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Pentadentate Ligands. II. Nickel(II) Complexes of the Linear Schiff Base Ligand Derived from 2-Pyridinecarboxaldehyde and Bis(3,3′-aminopropyl)amine

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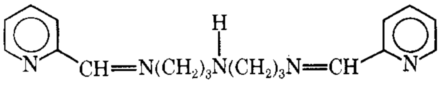
Nickel(II) complexes employing the linear potentially pentadentate ligand (pyDPT) derived from 2-pyridinecarboxaldehyde and bis(3,3′-aminopropyl)amine have been prepared. Complexes of general formula [Ni(pyDPT)X]X and [Ni(pyDPT)Y]PF_6, where X^- = Cl^-, Br^-, I^-, NO_3^-, and SCN^- and Y^- = Cl^-, Br^-, NO_3^-, and SCN^-, have been isolated. When X^- = PF_6^-, a complex of composition [Ni(pyDPT)(H_2O)]$(PF_6)_2$ is formed. All complexes have been characterized by infrared and visible spectral, magnetic susceptibility, and conductometric measurements. Both in solution and in the solid state the materials give rise to a pseudooctahedral coordination environment about the nickel(II) ion. The position of the lowest energy d–d transition in the solid state can be correlated with the relative location of X and Y in the spectrochemical series. In methanol solution, conductance measurements suggest the replacement of X or Y by a solvent molecule to complete the six-coordinate structure. In nitromethane the complexes behave as 1:1 electrolytes.

Introduction

Transition metal complexes of linear potentially pentadentate ligands have not been investigated to a great extent.[1] The most heavily studied ligands of this type to date have been those Schiff bases derived from variously substituted salicylaldehydes and tridentate polyamines.[2-4] The resulting metal(II) complexes have been shown to be neutral materials wherein the ligand is dinegatively charged. Limited study has revealed that the chain of atoms joining the two azomethine linkages determines whether the ligand functions as a pentadentate, tetradentate, or some lower polydentate chelating group.[3-5]

We wish to report here our results concerning the cationic nickel(II) complexes of the neutral pentadentate ligand derived from 2-pyridinecarboxaldehyde and bis(3,3′-aminopropyl)amine, structure I, hereafter referred to as pyDPT.



I

Experimental Section

Materials.—2-Pyridinecarboxaldehyde and bis(3,3′-aminopropyl)amine (DPT) were obtained from the Aldrich Chemical Co., Milwaukee, Wis. Before use, the 2-pyridinecarboxaldehyde was distilled *in vacuo* collecting the fraction which boiled at 40–41° (5 mm). KSeCN was obtained from Alfa Inorganics, Inc., Beverly, Mass. All other chemicals and solvents were of reagent grade or equivalent.

Preparation of [Ni(pyDPT)Cl]Cl.—To a stirred solution of 2-pyridinecarboxaldehyde (5.35 g, 0.05 mol) dissolved in 50 ml of absolute ethanol was added DPT (3.28 g, 0.025 mol). The solution was refluxed for 10 min, turning from pale yellow to dull orange. To this refluxed solution was added dropwise a solution prepared by adding $NiCl_2 \cdot 6H_2O$ (5.94 g, 0.025 mol) to a minimum amount of ethanol plus 5 ml of triethyl orthoformate. The solution immediately became dark red and was refluxed for 50 min. No solid appeared upon cooling the solution to room temperature. Ethyl ether was added to the solution until a definite cloudiness appeared; also, scratching was employed. Upon cooling the solution overnight, a brown powdery material precipitated. The product was filtered in a water-free atmosphere, recrystallized from hot ethanol, filtered again as previously described, and dried at 100° for 12 hr at reduced pressure.

Preparation of [Ni(pyDPT)(NO_3)]NO_3.—This material was prepared as described above with the minor modification that $Ni(NO_3)_2 \cdot 6H_2O$ was substituted for $NiCl_2 \cdot 6H_2O$.

Preparation of [Ni(pyDPT)I]I.—To a stirred solution of 2-pyridinecarboxaldehyde (5.35 g, 0.05 mol) dissolved in 50 ml of absolute ethanol was added DPT (3.28 g, 0.025 mol). The solution was refluxed for 10 min, turning from pale yellow to dull orange. To this refluxed solution was added dropwise a solution prepared by adding $Ni(NO_3)_2 \cdot 6H_2O$ (7.27 g, 0.025 mol) to a minimum amount of absolute ethanol which contained 5 ml of triethyl orthoformate. The solution immediately became dark red and was allowed to reflux for 50 min. The resulting solution was cooled to room temperature and saturated with a methanol solution of NaI. Upon cooling overnight, a brownish red powdery material precipitated. The product was recrystallized from hot water, filtered, and dried as described above.

Preparation of [Ni(pyDPT)Br]Br.—This material was prepared as described above except that a methanol solution of LiBr was used instead of NaI.

Preparation of [Ni(pyDPT)(SCN)]SCN.—This material was prepared as described above except that a methanol solution of NaSCN was used instead of NaI.

Preparation of [Ni(pyDPT)(H_2O)]$(PF_6)_2$.—To a stirred solution of 2-pyridinecarboxaldehyde (5.35 g, 0.05 mol) dissolved in 50 ml of absolute ethanol was added DPT (3.28 g, 0.025 mol). The solution was refluxed for 10 min, turning from pale yellow to dull orange. To this refluxed solution was added dropwise a solution prepared by dissolving $Ni(C_2H_3O_2)_2 \cdot 4H_2O$ (6.22 g, 0.025 mol) and 5 ml of triethyl orthoformate in a minimum amount of absolute ethanol. The solution immediately became a rich brown color and was refluxed for 50 min. The resulting solution was cooled to room temperature and saturated with an absolute ethanol solution of NH_4PF_6. Upon cooling overnight, a reddish material precipitated. The product was recrystallized from hot methanol, filtered, and dried as previously described.

Preparation of [Ni(pyDPT)Cl]PF_6.—This material was prepared as described above except that $NiCl_2 \cdot 6H_2O$ was used in place of $Ni(C_2H_3O_2)_2 \cdot 4H_2O$.

Preparation of [Ni(pyDPT)(NO_3)]PF_6.—This material was prepared following the procedure described for the preparation of [Ni(pyDPT)Cl]PF_6 except that $Ni(NO_3)_2 \cdot 6H_2O$ was substituted for $NiCl_2 \cdot 6H_2O$.

Preparation of [Ni(pyDPT)Br]PF_6.—This material was prepared following the procedure described for the preparation of [Ni(pyDPT)Cl]PF_6 except that $NiBr_2 \cdot 6H_2O$ was substituted for $NiCl_2 \cdot 6H_2O$.

Preparation of [Ni(pyDPT)(SCN)]PF_6.—[Ni(pyDPT)(SCN)]SCN (5 g, 0.01 mol) was dissolved in a minimum amount of hot water and cooled to room temperature. The resulting reddish brown solution was filtered by gravity and saturated with an aqueous solution of NH_4PF_6. An orange material readily precipitated. The product was recrystallized from hot methanol–water, filtered, and dried at 100° for 12 hr at reduced pressure.

Physical Measurements.—Infrared absorption spectra in the

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[1] H. A. Goodwin, "Chelating Agents and Metal Chelates," F. Dwyer and D. Mellor, Ed., Academic Press, New York, N. Y., 1964.

[2] L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, **88**, 5180 (1966).

[3] W. M. Coleman and L. T. Taylor, *ibid.*, **92**, 1449 (1970).

[4] W. M. Coleman and L. T. Taylor, *Inorg. Chem.*, **10**, 2195 (1971).

[5] M. K. Akhtar, E. D. McKenzie, R. E. Paine, and A. J. Smith, *Inorg. Nucl. Chem. Lett.*, **5**, 673 (1969).

TABLE I

ANALYTICAL DATA FOR THE NICKEL(II) COMPLEXES

	Analyses, %						
	C		H		N		
Compound	Calcd	Found	Calcd	Found	Calcd	Found	μ_{eff}, BM
$[\text{Ni(pyDPT)Cl}]\text{Cl}$	47.26	47.28	5.47	5.74	15.32	15.17	3.19
$[\text{Ni(pyDPT)(NO}_3)]\text{NO}_3$	42.35	42.11	4.90	4.65	19.22	19.34	3.25
$[\text{Ni(pyDPT)I}]\text{I}$	33.75	33.78	3.91	3.78	10.94	10.98	3.24
$[\text{Ni(pyDPT)Br}]\text{Br}$	39.56	39.34	4.58	4.49	12.82	12.67	3.22
$[\text{Ni(pyDPT)(SCN)}]\text{SCN}$	49.59	49.87	4.79	4.77	20.25	20.43	3.23
$[\text{Ni(pyDPT)(H}_2\text{O)}](\text{PF}_6)_2$	31.98	32.01	3.73	3.84	10.36	10.49	3.31
$\text{Ni(pyDPT)Cl}]\text{PF}_6{}^a$	39.91	39.71	4.23	4.49	12.77	12.93	3.25
$[\text{Ni(pyDPT)(NO}_3)]\text{PF}_6$	37.59	37.80	4.03	3.99	14.61	14.79	3.23
$[\text{Ni(pyDPT)Br}]\text{PF}_6{}^b$	36.45	36.12	3.91	3.93	11.91	11.94	3.24
$[\text{Ni(pyDPT)(SCN)}]\text{PF}_6$	39.95	39.87	4.06	3.95	14.71	14.46	3.20

[a] Analysis for Cl^-: calcd, 6.46; found, 6.45. [b] Analysis for Br^-: calcd, 13.49; found, 13.46.

TABLE II

MOLAR CONDUCTANCES OF $[\text{Ni(pyDPT)X}]\text{X}$ AND $[\text{Ni(pyDPT)X}]\text{PF}_6$ (23°)

Compound	Solvent	Concn, m*M*	Λ_m, $\text{ohm}^{-1}\ \text{cm}^{-1}\ \text{mol}^{-1}$
$[\text{Ni(pyDPT)Cl}]\text{Cl}$	CH_3OH^a	1	160
		10	88.5
	$\text{CH}_3\text{NO}_2{}^b$	1	68
		10	47
$[\text{Ni(pyDPT)(NO}_3)]\text{NO}_3$	CH_3OH	1	155
		10	94.7
	CH_3NO_2	10	50.3
		1	85
$[\text{Ni(pyDPT)I}]\text{I}$	CH_3OH	1	190.6
		10	108.3
	CH_3NO_2	10	48.1
		1	89
$[\text{Ni(pyDPT)Br}]\text{Br}$	CH_3OH	1	175
		10	103.1
	CH_3NO_2	1	82
		10	50
$[\text{Ni(pyDPT)(SCN)}]\text{SCN}$	CH_3OH	1	90.7
		2	87.5
$[\text{Ni(pyDPT)(H}_2\text{O)}](\text{PF}_6)_2$	CH_3OH	1	189
		10	106.8
	CH_3NO_2	1	179
$[\text{Ni(pyDPT)Cl}]\text{PF}_6$	CH_3OH	6	107.6
	CH_3NO_2	4	89.7
$[\text{Ni(pyDPT)(NO}_3)]\text{PF}_6$	CH_3OH	6	124
	CH_3NO_2	5	97
$[\text{Ni(pyDPT)Br}]\text{PF}_6$	CH_3OH	6	118
	CH_3NO_2	5	83
$[\text{Ni(pyDPT)(SCN)}]\text{PF}_6$	CH_3OH	2	58

[a] Molar conductivity of a methanol solution of NaSCN (0.00087 *M*) is 64.3 $\text{ohm}^{-1}\ \text{cm}^{-1}\ \text{mol}^{-1}$. Molar conductivity of a methanol solution of CaCl_2 (0.00098 *M*) is 131.6 $\text{ohm}^{-1}\ \text{cm}^{-1}\ \text{mol}^{-1}$. [b] For a 1:1 electrolyte, Λ_m = 85–97 $\text{ohm}^{-1}\ \text{cm}^{-1}\ \text{mol}^{-1}$; for a 2:1 electrolyte, Λ_m = 177 $\text{ohm}^{-1}\ \text{cm}^{-1}\ \text{mol}^{-1}$: N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3999 (1959).

region 5000–450 cm^{-1} were determined employing a Nujol or hexachlorobutadiene mull technique with a Perkin-Elmer Model 621 grating spectrophotometer and a Beckman IR-5A recording spectrophotometer.

Ultraviolet–visible–near-infrared spectra at room temperature were obtained using a Cary 14 recording spectrophotometer. Solution spectra were taken utilizing spectroquality solvents in matched solution cells. Diffuse transmittance spectra were obtained using Nujol mulls supported on Whatman No. 1 filter paper.[6]

Magnetic susceptibility data were obtained at room temperature by the Faraday method using mercury(II) tetrathiocyanatocobaltate(II) as the calibrant. Diamagnetic corrections were made employing Pascal's constants.[7]

Molar conductances were measured using a Barnstead Model PM-70CB conductivity bridge with a cell constant of 1.50 cm^{-1}. The distilled water, methanol, and nitromethane used for these measurements had a specific conductance of less than 10^{-6} ohm^{-1}.

Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, Tenn., and in this laboratory using a Perkin-Elmer Model 240 carbon, hydrogen, and nitrogen analyzer.

Results and Discussion

The subject nickel complexes, Table I, are highly crystalline and range in color from reddish orange to light brown or tan. All of the complexes are insoluble in cold water but dissolve readily upon heating. The complexes are moderately soluble in methanol, ethanol, nitromethane, and dimethyl sulfoxide; but, they are very insoluble in hot chloroform, benzene, or acetone. They are slightly soluble in hot pyridine.

The complexes are relatively thermally stable, melting above 200° with decomposition. Several fruitless attempts were made at removing the water of hydration from the $[\text{Ni(pyDPT)(H}_2\text{O)}](\text{PF}_6)_2$ complex. However, the complex appears to undergo decomposition with loss of water around 284°.

Conductivity data in methanol and nitromethane for the complexes are tabulated in Table II. The data indicate that the $[\text{Ni(pyDPT)Cl}]\text{Cl}$, $[\text{Ni(pyDPT)NO}_3]\text{NO}_3$, $[\text{Ni(pyDPT)I}]\text{I}$, $[\text{Ni(pyDPT)Br}]\text{Br}$, and $[\text{Ni(pyDPT)H}_2\text{O}](\text{PF}_6)_2$ complexes are all 2:1 electrolytes in methanol, suggesting that a molecule of methanol is probably attached to the sixth coordination position around the nickel ion rather than one of the two anions present in each of the above cases. This solvolysis may be envisioned to proceed as

$$\text{Ni(pyDPT)X}^+ + \text{CH}_3\text{OH} \rightleftharpoons \text{Ni(pyDPT)(CH}_3\text{OH)}^{2+} + \text{X}^-$$

In nitromethane, however, all of the above complexes appear to be 1:1 electrolytes, indicating that one anion is coordinated to the metal ion thereby satisfying a primary and secondary valence whereas the second anion satisfies only the primary valence. In addition, the mixed complex salts $[\text{Ni(pyDPT)Cl}]\text{PF}_6$, $[\text{Ni(pyDPT)NO}_3]\text{PF}_6$, and $[\text{Ni(pyDPT)Br}]\text{PF}_6$ also are 1:1 electrolytes in nitromethane. Hexafluorophosphate is known to be a rather poor ligand; therefore, it is reasonable to assume that the chloride, bromide, and nitrate ions are all coordinated in the sixth position rather than the hexafluorophosphate. Both the $[\text{Ni(pyDPT)SCN}]\text{SCN}$ complex and $[\text{Ni(pyDPT)SCN}]\text{PF}_6$, are 1:1 electrolytes even in methanol suggesting a thiocyanate ion must be coordinated to the nickel ion in both cases. This observation is consistent with the position of thiocyanate ion in the spectrochemical series above methanol.

Infrared spectra were obtained as Nujol and hexa-

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(6) R. H. Lee, E. Griswold, and J. K. Kleinberg, *Inorg. Chem.*, **3**, 1278 (1964).

(7) B. N. Figgis and J. Lewis, "Modern Coordination Chemistry," J. Lewis and R. J. Wilkins, Ed., Interscience, New York, N. Y., 1960.

chlorobutadiene mulls. The vibrational frequencies of the pyridine ring and the Schiff base linkage of the acyclic side chain should be found in the region of the spectrum between 1700 and 1400 cm^{-1}.[8] For the nickel complexes the assignment of the C=N stretching frequency ranges from 1635 to 1648 cm^{-1}. Ordinarily, the C=N stretching frequency for the free ligand would be expected to occur at somewhat higher energy than the C=N stretching mode for the metal complex[9] if the Schiff base linkage is coordinated. However the acyclic C=N group in pyDPT is conjugated and the interaction of the π electron of the side chain azomethine linkage with the π electron system of the pyridine ring is expected to lower the C=N stretching frequency somewhat. Upon coordination to nickel(II), π-electron interaction is expected to be diminished.[10]

The infrared spectra of the [Ni(pyDPT)X]X complexes also show a medium weak, sharp band in the range 3170–3320 cm^{-1} which may be assigned to the N–H stretching mode. Absorption in this frequency range is low when compared with values reported for nonhydrogen bonded secondary amines which usually absorb weakly in the range 3350–3310 cm^{-1}. The free ligand pyDPT has an N–H stretching band around 3200 cm^{-1}. The weakness and broadness of this band suggests a highly hydrogen-bonded structure for this material in solution. Since the sharpness of this band in the complexes excludes the presence of extensive hydrogen bonding, the lowering of its frequency must be attributed to the formation of a metal–secondary nitrogen coordinate bond.[9]

On the basis of the previously reported four ring vibrations[10] of the pyridine nucleus, the bands at 1587, 1567, 1468, and 1435 cm^{-1} in the spectrum of pyDPT are assigned to the pyridine ring. The basic pattern of these four bands is evident throughout the spectra of all the complexes, although some shifting of bands and changes in intensities do occur. In all of the complexes, band I is the strongest of the four and it is the one which exhibits the strongest absorption in the double-bond region. Band II in the complexes is greatly reduced in intensity and often is hardly more than a shoulder. Bands III and IV are usually of medium or strong intensity with band IV being the stronger of the two.

The infrared spectrum for $[Ni(pyDPT)(H_2O)](PF_6)_2$ shows a very broad band spanning the 900–800-cm^{-1} region. This band is assigned as being due to uncoordinated hexafluorophosphate.[9] This band is also present in the infrared spectra of the four mixed complex salts and the anion appears not to be coordinated in these materials as well. Absorption in the 3400-cm^{-1} region is consistent with the presence of water in the formulation.

For $[Ni(pyDPT)NO_3]NO_3$, the infrared spectrum shows a sharp band at 1740 cm^{-1}. This band is not found in the infrared spectrum of any of the other nickel(II) complexes, including the $[Ni(pyDPT)NO_3]PF_6$ complex salt, and, therefore, it is assigned to ionic nitrate.[11] Another band indicative of ionic nitrate is found as a medium sharp band around 1368 cm^{-1}. The spectrum of the $[Ni(pyDPT)NO_3]NO_3$ complex also exhibits two weak broad bands in the range 1400–1300 cm^{-1} assignable to coordinated nitrate (*i.e.*, one at about 1305 cm^{-1} and the other at 1385 cm^{-1}). Therefore, in this complex, we postulate that one nitrate ion is ionic and the other one is functioning as monodentate nitrate. The conductivity data in nitromethane supports this assignment. A single medium broad band from 1360 to 1355 cm^{-1} is present in $[Ni(pyDPT)(NO_3)]PF_6$ which also can be attributed to monodentate nitrate.

In the complex [Ni(pyDPT)SCN]SCN two intense bands occur, each of which is split into two distinct components. One band has peaks at 2030 and 2050 cm^{-1} and is assigned to ionic thiocyanate. The other band, with peaks at 2060 and 2080 cm^{-1}, is assigned as coordinated thiocyanate.[12] In the complex salt $[Ni(pyDPT)SCN]PF_6$, a single sharp band at 2080 cm^{-1} is observed indicative of coordinated thiocyanate. Here, too, a very broad band spanning 900–800 cm^{-1} provides proof of the presence and noncoordination of hexafluorophosphate anion.

The broad band due to hexafluorophosphate also appears in the spectra of the complex salts $[Ni(pyDPT)Cl]PF_6$ and $[Ni(pyDPT)Br]PF_6$. However, the infrared spectrum of each does not provide information as to whether chloride and bromide ions are present and, if so, whether the halide ions are coordinated. A glance at the analytical data in Table I shows that the found percentages for chloride and bromide are very close to the calculated percentages for these complexes. Furthermore, the spectrochemical series suggests both chloride and bromide ion are better ligands than hexafluorophosphate. Therefore, if the chloride and bromide are present in the complex, they would coordinate in preference to the hexafluorophosphate. Additional proof that chloride and bromide are actually present in these complex salts was supported by positive silver halide tests.

Magnetic susceptibility measurements, Table I, indicate that all the nickel(II) complexes are high-spin octahedral ones.[13] The pseudooctahedral structure may be envisioned for each complex by having five coordinate positions filled by the pentadentate ligand and an anion or a solvent molecule satisfying the remaining sixth position, structure II.

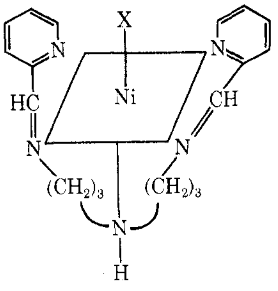

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Table III lists the solid-state and solution electronic spectra for the simple and mixed nickel(II) complexes,

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[8] R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Boston, Mass., 1966.

[9] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley, New York, N. Y., 1963.

[10] P. E. Figgins and D. J. Busch, *J. Phys. Chem.*, **65**, 2236 (1961).

[11] N. F. Curtius and Y. M. Curtius, *Inorg. Chem.*, **4**, 804 (1965).

[12] P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960); M. E. Farago and J. M. James, *Inorg. Chem.*, **4**, 1706 (1965).

[13] B. N. Figgis, "Introduction to Ligand Fields," Interscience, New York, N. Y., 1968.

TABLE III

ELECTRONIC SPECTRA[a,b] (cm^{-1}) OF $[Ni(pyDPT)X]X$ AND $[Ni(pyDPT)X]PF_6$

Compound	Medium	Band max ν_1	ν_2	ν_3	ν_4	ν_5
$[Ni(pyDPT)Cl]Cl$	Nujol	9,800	12,050	20,000	...	...
	CH_3OH	10,950	12,990	22,900 sh	27,870 sh	35,090
		(9)	(10.2)	(35)	(5400)	(15,000)
$[Ni(pyDPT)NO_3]NO_3$	Nujol	10,260	12,350	23,260	...	...
	CH_3OH	10,530	13,040	23,260	27,780	35,090
		(6.8)	(5.2)	(70)	(200)	15,000)
$[Ni(pyDPT)I]I$	Nujol	9,710 vb	12,500 sh	22,220	...	...
	CH_3OH	10,385	13,120	22,990	27,780	35,090
		(8.6)	(6.2)	(110)	(550)	(18,300)
$[Ni(pyDPT)Br]Br$	Nujol	9,520	12,990	20,620	...	...
	CH_3OH	10,420	13,070	22,730	...	35,090
		(7.8)	(5.8)	(154)		(16,500)
$[Ni(pyDPT)SCN]SCN$	Nujol	11,240	12,350	20,830	...	...
	CH_3OH	11,110	12,270	...	...	35,090
		(15)	(145)			(36,000)
$[Ni(pyDPT)H_2O](PF_6)_2$	Nujol	10,640	12,350	22,730	...	...
	CH_3OH	10,410	13,070	22,990	27,880 sh	35,090
		(8)	(6.3)	(28)	(55)	(18,000)
$[Ni(pyDPT)Br]PF_6$	Nujol	9,620	...	20,000	25,640	
	CH_3NO_2	9,800	12,660	19,420	...	
		(9.8)	(5.3)	(102)		
$[Ni(pyDPT)SCN]PF_6$	Nujol	10,990	12,350	20,830	26,300	
	CH_3OH	10,990	12,350	20,000	...	
		(16)	(15)	(127)		
$[Ni(pyDPT)Cl]PF_6$	Nujol	9,900	12,050	20,000	25,640	
	CH_3NO_2	10,000	12,660 sh	19,800 sh	...	
		(8)	(6)	(105)		
$[Ni(pyDPT)NO_3]PF_6$	Nujol	10,100	12,270	21,270	...	
	CH_3NO_2	10,410	12,520 sh	22,730 sh	...	
		(9.2)	(7.2)	(140)		

[a] Numbers in parentheses are molar extinction coefficients. [b] Abbreviations used: sh, shoulder; vb, very broad.

respectively. Solid-state spectra for all the complexes were obtained employing the Nujol mull diffuse-transmittance method. Solution spectra were obtained in methanol for complexes of the general formula $[Ni(pyDPT)X]X$ and $[Ni(pyDPT)(SCN)]PF_6$ and in nitromethane for complexes of the general formula $[Ni(pyDPT)X]PF_6$. Some of the mixed complex salts were not sufficiently soluble in methanol to permit its use. The general features of each derivative's spectrum both in the solid state and in solution are the same. A very broad band is observed in the 10,000-cm^{-1} region, ν_1, which may or may not have a number of shoulders associated with it. Rather broad shoulders are also observed in the regions 20,000 cm^{-1}, ν_3, and 28,000 cm^{-1}, ν_4. Finally, a very intense ligand band appears at 35,090 cm^{-1} in solution and "tails off" very strongly into the visible region. The high molar extinction coefficient supports the assignment of this band as a Laporte-allowed transition.[13] The position of these bands is consistent with the postulation that the nickel(II) ion has essentially an octahedral environment about it.[14] Extinction coefficients obtained from the solution spectra are also in the range predicted for six-coordinate nickel(II).[15] Therefore, the following assignments are made assuming an octahedral environment for the metal ion

$$\begin{aligned} &\nu_1 \quad {}^3A_{2g} \longrightarrow {}^3T_{2g} \\ &\nu_3 \quad {}^3A_{2g} \longrightarrow {}^3T_{1g}(F) \\ &\nu_4 \quad {}^3A_{2g} \longrightarrow {}^3T_{1g}(P) \end{aligned}$$

The spectral data show several features and trends which are noteworthy. The solid-state spectra of $[Ni(pyDPT)X]X$ are similar to the solid spectra of the corresponding $[Ni(pyDPT)X]PF_6$ if X is the same. In all but two of the complexes, a relatively weak band occurs around 12,500 cm^{-1} which may be assigned as a spin-forbidden transition (*i.e.*, ${}^1E_g \rightarrow {}^3A_{2g}$). Since each $[Ni(pyDPT)X]X$ has five common donor atoms, the trend in the lowest energy transition reflects the different ligand field strengths of the various anions. Similarly, it can be seen that the spectrochemical series also holds in the mixed complexes in the solid state $[Ni(pyDPT)X]PF_6$.

In methanol the solution spectra are approximately the same except for $[Ni(pyDPT)SCN]SCN$. Conductivity measurements indicate that all the complexes are 2:1 electrolytes in methanol, except for the thiocyanate which appears to be a 1:1 electrolyte. Thus, a molecule of methanol is predicted to be coordinated in the sixth position of the nickel ion in all but the one exception mentioned. For these 2:1 electrolytes, the same species $Ni(pyDPT)CH_3OH^+$ is anticipated in solution for each derivative. Therefore, the spectra should be almost identical which is the case. The methanol solution spectrum of $[Ni(pyDPT)SCN]SCN$ is different from that of the other $[Ni(pyDPT)X]X$ complexes. The ν_1 band appears at the same position for the SCN^- derivative both in the solid state and in solution.

In nitromethane the mixed salts have been shown to be 1:1 electrolytes. Thus, their spectra should not be exactly identical in solution since a different anion is coordinated in the sixth position for each complex Here, too, the spectrochemical series is adhered to closely with ν_1 for the thiocyanate derivative occurring at 10,990 cm^{-1}, for the nitrate derivative at 10,410 cm^{-1}, for the chloride derivative at 10,100 cm^{-1}, and for the bromide derivative at 9800 cm^{-1}.

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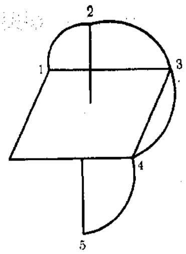
(14) M. Kilner and J. M. Smith, *J. Chem. Educ.*, **45**, 94 (1968).

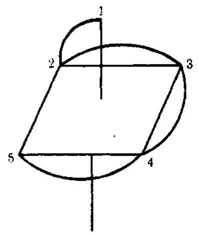
(15) D. H. Busch, *ibid.*, **41**, 77 (1964).

As noted previously the lowest energy band is extremely broad with from zero to three relatively sharp bands superimposed on it. These bands usually appear as shoulders rather than as isolated bands. This so-called "fine structure" is especially noticeable in methanol solution, less so in nitromethane, and practically undetectable in Nujol. The splitting of this band may arise *via* one or some combination of the following rationalizations. The broad band may contain a number of component vibrational transitions which are sufficiently widely spaced so that they may be observed as poorly resolved shoulders.[16] Since these spectral features appear to be solvent dependent, this argument seems quite tenable. Alternatively, some splitting of the lowest energy band could arise from tetragonal distortion of the formally octahedral complex. The symmetry of these complexes is, at best, C_{4v} and some of the splitting of the first octahedral band may be attributed to the effects of lower symmetry.[17]

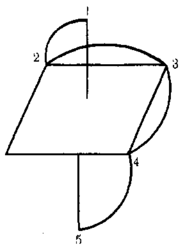
Finally, it may be interesting to speculate how the pyDPT ligand attaches itself to the octahedral nickel(II) ion. A linear pentadentate ligand in which the donor atoms are members of a continuous chain of atoms as pyDPT may attach itself to an octahedral metal ion in one or several manners, structures IIIA–IIID. In order for any of these structures to be adopted, a twist must occur at one or more donor atoms in the coordinating molecule, for example at the 2 and 4 positions in IIIA. Therefore, if the molecule is not flexible enough to allow for this stereochemical twist, it may not function as a pentadentate ligand but rather as a quadridentate or tridentate ligand.[4]



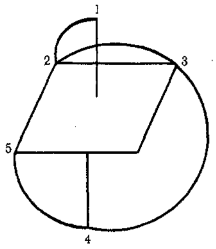
IIIA



IIIB



IIIC



IIID

The greatest amount of twist must occur at the azomethine linkages (*i.e.*, the 2 and 4 positions) in the pyDPT ligand in order for it to function as a pentadentate ligand. A study of Dreiding stereomodels shows that of the four arrangements IIIB and IIIC are the least favored sterically. It is possible to construct a model of IIIA although some strain is apparent. Perhaps the most favored arrangement is IIID which is quite easy to achieve using the stereomodels and presents the least strain on the ligand.

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Circular Dichroic Spectral Studies of Mixed Amino Acid–Acetylacetone Complexes of Nickel(II) and Observations on the Proline–Nickel(II) Complexes[1]

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Circular dichroic spectra demonstrate formation of mixed amino acid–acetylacetone complexes of Ni(II), containing one moiety each of the chelants. Group theoretical arguments are used to deduce from the CD spectra that the arrangement of the chelants is trans, or equatorial. Amino acids used are valine, serine, arginine, ornithine, proline, aspartic acid, and asparagine. CD spectra of prolinatonickel(II) may differ from those of the normal amino acid complexes due to the dissymmetric nitrogen of the complex. Spectra of *trans*-bis(prolinato)bis(aquo)nickel(II) and *cis*-bis(prolinato)nickel(II) are identified through group theoretical arguments. A possible mechanism for change from the trans bis-prolinato complex to the cis form is suggested.

Introduction

We have shown earlier[2] that 1:1 complexes between Ni(II) and the normal amino acids have a characteristic circular dichroism in the visible Ni(II) absorption bands. Potentially tridentate aspartic acid and asparagine induce a markedly different CD spectrum. Group theoretical arguments could be invoked to deduce from the splitting pattern of the $T_{1g}(O_h)$ upper state in the red region of the spectrum that these last complexes show cis tridentate chelation. When L-lactic acid, with the same spatial geometry as L-alanine, complexes with

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] L. I. Katzin and E. Gulyas, *J. Amer. Chem. Soc.*, **91**, 6940 (1969).