Pyridine Complexes of Nickel(II)

By MICHAEL R. ROSENTHAL[1] and RUSSELL S. DRAGO

In this article conclusive evidence for the existence of $Ni(C_5H_5N)_6^{2+}$ is presented for the first time. This permits direct calculation of the spectrochemical parameters for pyridine. The complexes $Ni(C_5H_5N)_4(ClO_4)_2$ and $Ni(C_5H_5N)_4(BF_4)_2$ were prepared and found to be high-spin at room temperature with coordinated perchlorate and tetrafluoroborate. A nitrate complex of formula $Ni(C_5H_5N)_3(NO_3)_2$ was prepared. The behavior of these complexes in solution and their reactions in solution with excess pyridine are reported.

Introduction

Pyridine is an interesting nonaqueous solvent because it is a good base ($pK_B = 8.81$) with a low dielectric constant ($\epsilon = 12.3$). Consequently, it was of interest to examine in detail some of the transition metal ion complexes formed by this material and to evaluate its spectrochemical parameters. In this connection, there is no conclusive evidence in the literature regarding the existence of a six-coordinate pyridine complex of nickel(II), an ion that would be desirable for the spectrochemical calculations. Most of the nickel complexes studied contain anions, X, that are good coordinating agents, *e.g.*, halide, thiocyanate, etc. Under these conditions tetragonal complexes of general formula $Ni(C_5H_5N)_4X_2$ are formed. Even though the anions perchlorate and tetrafluoroborate were employed in this study, it was still observed that the solid complexes isolated contain coordinated anions. In certain solvents these anions can be displaced by solvent or pyridine, and data presented here provide the first conclusive evidence for the existence of a six-coordinate pyridine complex of nickel(II). The spectrochemical parameters were evaluated from the electronic spectrum of this complex.

Experimental

Reagents.—Reagent grade acetonitrile, benzonitrile, ether, and nitromethane were used without further purification. Spectral reagent grade dichloromethane (Merck) stored over Linde 4A molecular sieves, was employed. Reagent grade pyridine was dried over barium oxide, distilled, and stored over molecular sieves. The 2,2-dimethoxypropane employed was practical grade (Eastman) and was used without further purification. Nickel(II) chloride was dehydrated at 120° for several days.

Bis(perchlorato)tetrakis(pyridine)nickel(II).—Hexaaquonickel(II) perchlorate (20 g.), dissolved in 140 ml. of 2,2-dimethoxypropane, was stirred 3 hr. to dehydrate the salt. Pyridine (70 ml.) was then added and a pale blue precipitate immediately formed. The precipitate was removed by filtration on a sintered glass funnel and washed repeatedly with small portions of ether. The dried crystals were then suspended in ether, filtered, washed, and dried for 12 hr. *in vacuo* at 25°.

Bis(tetrafluoroborato)tetrakis(pyridine)nickel(II).—The same procedure as described for the perchlorate was followed, with the exception that the pale blue crystals required about 15 min. to precipitate. The starting material was hexaaquonickel(II) tetrafluoroborate (Alfa Inorganics).
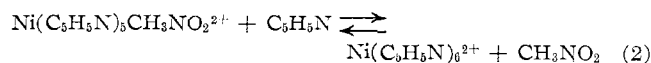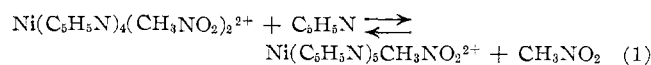
Dinitratotris(pyridine)nickel(II).—To a solution of 3.4 g. of anhydrous silver nitrate in 25 ml. of acetonitrile was added 1.3 g. of nickel(II) chloride suspended in 15 ml. of acetonitrile. The white precipitate of silver chloride was then removed by centrifugation, leaving a deep green solution of $Ni(CH_3CN)_6^{2+}Ni(NO_3)_4^{2-}$; 5 ml. of pyridine was added to this solution. The solution, now blue, was reduced to one-third in volume *in vacuo* at room temperature, and the precipitated blue crystals were removed by filtration. These crystals were then washed with ether and dried for 12 hr. *in vacuo* at 25°. They were then suspended in ether, filtered, washed, and dried as above. The same compound was also prepared in 2,2-dimethoxypropane, starting with $Ni(NO_3)_2 \cdot 6H_2O$.

Dicyanatotetrakis(pyridine)nickel(II).—$NiCl_2 \cdot 6H_2O$ (5 g.) and 3.2 g. of KNCO were dissolved in 200 ml. of water. Pyridine (13 ml.) was added, and the solution was extracted with chloroform. One-third of the solvent was removed *in vacuo*, and the pale blue crystals were filtered, washed with ether, and dried for 12 hr. *in vacuo*.

Spectral Measurements.—Electronic spectra were obtained with a Cary Model 14M recording spectrometer. Mull spectra were obtained by using a Nujol-soaked filter disk as reference and a glass plate for the sample. Infrared spectra were obtained with a Perkin-Elmer Model 521 spectrometer with potassium bromide plates and a Beckman IR5A spectrometer with CsBr optics. The compounds were mulled in Nujol. Nuclear magnetic resonance measurements were made with a Varian A-60 spectrometer, using tetramethylsilane as an internal standard. Absorbance measurements for equilibrium constant calculations were performed with a Beckman Model DU spectrophotometer at $28.0 \pm 0.5°$.

Magnetic and Conductance Measurements.—Magnetic susceptibilities were determined by the Gouy method,[2] and the moments are reported at 25°. Molar conductances of dilute nitromethane and dichloromethane solutions were measured and are compared to values reported in the literature.[3-5]

Calculations.—The procedure employed in making the spectrochemical calculations for nickel(II) has been previously described.[6] Equilibrium constants were calculated from spectral data for the following possible equilibria

$$Ni(C_5H_5N)_4(CH_3NO_2)_2^{2+} + C_5H_5N \rightleftarrows$$
$$Ni(C_5H_5N)_5CH_3NO_2^{2+} + CH_3NO_2 \quad (1)$$

$$Ni(C_5H_5N)_5CH_3NO_2^{2+} + C_5H_5N \rightleftarrows$$
$$Ni(C_5H_5N)_6^{2+} + CH_3NO_2 \quad (2)$$

by using a procedure which has been previously described.[7] The following equation was utilized.

(2) B. N. Figgis and J. Lewis, "Modern Co-ordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, New York, N. Y., 1960.
(3) J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **2**, 572 (1963).
(4) J. T. Donoghue, Ph.D. Thesis, University of Illinois, 1963.
(5) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).
(6) D. W. Meek, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, **1**, 285 (1962)
(7) N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959).

(1) Abstracted in part from the Ph.D. thesis of M. R. Rosenthal, University of Illinois, Urbana, Ill., 1965.

TABLE I

ANALYTICAL DATA AND MAGNETIC PROPERTIES OF THE COMPLEXES

	%C		%H		%N		μ_{eff},
Complex[a]	Found	Calcd.	Found	Calcd.	Found	Calcd.	B.M.
$Ni(py)_4(ClO_4)_2$	41.7	41.8	3.59	3.48	9.50	9.76	3.24
$Ni(py)_4(BF_4)_2$	43.6	43.7	3.68	3.74	9.66	10.2	3.04
$Ni(py)_3(NO_3)_2$	42.9	42.9	3.58	3.57	16.7	16.7	3.14
$Ni(py)_4(NCO)_2$	56.8	57.4	4.45	4.36	18.3	18.3	3.04

[a] $py = C_5H_5N$.

TABLE II

ELECTRONIC SPECTRAL DATA

Complex	Solvent	λ_{max}, mμ
$Ni(py)_4(ClO_4)_2$	CH_2Cl_2	372 (15),[a] 608 (5), [740 (4), 800 (4)],[b] 1360 (2)
$Ni(py)_4(ClO_4)_2$ + py	CH_2Cl_2	374 (15), 603 (5), [750 (3), 811 (3)], 1355 (2)
$Ni(py)_4(ClO_4)_2$	Mull	373, 600, [745, 800], 1392
$Ni(py)_4(ClO_4)_2$	CH_3NO_2	370 (24), 590 (8), 975 (5)
$Ni(py)_4(ClO_4)_2$ + large excess py	CH_3NO_2	375 (32), 606 (18), 1017 (10)
$Ni(py)_4(BF_4)_2$	Mull	365, 588, [725, 775], ...[c]
$Ni(py)_4(BF_4)_2$	CH_3NO_2	373 (25), 600 (12), 985 (7)
$Ni(py)_4(BF_4)_2$ + large excess py	CH_3NO_2	375 (31), 606 (15), 1012 (9)
$Ni(py)_4(BF_4)_2$	py	374, 607, 1045
$Ni(py)_3(NO_3)_2$	CH_2Cl_2	375 (39), 608 (21), 1097 (9)
$Ni(py)_3(NO_3)_2$ + py	CH_2Cl_2	375 (29), 610 (16), 1097 (6)
$Ni(py)_3(NO_3)_2$	CH_3NO_2	375 (40), 620 (22), 1075 (8)
$Ni(py)_3(NO_3)_2$ + py	CH_3NO_2	375 (40), 605 (22), 1020 (6)
$Ni(py)_3(NO_3)_2$	Mull	365, 605, 900[d]
$Ni(py)_4(ClO_4)_2$	C_6H_5CN	365 (17), 580 (8), 944 (3)
$Ni(py)_4(ClO_4)_2$ + py	C_6H_5CN	365 (15), 580 (7), 942 (5)
$Ni(py)_4(ClO_4)_2$	CH_3CN	355 (11), 566 (7), 915 (6)
$Ni(py)_4(ClO_4)_2$ + py	CH_3CN	355 (10), 565 (7), 905 (6)
$Ni(py)_4(NCO)_2$ + py	CH_2Cl_2	373 (15), 610 (8), 994 (9)
$Ni(py)_4(NCO)_2$ + py	CH_3NO_2	375 (15), 608 (8), 998 (9)

[a] Parentheses enclose molar absorptivity at λ_{max}.   [b] Brackets denote peaks of a doublet.   [c] Absorption too low and broad to resolve λ_{max}.   [d] Very broad.

$$K^{-1} = \frac{A - A^0}{\epsilon_2 - \epsilon_1} - C_a - C_b + \frac{C_a C_b(\epsilon_2 - \epsilon_1)}{A - A^0}$$

where $A - A^0$ is the observed absorbance, A, minus the absorbance of the species in the equilibria 1 or 2 containing the lesser amount of coordinated pyridine. A correction is applied to A^0 to account for differences in the Ni^{2+} concentration in the various solutions by using the molar absorptivity of this species, ϵ_1. The molar absorptivity of the species containing the higher amount of coordinated pyridine, ϵ_2, is unknown, and C_a and C_b are the initial concentrations of nickel complex and free pyridine. Simultaneous equations are solved graphically to produce values for the two unknowns, K and ϵ_2.

Results

The analytical data for and room temperature magnetic moments of these complexes are reported in Table I. Table II contains the electronic spectral data and Table III the results of conductance studies.

The infrared spectra of Nujol mulls of the perchlorate and the tetrafluoroborate complexes indicate splitting of the ν_3 absorption of the anion in tetrahedral symmetry into ν_1 and ν_4 in C_{3v} symmetry. The infrared spectrum of the nitrate complex in a Nujol mull indicates that all the pyridine and both nitrate ions are coordinated. When pyridine is coordinated to a transition metal ion, there is a considerable frequency shift in its infrared absorptions, relative to uncomplexed pyridine. A doublet at 802 and 810

TABLE III

CONDUCTANCE DATA

Complex	Solvent	Λ_{molar}	Temp., °C.	Concn. $\times$ 10³, M
$Ni(py)_4(ClO_4)_2$	CH_2Cl_2[a]	1.72	22.4	0.292
$Ni(py)_4(ClO_4)_2$	CH_3NO_2	169	24.6	1.75
$Ni(py)_4(ClO_4)_2$ + py	CH_3NO_2	179	25.8	1.60
$Ni(py)_4(BF_4)_2$	CH_3NO_2	155	26.4	1.90
$Ni(py)_4(BF_4)_2$ + py	CH_3NO_2	153	26.0	2.45
$Ni(py)_3(NO_3)_2$	CH_2Cl_2[a]	0.194	22.6	0.324
$Ni(py)_3(NO_3)_2$	CH_3NO_2	7.25	25.6	7.58
$Ni(py)_3(NO_3)_2$ + py	CH_3NO_2	99	25.0	0.904
$Ni(py)_4(ClO_4)_2$ + C_6H_5CN	CH_2Cl_2[a]	24.9	26.6	0.161
$Ni(py)_4(ClO_4)_2$ + CH_3CN	CH_2Cl_2[a]	24.4	24.8	0.147
$Ni(py)_4(NCO)_2$ + py	CH_3NO_2	3.43	25.0	1.17
$Co(py)_2Cl_2$	CH_2Cl_2[a]	<0.226	22.8	0.236
$[(C_6H_5)_3AsCH_3]I$	CH_2Cl_2[a]	33.9	23.5	0.750
$[(C_6H_5)_3AsCH_3]_2Co(NO_3)_4$	CH_2Cl_2[a]	43.7	22.8	0.481
$[(C_6H_5)_3AsCH_3]_2Ni(NO_3)_4$	CH_2Cl_2[a]	71.1	23.2	0.413

[a] Extensive ion pairing occurs even at low concentration in this solvent due to the low dielectric constant and poor solvating properties. Thus, these values in CH_2Cl_2 should only be used to differentiate between nonionic and ionic species, not between types of ionic species.

cm.$^{-1}$ is assigned to ν_6 of a coordinated C_{2v} nitrate, a band at 1030 cm.$^{-1}$ to ν_2, and a band at 1305 cm.$^{-1}$ to ν_1.

When the nitrate complex is dissolved in dichloromethane, a blue-green solution is obtained. It was

found, from studying the far-infrared spectrum of this solution, that free pyridine is present. A band at 401 cm.$^{-1}$ appears in free pyridine which is shifted to 430 cm.$^{-1}$ in the complex. By examining solutions of pyridine at the proper concentrations, it was determined that Beer's law is obeyed, allowing a quantitative determination of free pyridine in the solution of the complex to be made. One mole of free pyridine is found for each mole of Ni(II).

The tetrafluoroborate complex is insoluble in dichloromethane. When either the perchlorate or tetrafluoroborate complex is dissolved in nitromethane, a blue-green solution is formed which becomes greener upon standing. However, when a solution is prepared containing equimolar amounts of either the perchlorate or tetrafluoroborate complex and excess pyridine, a blue solution results which is much more stable toward decomposition with respect to time. As the pyridine/Ni^{2+} molar ratio is increased, the solutions become more deeply blue, their electronic absorption bands shift to slightly longer wave lengths, and their molar absorptivities at the band maxima increase. The electronic absorption spectra of these complexes as a function of added pyridine are presented in Figure 1.
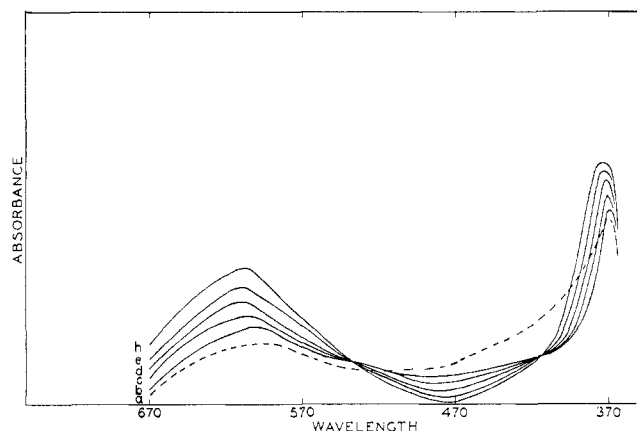

Figure 1.—Electronic spectrum of Ni(C$_5$H$_5$N)$_4$(ClO$_4$)$_2$ in CH$_3$NO$_2$ solution as a function of added pyridine. Mole ratio of added pyridine to Ni(C$_5$H$_5$N)$_4$(ClO$_4$)$_2$: a, 0; b, 1; c, 2; d, 4; e, 9; h, 205.

The presence of two isosbestic points indicates that an equilibrium exists between only two species, for solutions in this concentration range. The electronic spectrum of the solution containing only the Ni(II) complex does not pass through the isosbestic points. Equilibrium constant calculations were carried out to identify this equilibrium by considering the two possibilities shown in eq. 1 and 2. Taking A^0 as the absorbance of the four- and five-coordinate pyridine complex for eq. 1 and 2, respectively, the equilibrium constants and error limits were calculated. The data were found to fit the equilibrium represented by eq. 2 to a high degree of precision, while the calculation assuming eq. 1 produced very poor results. Even poorer results are obtained for equilibria involving complexes with 2 and 3 or 3 and 4 moles of coordinated pyridine. The data used in this calculation are presented in

Table IV, and the results of the graphical solution for K and $\Delta\epsilon$ are presented in Figure 2. Values of $K = 8.9 \pm 0.5$ (at 90% confidence level), $\epsilon_5 = 10.5$, and $\epsilon_6 = 16.3$ were obtained. A solution of approximately 0.001 M Ni(C$_5$H$_5$N)$_4$(BF$_4$)$_2$ in pyridine as a solvent has the same electronic spectrum as does the complex in nitromethane with a large excess of pyridine added.

TABLE IV
DATA FOR EQUILIBRIUM CONSTANT CALCULATIONS[a]

$M_{Ni^{+2}}$	$M_{py\ added}$	$M_{py\ total}$[b]	$A_{605\ m\mu}$[c]	A^0_{cor}
0.0295	0.0303	0.1483	0.311	0.311
0.0302	0.0638	0.1846	0.355	0.318
0.0301	0.1399	0.2603	0.399	0.317
0.0304	0.2674	0.3890	0.440	0.320
0.0301	0.5777	0.6981	0.469	0.317
0.0302	0.8365	0.9573	0.478	0.318
0.0302	6.2044	6.3252	0.499	0.317

[a] Temperature 28.0 ± 0.5° in CH$_3$NO$_2$ solution. [b] $M_{py\ total} = 4(M_{Ni^{+2}} + M_{py\ added}$. [b] Measurements were performed using 1-cm. matched cells.

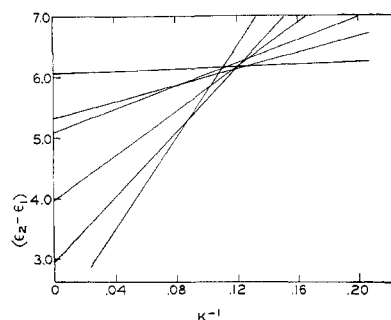Figure 2.—Plot of K^{-1} vs. $\epsilon_2 - \epsilon_1$ at 605 mμ for the equilibrium Ni(C$_5$H$_5$N)$_5$(CH$_3$NO$_2$)$^{+2}$ + C$_5$H$_5$N $\rightleftarrows$ Ni(C$_5$H$_5$N)$_6$$^{+2}$ + CH$_3$NO$_2$.

The spectrochemical parameters Dq and $\beta = B'/B$ were calculated from the spectrum assigned to octahedral Ni(C$_5$H$_5$N)$_6$$^{2+}$. Values of $\Delta(10Dq) = 9850$ cm.$^{-1}$ and $\beta = 0.83$ were obtained.

A far-infrared study upon a solution of the perchlorate complex in benzonitrile indicated that no free pyridine is present in solution. The nuclear magnetic resonance spectrum of this solution showed a shift to higher field and an increase in line width for the aromatic protons of the nitrile. Similar studies conducted in acetonitrile solvent indicated that free pyridine is present, but the quantity could not be accurately determined due to nitrile absorption. Crude measurements indicate an average stoichiometry of Ni(C$_5$H$_5$N)$_2$-(CH$_3$CN)$_4$.$^{2+}$ Attempts to isolate the mixed complex were unsuccessful. The nuclear magnetic resonance spectrum of this solution showed a broadened signal shifted to higher field for the acetonitrile protons.

Discussion

Structures of the Complexes in the Solid State.—
The infrared spectra of both the perchlorate and the tetrafluoroborate complexes in Nujol mulls indicate that the anions are coordinated. The magnetic moments of these complexes are typical of six-coordinate nickel(II) complexes.[8] The electronic mull spectra of

(8) B. N. Figgis, *Nature*, **182**, 1568 (1958).

both these complexes depart from typical spectra for octahedral nickel(II). Instead of three, there are four d–d absorption bands in the spectra. The extra band, a doublet at approximately 800 mμ, results from the large tetragonal distortion present. Additional bands have been observed in the electronic spectra of $Ni(C_5H_5N)_4Cl_2$ and $Cr(en)_2Cl_2^+$ and were attributed to tetragonal distortions.[9]

Unlike the corresponding complexes of lutidines,[10,11] the nitrate complex contains three molecules of pyridine per nickel ion. This compound is prepared by two methods and can be crystallized unchanged from dichloromethane. The magnetic moment and electronic mull spectrum indicate six-coordinate nickel(II). The infrared spectrum indicates, as previously discussed, that the nitrate ions and all the pyridine are coordinated. This complex, then, may be formulated as either $Ni(C_5H_5N)_6^{2+}Ni(NO_3)_4^{2-}$ or $Ni(C_5H_5N)_3(NO_3)_2$. It has been shown that $Ni(NO_3)_4^{2-}$ has a typical octahedral spectrum and magnetic moment.[12] The possible structure for the pyridine complex containing tetranitratonickelate(II) is eliminated on the basis of the absence of electronic absorptions characteristic of $Ni(NO_3)_4^{2-}$ in the mull spectrum. The pyridine complex is thus formulated as a six-coordinate complex containing a monodentate and a bidentate nitrate group.

The cyanate complex has a magnetic moment typical of six-coordinate nickel(II) and undoubtedly contains coordinated cyanate.

Structures of the Complexes in Solution. Dichloromethane.—When the perchlorate complex is dissolved in dichloromethane, a blue solution is obtained whose electronic spectrum is very similar to that of the Nujol mull. A conductance measurement indicates that no ionic species are present. Addition of a large excess of pyridine has no effect upon either of these measurements. This is not surprising when one considers that anion displacement would not be expected in the poorly solvating, low dielectric constant solvent dichloromethane. The species in solution is thus formulated as $Ni(C_5H_5N)_4(ClO_4)_2$.

As previously discussed, the nitrate complex dissolves in dichloromethane, liberating pyridine into the solution. The fact that the electronic spectrum of this solution is consistent with a six-coordinate species, and the fact that the molar conductance value indicates that no ionic species are present, leads us to believe that the following reaction is taking place.

$$Ni(C_5H_5N)_3(NO_3)_2 \longrightarrow Ni(C_5H_5N)_2(NO_3)_2 + C_5H_5N$$
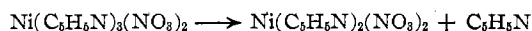
The electronic spectrum of this solution is very similar to those reported for dichloromethane solutions of $Ni(2,4\text{-lutidine})_2(NO_3)_2$ and $Ni(2,5\text{-lutidine})_2(NO_3)_2$.[10] Addition of excess pyridine has no effect upon the electronic spectrum or conductance value of this solution.

The cyanate complex is soluble in dichloromethane

with a slight excess of pyridine added. The electronic spectrum is identical with that of a similar solution in nitromethane, whose conductance value indicates that no ionic species are present. The structure of the species is thus formulated as $Ni(C_5H_5N)_4(NCO)_2$.

Nitromethane.—Conductance measurements on the solutions of both the perchlorate and the tetrafluoroborate complexes in nitromethane solution, with and without excess pyridine added, indicate that no anion coordination is taking place. The absence of the extra band in the electronic spectrum is further evidence that anion displacement has taken place. This behavior, different from that in dichloromethane, is readily understood when one considers the coordinating ability of nitromethane and its relatively high dielectric constant. The fact that both the perchlorate and tetrafluoroborate complexes produce identical spectra in nitromethane solution, when dissolved at the same molar concentration with the same molar concentration of added pyridine, is further evidence for the lack of anion coordination. Since the solution containing no excess pyridine produces a spectrum that does not pass through the isosbestic points, other species are present in this solution, and a more complex equilibrium exists. We have not concerned ourselves with all the possible species that can exist in the Ni^{2+}–pyridine system in solution but merely wish to establish the existence of a six-coordinate pyridine complex.

The results obtained in the equilibrium study (Table IV) are most definitive for solutions that contain smaller amounts of excess pyridine, for in these solutions the free pyridine concentration used in the calculation of K is greatly affected by the amount of pyridine complexed. These results strongly support formulating the equilibrium in excess pyridine by eq. 2 and hence support the existence of a six-coordinate pyridine complex of Ni(II). Further evidence is presented in the fact that the solution of the tetrafluoroborate complex in pyridine has the same electronic spectrum as the complex in nitromethane with the large excess of pyridine added. It is important that the solution of the tetrafluoroborate complex in pyridine has an electronic spectrum different from the Nujol mull electronic spectrum, indicating that anion displacement has taken place in the pyridine solution. If, then, these two solutions contain the same species, nitromethane coordination is eliminated as a possibility in the solution containing the large excess of pyridine in nitromethane.

The value for Δ obtained (9850 cm.$^{-1}$) is to be contrasted with a value of 10,150 cm.$^{-1}$ previously reported.[11] This higher value apparently arose from calculations on a species other than $Ni(C_5H_5N)_6^{2+}$. The solution spectrum reported for $Ni(C_5H_5N)_6^{2+}$ on which calculations leading to the large Δ value were made is identical with the spectrum reported[9] for a solution of $Ni(NO_3)_2$ in pyridine, which is proposed[9] to be $Ni(C_5H_5N)_4(H_2O)_2^{2+}$.

Additional support for the existence of the octahedral complex of Ni(II) and pyridine in our system can be obtained from the spectrochemical data. Using the

(9) O. Böstrup and C. K. Jørgensen, *Acta Chem. Scand.*, **11**, 1223 (1957).

(10) S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chem.*, **3**, 480 (1964).

(11) S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *ibid.*, **3**, 671 (1964).

(12) D. K. Straub, R. S. Drago, and J. T. Donoghue, *ibid.*, **1**, 848 (1962).

frequencies of the $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^4T_{1g}(P)$ to calculate[6] $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ for an octahedral complex, a value of 15,993 cm.$^{-1}$ is obtained compared to an experimental value of 16,502 cm.$^{-1}$. The ratio of the frequencies for the transitions to $^3T_{1g}(F)$ and $^3T_{2g}$ is 1.68, which is in agreement with that expected for an octahedral complex.

When the nitrate complex is dissolved in nitromethane, a blue-green solution is obtained whose electronic spectrum and conductance value indicate that the same species is formed as in dichloromethane solution. When excess pyridine is added, a solution is obtained whose color is blue and whose electronic spectrum has shifted to lower wave lengths. A conductance measurement indicates that one nitrate ion has been removed from the coordination sphere of the nickel ion. This phenomenon, which does not occur in dichloromethane, can be attributed to the higher dielectric constant of nitromethane.

The cyanate complex is soluble in nitromethane with excess pyridine added. The electronic spectrum is identical with that of the dichloromethane solution previously mentioned. The conductance value indicates that no ionic species are present despite the excess pyridine and suggests that the species present is Ni-$(C_5H_5N)_4(NCO)_2$.

Acetonitrile and Benzonitrile.—The absence of free pyridine in the solution of the perchlorate complex in benzonitrile and the marked difference in the electronic spectrum of this solution and the mull spectrum of the perchlorate complex indicate that the

species in solution is $Ni(C_5H_5N)_4(C_6H_5CN)_2^{2+}$. The addition of excess pyridine has no effect upon the electronic spectrum of this solution. The behavior of the n.m.r. signal is further evidence for benzonitrile coordination as manifested by a contact shift. The contact shift, an increase in line width and a shift to higher or lower fields, is typical for ligand protons in complexes of paramagnetic metal ions.[13] Unpaired electron spin is delocalized onto the ligand through σ or π electron systems, affecting shielding and relaxation times. The stability of this species in the presence of excess pyridine is probably due to less steric strain when the ligands on the z axis are benzonitrile than when they are pyridine.

In acetonitrile, a better base than benzonitrile for electronic and steric reasons, the species produced when the perchlorate complex is dissolved contains less than four coordinated pyridine molecules. Addition of excess pyridine does not change the electronic spectrum. The complex is formulated on the basis of the far-infrared measurements as $Ni(C_5H_5N)_2(CH_3CN)_4^{2+}$. As in the case of the benzonitrile solvent, acetonitrile coordination is indicated by the n.m.r. contact shift of the acetonitrile protons.

(13) B. B. Wayland and R. S. Drago, *J. Am. Chem. Soc.*, **87**, 2372 (1965).

The Preparation and Infrared Examination of the 2-, 3-, and 4-Cyanopyridine Complexes of Copper(I), Silver(I), and Gold(I) Perchlorates

BY FLOYD FARHA, JR., AND REYNOLD T. IWAMOTO

The preparation of the bis 2-, 3-, and 4-cyanopyridine complexes of copper(I), silver(I), and gold(I) perchlorates and the tris 3-cyanopyridine complex of silver(I) perchlorate is described. Because both the nitrile group and the pyridine group in the cyanopyridine are capable of coordinating strongly with these ions, the infrared spectra of the complexes were examined to determine the coordination site of the metal ions. In 3- and 4-cyanopyridine, the metal ions are bound to the pyridine nitrogen, and in 2-cyanopyridine they are bound to the nitrile nitrogen.

An attempted extension of a previously reported study from this laboratory[1] on solvent-effected reorientation in the coordination sphere of metal ions of organic ligands with two active functional groups has led us into this study of the cyanopyridine complexes of copper(I), silver(I), and gold(I) ions. Both the nitrile group and the pyridine group in the cyanopyridine

are capable of coordinating strongly with these ions. The preferential coordination of metal ions by one group rather than by the other and the relative ability of the three cyanopyridines to form complexes with these metal ions depend upon polar, resonance, and steric effects. Preparation and analysis of ten metal complexes of 2-, 3-, and 4-cyanopyridine are reported. The position of the metal ion in these complexes is deduced from infrared spectral data.

(1) F. Farha and R. T. Iwamoto, *J. Electroanal. Chem.*, **8**, 55 (1964).