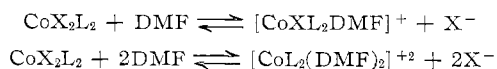


that the strong band in the visible region in $(\text{CoX}_4)^{-2}$ in the tetrahedral complexes may not be due to crystal field effects at all.

No attempt is therefore made to assign the spectral bands of the tetrahedral cobalt(II) complexes which seem to occur in chloride and bromide complexes only.

Two other possible structures are an oxygen or a chloride bridged structure similar to those found in copper(II) pyridine N-oxide complexes² and in $\text{Co}(\text{py})_2\text{Cl}_2$ (violet),²⁰ respectively. The infrared and magnetic susceptibility data, however, seem not to support these two types of bonding.⁴ Quite unexpectedly the halide complexes seem to maintain a tetrahedral structure in N,N-dimethylformamide²¹ (Figure 2).

This may be due to a mechanism similar to that observed by Buffagni and Dunn²² for CoCl_2 in dimethylformamide. It seems reasonable that a similar displacement occurs with the CoX_2L_2 complexes ($\text{X} = \text{Cl}, \text{Br}$).



This does not occur in methanol, since its coordina-

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tion tendency is smaller than that of dimethylformamide.

Nitrate Complexes.—The single-crystal X-ray analysis²³ of $\text{Co}[(\text{CH}_3)_3\text{PO}]_2(\text{NO}_3)_2$ has established that the cobalt(II) ion is surrounded by an irregular arrangement of six oxygen atoms, with each nitrate ion acting as a bidentate ligand.

The spectra of the 2,6-DPNO and 2,4,6-TPNO cobalt(II) nitrate complexes are similar to the spectra of $\text{Co}[(\text{CH}_3)_3\text{PO}]_2(\text{NO}_3)_2$. The absorption bands observed for these two nitrate complexes at 565 and 320 $m\mu$ were also observed for the above complex. The solids obey the Curie-Weiss law as shown by the determination of magnetic susceptibility at different temperatures, and the effective magnetic moments fall in the same range as those of the triphenylphosphine oxide complexes.^{1b} The spectra of the solid in lithium fluoride and in solution in nitromethane are superimposable except for the intensity, indicating that the complex does not change in the solvent (Figure 1). This seems to indicate that the 2,6-DPNO and 2,4,6-TPNO complexes also have distorted octahedral structures.

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Coordination Compounds of Nickel(II) Salts with Substituted Pyridines. Complexes of 2-, 3-, and 4-Methylpyridine

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Complexes of 2-, 3-, and 4-methylpyridine (2-pic, 3-pic, and 4-pic) with a number of Ni(II) salts (chloride, bromide, iodide, nitrate, perchlorate, and tetrafluoroborate) were prepared and investigated. Three series of complexes were obtained, $\text{Ni}(\text{pic})\text{X}_2$ (pic = 2-pic, 3-pic; $\text{X} = \text{Cl}, \text{Br}$); $\text{Ni}(\text{pic})_2\text{X}_2$ (pic = 2-pic, 3-pic, 4-pic; $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_3$); $\text{Ni}(\text{pic})_4\text{X}_2$ (pic = 3-pic, 4-pic; $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NO}_3, \text{ClO}_4, \text{BF}_4$). The complex $\text{Ni}(\text{3-pic})_4\text{X}_2$ ($\text{X} = \text{ClO}_4, \text{BF}_4$) was obtained in two isomeric forms, identified as $[\text{Ni}(\text{3-pic})_4\text{X}_2]$ and $[\text{Ni}(\text{3-pic})_4]\text{X}_2$, respectively. The complexes of 4-aminopyridine, $\text{Ni}(\text{4-NH}_2\text{py})_4\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{ClO}_4$), were also prepared and investigated. The stoichiometry and stereochemistry of the complexes were correlated with the properties of the anion and ligand, in particular with the basicity and steric requirements of the latter.

Introduction

This investigation is part of a study on the coordination compounds of substituted pyridines with Ni(II) salts, to establish a correlation between the stoichiometry and stereochemistry of Ni(II) complexes and the properties of the ligands and anions. Some previous results of this study have been published.¹⁻³ The

present paper describes the preparation and properties of the complexes of isomeric methylpyridines (picolines, abbreviated as 2-pic, 3-pic, and 4-pic) with a number of Ni(II) salts. The analogous complexes of 4-aminopyridine are also reported, as they are helpful in establishing a correlation between the stereochemistry of the NiL_4X_2 complexes and the basicity of the ligand L.

Experimental

Starting Materials.—The picolines (Brothers Chemical Co.) were dried over potassium hydroxide for 3 days, distilled under

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TABLE I
 ANALYTICAL DATA FOR THE NICKEL(II)-PICOLINE COMPLEXES

Compound ^a	Color	μ_{eff} , B.M. ^b	—Ni, %—		Halogen, %		—N, %—		—C, %—		—H, %—	
			Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
{Ni(2-pic)Cl ₂ } _n	Brick-red	3.44	26.35	26.20	31.84	31.58	6.29	6.25				
[Ni(2-pic) ₂ Cl ₂]	Deep blue	3.48	18.58	18.36	22.45	22.56	8.87	8.53				
{Ni(3-pic) ₂ Cl ₂ } _n	Pale yellow-green	3.39	18.58	18.39	22.45	22.56	8.87	8.75	45.62	45.41	4.48	4.37
{Ni(3-pic)Br ₂ } _n	Brick-red	3.19	18.84	18.40	51.35	51.28	4.49	4.32				
[Ni(2-pic) ₂ Br ₂]	Deep blue	3.47	14.50	14.46	39.48	39.46	6.92	6.78				
{Ni(3-pic) ₂ Br ₂ } _n	Yellow	3.43	14.50	14.70	39.48	39.59	6.92	6.84				
[Ni(4-pic) ₂ Br ₂] _n	Yellow	3.38	14.50	14.33	39.48	39.39	6.92	7.10	35.60	36.10	3.49	3.60
[Ni(2-pic) ₂ I ₂]	Dark green	Diamag.	11.77	11.85	50.89	50.38	5.62	5.84	28.89	28.80	2.83	2.90
[Ni(3-pic) ₂ I ₂]	Dark green	3.47	11.77	11.62	50.89	50.83	5.62	5.80	28.89	28.12	2.83	3.13
[Ni(4-pic) ₂ I ₂]	Dark green	3.38	11.77	11.41	50.89	50.75	5.62	5.67				
[Ni(3-pic) ₂ Cl ₂]	Blue-green	3.15	11.69	11.73	14.12	14.11	11.16	11.32	57.40	57.66	5.63	5.66
[Ni(4-pic) ₂ Cl ₂]	Pale blue	3.28	11.69	11.85	14.12	14.01	11.16	11.18				
[Ni(3-pic) ₂ Br ₂]	Blue-green	3.17	9.93	9.98	27.04	26.90	9.48	9.67	48.76	49.04	4.78	4.79
[Ni(4-pic) ₂ Br ₂]	Pale blue	3.30	9.93	9.53	27.04	27.29	9.48	9.32	48.76	46.39	4.76	4.72
[Ni(3-pic) ₂ I ₂]	Yellow-green	3.21	8.57	8.52	37.05	36.98	8.18	7.94	42.07	41.48	4.13	4.13
[Ni(4-pic) ₂ I ₂]	Yellow-green	3.34	8.57	8.49	37.05	37.20	8.18	7.72	42.07	42.06	4.13	4.25
[Ni(2-pic) ₂ (NO ₃) ₂]	Green	3.23	15.95	15.40			15.19	15.62				
[Ni(3-pic) ₂ (NO ₃) ₂]	Blue	3.13	12.70	12.50			15.14	15.52				
[Ni(4-pic) ₂ (NO ₃) ₂]	Blue	3.31	10.57	10.43			15.14	15.45				
[Ni(3-pic) ₂ (ClO ₄) ₂]	Yellow	Diamag.	9.32	9.31			8.89	8.75				
[Ni(3-pic) ₂ (ClO ₄) ₂]	Blue	3.14	9.32	9.31			8.89	8.75				
[Ni(3-pic) ₂ (BF ₄) ₂]	Yellow	Diamag.	9.71	9.65			9.27	9.35				
[Ni(3-pic) ₂ (BF ₄) ₂]	Blue	3.18	9.71	9.65			9.27	9.35				
[Ni(4-pic) ₂ (ClO ₄) ₂]	Bright yellow	Diamag.	9.32	9.07			8.89	8.69				
[Ni(4-pic) ₂ (BF ₄) ₂]	Bright yellow	Diamag.	9.71	9.55			9.27	9.23				
[Ni(H ₂ O) ₂ (3-pic) ₂ (ClO ₄) ₂]	Blue	3.23	8.81	8.46			8.41	8.28				
[Ni(H ₂ O) ₂ (3-pic) ₂ (BF ₄) ₂]	Blue	3.09	9.16	9.02			8.74	8.55				
[Ni(H ₂ O) ₂ (4-pic) ₂ (ClO ₄) ₂]	Blue	3.13	8.81	8.95			8.41	8.39				
[Ni(H ₂ O) ₂ (4-pic) ₂ (BF ₄) ₂]	Blue	3.16	9.16	9.25			8.74	8.70				
[Ni(4-NH ₂ py) ₂ Cl ₂]	Orange	Diamag.	11.60	11.21	14.01	14.12	22.13	22.05				
[Ni(4-NH ₂ py) ₂ Cl ₂]	Blue	3.18	11.60	11.81	14.01	13.90	22.13	22.15				
[Ni(4-NH ₂ py) ₂ Br ₂]	Orange	Diamag.	9.86	9.83	26.86	26.95	18.82	18.75				
[Ni(4-NH ₂ py) ₂ Br ₂]	Blue-green	3.26	9.86	9.73	26.86	27.06	18.82	18.68				
[Ni(4-NH ₂ py) ₂ I ₂]	Orange	Diamag.	8.51	8.56	36.83	36.50	16.25	16.50				
[Ni(4-NH ₂ py) ₂ (ClO ₄) ₂]	Yellow	Diamag.	9.25	9.47			17.38	17.64				

^a 2-pic = 2-methylpyridine, 3-pic = 3-methylpyridine, 4-pic = 4-methylpyridine, 4-NH₂py = 4-aminopyridine. ^b Diamagnetic corrections were made.

reduced pressure, and stored over molecular sieves. The 4-aminopyridine (abbreviated as 4-NH₂py) (Aldrich Chem. Co.) was purified by chromatography over alumina (Wohelm grade 1) in benzene solution. The boiling and melting points and infra-red spectra of the purified compounds were in good agreement with those reported in the literature.^{4,5}

Preparation of the Complexes.—The compounds prepared, together with their colors, magnetic moments, and analytical data, are listed in Table I.

The complexes of the general formula [Ni(pic)₂X₂] (pic = 3-pic and 4-pic; X = Cl, Br, I) were prepared by the dropwise addition of an excess of the picoline to a boiling solution of the anhydrous nickel(II) halide in ethanol, under constant stirring. The precipitate which formed immediately or on cooling was filtered off, washed with cold ethanol, and dried *in vacuo* over P₄O₁₀. The chloro and bromo complexes were recrystallized by dissolution in dichloromethane containing a small amount of the picoline and reprecipitated with ethyl ether. The iodo complexes were not recrystallized.

The complexes [Ni(2-pic)₂Cl₂] and [Ni(2-pic)₂Br₂] were obtained as previously described¹; [Ni(2-pic)₂I₂] was prepared similarly to the [Ni(pic)₂X₂] compounds, except that it was not washed nor recrystallized. It was dried *in vacuo* over P₄O₁₀.

The complexes {Ni(3-pic)₂Br₂}_n and [Ni(4-pic)₂I₂] were prepared by heating the finely powdered corresponding complexes of the type [Ni(pic)₂X₂] at 110° under vacuum. The heating times required for complete transformation were 2 hr. for {Ni(3-pic)₂Br₂}_n and 1 day for [Ni(4-pic)₂I₂]. The complex [Ni(3-pic)₂I₂] was prepared by heating [Ni(3-pic)₂Cl₂] in an oven at 90° for 3 days.

The complexes {Ni(4-pic)₂Br₂}_n and {Ni(3-pic)₂Cl₂}_n were prepared by the dropwise addition, with constant stirring, of a

dilute ethanol solution of picoline (2 moles) to a boiling ethanol solution of nickel(II) halide (1 mole). The precipitate which formed was filtered off, washed with hot ethanol, and dried *in vacuo* over P₄O₁₀.

The {Ni(3-pic)Br₂}_n complex was prepared by heating the finely ground [Ni(3-pic)₂Br₂] in an oven at 90° for 5 days. To obtain a homogeneous product, frequent stirring and regrinding of the powder was necessary. The complex {Ni(2-pic)Cl₂}_n was obtained by repeatedly washing [Ni(2-pic)₂Cl] with ethyl ether.

The complex [Ni(2-pic)₂(NO₃)₂] was prepared by the addition of excess picoline to an ethanol solution of anhydrous nickel(II) nitrate. The solution was diluted with ethyl ether and cooled in a refrigerator; crystals precipitated which were filtered off, washed with ethyl ether, and dried *in vacuo* over P₄O₁₀.

The complexes [Ni(3-pic)₂(NO₃)₂] and [Ni(4-pic)₂(NO₃)₂] were obtained by concentrating almost to dryness, under reduced pressure, an ethanol solution of anhydrous Ni(II) nitrate containing excess picoline. The compounds were dried *in vacuo* over P₄O₁₀.

The complexes [Ni(4-pic)₂X₂] (X = ClO₄, BF₄) were obtained by the addition of ethyl ether to an ethanol solution of the corresponding aquo complex [Ni(H₂O)₆]X₂, containing an excess of picoline. The compounds were repeatedly washed with ethyl ether and dried *in vacuo* over P₄O₁₀.

The complexes [Ni(H₂O)₂(4-pic)₂X₂] (X = ClO₄, BF₄) were prepared by the slow evaporation of a solution of the corresponding [Ni(4-pic)₂]X₂ in dichloromethane saturated with water. The compounds were dried in air at room temperature for 1 day.

The complexes [Ni(H₂O)₂(3-pic)₂X₂] (X = NO₃, ClO₄, BF₄) were obtained by the addition of ethyl ether to an ethanol solution of the corresponding [Ni(H₂O)₆]X₂, containing an excess of picoline. The compounds were repeatedly washed with ether and dried *in vacuo* over P₄O₁₀.

The complexes [Ni(3-pic)₂(ClO₄)₂] and [Ni(3-pic)₂(BF₄)₂] were

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prepared by heating the corresponding $[\text{Ni}(\text{H}_2\text{O})_2(3\text{-pic})_4]\text{X}_2$ in *vacuo* at 110 and 80°, respectively.

The complexes $[\text{Ni}(3\text{-pic})_4(\text{ClO}_4)_2]$ and $[\text{Ni}(3\text{-pic})_4(\text{BF}_4)_2]$ were prepared by refluxing for 1 hr. the corresponding $[\text{Ni}(\text{H}_2\text{O})_2(3\text{-pic})_4]\text{X}_2$ in a 1:1 mixture of benzene and 2,2-dimethoxypropane. After cooling the solution in a refrigerator overnight large crystals separated which were filtered and dried in *vacuo*.

The yellow-orange complexes $[\text{Ni}(4\text{-NH}_2\text{py})_4]\text{X}_2$ (X = Br, I, ClO_4) and the greenish blue $[\text{Ni}(4\text{-NH}_2\text{py})_4\text{Cl}_2]$ were prepared by heating on a steam bath an ethanol solution of anhydrous nickel(II) halide, or $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$, containing an excess of 4-aminopyridine. The yellow crystals which formed were separated by decantation from a small amount of a powdery greenish impurity, washed several times with ethanol, and dried in *vacuo*. The yellow-orange complex $[\text{Ni}(4\text{-NH}_2\text{py})_4]\text{Br}_2$ on standing 2 days in a desiccator changed into the greenish blue $[\text{Ni}(4\text{-NH}_2\text{py})_4\text{Br}_2]$. The reaction of NiCl_2 with 4-aminopyridine in ethanol at -20° yielded golden yellow needles which rapidly changed to the greenish blue $[\text{Ni}(4\text{-NH}_2\text{py})_4\text{Cl}_2]$.

Stability toward Atmospheric Moisture.—The complexes $[\text{Ni}(3\text{-pic})_4]\text{X}_2$ (X = ClO_4 , BF_4) and $[\text{Ni}(3\text{-pic})_4]\text{X}_2$ (X = I, ClO_4 , BF_4) are very sensitive to moisture, which transforms them into the corresponding $[\text{Ni}(\text{H}_2\text{O})_2(3\text{-pic})_4]\text{X}_2$. The complexes $[\text{Ni}(2\text{-pic})_2\text{Cl}_2]_n$ and $[\text{Ni}(2\text{-pic})_2\text{X}_2]$ (X = Cl, Br, I, NO_3) react rapidly with moisture to give greenish amorphous decomposition products. These moisture sensitive compounds were prepared and handled in a drybox. The complexes $[\text{Ni}(3\text{-pic})_2(\text{NO}_3)_2]$ and $[\text{Ni}(4\text{-pic})_2\text{X}_2]$ (X = I, NO_3) are only moderately sensitive to moisture. All other complexes are fairly stable but decompose on prolonged exposure.

Analyses.—Halogens were determined by the Volhard method, nickel by titration with EDTA, nitrogen by the semimicro Dumas method, and carbon and hydrogen by microanalyses.

Magnetic susceptibility measurements were made by the Gouy method. The values of the magnetic moment, μ_{eff} , of the solid compounds are listed in Table I.

Infrared absorption spectra were taken with a Perkin-Elmer Model 221 recording spectrophotometer. The spectra of the solid complexes were obtained both in Nujol mulls and in KBr disks. The absorption frequencies are reported elsewhere.⁶

Electronic Spectra.—Transmission spectra were taken both in solution and in Nujol mull with a Cary Model 14 recording spectrophotometer. Diffuse reflectance spectra of the finely powdered solids were obtained with a Beckman Model DU quartz spectrophotometer equipped with a diffuse reflectance attachment, using magnesium carbonate as the reference. For the solid compounds, poor resolution was generally obtained below 10,000 cm^{-1} and therefore in the spectra of the octahedral complexes the band corresponding to the transition ${}^3\text{A}_2 \rightarrow {}^3\text{T}_2$ was not observed. The absorption maxima of the solid complexes, of the dichloromethane solutions, and of solutions containing added amounts of picolines are reported elsewhere.⁶

Conductivity measurements were made at 25° by the standard procedure using Spectrograde dichloromethane as the solvent. The following values were obtained (Λ_M in $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$): CH_2Cl_2 , specific conductivity $< 10^{-5} \text{ohm}^{-1} \text{cm}^{-1}$; $\text{CH}_2\text{Cl}_2 + 4\text{-pic}$ (10.0 M), specific conductivity $< 10^{-5} \text{ohm}^{-1} \text{cm}^{-1}$; $\{\text{Ni}(4\text{-pic})_2\text{Br}_2\}_n$, $0.98 \times 10^{-3} M$, no conductivity; $[\text{Ni}(4\text{-pic})_4\text{Br}_2]$, $1.42 \times 10^{-2} M$, $\Lambda_M = 0.19$; $[\text{Ni}(4\text{-pic})_4\text{Cl}_2]$, $1.31 \times 10^{-2} M$, $\Lambda_M = 0.17$; $[\text{Ni}(4\text{-pic})_4\text{Br}_2]$, $1.42 \times 10^{-2} M$ with added 4-pic (10.0 M), $\Lambda_M = 0.26$; $[\text{Ni}(2\text{-pic})_2(\text{NO}_3)_2]$, $0.93 \times 10^{-2} M$, no conductivity; $[\text{Ni}(3\text{-pic})_2(\text{NO}_3)_2]$, $0.98 \times 10^{-2} M$, $\Lambda_M = 0.13$; $[\text{Ni}(4\text{-pic})_4(\text{NO}_3)_2]$, $0.91 \times 10^{-2} M$, $\Lambda_M = 0.43$; $[\text{Ni}(4\text{-pic})_4](\text{ClO}_4)_2$, $0.97 \times 10^{-2} M$, $\Lambda_M = 6.71$; $[\text{Ni}(4\text{-pic})_4](\text{ClO}_4)_2$, $1.04 \times 10^{-2} M$ with added 4-pic (10.0 M), $\Lambda_M = 14.36$. For compari-

son, the molar conductivities of the following salts were determined: $[(n\text{-C}_4\text{H}_9)_4\text{N}]\text{I}$, $1.05 \times 10^{-2} M$, $\Lambda_M = 9.85$; $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2[\text{CoBr}_4]$, $0.97 \times 10^{-2} M$, $\Lambda_M = 5.8$; $[(\text{C}_2\text{H}_5)_4\text{N}]\text{ClO}_4$, $0.97 \times 10^{-2} M$, $\Lambda_M = 10.37$.

Results

Halo Complexes.—The crystalline $\text{Ni}(\text{pic})_4\text{X}_2$ (where pic is 3-picoline or 4-picoline and X = Cl, Br, or I) have magnetic moments and electronic spectra typical of Ni(II) in an octahedral ligand field. Similar to the $[\text{Ni}(\text{py})_4\text{Cl}_2]$ complex,⁷ they may therefore be considered to have a "trans," essentially octahedral configuration. The spectra of some of these complexes depart slightly from the usual pattern of octahedral Ni(II). In addition to the three absorptions corresponding to the transitions to the excited states ${}^3\text{T}_2$, ${}^3\text{T}_1(\text{F})$, and ${}^3\text{T}_1(\text{P})$, a weak band or shoulder appears in the 11,000–10,000 cm^{-1} region. A similar spectrum has been reported for $\text{Ni}(\text{py})_4\text{Cl}_2$ and attributed⁸ to tetragonal distortion of the octahedral symmetry, resulting from the appreciable difference in the ligand field strengths of pyridine and chloride ion.

The $[\text{Ni}(\text{pic})_4\text{X}_2]$ complexes are stable in dry air at room temperature and at higher temperatures (110–200°) lose some of the coordinated picoline. The loss of picoline generally takes place stepwise, with formation of either $\text{Ni}(\text{pic})_2\text{X}_2$ or $\text{Ni}(\text{pic})\text{X}_2$, or both. Finally, above 200° only the nickel(II) halide remains. The $[\text{Ni}(\text{pic})_4\text{X}_2]$ complexes are readily soluble in organic solvents except ethers and hydrocarbons, but their solution spectra indicate that extensive solvolysis occurs if the solvent has coordinating ability. When the donor character of the solvent is very poor, such as for dichloromethane, the complexes dissolve without solvolysis but with partial dissociation and rearrangement, as discussed later.

In the crystalline $\text{Ni}(\text{pic})\text{X}_2$ the arrangement of the ligands around Ni(II) depends upon both the picoline and the halide. The deep blue complexes $[\text{Ni}(2\text{-pic})_2\text{Cl}_2]$ and $[\text{Ni}(2\text{-pic})_2\text{Br}_2]$ have magnetic moments and electronic spectra which indicate a pseudo-tetrahedral configuration.¹ The dark green $[\text{Ni}(2\text{-pic})_2\text{I}_2]$, the color of which results mostly from charge-transfer absorptions, is diamagnetic and can be considered to have a distorted square-planar configuration. The pale yellow or yellow-green compounds $\{\text{Ni}(3\text{-pic})_2\text{Cl}_2\}_n$, $\{\text{Ni}(3\text{-pic})_2\text{Br}_2\}_n$, and $\{\text{Ni}(4\text{-pic})_2\text{Br}_2\}_n$ have magnetic moments and electronic spectra corresponding to an essentially octahedral environment of ligands around the Ni(II) and can be considered to have a polymeric structure with double halogen bridges, similar to the analogous pyridine compounds.⁹ The very low solubility of these complexes in most poor donor solvents is consistent with a polymeric structure. Finally, the dark green iodo complexes $[\text{Ni}(3\text{-pic})_2\text{I}_2]$ and $[\text{Ni}(4\text{-pic})_2\text{I}_2]$ have magnetic moments in the range expected for distorted tetrahedral Ni(II) compounds, and their

(6) Supplementary material (infrared and electronic spectra data) has been deposited as Document No. 8505 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting \$1.25 for photoprints or \$1.25 for 35-mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

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spectra, though largely obscured by charge-transfer bands, also indicate a tetrahedral configuration.

The general behavior of the $\text{Ni}(\text{pic})_2\text{X}_2$ complexes is similar to that of the $[\text{Ni}(\text{pic})_4\text{X}_2]$ compounds. They are stable in dry air at room temperature, but at higher temperatures lose the coordinated picoline, either stepwise to form an intermediate $\text{Ni}(\text{pic})\text{X}_2$ or gradually to yield the $\text{Ni}(\text{II})$ halide. The $\text{Ni}(\text{pic})_2\text{X}_2$ complexes either do not dissolve or undergo solvolysis in most organic solvents. In dichloromethane, they are soluble without solvolysis, except for $\{\text{Ni}(\text{3-pic})_2\text{Cl}_2\}_n$, which does not dissolve, and for $[\text{Ni}(\text{2-pic})_2\text{X}_2]$ ($\text{X} = \text{Cl}, \text{I}$), which partially dissociate leaving a small residue of nickel(II) halide. Some complexes, however, dissolve in dichloromethane with structural changes, as discussed later.

The brick-red $\text{Ni}(\text{2-pic})\text{Cl}_2$ and $\text{Ni}(\text{3-pic})\text{Br}_2$ have magnetic moments of 3.44 and 3.19 B.M., respectively, and their electronic spectra have bands at 21.0×10^3 and $10.2 \times 10^3 \text{ cm}^{-1}$ and at 20.6×10^3 and $11.7 \times 10^3 \text{ cm}^{-1}$, respectively. When compared with the values of $\{\text{Ni}(\text{3-pic})_2\text{Br}_2\}_n$ ($\mu_{\text{eff}} = 3.39$ B.M., ν_4 (${}^3\text{A}_2 \rightarrow {}^3\text{T}_1(\text{P})) = 23.2 \times 10^3$, ν_3 (${}^3\text{A}_2 \rightarrow {}^3\text{T}_1(\text{F})) = 13.3 \times 10^3 \text{ cm}^{-1}$), and of the polymeric NiCl_2 ($\nu_4 = 22.1 \times 10^3$, $\nu_1 = 12.9 \times 10^3 \text{ cm}^{-1}$) and NiBr_2 ($\nu_4 = 20.7 \times 10^3$, $\nu_3 = 12.1 \times 10^3 \text{ cm}^{-1}$), the magnetic moments and visible spectra of the $\text{Ni}(\text{pic})\text{X}_2$ complexes suggest a tridimensional polymeric structure not appreciably distorted from octahedral symmetry. A similar structure has been assigned¹⁰ to $\text{Ni}(\text{py})\text{Cl}_2$. These complexes are insoluble in organic solvents, but rapidly become pale green or bluish when exposed either to moisture or polar solvents.

Solution Behavior of the Halo Complexes in Dichloromethane.—Dichloromethane is a particularly suitable solvent for the solution study of these complexes because solvolysis does not take place to any detectable extent. Although the crystalline halo complexes have different stereochemistries depending on their stoichiometry, the picoline, and the halide, the dichloromethane solutions of all complexes contain the nonionic $[\text{Ni}(\text{pic})_2\text{X}_2]$ of essentially tetrahedral configuration. Thus the visible absorption spectra show the presence of one tetrahedral species not only for solutions of the $[\text{Ni}(\text{pic})_2\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}$) and $[\text{Ni}(\text{pic})_2\text{I}_2]$ ($\text{pic} = \text{3-pic}, \text{4-pic}$) complexes, which are tetrahedral in the solid state, but also for solutions of $[\text{Ni}(\text{2-pic})_2\text{I}_2]$, which is square-planar in the solid state, and of $\{\text{Ni}(\text{3-pic})_2\text{Br}_2\}_n$ and $\{\text{Ni}(\text{4-pic})_2\text{Br}_2\}_n$, which in the solid have an octahedral polymeric structure. Dissociation of $[\text{Ni}(\text{pic})_4\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) in solution also yields tetrahedral $[\text{Ni}(\text{pic})_2\text{X}_2]$. The dissociation, $[\text{Ni}(\text{pic})_4\text{X}_2] \rightarrow 2(\text{pic}) + [\text{Ni}(\text{pic})_2\text{X}_2]$, is complete in solutions of the iodo complexes, whereas solutions of the chloro and bromo complexes contain tetrahedral $[\text{Ni}(\text{pic})_2\text{X}_2]$ together with another nonionic species of octahedral configuration. The approximate molar ratio between these two species in solutions of $[\text{Ni}(\text{4-}$

$\text{pic})_4\text{Br}_2]$ can be calculated from their relative absorbancies and from the extinction coefficient of the tetrahedral $[\text{Ni}(\text{4-pic})_2\text{Br}_2]$, obtained from the solution spectra of the polymeric $\{\text{Ni}(\text{4-pic})_2\text{Br}_2\}_n$. The ratio, O_h/T_d , decreases with dilution and was found to be 3.2 at 0.120 *M*, 1.8 at 0.006 *M*, 1.3 at 0.0025 *M*, and 0.72 at 0.0012 *M*. Of the absorption bands of the octahedral species, only ν_4 could be clearly identified since ν_3 appears as a shoulder on the low-frequency side of the major tetrahedral absorption (${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$) and ν_1 (${}^3\text{A}_2 \rightarrow {}^3\text{T}_2$) is hidden (or overlaid) by the lower energy tetrahedral absorption, (${}^3\text{T}_1(\text{F}) \rightarrow {}^3\text{T}_2$). The values of ν_4 indicate that the average field around the $\text{Ni}(\text{II})$ is weaker than in the $[\text{Ni}(\text{pic})_4\text{X}_2]$ complexes (4N, 2X), and close to that of the solid $\{\text{Ni}(\text{pic})_2\text{X}_2\}$ (2N, 4X) polymeric compounds. Since the polymeric $\{\text{Ni}(\text{pic})_2\text{X}_2\}$ complexes are either insoluble or completely broken down to the monomeric tetrahedral species upon dissolution, it is reasonable to assume that the octahedral species observed in the solution of $[\text{Ni}(\text{pic})_4\text{X}_2]$ is a dimer of the type $\{\text{Ni}(\text{pic})_3\text{Cl}\}_2$ (3N, 3X). In agreement with the proposed scheme dichloromethane solutions of $[\text{Ni}(\text{pic})_4\text{X}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), in the presence of an excess of picoline to prevent dissociation, contain a single nonionic species which from its spectrum is identified as the octahedral $[\text{Ni}(\text{pic})_4\text{X}_2]$.

Nitrato Complexes.—Anhydrous nickel(II) nitrate in ethanol solution reacts with the picolines to form complexes of the formulas $\text{Ni}(\text{2-pic})_2(\text{NO}_3)_2$, $\text{Ni}(\text{3-pic})_3(\text{NO}_3)_2$, and $\text{Ni}(\text{4-pic})_4(\text{NO}_3)_2$. The crystalline compounds have magnetic moments and electronic absorption spectra indicating an octahedral coordination for $\text{Ni}(\text{II})$, and their infrared spectra show the absorptions typical of coordinated NO_3 groups.¹¹ The complexes are very soluble in organic solvents except ethers and hydrocarbons, but generally undergo extensive solvolysis. In dichloromethane they remain unchanged as shown by their visible spectra, and their solutions are nonconducting. It is therefore possible to formulate them as nonionic octahedral complexes, with coordinated NO_3 groups. Undoubtedly, both nitrato groups act as bidentate ligands in the complex $[\text{Ni}(\text{2-pic})_2(\text{NO}_3)_2]$ and as monodentate ligands in $[\text{Ni}(\text{4-pic})_4(\text{NO}_3)_2]$. In the complex $[\text{Ni}(\text{3-pic})_3(\text{NO}_3)_2]$, it must be assumed that one nitrato group acts as a monodentate and the other as a bidentate ligand. A similar complex, $[\text{Ni}(\text{py})_3(\text{NO}_3)_2]$, has recently been obtained¹² with pyridine.

Complexes of Nickel(II) Perchlorate and Tetrafluoroborate.—The hydrated nickel(II) perchlorate, $[\text{Ni}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$, reacts with 3-picoline to give a blue complex which on the basis of its magnetic moment and visible and infrared spectra can be formulated as *trans*- $[\text{Ni}(\text{H}_2\text{O})_2(\text{3-pic})_4](\text{ClO}_4)_2$, similar to the analogous pyridine complex.⁸ The $[\text{Ni}(\text{H}_2\text{O})_2(\text{3-pic})_4](\text{ClO}_4)_2$ is slightly soluble (with solvolysis) in organic solvents

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(11) B. O. Field and C. J. Hardy, *Quart. Rev. (London)*, **18**, 361 (1965), and references therein.

(12) M. R. Rosenthal and R. S. Drago, personal communication.

of good donor character; it is insoluble in the others, including dichloromethane. When this complex is refluxed in a 1:1 mixture of benzene and 2,2-dimethoxypropane the coordinated water is lost and blue crystals of $\text{Ni}(\text{3-pic})_4(\text{ClO}_4)_2$ are formed. This anhydrous complex has a magnetic moment of 3.14 B.M., an infrared spectrum which shows the presence of coordinated (unidentate) ClO_4 groups,¹³ and a visible spectrum similar to those reported for some tetragonal nickel(II) complexes.^{12,14,15} It is therefore possible to formulate it as the nonionic, tetragonally distorted octahedral $[\text{Ni}(\text{3-pic})_4(\text{ClO}_4)_2]$. On the other hand, when $[\text{Ni}(\text{H}_2\text{O})_2(\text{3-pic})_4](\text{ClO}_4)_2$ is dehydrated by heating under vacuum a bright yellow powder is obtained, again having the composition $\text{Ni}(\text{3-pic})_4(\text{ClO}_4)_2$. This yellow powder is diamagnetic, its visible spectrum has a single absorption at $23.0 \times 10^3 \text{ cm.}^{-1}$, and its infrared spectrum shows absorptions typical of the free ClO_4^- ion. The compound can be formulated therefore as square-planar $[\text{Ni}(\text{3-pic})_4](\text{ClO}_4)_2$. Both the yellow $[\text{Ni}(\text{3-pic})_4](\text{ClO}_4)_2$ and the blue $[\text{Ni}(\text{3-pic})_4(\text{ClO}_4)_2]$ are soluble in organic solvents of good donor character, but the spectra of the solutions indicate that coordination of the solvent and/or solvolysis takes place to a large extent. In dichloromethane both complexes dissolve to form identical, yellow-green solutions, the spectra of which show the presence of both square-planar (yellow) and tetragonal (blue) species. The ratio of the square-planar and tetragonal species in solution does not vary with concentration and is independent of the structure of the solid. On evaporation to dryness under reduced pressure, the solutions give $[\text{Ni}(\text{3-pic})_4(\text{ClO}_4)_2]$ as a pale blue powder which slowly changes to the yellow $[\text{Ni}(\text{3-pic})_4](\text{ClO}_4)_2$. Both isomers are very sensitive to moisture, being transformed into the same diaquo complex, $[\text{Ni}(\text{H}_2\text{O})_2(\text{3-pic})_4](\text{ClO}_4)_2$, used as the starting material in their preparation.

Nickel(II) tetrafluoroborate gives an analogous series of complexes. The blue paramagnetic $[\text{Ni}(\text{H}_2\text{O})_2(\text{3-pic})_4](\text{BF}_4)_2$ yields yellow diamagnetic $[\text{Ni}(\text{3-pic})_4](\text{BF}_4)_2$ when heated under vacuum at 80° and blue paramagnetic $[\text{Ni}(\text{3-pic})_4(\text{BF}_4)_2]$ when refluxed with a benzene-dimethoxypropane mixture. Again, both the yellow and blue isomers dissolve in dichloromethane to give identical solutions, containing the two species in a constant ratio. On evaporating the dichloromethane solution, a solid separates which at first is yellow (as long as some solvent is present), becomes blue on drying, and then rapidly (in about 30 min.) changes again to yellow. Both the yellow and blue isomers are extremely sensitive to moisture, which re-forms the diaquo complex $[\text{Ni}(\text{H}_2\text{O})_2(\text{3-pic})_4](\text{BF}_4)_2$.

Somewhat different results are obtained with 4-picoline. When nickel(II) perchlorate, either hydrated or anhydrous, reacts with an excess of 4-picoline, a blue solution results from which yellow crystals of $\text{Ni}(\text{4-}$

$\text{pic})_4(\text{ClO}_4)_2$ separate by addition of a large volume of ethyl ether. On the basis of its magnetic and spectral properties the yellow compound is formulated as the square-planar $[\text{Ni}(\text{4-pic})_4](\text{ClO}_4)_2$. The behavior of this compound toward organic solvents is similar to that of the analogous 3-picoline complex. The dichloromethane solution is yellow-green and its electronic spectrum, in addition to the absorption typical of the square-planar $[\text{Ni}(\text{4-pic})_4]^{+2}$, shows other bands which are ascribed to the tetragonal nonionic species $[\text{Ni}(\text{4-pic})_4(\text{ClO}_4)_2]$. As for the 3-picoline complexes, the ratio between the yellow and blue isomers is independent of the total concentration. The original yellow crystals re-form when the dichloromethane solution is evaporated under vacuum. Although $[\text{Ni}(\text{4-pic})_4](\text{ClO}_4)_2$ does not react with atmospheric moisture in the solid state, its solution readily absorbs moisture to form the blue paramagnetic $[\text{Ni}(\text{H}_2\text{O})_2(\text{4-pic})_4](\text{ClO}_4)_2$. When stored over a dehydrating agent or *in vacuo* $[\text{Ni}(\text{H}_2\text{O})_2(\text{4-pic})_4](\text{ClO}_4)_2$ rapidly loses its coordinated water to re-form $[\text{Ni}(\text{4-pic})_4](\text{ClO}_4)_2$, which is also obtained when the diaquo complex is dehydrated by refluxing with a mixture of benzene and dimethoxypropane. Unlike the corresponding 3-picoline complex, the diaquo compound $[\text{Ni}(\text{H}_2\text{O})_2(\text{4-pic})_4](\text{ClO}_4)_2$ is readily soluble in dichloromethane, but the spectrum of its solution shows that water is partially lost and a mixture of the square-planar and tetragonal $\text{Ni}(\text{4-pic})_4(\text{ClO}_4)_2$ results. An analogous series of complexes is formed by nickel(II) tetrafluoroborate with 4-picoline.

The ratio between the tetragonal and square-planar species in dichloromethane solution was approximately estimated to be 80/20 for $\text{Ni}(\text{3-pic})_4(\text{ClO}_4)_2$, 75/25 for $\text{Ni}(\text{3-pic})_4(\text{BF}_4)_2$, 95/5 for $\text{Ni}(\text{4-pic})_4(\text{ClO}_4)_2$, and 85/15 for $\text{Ni}(\text{4-pic})_4(\text{BF}_4)_2$. These values were obtained by assuming the extinction coefficient, ϵ , of the square-planar absorption to be 100 for the perchlorate and 110 for the tetrafluoroborate complexes, by analogy with the values of ϵ observed³ for the NiL_4X_2 complexes ($\text{L} = 3,4\text{- and }3,5\text{-lutidine}$; $\text{X} = \text{ClO}_4$ and BF_4). The extinction coefficient of the major absorption band of the tetragonal species is then calculated to be 18–20, in good agreement with the values observed for $[\text{Ni}(\text{3-bromopyridine})_4(\text{ClO}_4)_2]$ (ϵ 15)¹⁶ and $[\text{Ni}(\text{pyridine})_4(\text{ClO}_4)_2]$ (ϵ 15).¹⁴

The addition of a rather large excess of picoline to the dichloromethane solutions of the complexes $\text{Ni}(\text{pic})_4\text{X}_2$ ($\text{pic} = 3\text{-pic and }4\text{-pic}$; $\text{X} = \text{ClO}_4$ and BF_4) causes a change in color from yellow-green to blue, accompanied by a marked increase in conductivity. The spectra of the blue solutions show the presence of one octahedral species, and the frequencies of the absorption bands indicate a field strength close to that expected for Ni(II) surrounded by six N donor atoms. The complex species present in these solutions is assigned the formula $[\text{Ni}(\text{pic})_6]^{+2}$, but attempts to isolate its salts have been unsuccessful.

Complexes of 4-Aminopyridine.—The anhydrous halides and the hydrated perchlorate of nickel(II)

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(15) N. F. Curtis and Y. M. Curtis, personal communication.

(16) L. M. Vallarino and J. V. Quagliano, unpublished work.

react with an excess of 4-aminopyridine in boiling ethanol to give complexes of the general formula $\text{Ni}(4\text{-NH}_2\text{py})_4\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{ClO}_4$), insoluble in organic solvents. The compounds with $\text{X} = \text{I}$ and ClO_4 are orange-yellow, and from their magnetic and spectral properties are formulated as salts of the square-planar cation $[\text{Ni}(4\text{-NH}_2\text{py})_4]^{2+}$. The compounds with $\text{X} = \text{Br}$ and Cl are obtained in two forms; one is metastable, yellow, and diamagnetic, and the other is stable, blue-green, and paramagnetic. Again, the yellow isomers are formulated as $[\text{Ni}(4\text{-NH}_2\text{py})_4]\text{X}_2$, and the blue-green isomers as the nonionic, tetragonally distorted octahedral $[\text{Ni}(4\text{-NH}_2\text{py})_4\text{X}_2]$. For $\text{X} = \text{Cl}$, the yellow crystals are very unstable and transform into the blue-green isomer in a few minutes, and immediately on grinding. For $\text{X} = \text{Br}$, the yellow crystals are stable for 1 or 2 days, then gradually change into the blue-green form. The infrared spectra of these complexes of 4-aminopyridine indicate that the amino group in the 4 position is not involved in coordination to the nickel(II), but very likely is hydrogen-bonded to neighboring anions. Hydrogen bonding would account for the insolubility of these complexes in most solvents. Other complexes of the type NiL_4X_2 , where the ligand L contains a noncoordinated NH_2 group, for example 3-aminopyridine and isonicotinamide, are also found to be insoluble.¹⁶

to give the complexes NiL_4X_2 ($\text{X} = \text{halide}, \text{NCS}, \text{NO}_3, \text{ClO}_4, \text{BF}_4$), whereas in solution up to six ligands can coordinate to Ni(II) to form $[\text{NiL}_6]\text{X}_2$, if the anion X has poor donor character ($\text{X} = \text{ClO}_4, \text{BF}_4$).

In the solid state the NiL_2X_2 complexes exist in a variety of structures. For example, solid $[\text{Ni}(\text{py})_2\text{Cl}_2]_n$ has a polymeric, octahedral structure with double Cl bridges⁹; solid $[\text{Ni}(2\text{-pic})_2(\text{NO}_3)_2]$ is assigned a (monomeric) octahedral configuration with bidentate NO_3 groups; solid $[\text{Ni}(2,5\text{-lutidine})_2\text{Cl}_2]$ is square-planar²; and solid $[\text{Ni}(2\text{-pic})_2\text{Cl}_2]$ is tetrahedral.¹ Several compounds, among them $\text{Ni}(\text{quinoline})_2\text{Cl}_2$ and $\text{Ni}(3,4\text{-lutidine})_2\text{Br}_2$, have been isolated^{8,14,17} in two isomeric forms, the one polymeric octahedral and the other tetrahedral. No well-defined relationship is so far apparent between the structure of the solid NiL_2X_2 compounds and the properties of the ligand and anion. On the other hand, all the NiL_2X_2 compounds investigated in solutions of noncoordinating solvents were found to have a tetrahedral (somewhat distorted) configuration.

The stereochemistry of the NiL_4X_2 complexes appears to vary regularly with the properties of the ligand and anion, as shown in Table II. This table lists the ligands L in the order of their increasing basicity¹⁸ and the anions X in the order of their decreasing tendency to coordinate to Ni(II). The table shows that the

TABLE II

STEREOCHEMISTRY OF THE NiL_4X_2 COMPLEXES

Ligand ^a	pK_A^b	X = Cl		X = Br		X = I		X = ClO ₄		X = BF ₄	
		Solid	CH ₂ Cl ₂ soln.	Solid	CH ₂ Cl ₂ soln.	Solid	CH ₂ Cl ₂ soln.	Solid	CH ₂ Cl ₂ soln.	Solid	CH ₂ Cl ₂ soln.
py	5.17	Oct. ^c	Oct.	Oct.	Oct.	Oct.	Oct.	Oct. ^{d,e}	Oct. ^{d,g}	Oct. ^{d,e}	Oct. ^{d,h}
3-pic	5.68	{ Oct.	Oct.	Oct.	Oct.	Oct.	Oct.	Oct. ^{d,h}	Oct., ^d 80%	Oct. ^{d,h}	Oct., ^d 75%
4-pic	6.02	{ Oct.	Oct.	Oct.	Oct.	Oct.	Oct.	Sq.-pl.	Sq.-pl., 20% Oct., ^d 95%	Sq.-pl.	Sq.pl., 25% Oct., ^d 85%
3,5-L ^f	6.15	Oct.	Oct.	Oct.	Oct.	Oct.	Oct.	Sq.-pl. ⁱ	Sq.-pl., 5%	Sq.-pl.	Sq.-pl., 15%
3,4-L ^f	6.46	Oct.	Oct.	Oct.	Oct.	Sq.-pl.	Oct.	Oct. ^g	Sq.-pl.	Oct. ^d	Sq.-pl.
4-NH ₂ py	9.17	{ Sq.-pl. ^h		Sq.-pl. ^h		Sq.-pl.		Sq.-pl. ⁱ		Sq.-pl.	
		{ Oct.	g	Oct.	g		g		g		g

^a py = pyridine, 3-pic = 3-picoline, 4-pic = 4-picoline, 3,5-L = 3,5-lutidine, 3,4-L = 3,4-lutidine, 4-NH₂py = 4-aminopyridine.
^b Ref. 17. ^c Ref. 7. ^d Spectrum shows marked tetragonal distortion. ^e Ref. 14. ^f Ref. 3. ^g Not soluble. ^h Unstable. ⁱ Ref. 19.

Conclusions

Some interesting regularities for the Ni(II) complexes of pyridine bases emerge from the results of the present and previous investigations. The steric requirements of the ligand appear to determine the maximum number of ligands which coordinate to Ni(II). In general no more than two molecules of an α -substituted pyridine, including fused ring compounds such as quinoline, coordinate to Ni(II), and the resulting complexes have the formula NiL_2X_2 ($\text{X} = \text{halide}, \text{NCS}, \text{NO}_3$). Compounds of this formula with $\text{X} = \text{Cl}, \text{Br}$, and I are also obtained with ligands which do not have substituents in the the α positions. When both α -positions of the pyridine system are free, a maximum of four ligands coordinates to Ni(II) in the solid state

and the stereochemistry of the NiL_4X_2 complexes is generally the same in the solid state as in dichloromethane solutions, though differences are observed in a few cases. Also, the dependence of the stereochemistry on the properties of L and X is more regular for the solutions than for the solid complexes. In solution, all halide complexes are octahedral, whereas the perchlorate and the tetrafluoroborate complexes are octahedral with marked tetragonal distortion for ligands of pK_A lower than ~ 5.5 and square-planar for ligands of pK_A higher than ~ 6.1 . When the ligands have pK_A values within this range the solutions contain an equilibrium mixture of the square-planar and the octahedral isomers.

(17) D. M. L. Goodgame and M. Goodgame, *J. Chem. Soc.*, 207 (1963).

(18) A. P. Katritzky, "Physical Methods in Heterocyclic Chemistry," Vol. 1, Academic Press, New York, N. Y., 1963, pp. 64-106.

For the same ligand the ratio, square-planar/octahedral, increases from the perchlorate to the tetrafluoroborate, in agreement with the lower coordinating ability expected for the latter. The stereochemistry of the solid complexes varies with the basicity of the ligand following a trend similar to, though not quite so regular as, that observed in solution. Thus, $\text{Ni}(3,5\text{-L})_4\text{X}_2$ ($\text{X} = \text{ClO}_4, \text{BF}_4$) is octahedral in the solid state but square-planar in solution; $\text{Ni}(4\text{-pic})_4\text{X}_2$ ($\text{X} = \text{ClO}_4, \text{BF}_4$) is square-planar in the solid state but predominantly octahedral in solution; and $\text{Ni}(3\text{-pic})_4\text{X}_2$ ($\text{X} = \text{ClO}_4, \text{BF}_4$) gives, in the solid state, both octahedral and square-planar isomers, but the octahedral form is unstable in the solid state though predominant in solution. This points out that for crystalline compounds an intrinsically slightly less stable configuration may be favored because of lattice energy effects. It may be observed that for ligands with $\text{p}K_A$ not included in, nor close to, the borderline region, ~ 5.5 to ~ 6.1 , the perchlorate and tetrafluoroborate complexes have the same structure both in the solid and in solution. As the basicity of the ligand increases, the solid complexes may have a square-planar configuration, even when X is a halide. The 3,4-lutidine forms a square-planar complex for $\text{X} = \text{I}$, and the more basic 4-aminopyridine gives a square-planar complex also for $\text{X} = \text{Br}$ and even for $\text{X} = \text{Cl}$, although the latter is very unstable.

On the basis of this observed trend, it now appears possible to predict the stereochemistry of a complex of the type NiL_4X_2 , where L is a nitrogen-donor aro-

matic heterocyclic ligand and X is an anion listed in Table II. The chloride complexes should be octahedral for ligands with a $\text{p}K_A$ lower than about 9.0, the iodide complexes should be octahedral for ligands with $\text{p}K_A$ lower than about 6.5, and for bromide complexes the change from octahedral to square-planar should take place at an intermediate $\text{p}K_A$ value. The perchlorate and tetrafluoroborate complexes should be octahedral for ligands with $\text{p}K_A$ lower than 5.5 and square-planar for ligands with $\text{p}K_A$ higher than 6.2, and within this range either or both configurations may be expected. Although these predictions refer to complexes in solution, they may also be extended to solid complexes, if it is kept in mind that near the borderline regions lattice effects may determine the actual structure. In agreement with the above predictions we find that the perchlorate complex of 3-bromopyridine ($\text{p}K_A = 2.84$) reported as octahedral in the solid state¹⁹ is also octahedral in solution (with strong tetragonal distortion). Investigations are now in progress to establish the ligand $\text{p}K_A$ values at which the change of structure from octahedral to square-planar occurs for the halide complexes.

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The Coordination of Substituted Pyridine N-Oxides with Oxovanadium(IV) Cations¹

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Complexes of oxovanadium(IV) chloride, bromide, and perchlorate with various substituted pyridine N-oxide ligands have been prepared and characterized. The variation in stoichiometry with changes in the 4-substituent for a series of these N-oxides allowed a relative coordination stability for the ligands to be established. Activator substituted molecules (CH_3O - and CH_3 -) as well as the parent gave only highly coordinated species of the type VOL_4^{2+} and VOL_5^{2+} ($\text{L} = 4\text{-Z-C}_5\text{H}_4\text{NO}$). Deactivator substitution (Cl -, Br -, and NO_2 -) gave species of the type $\text{VOL}_2\text{X}_2\cdot\text{H}_2\text{O}$ ($\text{X} = \text{Cl}$ or Br). In all cases only the higher coordination was observed for $\text{X} = \text{ClO}_4$.

Introduction

The donor properties of pyridine N-oxide have been studied for many transition metal ions³⁻⁶ including

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selected oxometal cations.⁶⁻⁸ Diverse stoichiometries were often observed for a particular metal ion. Ap-

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