Geometrically Specific Multidentate Ligands and Their Complexes. I. A Nickel(II) Complex of the Potentially Heptadentate Schiff Base Derived from 2,2′,2″-Triaminotriethylamine and 2-Pyridinecarboxaldehyde[1]

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Abstract: Nickel complexes of the potentially heptadentate ligand tren-py, $N(CH_2CH_2N{=}CHC_5H_4N)_3$, have been prepared and characterized by elemental analyses, conductivity measurements, magnetic measurements, infrared spectroscopy, electronic spectroscopy, and a single-crystal X-ray study performed M. F. Bailey and E. C. Lingafelter. This ligand was selected because inspection of molecular models suggested that the most likely mode of chelation would be heptadentate with the nitrogen donor atoms at the apices of a monocapped octahedron. Basically, the X-ray study substantiated this expectation except that the Ni(II)–unique nitrogen distance is 3.25 Å, whereas the other Ni(II)–nitrogen distances are 2.10 Å. In spite of the long Ni(II)–unique nitrogen distance, the lone pair of electrons on the nitrogen atom is directed toward the metal atom as evidenced by a Ni–N–C angle of 97°. The magnetic and spectral properties of the $[Ni(tren\text{-}py)]^{2+}$ salts have been compared to those of a series of the closely related, pseudo-octahedral $[Ni(\alpha\text{-diimine})_3]^{2+}$ complexes.

The recent emergence of a large body of research concerning unusual coordination polyhedra for complex compounds has altered the chemist's classic predilection to think in terms of four- and six-coordinate structures.[3,4] The studies of Hoard and his coworkers are especially noteworthy for their explicit attention to the role of ligand configuration in determining the geometry of the complex itself.[5] Their research has set the stage for attempting to premeditatively generate chelates of specific geometry by giving careful attention to the design of the multidentate ligands from which the chelates are derived. The influence of such ligands is expected to be most strongly felt where the energetic factors discriminating between various geometries are small. In the case of heptacoordinate species, MX_7, energies based on repulsive interactions are very similar for four of the geometries known to exist for seven-coordination, D_{5h}, C_{2v}, C_s, and C_{3v}.[3] Using the notation of Muetterties, these relationships are shown graphically in Figure 1A.[6] The adjacent diagram, Figure 1B, reflects the expected rearrangement of the relative energies attending complex formation for the case of a heptadentate ligand designed or tailored for C_{3v} symmetry.

We have selected the capped octahedron (C_{3v}) and the first-row transition metals respectively as the style and size template for which geometrically specific ligands will be designed and used to test the concept represented in Figure 1. Heptacoordination was chosen because the energies of the MX_7 species are similar and because relatively few examples of this coordination are known for the first transition series metals. These examples include the hydrated iron and manganese complexes of sexadentate polyaminopolycarboxylic acid complexes, the donor atom positions of which can generally be defined in terms of either the pentagonal bipyramid (D_{5h}) or the capped trigonal prism (C_{2v}).[5] The donor atoms of the chromium complex, $K_3[Cr(O_2)_2(CN)_3]$, assume a pentagonal array, as do the donor atoms of a novel iron complex containing a pentadentate macrocyclic ligand.[7,8] The only discrete (nonbridging) complex of any transition period exhibiting the capped octahedral configuration is the $[Ho(C_6H_5COCHCOC_6H_5)_3H_2O]$ complex.[9] In the seven-coordinate compounds just mentioned and in all others known to these authors, there is no complex for which a structure has been determined in which the seven donor atoms are all members of a single ligand, a heptadentate ligand.

The amine 2,2′,2″-triaminotriethylamine (hereafter tren), $[N(CH_2CH_2NH_2)_3]$, was chosen for one component of such a ligand because it seemed well suited for occupying the unique donor site and the top three octahedral sites in the C_{3v} model (see Figure 2). In the [Cu(tren)NCS]NCS and the [Zn(tren)NCS]NCS structures, tren is known to adopt a similar configuration in that its tertiary amine nitrogen serves as an apical donor in a trigonal bipyramid, whereas the three primary amine nitrogens are located in equatorial sites.[10] The other component of the ligand, 2-pyridinecarboxaldehyde, was selected because its condensation product with tren (hereafter called tren-py) would lead to the formation of three α-diimine linkages in the resulting Schiff base of potentially heptadentate character. The α-diimine linkages are thought to be desirable for primarily two reasons: (1) such groups

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[3] E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966).

[4] E. L. Muetterties and C. M. Wright, *ibid.*, **21**, 109 (1967).

[5] (a) G. H. Cohen and J. L. Hoard, *J. Am. Chem. Soc.*, **88**, 3228 (1966); (b) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963).

[6] E. L. Muetterties, presentation at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

[7] R. Stomberg, *Arkiv Kemi*, **23**, 401 (1964).

[8] E. Fleischer and S. Hawkinson, *J. Am. Chem. Soc.*, **89**, 720 (1967).

[9] A. Zalkin and D. H. Templeton, American Crystallographic Association, Summer Meeting, Aug 1967.

[10] (a) P. C. Jain and E. C. Lingafelter, *J. Am. Chem. Soc.*, **89**, 6131 (1967); (b) P. C. Jain, P. Paoletti, and E. C. Lingafelter, *ibid.*, **90**, 519 (1968).

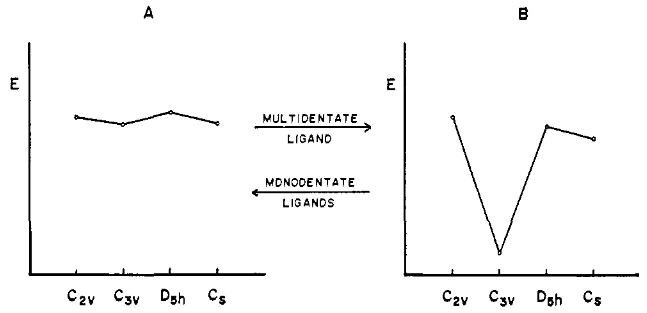

Figure 1. Energy arising from ligand–ligand repulsion *vs.* geometry for heptacoordinate complexes: (A) diagram based on idealized heptacoordinate models with seven monodentate ligands; (B) diagram representing the case of a heptadentate ligand geometrically specific for the C_{3v} model.

characteristically give rise to robust complexes in the first transition series, and (2) a large amount of data is available for the pseudo-octahedral complexes of the tris(α-diimine) type.[11] Because the tris(α-diimine) complexes are very closely related to the idealized, capped octahedral structure which tren-py was designed to adopt, the data available for the former are uniquely useful for comparative purposes.

We report here the preparation and properties for $[Ni(tren\text{-}py)]^{2+}$ salts as well as the major features of the structure of the complex as found in the X-ray determination by Bailey.[12] The preparation of an iron complex containing a ligand derived from tren and salicylaldehyde has been reported recently by Broomhead and Robinson.[13]

Experimental Section

The reagents used as starting materials were obtained commercially and used without further purification. All solvents were reagent grade. The products were dried at room temperature for 12 hr over P_4O_{10} at 1 mm.

2,2′,2′′-Triaminotriethylamine·3HCl (tren·3HCl). A procedure similar to that employed by Jonassen and Strickland was adopted.[14] Triethylenetetramine (200 g) obtained from Union Carbide was dissolved in 750 ml of 95% EtOH and cooled to 5° in an ice–salt bath. Concentrated HCl was added dropwise at such a rate that the temperature was kept below 10°. Upon the addition of approximately 50 ml of the concentrated HCl, initial precipitation began, and the white crystalline product of tren·3HCl was collected in fractions with each 2-ml addition of acid. Only the middle fractions were used since continued addition of HCl produces a thick, creamy white precipitate of trien·4HCl (trien = triethylenetetramine).

The tren·3HCl (20 g) was recrystallized from approximately 20 ml of boiling water by the addition of cold 95% EtOH, collected, and washed several times with anhydrous ether (13 g, 11.6% yield). *Anal.* Calcd for tren·3HCl: C, 28.15; H, 8.28; N, 21.92. Found: C, 28.32; H, 8.10; N, 21.85.

Tris[1-(2-pyridyl)-2-azabuten-4-yl]aminenickel(II) Hexafluorophosphate [Ni(tren-py)(PF_6)$_2$]. The following procedure was done at room temperature. 2-Pyridinecarboxaldehyde (1.25 g; 11.7 mm) was added to a mixture of tren·3HCl (1.00 g, 3.9 mm) and NaOH (0.47 g) dissolved in 100 ml of water. The resulting yellow solution was filtered and to the filtrate a solution of $NiCl_2 \cdot 6H_2O$ (0.93 g, 3.9 mm) dissolved in 20 ml of water was added with stirring. Upon addition of a filtered solution of $NaPF_6$ (1.35 g, 8.0 mm) in 20 ml of water, a yellow-brown crystalline solid was obtained. This solid was recrystallized from a 1:1 (by volume) acetone–hexane mixture, yield 1.43 g (48%). *Anal.* Calcd for Ni(tren-py)(PF_6)$_2$: C, 37.90; H, 3.58; N, 12.85; F, 29.90. Found: C, 38.06; H, 3.81; N, 12.81; F, 29.74. The molar conductance was 323 ohm^{-1} M^{-1} cm^2 for a 1 × 10^{-4} *M* acetone solution (comparative value[15] 322 ohm^{-1} M^{-1} cm^2 for a 1.9 × 10^{-4} *M* solution of bis(terpyridyl)-copper(II) hexafluorophosphate).

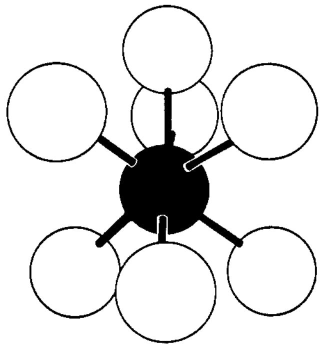

Figure 2. Ball model representing capped octahedron (C_{3v}).

Tris[1-(2-pyridyl)-2-azabuten-4-yl]aminenickel(II) Iodide [Ni(tren-py)I_2]. The following procedure was done at room temperature. To a filtered solution of 50 ml of acetone and NaI (0.33 g, 2.12 mm) was added a filtered solution of Ni(tren-py)(PF_6)$_2$ (0.80 g, 1.06 mm) in 100 ml of acetone. The yellow-brown crystals that separated were collected and washed with anhydrous ether, yield 0.66 g (87%). *Anal.* Calcd for Ni(tren-py)I_2: C, 39.67; H, 3.75; N, 13.51; I, 34.97. Found: C, 39.68; H, 3.66; N, 13.35; I, 35.19. The molar conductance was 262 ohm^{-1} M^{-1} cm^2 for a 1 × 10^{-4} *M* water solution (lit.[16] 225–270 ohm^{-1} M^{-1} cm^2 for 1 × 10^{-3} *M* solution).

Physical Measurements. Using KBr plates infrared spectra were obtained with a Beckman IR-10 recording spectrophotometer as Fluorolube mulls between 4000 and 1300 cm^{-1} and as Nujol mulls in the range 4000 to 400 cm^{-1}. A Cary Model 14 spectrophotometer was used for measurements in the ultraviolet, visible, and near-infrared spectral ranges. The electronic spectra were resolved using a Du Pont 310 curve resolver programmed for gaussian distribution. Electronic spectra of the solids were obtained as Nujol mulls.[17] Solution conductivities were obtained with an Industrial Instruments, Inc., Model RC-16B2 conductivity bridge at 25° in reagent grade acetone and conductivity water. Magnetic susceptibilities were obtained on the solid samples at 21° by the Faraday technique using $Hg[Co(SCN)_4]$[18] as a calibrant and in solution at 25° by the nmr technique of Evans[19] with the HA-60/DA-60 NMR. The molar diamagnetic corrections used in calculating μ_{eff} are for tren-py, -169×10^{-6} cgs unit; for hexafluorophosphate anion, -64×10^{-6} cgs unit; for iodide anion, -51×10^{-6} cgs unit.[24] Elemental analyses were determined by Alfred Bernhardt Mikroanalytisches Laboratorium, West Germany.

Results and Discussion

Synthesis and Structure. The synthesis of the $[Ni(tren\text{-}py)]^{2+}$ salts is straightforward once a pure source of tren has been isolated. As indicated in Figure 3, the complex is prepared by adding nickel chloride to a mixture of tren and 2-pyridinecarboxaldehyde in water. Upon addition of sodium hexafluorophosphate, the corresponding salt of the complex is immediately obtained. Slow evaporation of an acetone–water solution of the $[Ni(tren\text{-}py)][PF_6]_2$ affords single crystals suitable for X-ray structural determination.

Using crystals so obtained, Dr. Marcia Bailey in collaboration with Professor E. C. Lingafelter deter-

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[11] M. A. Robinson, J. D. Curry, and D. H. Busch, *Inorg. Chem.*, 2, 1178 (1963).

[12] M. Bailey and E. C. Lingafelter, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

[13] J. Broomhead and D. Robinson, *Australian J. Chem.*, 21, 1365 (1968).

[14] H. B. Jonassen and G. T. Strickland, *J. Am. Chem. Soc.*, 80, 312 (1958).

[15] J. A. Nusz, private communication.

[16] M. M. Jones, "Elementary Coordination Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1964.

[17] R. H. Lee, E. Griswold, and J. Kleinberg, *Inorg. Chem.*, 3, 1278 (1964).

[18] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

[19] D. F. Evans, *ibid.*, 2003 (1959).

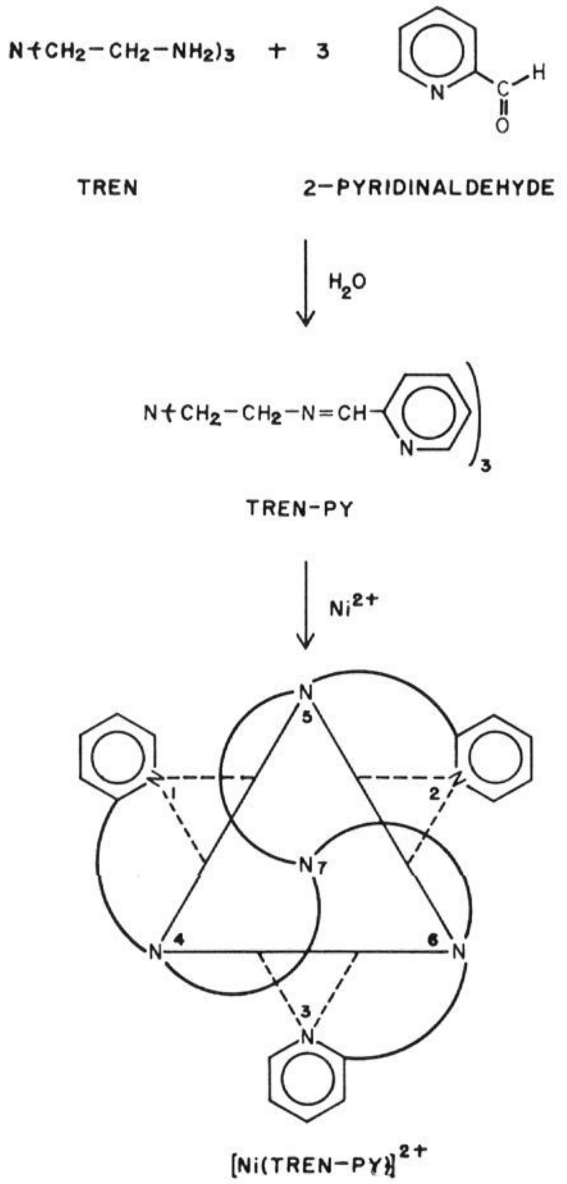

Figure 3. Preparation of Ni(II) complex of tren-py.

mined the structure of the [Ni(tren-py)][PF_6]$_2$ salt. As the idealized model shown in Figure 4 indicates, the complex cation does assume the helical C_3 geometry for which the parent ligand was designed (see also Figure 3). The three imine nitrogen atoms along with the three pyridine nitrogen atoms are disposed approximately at the apices of an octahedron with metal–nitrogen distances of 2.10 Å. This distance is close to that predicted by Pauling's covalent radii and very similar to nickel–nitrogen distances found for related complexes.[20,21] The unique nitrogen, N(7), is at a significantly greater distance from the nickel, 3.25 Å, but apparently has its lone pair of electrons pointed toward the nickel as is indicated by a Ni–N(7)–C angle of 97°. The latter value is considerably smaller than the nominal tetrahedral angle and is therefore suggestive of some sort of strain at the N(7) bridgehead. The N(7) separation from the three nearest nitrogen atoms [N(4), N(5), and N(6)] is only 2.85 Å, a value within twice the van der Waals radius of nitrogen but longer than the corresponding distances (2.829, 2.805, and 2.829 Å) found in [Zn(tren)NCS]NCS.[10b,20] In some ethylenediamine-type complexes the N–N distance is even closer, and it is therefore clear that nitrogen nonbonding interactions alone are not responsible for the relatively large N(7)–Ni distance. A consideration of the molecular models shows that the N(7)–Ni distance is greater when the ethylenic units adopt their characteristic *gauche* configuration than when the hydrogen atoms of these units are in an eclipsed conformation.[22] It should be noted that the hydrogen atoms of the ethylenic unit in the [Ni(tren-py)]$^{2+}$ structure adopt the *gauche* configuration although the stick model depicted in Figure 4 shows them to be eclipsed.

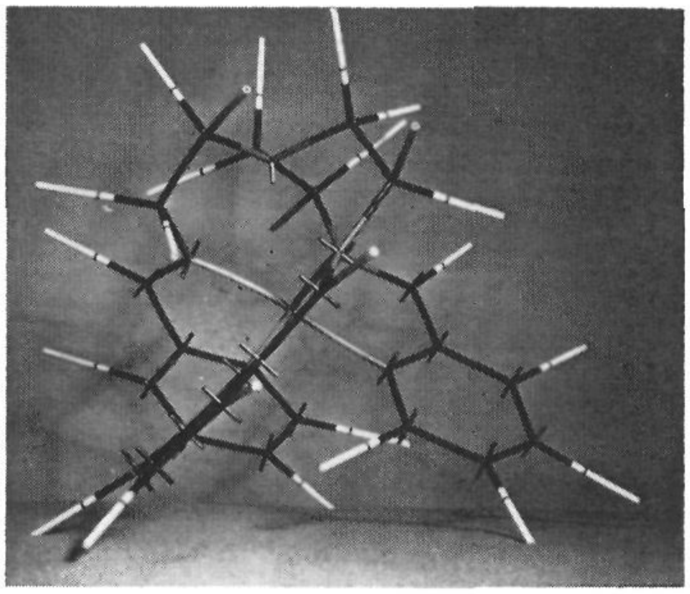

Figure 4. Idealized stick model representing structure of [Ni-(tren-py)]$^{2+}$ with hydrogen atoms of the ethylenic units in the eclipsed configuration.

The long Ni–N(7) bond distance certainly precludes any strong perturbation of the ligand field by the lone pair of electrons on that nitrogen atom. Thus the primary function of the N(7) atom might properly be considered the common link in the eight-membered chelate rings which contain the imine nitrogen atoms. An attempt to test this view of the role of the tren linkage is appropriately made by comparing the

Table I. Infrared Spectra of Ni(II) Complexes[a]

Assignment	[Ni(PMI)$_3$]-(BF_4)$_2$[b]	Ni(tren-py)-(PF_6)$_2$	Ni(tren-py)I_2
C=N, str	1654 (s)	1645 (s)	1632 (s)
py,[c] band I	1604 (s)	1600 (s)	1595 (s)
py,[c] band II	1570 (w)	1570 (w)	1565 (w)
py,[c] band III	1482 (m)	1475 (m)	1473 (m)
py,[c] band IV	1441 (s)	1442 (s)	1435 (s)

[a] s = strong, m = medium, w = weak; all values reported in cm^{-1}. [b] PMI = 2-pyridinecarboxaldehyde methylimine; for assignments, see W. J. Stratton and D. H. Busch, *J. Am. Chem. Soc.*, **82,** 4834 (1960). [c] py = pyridine.

Table II. Magnetic Moments for Ni(II) Complexes

Complex	μ_{eff}, BM	Symmetry	Ref
Ni(bipy)$_3$(ClO_4)$_2$[a]	3.10	D_3	*e*
Ni(bipy)$_3I_2\cdot 6H_2O$[a]	3.10	D_3	*e*
Ni(PMI)$_3$(BF_4)$_2$[b]	3.12	C_1[d]	*f*
Ni(PiPI)$_3$(BF_4)$_2\cdot 1.5H_2O$[c]	3.18	C_1[d]	11
Ni(tren-py)(PF_6)$_2$	2.98	C_3	This work
Ni(tren-py)I_2	2.96	C_3	This work

[a] bipy = bipyridyl. [b] PMI = 2-pyridinecarboxaldehyde methylimine. [c] PiPI = 2-pyridinecarboxaldehyde isopropylimine. [d] This symmetry assigned based on work with similar ligands on V(III): F. Röhrscheid, R. E. Ernst, and R. H. Holm, *Inorg. Chem.*, **6,** 1607 (1967). [e] F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3570 (1952). [f] P. E. Figgins and D. H. Busch, *J. Am. Chem. Soc.*, **82,** 820 (1960).

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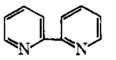
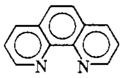
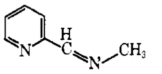
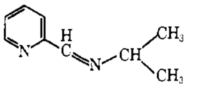
(20) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

(21) M. DiVaira and P. L. Orioli, *Inorg. Chem.*, **6,** 490 (1967).

(22) E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81,** 2620 (1959).

Table III. Electronic Spectra and Related Parameters for $[NiL]^{2+}$ Salts

L	ν, cm^{-1} (ϵ) $^1E_g(D) \leftarrow {}^3A_{2g}$	ν_1, cm^{-1} (ϵ) $^3T_{2g}(F) \leftarrow {}^3A_{2g}$	ν_2, cm^{-1} (ϵ) $^3T_{1g}(F) \leftarrow {}^3A_{2g}$	*Dq*, cm^{-1}	*B*,[a] cm^{-1}	% lowering of B from Ni(II) free-ion value
3 	11,500 (5.7)	12,650 (7.1)	19,200 (11.6)	1265	750	29
3 	11,550 (5.5)	12,700 (6.8)	19,300 (11.9)	1270	750	29
3 	11,710 (7.3)	12,670 (8.9)	≈19,510 (14.6)	1267	803	24
3 	11,490 (7.6)	12,380 (7.2)	19,100 (10.5)	1238	792	25
tren-py[b]	11,000 (5.0)	12,500 (6.4)	18,200 (13.2)	1250	602	43
tren-py[c]	11,100 (4.8)	12,500 (6.4)	18,200 (11.6)	1250	602	43

[a] Racah parameter calculated from ν_1 and ν_2, free-ion value for Ni(II) = 15,840/15 cm^{-1}: R. S. Drago, "Physical Methods in Inorganic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1965, p 410. [b] 10^{-2} *M* in acetone, PF_6^- salt. [c] 10^{-2} *M* in water, I^- salt.

properties of $[Ni(tren\text{-}py)]^{2+}$ with those of the related tris(α-diimine) species. As can be seen in Tables I–III, there are obvious similarities between the complexes with respect to infrared spectra, magnetic moments at room temperature, and electronic spectra in the visible region. It is significantly more difficult to definitively establish any differences and to relate them to the presence of the tren moiety.

Magnetic Moments and Electronic Spectra. The magnetic moments of the $[Ni(tren\text{-}py)]^{2+}$ salts and of the tris(α-diimine) complexes are all in the range expected for a high-spin d^8 configuration and are all above the spin-only value of 2.83 BM. In spite of the fact that the actual symmetries of the latter group are undoubtedly either D_3 or C_1, they have been effectively treated as cubic complexes in the analysis of their electronic spectra.[11,23] If a different conclusion for the effective environment of the $[Ni(tren\text{-}py)]^{2+}$ species is to be based on magnetic moments, it will have to rest on a thorough temperature-dependent study although the lower value at room temperature might suggest a stereochemistry of lower effective symmetry than that for the tris complexes.[24]

In solution the $[Ni(tren\text{-}py)]^{2+}$ ion gives every indication of maintaining its solid-state configuration as is evidenced by the following: (1) the conductometric behavior of the salts in acetone and water is that expected of a di-univalent electrolyte (see Experimental Section); (2) a value of 3.2 ± 0.3 BM for the magnetic moment of the PF_6^- salt in acetone is well within the experimental error of those obtained for the solid samples; and (3) the electronic spectra of the salts in solution are very nearly like those in the solid state (in mulls) except that the former are somewhat better resolved.

The absorption envelope for the $[Ni(tren\text{-}py)]^{2+}$ salts in the 11,000–13,000-cm^{-1} region of the spectrum is very similar in position and shape to that recorded for a closely related complex, tris(2-pyridinecarboxaldehyde isopropylimine)nickel(II).[25] A further similarity exists in that this portion of the spectrum can be resolved into two gaussian components, whereas two components are also listed for the 2-pyridinecarboxaldehyde isopropylimine complex.[11] The positions and extinction coefficients of these components and those of a higher energy band observed in the spectrum are recorded in Table III along with the corresponding data for other tris(α-diimine) species. The band assignments reported in Table III for the latter complexes are those of Robinson, Curry, and Busch and are predicated on an O_h crystal-field model.[11] Because of the similarity noted above and the structural information previously stated, the band assignments for the $[Ni(tren\text{-}py)]^{2+}$ salts are tentatively made on an O_h model. It should be noted that in all cases listed in the table, the band expected for the third spin-allowed transition is apparently masked by intense parity-allowed transitions. The experimental energies corresponding to ν_1 and ν_2 along with the well-known expression relating the energies of octahedral terms to *Dq* and the Racah parameter, *B*, were used to estimate *Dq* and *B* for all the complexes listed.[26] That these estimated values are reasonably reliable for the tris species is suggested by the fact that the values so obtained for *Dq* and *B* of tris(bipyridyl)nickel(II) are very close to the corresponding numbers calculated by Palmer and Piper from spectral data gathered under the more nearly ideal conditions afforded by low temperatures.[23,27] The similarities in the *Dq* values listed in the table are quite striking; however, the position of ν_2 for $[Ni(tren\text{-}py)]^{2+}$ is significantly lower than that for the tris complexes and consequently the apparent *B* value is unusually small. Because of the lack of

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(23) R. A. Palmer and T. S. Piper, *Inorg. Chem.*, 5, 864 (1966). These researchers were unable to find a trigonal splitting in the electronic transitions of tris(bipyridyl)nickel(II) even though relative intensity data from polarized spectra could be interpreted on a D_3 model. Thus the trigonal perturbation of an essentially O_h field was judged to be small.

(24) B. N. Figgis and J. Lewis in "Technique of Inorganic Chemistry," Vol. IV, Interscience Publishers, New York, N. Y., 1965.

(25) See Figure 1 of ref 11.

(26) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, 9, 753, 766 (1965).

(27) A. B. P. Lever, "The Crystal Field Splitting Parameter Dq: Calculation and Significance," Advances in Chemistry Series, No. 62, American Chemical Society, Washington, D. C., 1966.

ν_3, none of the common calculations can be performed to test the validity of adopting an octahedral crystal-field model[28,29] and, consequently, one cannot tell whether the low B value reflects some special character of $[\mathrm{Ni(tren\text{-}py)}]^{2+}$ with respect to the tris species or whether it is just an artifact of a model inappropriately applied.

Acknowledgment. We are most grateful to Dr. M. Bailey and to Professor E. C. Lingafelter for their interest in this problem, for the structure determination, and for the many rewarding discussions held with them. Thanks are also due to Professor V. Shomaker for his helpful suggestions.

(28) R. S. Drago, D. W. Meek, M. D. Joesten, and L. LaRoche, *Inorg. Chem.*, **2**, 124 (1963).

(29) For another approach to analyzing O_h Ni(II) spectra, see C. K. Jørgensen, *Progr. Inorg. Chem.*, **4**, 96 (1962).

The Kinetics of Reaction of Nickel(II) Ion with a Variety of Amino Acids and Pyridinecarboxylates

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Abstract: The rate constants for the formation of the mono complex of nickel(II) with 22 different ligands have been determined by the stopped-flow method. The ligands studied included amino acids, polyamino carboxylates, peptides, and pyridinecarboxylates. The zwitterion form is shown to be extremely unreactive, and this striking result is discussed. The reactivity of the monoprotonated forms of pyridine-2-carboxylate and pyridine-2,6-dicarboxylate and the diprotonated EDTA and CyDTA is ascribed to the presence of small amounts of the neutral form with the proton associated with the carboxylate. An expected correlation of formation rate constant with the charge of the ligand is observed. Small deviations of some ligands are discussed in terms of the detailed structure of these ligands in solution.

The generally accepted mechanism[1] for the formation of many inner-sphere metal complexes $\mathrm{ML}^{(n-m)+}$ involves exchange of the ligand L for a molecule of water of the inner coordination sphere of the metal within the outer-sphere complex $\mathrm{M_{aq}}^{n+}\mathrm{L}^{m-}$.

$$\mathrm{M_{aq}}^{n+} + \mathrm{L_{aq}}^{m-} \underset{}{\overset{K_{\mathrm{os}}}{\rightleftharpoons}} \mathrm{M_{aq}}^{n+}\mathrm{L}^{m-} \underset{k_{\mathrm{r}}}{\overset{k_{\mathrm{H_2O}}}{\rightleftharpoons}} \mathrm{ML}^{(n-m)+} + \mathrm{H_2O} \quad (1)$$

The process is dominated by the value of $k_{\mathrm{H_2O}}$, and the results of a large number of studies of the kinetics of formation of metal complexes, particularly those of nickel(II), with a wide variety of ligands lend strong support to this mechanism.[2] The more recent tendency has therefore been to investigate the finer details of complex formation. This includes a study of the effects of charge and structure of the ligand, already coordinated as well as entering, on the rate and mechanism of the formation reaction.[3-8] The difference in five- and six-membered chelate formation[4,5] and the nature of the donor atoms[6-8] are among the structural factors which have been investigated.

In the present study we are concerned with the kinetics of reaction, over a range of pH, of nickel(II) ion with 22 ligands, which are listed with their abbreviations in Table I. Nearly all of the ligands contain one or more amino and/or carboxylate groups as part of aliphatic or heterocyclic systems. The aim is to have available, for comparative purposes, the reaction rate constants for a variety of ligands under a uniform set of conditions. We were hoping thus to examine the effect of (a) charge and its distribution in the ligand and (b) donor atom protonation on the mechanistic behavior.

Experimental Section

Materials. Commercial products of the highest quality available were used. Aminomalonic acid was prepared by hydrolysis of the ester (Aldrich)[9] and piperidine-2,6-dicarboxylate by hydrogenation of pyridine-2,6-dicarboxylate.[10]

Kinetic Experiments. Standard solutions of ligands, lutidine and acetate buffers, and sodium nitrate were prepared by weight. Nickel ion concentration was estimated by EDTA titration, and sodium perchlorate solutions were prepared by mixing standardized solutions of sodium carbonate and perchloric acid. A very small optical density change accompanied the formation of the mono complexes of the aliphatic ligands, but these reactions were attended by pH changes (eq 2), which were used to follow the progress of the reaction. An added buffer (2,6-lutidine, p$K \sim 6.7$, or acetate, p$K \sim 4.8$) limited the pH change to a small one, about 0.2 unit, which was registered with an appropriate indicator (bromothymol blue, p$K \sim 6.8$, λ 620 mμ, or methyl orange, p$K \sim 3.5$, λ 510 mμ). In detail, nickel nitrate solution (10^{-3}–10^{-1} M, buffered $\sim 10^{-2}$ M at ionic strength 0.3 M with added $\mathrm{NaNO_3}$ (or $\mathrm{NaClO_4}$ for uv work)) was mixed with ligand solution (10^{-4}–10^{-3} M, buffered $\sim 10^{-2}$ M,

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