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Synthesis and Characterization of Nickel(II) Complexes of Neutral, Tetradentate Schiff Base Ligands Derived from 1,3-Diamines[1]

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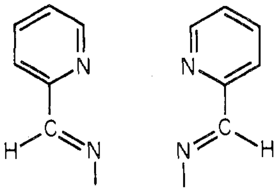
A series of hydrolytically stable nickel(II) complexes with the tetradentate ligand *N,N'*-bis(2-pyridylmethylene)-1,3-diaminopropane and four related Schiff bases is described. The nickel(II) complexes have been characterized in the solid state by elemental analysis, magnetic susceptibility, and infrared and electronic spectroscopy. All of the complexes contain a 1:1 ratio of tetradentate ligand to nickel(II) salt. Representative complexes exhibit magnetic moments typical of six-coordinate nickel(II). The infrared spectra of the complexes support the Schiff base formulation of the ligands and provide evidence for the coordination of the pyridyl groups. A tetragonal crystal field model provides a basis for the interpretation of the visible and near-infrared electronic spectra. The donor atoms of the tetradentate ligand are assumed to adopt an essentially planar arrangement about the nickel(II) ion with the remaining axial coordination sites occupied by anionic or neutral donors.

Introduction

Previous studies of the ionic transition metal complexes of neutral, tetradentate Schiff bases have dealt primarily with the ligands derived from ethylenediamine and pyridine-2-carboxaldehyde, pya$_2$en (**1**), or quinoline-8-aldehyde, quina$_2$en (**2**). A complex of stoichiometry Cu(pya$_2$en)Cl$_2$·2H$_2$O was reported by Busch and Bailar,[3] who postulated from infrared evidence that the two water molecules had added across the azomethine linkages. More recently the reaction of pya$_2$en with iron(II) and nickel(II) perchlorates was reported[4] to yield only the 2:1 complexes M(pya$_2$en)$_2$(ClO$_4$)$_2$ which decomposed in solution liberating pyridine-2-carboxaldehyde. Harris and McKenzie[5,6] studied the reaction of pya$_2$en with copper(II) salts and isolated three types of complexes: (a) Cu$_2$(pya$_2$en)Cl$_4$·H$_2$O and Cu$_2$(pya$_2$en)$_3$(ClO)$_4$, postulated to contain bridging ligands; (b) [Cu(pya$_2$en)Br]ClO$_4$, a five-coordinate complex in the solid state and in nitromethane solution; and (c) [Cu(pya$_2$en-CH$_3$OH)Br]ClO$_4$, a distorted trigonal-bipyramidal complex in which a methanol molecule has added across one of the azomethine linkages. Nickel(II), cobalt(II), and copper(II) complexes containing the intact tetradentate ligand quina$_2$en have been reported[7] together with complexes of quinaen, a tridentate ligand arising from the partial hydrolysis of the quina$_2$en complexes.



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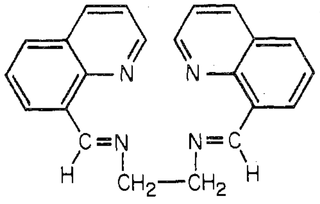

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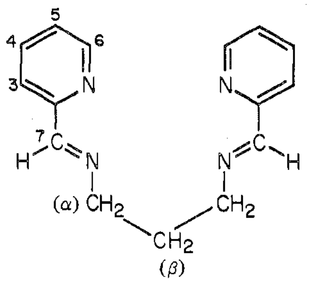
The hydrolytic instability exhibited by pya$_2$en and quina$_2$en in the presence of metal ions has been generally attributed to the steric strain induced in the ligands accompanying planar chelation.[5-7] Harris and McKenzie suggested[5] that the steric strain present in coordinated pya$_2$en could be reduced by enlarging the central, diamine chelate ring and proposed that planar coordination of the Schiff base ligand derived from pyridine-2-carboxaldehyde and 1,3-diaminopropane, pya$_2$tn, **3**, results in negligible bond angle strain.



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In support of this suggestion they reported[6] that the copper(II) complex of pya$_2$tn did not undergo the alcohol addition reaction found for the pya$_2$en complex. By comparison to [Cu(pya$_2$en)Br]ClO$_4$, [Cu(pya$_2$tn)I]ClO$_4$ was formulated as a distorted trigonal-bipyramidal complex in nitromethane solution. No other metal complexes of Schiff base ligands derived from 1,3-diamines and pyridine-2-carboxaldehyde have been reported.

The nickel(II) complexes described in this study form adducts with additional monodentate donors in aqueous solution without destroying the planar, tetradentate chelation of the neutral Schiff base ligands. In this regard they provide a suitable system for studies of ternary complex formation. This paper reports the synthesis and characterization of the nickel(II) complexes of five neutral, tetradentate Schiff base ligands. A determination of the solution stereochemistry of certain of these complexes and a kinetic study of ternary complex formation with selected additional donors will be presented in subsequent papers.

Experimental Section

Materials. Pyridine-2-carboxaldehyde, 2-acetylpyridine, 1,3-diaminopropane, and 1,3-dibromobutane were obtained from Aldrich Chemical Co.; 1,3-diamino-2-propanol was obtained from J. T. Baker Chemical Co. The pyridine-2-carboxaldehyde was distilled prior to

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(2) National Institutes of Health Predoctoral Fellow: Fellowship 5 F01 GM39525-02 from the National Institute of General Medical Sciences.

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Table I. Analytical Data for the Complexes

Compd	% C		% H		% N		% halogen	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$Ni(pya_2tnOH)Cl_2$	45.28	45.01	4.05	4.08	14.08	14.03	17.82	17.88
$Ni(pya_2tnOH)Br_2$	37.00	36.74	3.31	3.32	11.51	11.30	32.83	32.65
$Ni(pya_2tnOH)I_2$	31.02	31.10	2.78	2.76	9.65	9.54	43.70	43.80
$Ni(pya_2tnOH)(NO_2)_2$	42.99	43.28	3.85	3.66	20.06	20.11		
$Ni(pya_2tnOH)(N_3)_2$	43.83	44.01	3.92	4.03	34.07	34.21		
$Ni(pya_2tnOH)(NCS)_2$	46.07	45.89	3.63	3.80	18.96	18.81		
$Ni(pya_2tn)Cl_2 \cdot H_2O$	45.04	44.98	4.54	4.34	14.01	14.02	17.73	17.71
$Ni(pya_2tn)Br_2$	38.26	38.41	3.43	3.47				
$Ni(pya_2tn)I_2$	31.90	31.99	2.86	2.75	9.92	9.72	44.93	45.03
$Ni(pya_2tn)(NO_2)_2$	44.70	44.69	4.00	4.08				
$Ni(pya_2tn)(N_3)_2$	45.60	45.41	4.08	3.96				
$Ni(pya_2tn)(NCS)_2$ brown	47.80	48.00	3.77	3.96	19.67	19.52		
green		47.85		3.93		19.69		
$Ni(pya_2tn)(Im)_2I_2$	35.98	35.94	3.45	3.59	15.99	15.84		
$Ni(pya_2(+)tnCH_3)Cl_2 \cdot 2H_2O$	44.49	44.56	5.13	5.13	12.97	12.99	16.41	16.43
$Ni(pya_2(+)tnCH_3)(N_3)_2 \cdot H_2O$	45.00	44.94	4.73	4.75	32.80	32.77		
$Ni(7\text{-}CH_3pya_2tn)Cl_2$	49.80	49.57	4.92	4.90	13.67	13.63	17.29	17.48
$Ni(7\text{-}CH_3pya_2tnCH_3)Cl_2$	50.99	51.01	5.23	5.20	13.21	13.01		

use. Industrial grade *N,N*-dimethylformamide (Baker and Adamson) was used for the Gabriel synthesis. All other materials were of reagent grade or equivalent. Elemental analysis for the nickel(II) complexes prepared in this study are presented in Table I.

Syntheses. 1,3-Diaminobutane, $tnCH_3$. The following modified Gabriel synthesis was developed.

1,3-Bis(phthalimidyl)butane. To a stirred suspension of potassium phthalimide (964 g, 5.2 mol) in 4 l. of *N,N*-dimethylformamide was added dropwise 1,3-dibromobutane (305 ml, 2.5 mol) while maintaining a reaction temperature of 70–80°. After the addition was complete, the reaction mixture was stirred for 3.5 hr at 70–80° and then suction filtered while still warm. To the stirred filtrate was slowly added 19 l. of water causing precipitation of the crude product. The crude product was recovered by filtration and washed well with water. Recrystallization from 95° ethanol gave 526 g (60% yield) of white crystals, mp 129–133°.

Hydrazinolysis of 1,3-Bis(phthalimidyl)butane. To a slurry of 1,3-bis(phthalimidyl)butane (526 g, 1.56 mol) in 2 l. of 95% ethanol was added 97% hydrazine (110 ml, 3.36 mol). The slurry was warmed to 50° with stirring and became clear yellow after 0.5 hr; after 1 additional hr of stirring at 50° a white precipitate formed which partially dissolved upon the addition of 1 l. of water. The reaction mixture was heated to reflux and 315 ml of concentrated hydrochloric acid was slowly added, producing a dense white precipitate of phthalhydrazide. The mixture was refluxed for 2 hr, cooled to room temperature, and suction filtered. The phthalhydrazide was washed with water, and the combined washings and filtrate were evaporated to a volume of 2 l. The concentrated filtrate was saturated with KOH and continuously extracted with ether. Fractional distillation of the dried (Na_2SO_4) ether extract gave 83 g (62% yield) of 1,3-diaminobutane, bp 143–146° (lit. bp 138–141°,[8] 144–146.5°[9]). Treatment of 1,3-diaminobutane with dry HCl in 95% ethanol gave the dihydrochloride, mp 176° dec (lit. mp 169–170°,[8] 177°[10]).

(*S*)-(+)D-1,3-Diaminobutane, $(+)tnCH_3$. The racemic 1,3-diaminobutane was resolved by a method similar to that reported by Larsen together with a determination of the absolute configuration.[9] The less soluble bis((+)D-hydrogentartrate) salt was recovered by filtration and recrystallized three times from 50% aqueous ethanol. The (*S*)-(+)D-1,3-diaminobutane gave $[\alpha]^{26}D$ +1.52 ± 0.2° (benzene) and $\alpha^{26}D$ +19.11 ± 0.01° (neat, 2 dm); lit.[9] $\alpha^{25}D$ +1.80° (neat, 2 cm).

Schiff Bases. *N,N'*-Bis(2-pyridylmethylene)-1,3-diaminopropane, pya_2tn. Pyridine-2-carboxaldehyde (105 ml, 1.10 mol) was added dropwise to a solution of 1,3-diaminopropane (46.4 ml, 0.55 mol) in 25 ml of benzene. When the addition was complete, the dark red solution was distilled and the fraction boiling at 152–153° (0.14 Torr) was collected. This fraction is initially colorless, but rapidly yellows on standing; yield 63 g.

***N,N'*-Bis(2-pyridylmethylene)-1,3-diamino-2-propanol, pya_2tnOH.** 1,3-Diamino-2-propanol (5.86 g, 65 mmol) and pyridine-2-carboxaldehyde (12.4 ml, 130 mmol) were mixed and stirred at 50° until homogeneous. The resulting yellow oil was dried *in vacuo* (0.2 mm) for 2 hr, dissolved in 60 ml of absolute ethanol and cooled in a freezer until crystallization was complete. The yellow crystals were filtered, washed with 60 ml of cold absolute ethanol, and dried *in vacuo*; yield 9.6 g, mp 87–89°. Recrystallization from absolute ethanol gave pale yellow crystals, mp 89–91°.

***N,N'*-Bis(2-pyridylmethylene)-(*S*)-(+)-1,3-diaminobutane, $pya_2(+)tnCH_3$, *N,N'*-bis(7-methyl-2-pyridylmethylene)-1,3-diaminopropane, $7\text{-}CH_3pya_2tn$,** and racemic ***N,N'*-bis(7-methyl-2-pyridylmethylene)-1,3-diaminobutane, $7\text{-}CH_3pya_2tnCH_3$,** were prepared *in situ* and were not isolated.

Complexes. $Ni(pya_2tn)Cl_2 \cdot H_2O$. Pyridine-2-carboxaldehyde (9.6 ml, 100 mmol) dissolved in 10 ml of isopropyl alcohol was added dropwise to a solution of 1,3-diaminopropane (4.2 ml, 50 mmol) in 10 ml of isopropyl alcohol cooled in an ice–water bath. The resulting solution was stirred at room temperature for 45 min and then added to a hot solution of nickel(II) chloride hexahydrate (11.9 g, 50 mmol) in 100 ml of absolute ethanol. After slow evaporation to 100 ml, followed by cooling, green crystals were obtained which were filtered, washed with isopropyl alcohol, and dried *in vacuo* at 60°; yield 14 g.

$Ni(pya_2tn)Cl_2 \cdot 6H_2O$. Recrystallization of $Ni(pya_2tn)Cl_2 \cdot H_2O$ from water gave large green crystals which were dried in air at room temperature. These crystals lost 19.5% of their weight upon drying *in vacuo* at 60°, yielding $Ni(pya_2tn)Cl_2 \cdot H_2O$. The air-dried crystals were formulated as $Ni(pya_2tn)Cl_2 \cdot 6H_2O$.

$Ni(pya_2(+)tnCH_3)Cl_2 \cdot 2H_2O$ was prepared following the procedure used for $Ni(pya_2tn)Cl_2 \cdot H_2O$.

$Ni(7\text{-}CH_3pya_2tn)Cl_2$. 2-Acetylpyridine (7.0 g, 58 mmol) was added dropwise to a solution of 1,3-diaminopropane (2.1 g, 29 mmol) in 10 ml of absolute ethanol at *ca.* 5° and the mixture was then warmed to 50–60° under a stream of nitrogen for 1.5 hr. This mixture was added to a hot solution of nickel(II) chloride hexahydrate (6.9 g, 29 mmol) in 80 ml of 95% ethanol. Addition of 20 ml of *n*-butyl alcohol and slow evaporation gave green crystals which were filtered and washed with 95% alcohol. The crystals were recrystallized from a water–ethanol–butanol mixture and dried *in vacuo* at 75°; yield 1.7 g.

$Ni(7\text{-}CH_3pya_2tnCH_3)Cl_2$. Racemic 1,3-diaminobutane (2.00 g, 22.7 mmol) was added to a solution of 2-acetylpyridine (5.49 g, 45.4 mmol) in 100 ml of benzene, and this mixture was slowly distilled at 110° *in vacuo* to a yellow oil residue. This ligand residue was dissolved in 20 ml of 95% ethanol and added to a hot solution of nickel(II) chloride hexahydrate (5.40 g, 22.7 mmol) in 60 ml of 95% ethanol. The green crystals which formed upon cooling were recrystallized from water and then from absolute methanol and dried *in vacuo* at 75°; yield 1.5 g.

$Ni(pya_2tnOH)Cl_2$. Nickel(II) chloride hexahydrate (23.8 g, 100 mmol) was dissolved in 300 ml of absolute ethanol; 2,2-dimethoxypropane (104 g, 1.0 mol) was added and the solution was refluxed for 1.5 hr. A solution of pya_2tnOH (26.8 g, 100 mmol) in 30 ml of absolute ethanol was added to the hot nickel chloride solution. Large green crystals formed upon cooling which were filtered and washed with warm absolute ethanol and dried *in vacuo* (75°); yield 29 g.

$Ni(pya_2tnOH)Br_2$ and $Ni(pya_2tn)Br_2$. Anhydrous nickel(II)

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bromide (2.88 g, 13.2 mmol) was dissolved in 100 ml of hot methanol, and a stoichiometric amount of ligand (13.2 mmol) dissolved in methanol was added. Addition of butanol and slow evaporation gave green-orange crystals which were recrystallized from a methanol-butanol mixture and dried *in vacuo* at room temperature.

Ni(pya$_2$tnOH)I$_2$ and Ni(pya$_2$tn)I$_2$. These complexes were prepared by the procedure used for the bromides, using anhydrous nickel(II) iodide, or by addition of excess sodium iodide to methanol solutions of the chloride complexes.

Ni(pya$_2$tn)(NCS)$_2$. Brown Isomer. To a boiling solution of Ni(pya$_2$tn)Cl$_2$·H$_2$O (1.87 g, 4.67 mmol) in 700 ml of methanol containing 50 ml of 2,2-dimethoxypropane was added a solution of NaSCN (1.62 g, 20 mmol) in 40 ml of methanol. The small brown crystals which formed were separated by filtration, washed with methanol, and dried *in vacuo* at 90°. The brown crystals melt with decomposition at 311°.

Green Isomer. Recrystallization of the brown isomer from boiling water containing excess NaSCN gave green crystals which were washed with water and dried *in vacuo* at 90°. These green crystals melt with decomposition at 286°.

The following derivatives were obtained by metatheses from Ni(pya$_2$tn)Cl$_2$·H$_2$O with appropriate sodium salts: **Ni(pya$_2$tn)(N$_3$)$_2$**, dark red crystals from methanol, dried *in vacuo* at 75°; **Ni(pya$_2$tn)(NO$_2$)$_2$**, dark red crystals from methanol, air-dried at room temperature. The following derivatives were obtained by metatheses from Ni(pya$_2$tnOH)Cl$_2$ with appropriate sodium salts: **Ni(pya$_2$tnOH)(NCS)$_2$**, red-brown crystals from water or methanol, dried *in vacuo* at 90°; **Ni(pya$_2$tnOH)(N$_3$)$_2$**, dark red crystals from methanol, dried at room temperature *in vacuo*; **Ni(pya$_2$tnOH)(NO$_2$)$_2$**, dark red crystals from methanol, dried at room temperature *in vacuo*.

Ni(pya$_2$(+)tnCH$_3$)(N$_3$)$_2$·H$_2$O was prepared metathetically from NaN$_3$ and Ni(pya$_2$(+)tnCH$_3$)Cl$_2$·2H$_2$O in water. The product was recrystallized from methanol containing excess NaN$_3$ yielding dark red crystals which were dried in air at room temperature.

Ni(pya$_2$tn)(Im)$_2$I$_2$. An aqueous solution 16 m*M* in Ni(pya$_2$tn)I$_2$ and 143 m*M* in imidazole, Im, was allowed to evaporate slowly. Long, brown crystals formed which were filtered, washed with absolute ethanol, and dried in air at room temperature.

Physical Measurements. All temperatures and pressures reported are uncorrected. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Magnetic susceptibilities were determined at 20° at two magnetic field strengths by the Faraday or Gouy methods using Hg[Co(NCS)$_4$] as the calibrant. Diamagnetic corrections were calculated from tables of Pascal's constants. The magnetic moments were reproducible within ±0.05 BM.

Infrared spectra were recorded for the ligands and the complexes as Nujol mulls using a Beckman Model IR-8 or IR-12 recording spectrophotometer. Spectra for the nitrite complexes were also measured as hexachlorobutadiene mulls.

Electronic absorption spectra of the solid complexes were obtained as mulls using a Cary Model 14 recording spectrophotometer equipped with a high-intensity visible source. Mulls were prepared by grinding the sample with Dow Corning high-vacuum silicone lubricant and were run from 5.5 to 43 kK between glass or silica plates *vs.* neutral density filters. All of the spectra were corrected for base line absorptions found in the spectrum of CaCl$_2$·2H$_2$O.

Results and Discussion

Two series of crystalline nickel(II) complexes of pya$_2$tn and pya$_2$tnOH and representative nickel(II) complexes of the ligands pya$_2$(+)tnCH$_3$, 7-CH$_3$pya$_2$tn, and 7-CH$_3$pya$_2$tnCH$_3$ were isolated.[11] The analytical data (Table I) reveal a 1:1 ratio of Schiff base ligand to metal salt for all of the complexes.

The nickel(II) complexes of pya$_2$tn and derivatives exhibit a high degree of hydrolytic stability in contrast to the instability of the analogous complexes of pya$_2$en which contain a five-membered central chelate ring. Ni(pya$_2$tn)Cl$_2$ shows no spectral evidence[12] of decomposition in aqueous solution over the pH range 3-11. Generally, these complexes can be recrystallized from hot water without any evidence of decomposition. The increased stability of tetradentate ligand complexes containing linked 5-6-5 membered chelate rings compared to linked 5-5-5 membered rings has also been reported for other tetramine[13] and Schiff base[14] complexes and is attributed to less steric strain in the former compounds. The magnetic moments for the nickel(II) complexes of pya$_2$tn and pya$_2$tnOH (Table II) fall within the range 2.9-3.4 BM reported for octahedral complexes of nickel(II).[15]

Table II. Magnetic Moments for the pya$_2$tn- and pya$_2$tnOH-Ni^{II} Complexes

Complex		$10^6\chi_g$, cgsu	$10^6\chi_g^{cor}$, cgsu	μ'_{eff}, BM
Ni(pya$_2$tn)Cl$_2$·6H$_2$O		8.15	8.61	3.21
Ni(pya$_2$tn)Cl$_2$·H$_2$O		10.49	10.90	3.21
Ni(pya$_2$tn)Br$_2$		8.51	8.89	3.14
Ni(pya$_2$tn)I$_2$		6.92	7.29	3.12
Ni(pya$_2$tn)(NO$_2$)$_2$		10.39	10.71	3.19
Ni(pya$_2$tn)(N$_3$)$_2$		10.14	10.52	3.13
Ni(pya$_2$tn)(NCS)$_2$	green	9.46	9.86	3.15
	brown	9.81	10.21	3.21
Ni(pya$_2$tnOH)Cl$_2$		10.19	10.59	3.16
Ni(pya$_2$tnOH)Br$_2$		8.36	8.73	3.17
Ni(pya$_2$tnOH)I$_2$		6.90	7.27	3.16
Ni(pya$_2$tnOH)(NO$_2$)$_2$		9.89	10.21	3.18
Ni(pya$_2$tnOH)(N$_3$)$_2$		6.82	10.19	3.15
Ni(pya$_2$tnOH)(NCS)$_2$		9.23	9.63	3.17

Infrared Spectra. The infrared spectra of pya$_2$tn, pya$_2$tnOH, and all of the nickel(II) complexes prepared from these ligands and from the α- and 7-methyl-substituted pya$_2$tn ligands exhibit bands typical of 2-substituted pyridines.[16] These pyridine bands are the four ring stretching vibrations (1600-1430 cm^{-1}), the ring breathing vibration (~1000 cm^{-1}), and the out-of-plane C-H deformation (~780 cm^{-1}). These compounds also show a band near 1650 cm^{-1} assigned to the azomethine stretching vibration. The positions and assignments of these bands are in agreement with those reported[3,17,18] for pya$_2$en and *N*-methylpyridine-2-carboxaldimine.

The changes observed in the characteristic pyridine vibrations of pya$_2$tn and pya$_2$tnOH upon complexation are in accord with the extensive correlations made for coordinated pyridines.[19] These changes, together with the absence of splitting in the ring stretching modes,[20] indicate that both pyridine moieties are coordinated in all of the complexes. The presence of a strong C=N stretching band in the complexes, together with the absence of NH or C=O bands (arising as a result of the partial or complete hydrolysis of the C=N bond), confirms the Schiff base nature of the coordinated ligands.

All of the pya$_2$tnOH complexes and the complexes formulated as hydrates show OH stretching bands in the region 3200-3600 cm^{-1}. The azide derivates exhibit strong bands near 2000 cm^{-1} assigned[21] to the asymmetric N$_3^-$ stretching

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[11] See Experimental Section for ligand abbreviations.

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Table III. Infrared Frequency Assignments for the Nitrite and Thiocyanate Ions in the Nickel(II) Complexes

	Freq, cm^{-1}, and nitrite assignments		
	ν_{as}	ν_s	δ
$Ni(pya_2tn)(NO_2)_2$	1381	1150	822
$Ni(pya_2tnOH)(NO_2)_2$	1381	1195	821
	1349	1143	
	Freq, cm^{-1}, and thiocyanate assignments		
	C-N str	C-S str	NCS bend
$Ni(pya_2tn)(NCS)_2$			
Brown isomer	2092	792	477
Green isomer	2099	792	477
	2082	781	
$Ni(pya_2tnOH)(NCS)_2$	2104	809	[b]
	2094	794[a]	
		783[a]	

[a] Shoulder. [b] Obscured by ligand band.

vibration. In addition, weak bands are found in the 1150-1350-cm^{-1} region (where the symmetric stretching band and deformation overtones are expected) and a strong band at 617 cm^{-1} is assigned to an azide deformation.

For the thiocyanate and nitrite derivatives, an attempt was made to determine whether the anions were coordinated and the mode of coordination. The infrared spectra of these ambidentate ions have been reviewed along with the methods for determining their bonding modes.[22] Assignments (Table III) were made by comparison to the extensive literature data for nitrite[22-26] and thiocyanate[27-29] complexes, with the assumption that the asymmetric nitrite stretching vibration (ν_{as}) is always found at higher energies than the symmetric stretching vibration (ν_s) for both N- and O-bonded nitrite ions.[24,30]

$Ni(pya_2tn)(NO_2)_2$ and $Ni(pya_2tnOH)(NO_2)_2$ may be formulated as O-bonded (nitrito) complexes from the stretching frequency assignments. The frequencies observed for $Ni(pya_2tn)(NO_2)_2$ are similar to the values reported[23-26] for *trans*-$[Ni(py)_4(ONO)_2]$ and the analogous picoline complexes. No information regarding the source of the splitting observed for $Ni(pya_2tnOH)(NO_2)_2$ was obtained from the infrared data; no bands were found for this complex which could be ascribed to the presence of nonbonded nitrite,[31] which would be present for both bridging[32] and chelating[25] nitrite ions. The observed C-S stretching and NCS bending vibration frequencies indicate the presence of N-bonded thiocyanate for all three complexes. However, the infrared data again do not offer a conclusive explanation for the splitting seen for the thiocyanate stretching vibrations in $Ni(pya_2tn)(NCS)_2$ (green isomer) and $Ni(pya_2tnOH)(NCS)_2$. The splitting could be due to the presence of both bridging and nonbonded thiocyanate, or to the presence of cis, N-bonded thiocyanates.[28]

Table IV. Solid-State Electronic Spectral Data

	$\bar{\nu}$, kK		
Complex	ν_1	ν_2	Other bands
$Ni(pya_2tn)Cl_2 \cdot 6H_2O$	10.0,[a] 12.5, 13.2[b]	18.2	26.3,[a] 32.5, 33.9,[a] 40.8
$Ni(pya_2tn)Cl_2 \cdot H_2O$	8.9, 11.9,[b] 12.7	17.5[a]	26.3,[a] 31.8, 33.6,[a] 40.0
$Ni(pya_2tn)Br_2$	8.6, 11.4,[b] 13.2		24.4,[a] 31.0, 34.5[a]
$Ni(pya_2tn)I_2$	8.6, 13.8		20.4,[a] 24.5, 29.0, 38.4[a]
$Ni(pya_2tn)(N_3)_2$	10.5, 11.9[a]	16.7[a]	22.5,[a] 29.4, 34.5,[a] 40.2
$Ni(pya_2tn)(NO_2)_2$	12.5		30.0,[a] 33.0, 39.7
$Ni(pya_2tn)(NCS)_2$ green	11.4, 12.4[a]	18.9[a]	31.4, 40.3
$Ni(pya_2tn)(NCS)_2$ brown	11.4, 12.4[a]	18.9	27.0, 30.7, 34.4,[a] 39.8
$Ni(pya_2tn)(Im)_2I_2$	12.5	17.3[a]	
$Ni(pya_2tnOH)Cl_2$	9.1, 11.9,[b] 12.7	17.2[a]	31.8, 39.2
$Ni(pya_2tnOH)Br_2$	8.7, 12.1,[a] 12.6	17.7[a]	30.5, 38.6
$Ni(pya_2tnOH)I_2$	8.2, 11.6,[b] 13.7		24.9, 32.7, 39.2
$Ni(pya_2tnOH)(N_3)_2$	11.9		22.7,[a] 29.4, 32.8, 39.8
$Ni(pya_2tnOH)(NCS)_2$	11.2, 12.5[a]	18.5	32.2, 39.8[a]
$Ni(pya_2tnOH)(NO_2)_2$	12.5		31.2,[a] 33.0, 40.0

[a] Shoulder. [b] Narrow band.

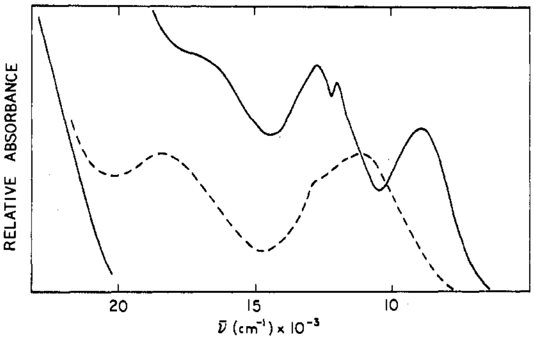

Figure 1. Solid-state diffuse transmittance spectra of $Ni(pya_2tn)Cl_2 \cdot H_2O$ (—) and $Ni(pya_2tnOH)(NCS)_2$ (- - -).

Electronic Spectra. The electronic spectral data for the solid nickel(II) complexes derived from pya_2tn and pya_2tnOH are presented in Table IV and representative near-infrared-visible spectra are illustrated in Figure 1. No attempt to assign the intense bands above 20,000 cm^{-1} has been made since red-shifted anion transitions,[33] charge-transfer transitions, ligand transitions, and nickel(II) transitions are all expected in this region. The weak features seen below 20,000 cm^{-1}, ν_1 and ν_2, have been assigned to nickel(II) d-d transitions. The pronounced splitting seen in ν_1 for the seven halide complexes is similar to the splitting observed in tetragonally distorted nickel(II) complexes.[34,35] A consistent interpretation of ν_1 and ν_2 in terms of octahedral or tetragonal[35] six-coordinate nickel(II) is possible for the entire series of complexes.

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In tetragonal[35] complexes the parent octahedral transition ($^3A_{2g} \rightarrow {}^3T_{2g}$) is split into two transitions, $^3B_{1g} \rightarrow {}^3B_{2g}$ and $^3B_{1g} \rightarrow {}^3E_g$. The energy of the former tetragonal component is a measure of the in-plane donor strength, whereas the latter component is a function of the axial donor strength. For a series of complexes in which only the weaker axial donors are varied, the energy of the in-plane transition should remain approximately constant while the energy of the axial transition decreases in going to poorer axial donors. For in-plane and axial ligands of comparable donor strength, the separation of the tetragonal levels becomes too small to be observed.

Although the number of nickel(II) bands observed in the solid-state spectra of the halide complexes is too low to permit a detailed analysis, a tentative assignment can be made using this tetragonal crystal field model assuming D_{4h} to be the donor atom symmetry.[36] The lowest energy component of ν_1 corresponds to the axial $^3B_{1g} \rightarrow {}^3E_g$ transition, and the remaining more intense higher energy component to the in-plane $^3B_{1g} \rightarrow {}^3B_{2g}$ transition. The third weaker feature seen in ν_1 for some of these complexes could arise from the $^1B_{1g} \rightarrow {}^1A_{1g}$, $^1B_{1g}$ transition. The method of calculation outlined by Lever[35] yields average values (cm^{-1}) of 305, 390, 530, and 750 for the axial ligand field strength of I^-, Br^-, Cl^-, and H_2O (in Ni(pya$_2$tn)Cl$_2$·6H$_2$O), respectively. These values are only approximate, but they do correspond to values reported for other tetragonal nickel(II) systems and to the order predicted by the spectrochemical series.[34,35] The average value of the ligand crystal field strength (1300 cm^{-1}) is close to that observed for bipyridyl (1265 cm^{-1}), which is expected because of the similarity of the ligands.

For the complexes containing azide, nitrite, thiocyanate, and imidazole, ν_1 and ν_2 may be assigned to the $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transitions of octahedral nickel(II), and the shoulder observed on ν_1 to the spin-forbidden $^3A_{2g} \rightarrow {}^1E_g$ transition. The apparent lack of tetragonal splitting in ν_1 can be ascribed to the smaller difference between the planar and axial ligand field strengths for these derivatives.

Registry No. Potassium phthalimide, 1074-82-4; 1,3-dibromobutane, 107-80-2; 1,3-bis(phthalimidyl)butane, 39489-17-3; hydrazine, 302-01-2; 1,3-diaminobutane, 590-88-5; pyridine-2-carboxaldehyde, 1121-60-4; pya$_2$tn, 39489-18-4; 1,3-diamino-2-propanol, 616-29-5; pya$_2$tnOH, 39489-19-5; Ni(pya$_2$tnOH)Cl$_2$, 39546-56-0; Ni(pya$_2$tnOH)Br$_2$, 39489-13-9; Ni(pya$_2$tnOH)I$_2$, 39489-12-8; Ni(pya$_2$tnOH)(NO$_2$)$_2$, 39546-55-9; Ni(pya$_2$tnOH)(N$_3$)$_2$, 39489-11-7; Ni(pya$_2$tnOH)(NCS)$_2$, 39489-10-6; Ni(pya$_2$tn)Cl$_2$, 39489-09-3; Ni(pya$_2$tn)Br$_2$, 39489-08-2; Ni(pya$_2$tn)I$_2$, 39489-07-1; Ni(pya$_2$tn)(NO$_2$)$_2$, 39489-06-0; Ni(pya$_2$tn)(N$_3$)$_2$, 39489-05-9; Ni(pya$_2$tn)(NCS)$_2$, 39489-04-8; Ni(pya$_2$tn)(Im)$_2$I$_2$, 39489-03-7; Ni(pya$_2$(+)tnCH$_3$)Cl$_2$, 39489-02-6; Ni(pya$_2$(+)tnCH$_3$)(N$_3$)$_2$, 39489-01-5; Ni(7-CH$_3$pya$_2$tn)Cl$_2$, 39489-00-4; Ni(7-CH$_3$pya$_2$tnCH$_3$)Cl$_2$, 39488-99-8.

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(36) The actual symmetry of the complexes is C_2 or lower depending on the central ring substituents.

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Electronic, Circular Dichroism, and Proton Magnetic Resonance Spectral Studies of the Nickel(II) Complexes of Some Neutral, Tetradentate Schiff Base Ligands Derived from 1,3-Diamines

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The nickel(II) complexes of the four neutral, tetradentate Schiff base ligands derived from pyridine-2-carboxaldehyde or 2-acetylpyridine and 1,3-diaminopropane or 1,3-diaminobutane were characterized in solution by conductivity measurements and absorption, circular dichroism, and proton magnetic resonance spectroscopy. The complexes [Ni(ligand)X$_2$]·nH$_2$O, where $X^- = Cl^-$, Br^-, I^-, or NO_2^-, behave as 2:1 electrolytes in aqueous solution and give rise to a common species formulated as [Ni(ligand)(H$_2$O)$_2$]$^{2+}$. The azide derivatives are formulated as [Ni(ligand)(N$_3$)(H$_2$O)]$^+$ in water and the chloride complexes as [Ni(ligand)(Cl)(CH$_3$OH)]$^+$ in methanol. In aqueous solution the complex ion [Ni(ligand)(H$_2$O)$_2$]$^{2+}$ reacts with additional neutral monodentate donors to yield [Ni(ligand)(donor)$_2$]$^{2+}$. The solution electronic spectra of the complexes exhibit a pronounced tetragonal splitting in the band attributed to the lowest energy octahedral nickel(II) transition. The circular dichroism spectra of the complexes with Schiff bases derived from (S)-(+)-1,3-diaminobutane show features similar to the electronic spectra and are consistent with a tetragonal model. The contact-shifted proton magnetic resonance spectra of the paramagnetic complexes confirm the Schiff base nature and tetradentate coordination of the ligands. The pmr studies indicate a preferred methyl axial conformation for the central chelate ring in the nickel(II) Schiff base complexes derived from 1,3-diaminobutane.

Introduction

In a previous paper[2] we reported the preparation and solid-state characterization of the nickel(II) complexes with the ligand N,N'-bis(2-pyridylmethylene)-1,3-diaminopropane and several related Schiff bases. This paper describes the studies undertaken to establish the stereochemistry of these complexes in solution.

Experimental Section

The following abbreviations are used for the tetradentate ligands: pya$_2$tn, N,N'-bis(2-pyridylmethylene)-1,3-diaminopropane; pya$_2$(+)tnCH$_3$, N,N'-bis(2-pyridylmethylene)-(S)-(+)-1,3-diaminobutane; 7-CH$_3$pya$_2$tn, N,N'-bis(7-methyl-2-pyridylmethylene)-1,3-diaminopropane; 7-CH$_3$pya$_2$tnCH$_3$, N,N'-bis(7-methyl-2-pyridylmethylene)-1,3-diaminobutane.

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