts of the β protons in $Ni((py)_3tach)^{2+}$. A spin-polarization mechanism, discussed by Milner and Pratt,[28] has been used to explain upfield β-proton shifts in six-membered chelate rings[28,29] and for the γ-proton shift of quinuclidine.[30] According to this mechanism, spin density will alternate in sign along a σ-bonded network, beginning with the donor atom which possesses positive spin. Nuclei experiencing positive spin density will be shifted to lower fields, whereas nuclei with negative spin density will be shifted upfield. The observed upfield shifts for the β protons in $Ni((py)_3tach)^{2+}$ may be rationalized by the spin polarization mechanism, Figure 2.

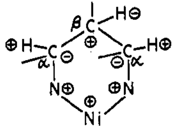

Figure 2.—The spin-polarization mechanism for spin delocalization in a fragment of $Ni((py)_3tach)^{2+}$. (+, − refer to the sign of spin density at nucleus.)

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[23] The usual assumption is made that nickel(II) complexes are magnetically isotropic and do not give rise to dipolar shifts.

[24] R. E. Cramer and R. S. Drago, *J. Amer. Chem. Soc.*, **92**, 66 (1970).

[25] G. N. La Mar and L. Sacconi, *ibid.*, **90**, 7216 (1968).

[26] R. H. Holm, G. W. Everett, Jr., and W. DeW. Horrocks, Jr., *ibid.*, **88**, 1071 (1966).

[27] T. G. Campbell, Ph.D. Thesis, Case Western Reserve University, 1970.

[28] R. S. Milner and L. Pratt, *Discuss. Faraday Soc.*, **34**, 88 (1962).

[29] L. Pratt and B. B. Smith, *Trans. Faraday Soc.*, **65**, 915 (1969).

[30] T. Yonezawa, I. Morishima, and Y. Ohmori, *J. Amer. Chem. Soc.*, **92**, 1267 (1970).

Recent empirical evidence[29,31–33] indicates that the delocalization of unpaired electron density from the metal ion to the α protons of the 1,2-diaminenickel(II) chelate ring depends on the dihedral angle of the Ni–N and C–H bonds in the Ni–N–C–H fragment. The extent of spin delocalization and hence the magnitude of the contact shift appear to fit a $\cos^2 \theta$ relationship,[32] where θ is the dihedral angle; protons with θ values close to 0 or 180° exhibit the largest contact shifts. The assignment of the α-CH resonance of $\mathrm{Ni((py)_3tach)^{2+}}$ at 300 ppm, one of the largest chemical shifts reported, is consistent with this dihedral angle relationship. This proton, which upon complexation is locked in an equatorial ring position, makes an angle of nearly 180° between the H–C–N and Ni–N–C planes. The β protons in $\mathrm{Ni((py)_3tach)^{2+}}$ exhibit a less pronounced dihedral angle dependence and give rise to different resonances.

The ligand field spectrum of $\mathrm{Ni((py)_3tame)^{2+}}$ (Figure 3) is slightly different from that reported[3,5] for $\mathrm{Ni((py)_3tach)^{2+}}$ and probably reflects the less rigid nature of the former complex ion. Whereas the spectrum of $\mathrm{Ni((py)_3tach)^{2+}}$ could not be assigned[3,5] readily by an octahedral model, the assignment of the 12,500-cm^{-1} band of $\mathrm{Ni((py)_3tame)^{2+}}$ to the $^3\mathrm{A}_{2g} \rightarrow {}^3\mathrm{T}_{2g}$ transition yields a Dq value (1250 cm^{-1}) in line with other tris(diimine)nickel(II) complexes.[34,35] The bands at 11,800 and 20,600 cm^{-1} are attributed to the $^3\mathrm{A}_{2g} \rightarrow {}^1\mathrm{E}_g$ and $^3\mathrm{A}_{2g} \rightarrow {}^3\mathrm{T}_{2g}(\mathrm{F})$ transitions, respectively. The calculation[36] of the Racah parameter B from the ratio of the two lowest spin-allowed transitions is not meaningful since the $^3\mathrm{A}_{2g} \rightarrow {}^3\mathrm{T}_{2g}(\mathrm{F})$ position is strongly influenced by an underlying intense transition. Although the band energies give a reasonable fit to an octahedral model, the molar absorptivity values (ϵ >20), which are similar to those observed for $\mathrm{Ni((py)_3tach)^{2+}}$[3,5] and a trigonal-prismatic, encapsulated Ni(II) complex,[6] suggest a significant trigonal distortion. The Ni(II) complex of the less rigid ligand (pic)$_3$tach exhibits significantly less intense ligand field transitions. Assignment of the spectrum of $\mathrm{Ni((pic)_3tach)^{2+}}$ on an octahedral model yields reasonable values of both Dq (1260 cm^{-1}) and B (840 cm^{-1}).

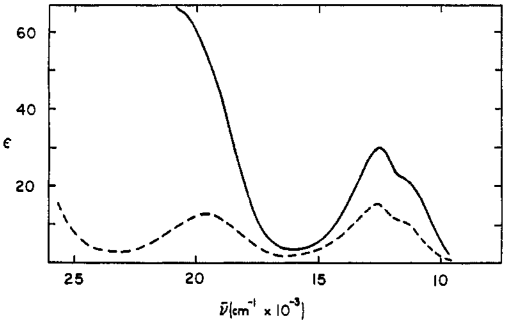

Figure 3.—Electronic spectra of $\mathrm{Ni((py)_3tame)^{2+}}$ (——) and $\mathrm{Ni((pic)_3tach)^{2+}}$ (- - -) in aqueous solution.

$\mathrm{Co((py)_3tame)I_3 \cdot 3H_2O}$.—A cobalt(III) complex of (py)$_3$tame was obtained upon hydrogen peroxide oxidation of a reaction mixture presumably containing $\mathrm{Co((py)_3tame)^{2+}}$. The ^{1}H nmr spectrum of diamagnetic $\mathrm{Co((py)_3tame)^{3+}}$ in dimethyl-d_6 sulfoxide (Figure 1) confirms the sexadentate coordination of the intact ligand and provides evidence for the pseudooctahedral geometry of this complex. The methylene protons exhibit an AB pattern indicating that these two protons are in diastereotopic environments. As described previously, this nonequivalence could only occur if the complex $\mathrm{Co((py)_3tame)^{3+}}$ possessed a chiral, pseudooctahedral geometry. The chemical shift difference between the two AB doublets decreases systematically with increasing temperature and coalescence of the quartet pattern is achieved at ~145° (Figure 4). This averaging of the nonequivalent methylene protons indicates that rapid interconversion of the two enantiomeric forms of the pseudooctahedral complex is occurring. From the observed decrease in separation of the AB doublets for $\mathrm{Co((py)_3tame)^{3+}}$ we have calculated the rate constants for this process at 80, 90, 100, 110, and 120° to be 678, 1238, 1415, 2010, and 2887 sec^{-1}, respectively, using the rate equation of Gutowsky and Holm[37] for intermediate exchange between two equally populated sites, $k = \tau^{-1} = \sqrt{2}\pi(\Delta\nu_0{}^2 - \Delta\nu^2)$. A plot of log k *vs.* $1/T$ yielded a straight line from which an Arrhenius activation energy (E_a) of 10.1 kcal/mol and a frequency factor of exp(9.0) sec^{-1} were calculated.

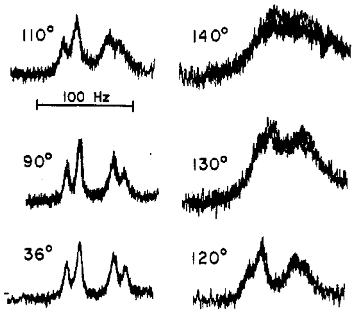

Figure 4.—Temperature dependence of the methylene resonances of $\mathrm{Co((py)_3tame)^{3+}}$ measured in DMSO-d_6 solution *vs.* DSS as an internal standard.

The values obtained for the exchange rates are subject to a relatively large uncertainty which arises from several sources. There exists the possibility of slight decomposition of $\mathrm{Co((py)_3tame)^{3+}}$ or dimethyl sulfoxide above 120°. In order to rule out the occurrence of extensive decomposition all samples for which spectra were obtained at high temperatures were cooled and the spectra were rerun at room temperature. The spectra before and after heating were virtually identical. Finally, the abnormally large separation of the AB doublets ($\Delta\nu_0$ = 46.5 Hz, J_{AB} = 13 Hz), which approaches an AX pattern, has made the calculation of the rate constants difficult for temperatures above 120°. Considering all of these possible sources of error, we estimate the uncertainty in the rate constants to be approximately 20%.

In the electronic absorption spectrum exhibited by $\mathrm{Co((py)_3tame)^{3+}}$, only the lowest energy absorption band (22,900 cm^{-1}) is assigned to a d–d transition

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(31) R. J. Fitzgerald and R. S. Drago, *J. Amer. Chem. Soc.*, **90**, 2523 (1968).

(32) F. F.-L. Ho and C. N. Reilley, *Anal. Chem.*, **41**, 1835 (1969); **42**, 600 (1970).

(33) F. F.-L. Ho, L. E. Erickson, S. R. Watkins, and C. N. Reilley, *Inorg. Chem.*, **9**, 1139 (1970).

(34) M. A. Robinson, J. D. Curry, and D. H. Busch, *ibid.*, **2**, 1178 (1963).

(35) L. J. Wilson and N. J. Rose, *J. Amer. Chem. Soc.*, **90**, 6041 (1968).

(36) A. B. P. Lever, "Inorganic Electronic Spectroscopy," Elsevier, Amsterdam, 1968, p 392.

(37) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

($^1A_{1g} \rightarrow {}^1T_{1g}$)[36,38] on the basis of its energy and low extinction coefficient (ϵ 260). No evidence of trigonal splitting was observed in this band. Beyond 26,000 cm^{-1}, any further d–d transitions are masked by the onset of strong bands attributed to parity-allowed intraligand or charge-transfer transitions.

$Fe((py)_3tame)Cl_2 \cdot 2H_2O$.—The synthesis of the iodide salt of this diamagnetic complex was reported[18] previously and the 60-MHz ^1H nmr spectrum of the complex supported the proposed mode of sexadentate coordination of the ligand. At 60 MHz, the methylene protons appeared as a broad singlet.[18] We have measured the 100-MHz ^1H nmr spectrum of $Fe((py)_3tame)^{2+}$, and with this increased resolution the AB nature of the methylene protons becomes apparent (Figure 1). This observation confirms the pseudooctahedral geometry previously assigned[2,18] to this complex. With increasing temperature the methylene AB pattern narrows and at ~95° collapses to a broad singlet (Figure 5). As in the case of $Co((py)_3tame)^{3+}$, this collapse of the AB multiplet is attributed to a facile racemization of the chiral complex ion. We have calculated[37] the rate constants at 60, 70, and 80° to be 27.5, 59.9, and 123 sec^{-1}, respectively. These data yield an activation energy of 18.4 kcal/mole^{-1} and a frequency factor of exp(13.5) sec^{-1}. An activation entropy of 1.0 cal deg^{-1} mol^{-1} was calculated.

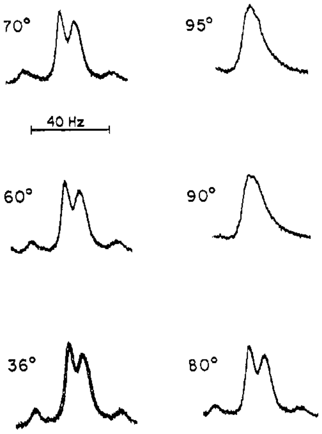

Figure 5.—Temperature dependence of the methylene resonances of $Fe((py)_3tame)^{2+}$ measured in D_2O *vs.* DSS as an internal standard.

The electronic spectrum (Figure 6) of $Fe((py)_3tame)^{2+}$ may be assigned on the basis of the pseudooctahedral coordination geometry indicated by the ^1H nmr results. The band positions and intensities (Table II) for $Fe((py)_3tame)^{2+}$ are in good agreement with those reported[5] for $Fe((py)_3tach)^{2+}$ and both spectra are similar to those reported for $Fe(bipy)_3{}^{2+}$,[5] $Fe(o\text{-}phen)_3{}^{2+}$,[39] and related tris($\alpha$-diimine)iron(II) complexes.[40] The close similarity in the spectra of $Fe((py)_3tame)^{2+}$ and $Fe((py)_3tach)^{2+}$ confirms the pseudooctahedral geometry suggested[5] for the latter complex.

The electronic spectra of several tris(α-diimine)iron(II) chelates have been assigned on the basis of theoretical calculations[40] and these results may be applied to an interpretation of the spectrum of $Fe((py)_3tame)^{2+}$. For tris(glyoxal-*N*-methylimine)iron(II) and related complexes, the intense bands appearing near 18,000 cm^{-1} were shown to be charge-transfer transitions from a $3d\pi$ atomic orbital to the lowest vacant π molecular orbital of the ligand. The expected d–d transitions ($^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1T_{2g}$) appear as weak bands (ϵ <500) in the region 25,000–28,000 cm^{-1}. Higher energy transitions are assigned mainly to intraligand $\pi \rightarrow \pi^*$ transitions. These assignments pertain equally well to $Fe((py)_3tame)^{2+}$, except that the intraligand $\pi \rightarrow \pi^*$ bands are shifted to lower energies and obscure the weak d–d bands. This lowering in energy of the $\pi \rightarrow \pi^*$ transitions may be attributed to the additional conjugation present in pyridinecarboxaldimine ligands compared to simple α-diimine ligands.

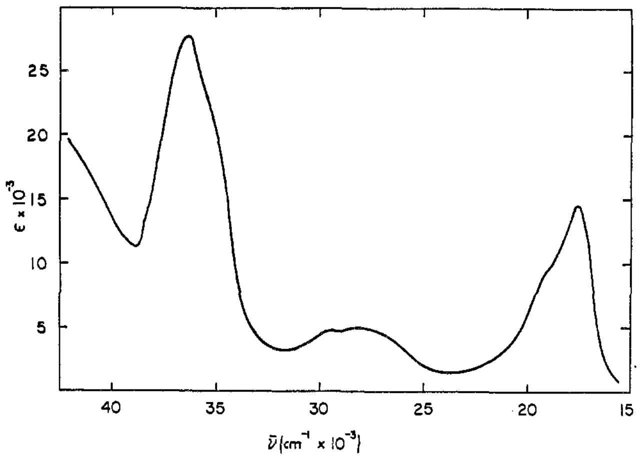

Figure 6.—Electronic spectrum of $Fe((py)_3tame)^{2+}$ in methanol solution.

Racemization Mechanisms in $M((py)_3tame)^{n+}$ Chelates.—The presence of the trigonal sexadentate ligand limits the possible racemization mechanisms which must be considered for $Fe((py)_3tame)^{2+}$ and $Co((py)_3tame)^{3+}$. Intermolecular processes are precluded because the total unwrapping of the sexadentate ligand is highly unfavorable and is likely to be quite slow. Any proposed bond rupture process must initially break a pyridine–metal bond and it is unlikely that more than one metal–ligand bond would be broken during the course of racemization. Finally, all racemization pathways, whether or not they involve bond rupture, which are accompanied by cis $\rightleftharpoons$ trans isomerization are ruled out since the ligand can only adopt a cis configuration.

Of the various intramolecular racemization mechanisms proposed for tris-bidentate chelates[10–14] only two pathways lead to the interconversion of enantiomers in pseudooctahedral $M((py)_3tame)^{n+}$ complexes. These mechanisms, depicted in Figure 7, are (1) a trigonal twisting[41] of one facial set of donor atoms with respect to the other about the real threefold axis of the complex, passing through a trigonal-prismatic (TP) transition (**3**), and (2) a bond rupture of one of the terminal pyridine–metal bonds followed by a rearrangement to a

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(38) A. Chakravorty, K. C. Kalia, and T. S. Kannan, *Inorg. Chem.*, **5**, 1623 (1966).

(39) P. Krumholz, *J. Amer. Chem. Soc.*, **75**, 2163 (1953).

(40) T. Ito, N. Tanaka, I. Hanazaki, and S. Nagakura, *Bull. Chem. Soc. Jap.*, **41**, 365 (1968).

(41) Besides the trigonal-twist mechanism, an additional intramolecular, non-bond-rupture mechanism (the Springer–Sievers twist)[11] can lead to the racemization of $M((py)_3tame)^{n+}$. This mechanism produces the same trigonal-prismatic transition state as the trigonal twist for these complexes. Although the Springer–Sievers twist appears to require more extensive bond reorganization to achieve the TP transition state, it cannot be ruled out as a contributing pathway and is tacitly included in the non-bond-rupture process.

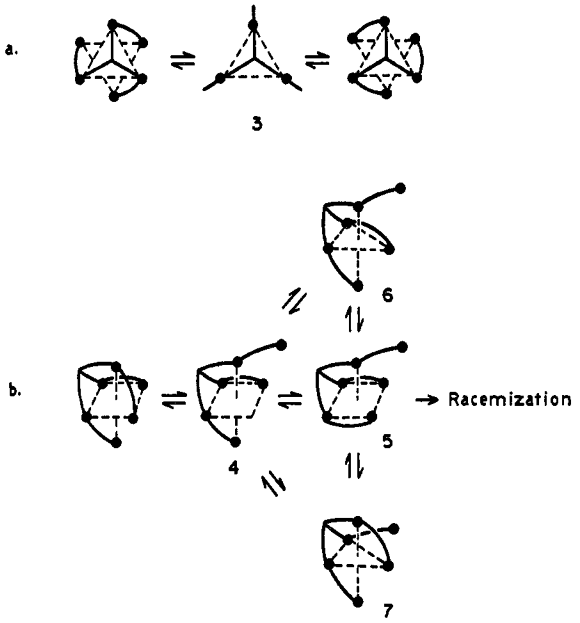

Figure 7.—Racemization mechanisms for M((py)$_3$tame)$^{n+}$ complexes: (a) trigonal-twist mechanism; (b) bond-rupture pathways.

symmetrical square-pyramidal intermediate (**5**). For M((py)$_3$tame)$^{n+}$, the initial square-pyramidal species, **4**, and the two possible trigonal-bipyramidal intermediates, **6** and **7**, which may be formed upon bond rupture are all dissymmetric and lead to retention of configuration upon bond recombination.

The M((py)$_3$tame)$^{n+}$ complexes provide a useful model system to examine intramolecular racemization processes. By analogy to the M((py)$_3$tach)$^{n+}$ complexes, which are trigonal prismatic in the absence of crystal field stabilization forces, (py)$_3$tame complexes should have a relatively accessible trigonal-prismatic transition state. Bond-rupture mechanisms are rendered less likely since the rigid nature of the sexadentate ligand would make breakage of a terminal bond more difficult than in the case of a tris-bidentate chelate. A twist mechanism is also favored by the fact that the two metal ions for which racemization has been observed, Fe(II) and Co(III), are generally inert to ligand substitution. Even if bond rupture occurs, the sexadentate chelate must undergo extensive stereochemical rearrangement to the symmetrical square-pyramidal intermediate in order to effect racemization. The only bond-rupture pathway which produces racemization may be viewed as a trigonal twist of the two bidentate chelate arms which remain coordinated. The question at hand is therefore whether the twisting process occurs with the ligand fully coordinated or with one terminal pyridine donor dangling free.

The activation parameters for the racemization of Co((py)$_3$tame)$^{3+}$ and, to a lesser degree, Fe((py)$_3$tame)$^{2+}$ are in line with the values of those parameters generally associated with twisting mechanisms.[42] With a few exceptions,[43] a negative activation entropy and low frequency factor have been found for those systems proposed to racemize by a twist process. For Fe((py)$_3$tame)$^{2+}$, evidence for a twist racemization mechanism without bond rupture over the pH range 2.5–9.4 is obtained from the acid independence of the racemization rate. This result is in contrast to the acid-dependent racemization of tris(bipyridine)iron(II) which proceeds by a bond-rupture process.[43b,44] For Fe(bipy)$_3^{2+}$, the addition of acid enhances the rate of racemization. Above pH 10 and in the presence of added salts, the racemization of Fe((py)$_3$tame)$^{2+}$ is accelerated.

In summary, Fe((py)$_3$tame)$^{2+}$ is postulated to undergo racemization *via* a twist mechanism without bond rupture over a wide pH range. Acid dependence studies were not possible for the racemization of Co((py)$_3$tame)$^{3+}$; however, the measured activation parameters suggest a similar twist mechanism for this complex ion.

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(42) P. C. Ray and N. K. Dutt, *J. Indian Chem. Soc.*, **20**, 81 (1943); J. J. Fortman and R. E. Sievers, *Inorg. Chem.*, **6**, 2022 (1967); L. H. Pignolet, R. A. Lewis, and R. H. Holm, *J. Amer. Chem. Soc.*, **93**, 360 (1971); D. C. Bradley and C. E. Holloway, *J. Chem. Soc. A*, 282 (1969).

(43) (a) D. W. Cooke, Y. A. Im, and D. H. Busch, *Inorg. Chem.*, **1**, 13 (1962); (b) F. Basolo, J. C. Hayes, and H. M. Neumann, *J. Amer. Chem. Soc.*, **76**, 3807 (1954).

(44) J. A. Broomhead and F. P. Dwyer, *Aust. J. Chem.*, **16**, 51 (1963); G. K. Schweitzer and J. M. Lee, *J. Phys. Chem.*, **56**, 195 (1952).