

The Nickel(II) - *syn*-Phenyl-2-Pyridyl Ketoxime System*

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Complexes of *syn*-phenyl-2-pyridyl ketoxime with nickel(II) have been prepared and characterized by analyses, infra-red, magnetic susceptibility measurements, conductance and potentiometric titration techniques. Three series of complexes have been prepared according to the molar ratio of the ligand to metal ion viz. 3:1, 2:1 and 1:1.

Introduction

Ligands coordinating to metal ions through the dimethine or α -diimine structural unit $-N=C-C=N-$ have been the subject of numerous investigations over the past three decades. Three authoritative reviews have been written on this structural unit dealing with the metal complexes of 1,10-phenanthroline and related heterocyclic ligands,¹ a comparison of the dimethine donor group with other donor groups in bidentate ligands,² and the magnetic susceptibility of iron(II), cobalt(II) and nickel(II) complexes with ligands containing this structural unit.³

Figure 1 summarizes some of the more widely investigated ligands containing the dimethine group.

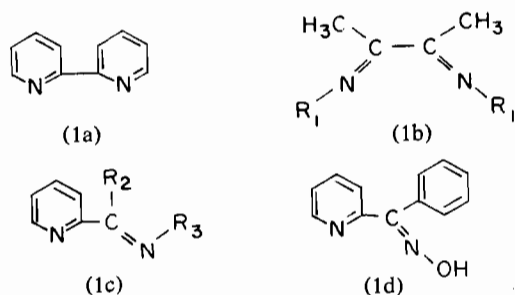


Figure 1. Typical Ligands Containing the Dimethine (α -Diimine) Structural Unit where R_1 is alkyl; R_2 is alkyl or aryl; R_3 is alkyl, aryl or hydrogen.

Included are those aromatic dimethine ligands typified by phen and 2,2'-bipyridine (1a); the aliphatic dimethine ligands, for example, biacetyl-bismeth-

thylimine (1b),⁴ and a class of ligands intermediate between these two types such as 2-pyridinalarylimines (1c) and 2-pyridinalkylimines (1c).⁵

Other functional groups which R_1 and R_3 may represent and which have been exhaustively studied are the amine, hydrazone and oxime. *syn*-phenyl-2-pyridyl ketoxime (HPPK, 1d) may thus be regarded as yet another variation on the fundamental dimethine structural unit. In addition, the incorporation of a single oxime group and a pyridine nitrogen as donor centers in the same ligand as contrasted with two oxime functionalities in the typical *vic*-dioximes facilitates the examination of the possible intra-molecular hydrogen bonds which may be formed by oxime containing ligands in coordination compounds.

This investigation reports the preparation and characterization of a series of nickel(II) complexes with HPPK.

Experimental Section

Materials. *syn*-Phenyl-2-pyridyl ketoxime was prepared from 2-benzoylpyridine according to the method of Huntress and Walter.⁶ 2-benzoylpyridine was obtained from Aldrich Chemical Co. and used without further purification. The nickel(II) salts were of reagent grade.

The 1,4-dioxane was purified as previously described.⁷ All other solvents were of reagent grade and purified by standard methods⁸ before used.

Preparation of Compounds. *Tris*-(*syn*-phenyl-2-pyridyl ketoxime)-nickel(II) Perchlorate. *syn*-phenyl-2-pyridyl ketoxime (4.0 g, 20 mm) was dissolved in 20 ml of hot absolute ethanol, and nickel(II) perchlorate hexahydrate (2.3 g, 6.2 mm) in 10 ml of absolute ethanol was added. The resulting solution was permitted to stand at room temperature until the formation of yellow crystals was judged to be complete, filtered, washed with solvent, and dried *in vacuo* over P_2O_5 , and then at 110°. *Anal.* Calcd. [Ni-($C_{12}H_{10}N_2O_3$)₃](ClO₄)₂: C, 50.69; H, 3.53; N, 9.86; Ni, 6.89. Found: C, 50.5; H, 3.64; N, 9.6; Ni, 6.96.

(*) Abstracted from the Thesis submitted by L. G. Ward in partial fulfillment of the requirements for the M. Sc. degree at Acadia University, June 1967.

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(2) C. M. Harris and S. E. Livingstone, in F. P. Dwyer and D. P. Mellor (Eds.) « Chelating Agents and Metal Chelates » Academic Press, New York 1964.

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(4) P. E. Figgins and D. H. Busch, *J. Am. Chem. Soc.*, **82**, 820 (1960).

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(8) A. I. Vogel « A Textbook of Practical Organic Chemistry ». Longmans, Green and Co., N. Y. 1956.

Tris-(syn-phenyl-2-pyridyl ketoxime)-nickel(II) Nitrate. Nickel(II) nitrate hexahydrate (3.6 g, 12.5 mm) was dissolved in 20 ml of absolute alcohol and added to a solution of *syn*-phenyl-2-pyridyl ketoxime (7.5 g, 37.5 mm) in 10 ml of absolute alcohol. The solution was refluxed with the formation of orange crystals, cooled and filtered. The crystals were washed with solvent and dried *in vacuo* over P_2O_5 , then at 110° . *Anal.* Calcd. for $[Ni(C_{12}H_{10}N_2O)_3](NO_3)_2$: C, 55.60; H, 3.86; N, 14.41; Ni, 7.55. Found: C, 55.63; H, 4.13; N, 14.15; Ni, 7.60.

Tris-(syn-phenyl-2-pyridyl ketoxime)-nickel(II) Iodide. Nickel(II) chloride hexahydrate (3.0 g, 12.5 mm) was dissolved in 10 ml of ethanol and added to a solution of *syn*-phenyl-2-pyridyl ketoxime (7.5 g, 37.5 mm) in 20 ml of ethanol. An aqueous solution of potassium iodide (20 g in 15 ml H_2O), and 3 drops of hydriodic acid was added to the ethanolic solution. The mixture was refluxed for 8-10 hours, and the orange precipitate which separated on standing, collected on a glass frit, washed with solvent and dried *in vacuo* over P_2O_5 , then at 110° . *Anal.* Calcd. for $[Ni(C_{12}H_{10}N_2O)_3]I_2$: C, 47.63; H, 3.31; N, 9.26; I, 28.00; Ni, 6.47. Found: C, 47.92; H, 3.66; N, 9.16; I, 27.82; Ni, 6.86.

Bis-(syn-phenyl-2-pyridyl ketoxime)-(syn-phenyl-2-pyridyl ketoximate) nickel(II) Nitrate. *Syn*-phenyl-2-pyridyl ketoxime (7.5 g, 37.5 mm) was dissolved in an ethanol solution containing approximately 15 mm ammonium hydroxide. Nickel(II) nitrate hexahydrate (3.6 g, 12.5 mm) was dissolved in ethanol containing ammonium hydroxide. These two solutions were mixed; allowed to stand for up to one week, seeded and the resulting brown precipitate was filtered on a glass frit, and dried *in vacuo* over P_2O_5 . *Anal.* Calcd. for $[Ni(C_{12}H_{10}N_2O)_2(C_{12}H_9N_2O)]NO_3$: C, 60.50; H, 4.06; N, 13.73; Ni, 8.22; O, 60.73; H, 4.38; N, 13.75; Ni, 8.03.

Dichloro-bis-(syn-phenyl-2-pyridyl ketoxime) nickel(II). *Method I.* A solution of anhydrous nickel(II) chloride (1.3 g, 10 mm) in 10 ml of absolute ethanol was added to a solution of *syn*-phenyl-2-pyridyl ketoxime (5.0 g, 25 mm) in 20 ml of absolute ethanol. The resulting solution was refluxed for several minutes, cooled, and the green crystals were collected on a glass frit, dried *in vacuo* over P_2O_5 and then at 110° . *Anal.* Calcd. for $[Ni(C_{12}H_{10}N_2O)_2]Cl_2$: C, 54.75; H, 3.80; N, 10.65; Cl, 13.50; Ni, 11.16. Found: C, 54.58; H, 4.16; N, 10.42; Cl, 13.68; Ni, 11.16.

Method II. The same procedure as Method I above except that 12.5 mm of nickel chloride hexahydrate was used rather than anhydrous nickel chloride.

Anal. Found: C, 55.09; H, 4.05; N, 10.41; Cl, 13.82; Ni, 10.69.

Bis-(syn-phenyl-2-pyridyl ketoxime) nickel(II) iodide. *Method I.* To a solution of *syn*-phenyl-2-pyridyl ketoxime (7.5 g, 37.5 mm) in 20 ml of ethanol was added an equal volume of an ethanol solution of nickel(II) nitrate hexahydrate (3.6 g, 12.5 mm). A solution of potassium iodide (20 g) in 15 ml of water

was added to the above 40 ml of ethanol solution and the resulting mixture refluxed for several hours. A green-brown solid separated on cooling, and the mixture was extracted with chloroform. The chloroform extract was evaporated, and bright green crystals were deposited. *Anal.* Calcd. for $[Ni(C_{12}H_{10}N_2O)_2]I_2$: N, 8.28. Found: Ni, 8.40.

Method II. To an ethanol solution (20 ml) of *syn*-phenyl-2-pyridyl ketoxime (7.5 g, 37.5 mm) was added 10 ml of an ethanol solution of nickel nitrate hexahydrate (3.6 g, 12.5 mm). Seven ml of hydriodic acid were then added, the mixture was refluxed until fine green crystals formed. The solution was cooled and the green precipitate collected on a glass frit, dried *in vacuo* over P_2O_5 and then at 110° . *Anal.* Calcd. for $[Ni(C_{12}H_{10}N_2O)_2]I_2$: C, 40.62; H, 2.82; N, 7.90; I, 35.83; Ni, 8.28. Found: C, 40.68; H, 3.05; N, 7.73; I, 35.65; Ni, 8.31.

Dichloro-bis-(syn-phenyl-2-pyridyl ketoxime) nickel(II) and Tris-(syn-phenyl-2-pyridyl ketoxime) nickel(II) chloride. Nickel chloride hexahydrate (3.0 g, 12.5 mm) and *syn*-phenyl-2-pyridyl ketoxime (7.5 g, 37.5 mm) were dissolved simultaneously in absolute ethanol and then refluxed until the solution darkened. On cooling, green and red crystals were deposited and collected on a glass frit. The red crystals were separated by washing with hot ethanol, and then collected from the cold solution by filtration. Both compounds were dried *in vacuo* over P_2O_5 and then at 110° . *Anal.* Calcd. for $[Ni(C_{12}H_{10}N_2O)_2]Cl_2$: Ni, 11.16. Found: Ni, 10.73. Calcd. for $Ni(C_{12}H_{10}N_2O)_3Cl_2$: Ni, 8.10. Found Ni, 8.00.

Bis-(syn-phenyl-2-pyridyl ketoxime) nickel(II) iodide *Tris-(syn-phenyl-2-pyridyl ketoxime) nickel(II) iodide.* To 20 ml of an ethanolic solution of *syn*-phenyl-2-pyridyl ketoxime (7.5 g, 37.5 mm) was added nickel chloride hexahydrate (3.0 g, 12.5 mm). An aqueous solution (15 ml) of potassium iodide (20 g) was added and the mixture refluxed for several hours. On cooling, fine light green, and large orange crystals separated. The large orange crystals which were flat and octagonal in shape were separated with tweezers. Both compounds were dried *in vacuo* over P_2O_5 , and then at 110° . *Anal.* Calcd. for $[Ni(C_{12}H_{10}N_2O)_2]I_2$: Ni, 8.28. Found Ni, 8.20. Calcd. for $[Ni(C_{12}H_{10}N_2O)_3]I_2$: Ni, 6.47. Found: Ni, 6.79.

Syn-phenyl-2-pyridyl ketoxime nickel(II) chloride. Five grams (25 mm) of *syn*-phenyl-2-pyridyl ketoxime was dissolved in 50 ml of absolute ethanol and the resulting solution was slowly added to 40 ml of an ethanol solution of nickel chloride hexahydrate (5.9 g, 25 mm) containing five drops of hydrochloric acid. The final solution was refluxed for half an hour, and then evaporated to a small volume. The complex was collected by filtration, dried *in vacuo* over P_2O_5 , and then at 110° . *Anal.* Calcd. for $Ni(C_{12}H_{10}N_2O)Cl_2$: C, 43.98; H, 3.05; N, 8.54; Cl, 20.65; Ni, 17.89. Found: C, 43.68; H, 3.02; N, 8.24; Cl, 21.83; Ni, 18.2.

The analyses for C, H, N, and halide were carried out by the Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. The nickel content of the com-

plexes was determined by digestion with HClO_4 - HNO_3 mixture,⁹ followed by titration with E.D.T.A. using murexide as indicator.¹⁰

Apparatus and Procedures. Potentiometric Titrations. Potentiometric titrations were carried out on solutions of *syn*-phenyl-2-pyridyl ketoxime and nickel(II) perchlorate using apparatus and procedures previously described.⁷ Titrations of the nickel(II) complexes prepared as described above were carried out at a concentration level of $10^{-2} M$ by transferring a weighed amount of complex to the titration vessel, dissolving in 50% V/V dioxane-water and titrating with standard sodium hydroxide.

Magnetic Measurements. The magnetic moments were obtained at room temperature by the Gouy method. Mercuric tetrathiocyanate cobaltate(II) was used as standard. The diamagnetic correction for the ligand HPPK was made directly, and Pascal's constants¹¹ were employed to correct for the diamagnetism of the anions. The reported values (Table I) are thus the moments attributable to the nickel(II) ion.

Table I. Magnetic Moments of Nickel(II) Complexes of *syn*-Phenyl-2-Pyridyl Ketoxime^a

Complex	μ_{eff} (oom Temp.)
$[\text{Ni}(\text{HPPK})_3](\text{ClO}_4)_2$	3.1 _a
$[\text{Ni}(\text{HPPK})_3](\text{NO}_3)_2$	3.1 _a
$[\text{Ni}(\text{HPPK})_3]\text{Cl}_2$	3.0 ₇
$[\text{Ni}(\text{HPPK})_3]\text{I}_2$	3.1 ₇
$[\text{Ni}(\text{HPPK})_2\text{Cl}_2]$	3.0 ₈
$[\text{Ni}(\text{HPPK})_2\text{I}_2]$	3.2 ₁
$[\text{Ni}(\text{HPPK})\text{Cl}_2]$	3.3 ₁
$[\text{Ni}(\text{HPPK})_2(\text{PPK})]\text{NO}_3$	2.9 ₈
$[\text{Ni}(\text{HPOX})_3]\text{I}_2 \cdot 2\text{H}_2\text{O}$	3.1 ₂ ^b
$[\text{Ni}(\text{PMI})_3](\text{BF}_4)_2$	3.1 ₂ ^c
$[\text{Ni}(\text{BMI})_3]\text{I}_2$	3.2 ₂ ^c

^a Corrected for the diamagnetism of HPPK: $131 \times 10^{-6} = \chi_{\text{M}}$ Pascal's constants used for anions. ^b R. A. Krause and D. H. Busch, *Nature*, 181, 1529 (1958). ^c Ref. 8. HPOX = 2-Pyridinaldoxime; BMI = biacetyl-bis-methylimine; PMI = 2-pyridinalmethylimine.

Conductivity Measurements. Molar conductances were obtained employing a Leeds and Northrup Co., No. 7651 potentiometer, a calibrated resistance box, and a 1000 cps oscillator. The conductivity cell was immersed in a constant temperature bath at $25.0 \pm 0.05^\circ\text{C}$. The cell constant was 0.3387 cm^{-1} . The absolute methanol used as solvent was protected from the atmosphere and had a specific conductance of less than 10^{-7} ohm^{-1} . The specific conductance of the water was found to be less than $2 \times 10^{-6} \text{ ohm}^{-1}$. The concentration of the solutions of the metal complexes employed on these measurements was $10^{-3} M$ based on the formula weight of the analyzed complex.

The results are reported in Table II.

Table II. Molar Conductances of Nickel(II) HPPK Complexes (ohms^{-1}) $1.0 \times 10^{-3} M$

	Λ_{M} CH ₃ OH	Λ_{M} H ₂ O
$[\text{Ni}(\text{HPPK})_3](\text{ClO}_4)_2$	171	181
$[\text{Ni}(\text{HPPK})_3](\text{NO}_3)_2$	158	227
$[\text{Ni}(\text{HPPK})_3]\text{I}_2$	165	57
$[\text{Ni}(\text{HPPK})_2\text{Cl}_2]$	92	261
$[\text{Ni}(\text{HPPK})_2\text{I}_2]$	161	255
$[\text{Ni}(\text{HPPK})\text{Cl}_2]$	101	260
$[\text{Ni}(\text{HPPK})_2(\text{PPK})]\text{NO}_3$	63	—

Spectrophotometric Measurements. Spectrophotometric measurements in the infrared-region were carried out with a Perkin-Elmer 21 equipped with sodium chloride optics, and a Perkin-Elmer 337 grating spectrophotometer. These results are reported in Table III.

Spectra in the region, 1250 $\text{m}\mu$ to 350 $\text{m}\mu$, were obtained using a Cary 14, and below 350 $\text{m}\mu$ with a Beckman DU equipped with photo multiplier. In all cases matched 1.0 cm quartz cells were employed for obtaining solution spectra, and nujol was used as the dispersion agent to obtain the diffuse transmittance spectra.

Results and Discussion

Synthesis. Three types of complexes formed by HPPK with nickel(II) may be distinguished on the basis of the stoichiometric ratio of HPPK to nickel(II) *viz.* 3:1, 2:1 and 1:1. The ensuing discussion of the properties of these complexes follows this order and is concerned with characteristics exhibited by these compounds in both the solid and solution phase.

Stable complexes of the type, $[\text{Ni}(\text{HPPK})_3]\text{X}_2$ where X = ClO_4^- , NO_3^- , I^- and Cl^- were readily isolated from ethanolic solutions as yellow to orange colored crystalline salts. Other solvent systems such as 50% aqueous-ethanol, 50% aqueous-dioxane both with controlled pH, and tetrahydrofuran did not prove to be satisfactory. Indeed, in the case of the preparation of $[\text{Ni}(\text{HPPK})_3](\text{ClO}_4)_2$ non aqueous conditions had to be maintained in order to avoid the formation of a heavy brown oil, whereas in the case of the preparation of $[\text{Ni}(\text{HPPK})_3](\text{NO}_3)_2$ no special precautions were required.

Under the conditions employed in this study it was not possible to isolate a bis-compound of HPPK and nickel(II) with perchlorate as the anion.

In the preparation of yellow $[\text{Ni}(\text{HPPK})_3]\text{Cl}_2$ and green $[\text{Ni}(\text{HPPK})_2]\text{Cl}_2$ it was found that both complexes could be isolated from the reaction mixture if HPPK and nickel(II) were mixed in a 3:1 ratio; however, from a 2:1 ratio of HPPK to nickel(II) just the green complex could be isolated. Since the green 2:1 complex was more soluble in hot ethanol than the yellow 3:1 complex, separation of these species was affected by hot filtration.

The preparations of $[\text{Ni}(\text{HPPK})_3]\text{I}_2$ and $[\text{Ni}(\text{HPPK})_2]\text{I}_2$ were similar to those for the chloride complexes, except that excess iodide as KI was used when both the orange 3:1 and green 2:1 complexes

(9) G. F. Smith. « The Wet Ashing of Organic Matter Employing Hot Concentrated Perchloric Acid ». The G. F. Smith Chemical Co., Columbus, Ohio (1954).

(10) F. J. Welcher. « The Analytical Uses of Ethylenediaminetetraacetic Acid », D. Van Nostrand Co. Inc., N. Y. (1958).

(11) J. Lewis and R. G. Wilkens, (Eds.) « Modern Coordination Chemistry », Interscience Pub. Inc. New York 1960, p. 403.

Table III. Infrared Bands and Assignments for Nickel(II)-HPPK. Complexes in 1600 cm^{-1} region

Compound	>C=N—	Py I	Py II	Phenyl	Py III	Py IV
HPPK	1618 w	1587 s, sp	1558 m	1490 m, sp	1471 s, sp	1431 s, sp
HPOX ^a	1520 s	1600 s, sp	1569 s, sp	—	1477 s, sp	1439 s, sp
[Ni(HPPK) ₃](ClO ₄) ₂	1618 m	1592 s, sp	1563 m, sp	1490 m, sp	1468 s, sp	1439 s, sp
[Ni(HPPK) ₃](NO ₃) ₂	—	1595 s	1565 w	1493 sh	1471 s, sp	1443 s, sp
[Ni(HPPK) ₃]I ₂	1605 s, sh	1587 s, sp	1560 m, sp	1486 m, sp	1466 s, sp	1439 s
[Ni(HPPK) ₃]Cl ₂	1608 m, sh	1587 s, sp	1560 m, sp	1486 m, sp	1466 s, sp	1437 s, sp
[Ni(HPPK) ₃]I ₂	1626 m	1597 m	1570 sh	1495 w	1475 s	1443 s, sp
[Ni(HPPK) ₃]Cl ₂	1639 m	1592 s, b	1563 m, sh	—	1458 s, vb	1439 s, sp
[Ni(HPPK) ₃]Cl ₂	1637 vb, sh	1592 m	1565 w, sp	1490 w	1468 s, sp	1437 s
[Ni(HPPK) ₃]PPK]NO ₃	1664 w, b	1587 s	1567 m, sh	1493 sh	1460 s, b	1437 s
[Ni(HPOX) ₃]I ₂	1633 w, sh	1599 s, sp	1563 w	—	1478 s, sp	1443 m
[Ni(HPOX) ₃]Cl ₂ ^a	1654 m, sp	1611 s, sp	1574 w	—	1490 s, sp	1438 wv

^a R. A. Krause, N. B. Colthup, and D. H. Busch, *J. Phys. Chem.*, 65, 2216 (1961). Abbreviations: s, strong; v, very; m, medium; sh, shoulder; sp, sharp; w, weak; b, broad.

were prepared; and HI was used as the source of iodide ion when the 2:1 complex was prepared exclusively. In all cases nickel(II) chloride was used as the source of the metal species.

The effective magnetic moments (μ_{eff}) of these compounds are reported in Table I. The values range from 3.1 to 3.2 Bohr Magnetons (B. M.) for the tris-complexes, with one exception, [Ni(HPPK)₂(PPK)]NO₃. Similar values obtained for the bis-HPPK complexes. In contrast, dichloro *syn*-phenyl-2-pyridyl ketoxime nickel(II) exhibits a slightly higher $\mu_{\text{eff}} = 3.3$ B.M.

The values reported here for the tris-HPPK complexes are strikingly similar to those reported for the analogous dimethine containing ligands: 2-pyridinaldoxime (HPOX); 2-pyridinalmethylamine (PMI), and bisacetyl-bis-(methylimine) (BMI). Values of μ_{eff} determined for the nickel(II) complexes of these latter three ligands are also recorded in Table I.

The range of values of μ_{eff} reported in Table I suggests octahedral structures about nickel(II) in all complexes except [Ni(HPPK)Cl₂] and [Ni(HPPK)₂(PPK)₂(PPK)]NO₃. This assignment of structure about nickel(II) is based on the fact¹² that μ_{eff} for a d⁸ system is grossly (*ca.*) 3.06 B.M. allowing for just spin-orbit coupling, and is (*ca.*) 3.23 B.M. if the ground term is ³A_{2g}. These computed values are in contrast to the « spin-only » value of $\mu_{\text{eff}} = 2.83$ B.M.

Conductance. In methanol, the tris-complexes of HPPK and nickel(II) exhibit a molar conductivity in the range 158 to 171 ohms⁻¹ (Table II) at a concentration level of 10⁻³ M based on the formula weight of the analyzed complex. Under these conditions, this range of conductance values may be attributed to di-univalent electrolytes. Stoufer¹³ established a range of 145 to 175 ohms⁻¹ for similar nickel(II) complexes under identical conditions, and Robinson and Busch¹⁴ have reported values up to 186 ohms⁻¹ for 3:1 nickel(II) complexes with ligands containing the dimethine structural unit. The conductance of the cation [Ni(HPPK)₃]²⁺ was calculated to vary between 40 and 48 ohms⁻¹ in methanol further substantiating a di-univalent electrolyte.

The cation conductance was computed from the difference between the measured value and those values estimated for the anions. The anion conductance values were calculated by comparing the conductance of a salt, *e.g.* NaCl, in water to that in absolute methanol at a concentration of 10⁻³ M at 25.0°. The values were found to be as follows: (ohms⁻¹): Cl⁻, 54.1; I⁻, 60.1; ClO₄⁻, 61.4; NO₃⁻, 70.6. The values employed for the anion conductances in water were obtained from standard tables.¹⁵ Values computed for the cation conductances on this basis tend to support this argument. Further, the increase in size of the halide ion resulting in an increase in conductance in non aqueous media suggesting an increase in solvation is not without precedent.¹⁶

The cation conductances computed for [Ni(HPPK)₂]²⁺ (41 ohms⁻¹) is in agreement with that for the tris-complexes, and the corresponding value for [Ni(HPPK)₂Cl]⁺ of 38 ohms⁻¹ is very close to values reported for similar compounds, by Robinson and Busch.¹⁴

The complex, [Ni(HPPK)Cl₂], has a molar conductance of 260 ohms⁻¹ in water which indicates a di-univalent electrolyte, and a value of 101 in methanol which resembles the values for a uni-univalent electrolyte. Again, it is suggested that methanol, as solvent, displaces just one of the chloride ions. The cation conductance calculated on this basis is 47 ohms⁻¹, similar to the values computed for the other complexes in this series.

The conductance of the tris-complexes in water showed a wide variation in both the molar and cation conductance. This indicates that more than a simple dissociation of the complex occurs.

The bis-complexes of HPPK and nickel(II) exhibit molar conductance values in water in the narrow range 255 to 261 ohms⁻¹. The corresponding cation conductance values are: 103 and 110 ohms⁻¹. These values are in the range expected for di-univalent electrolytes which may be interpreted to indicate that the halide ions are outside the coordination sphere in the solid complex, or displaced by the solvent in solution.

(12) Ref. 11 Chap. 6.

(13) R. C. Stoufer. Ph. D. Dissertation, The Ohio State University, Columbus, Ohio, 1958.

(14) M. A. Robinson and D. H. Busch, *Inorg. Chem.*, 2, 1171 (1963).

(15) Handbook of Chemistry and Physics, The Chemical Rubber Co., Cleveland, Ohio, 1962.

(16) M. O. Workman, G. Dyer and D. W. Meek, *Inorg. Chem.*, 6, 1543 (1967).

In absolute methanol a contrasting situation obtains; thus $[\text{Ni}(\text{HPPK})_2\text{I}_2]$ has $\Lambda_M = 161 \text{ ohms}^{-1}$, and $[\text{Ni}(\text{HPPK})_2\text{Cl}_2]$ has $\Lambda_M = 92 \text{ ohms}^{-1}$. The latter value indicates a uni-univalent electrolyte in this solvent and is interpreted as one chloride being displaced by the solvent. The former value of 161 ohms^{-1} is quite comparable to that obtained for the tris-complexes of HPPK. It is suggestive of a di-univalent electrolyte, and quite in accord with both iodide ions being replaced by solvent.

The compound $[\text{Ni}(\text{HPPK})_2(\text{PPK})]\text{NO}_3$ exhibits a molecular conductance of 63 ohms^{-1} in methanol. This value is low for a proposed uni-univalent electrolyte. The conductance of this compound could not be obtained in water due to color change followed by precipitation.

Infrared Spectra. The infrared absorption bands of HPPK and its nickel(II) complexes are reported in Table III. The corresponding absorption bands of the structurally related ligand pyridine-2-aldoxime, HPOX, and its nickel(II) complexes are included for comparative purposes.

It is convenient to discuss the infrared region according to the predominant functional groups present in the system. Thus, considered in order are: the hydroxyl group ($3500\text{-}3000 \text{ cm}^{-1}$) the $>\text{C}=\text{N}-$, pyridine ring, and phenyl ring ($1700\text{-}1400 \text{ cm}^{-1}$) and the $=\text{N}-\text{O}^-$ function (1200 cm^{-1}).

The frequency range generally ascribed to absorption by the free hydroxyl group is $3700\text{-}3500 \text{ cm}^{-1}$. In oximes, particularly aromatic ketoximes, the OH stretching frequencies are shifted to lower values, and appear in the range $3200\text{-}3100 \text{ cm}^{-1}$.^{17,18} In the case of HPOX, Krause *et al.*¹⁹ have noted that the broad OH band of a conventional oxime is replaced by multiple bands in the range $3194\text{-}2791 \text{ cm}^{-1}$. The strongest of these bands was found at 2791 cm^{-1} . The interpretation of this effect was that much stronger hydrogen bonding was involved in HPOX than in other oxime systems. More recently, Poziomek and Vaughan²⁰ separated *syn*- and *anti*-pyridine-2-aldoxime (pyridinealdehyde oxime) and assigned a broad OH absorption maximum at 2790 cm^{-1} to the *anti*-isomer, and a sharp band at 3574 cm^{-1} to a free OH absorption of the *syn*-isomer. This latter investigation was carried out in 5% CHCl_3 solutions. HPPK exhibits a similar behaviour to HPOX in that multiple bands are observed over the range $3226\text{-}2817 \text{ cm}^{-1}$. The multiplicity of these bands decreases in the spectrum of both the sodium salt and HPPK hydrochloride. It is noted that *anti*-phenyl-2-pyridyl ketoxime exhibits multiple absorption bands in the 3000 cm^{-1} region, and, insofar as they may be compared with similar bands of HPPK,²¹ they are at a slightly lower frequency and much less intense. In addition to the series of bands in the 3000 cm^{-1} region, *anti*-phe-

nyl-2-pyridyl ketoxime exhibits a broad band at 2550 cm^{-1} . It is suggested that intramolecular hydrogen bonding may give rise to the latter band since the OH group in *anti*-phenyl-2-pyridyl ketoxime should be more favourably oriented toward the pyridine nitrogen than that in HPPK. The series of bands around 3000 cm^{-1} may then be due to intermolecular hydrogen bonding in the case of HPPK.

Under the experimental conditions employed, it was not possible to distinguish unequivocally the aromatic C-H stretching modes which would be present in this region. The general range assignable here would be, however, 3075 to 3000 cm^{-1} with medium to weak intensity.

Molecular models suggest that the nickel complexes of HPPK would not intermolecularly hydrogen bond to the same extent as the free ligand. Thus the broad band in the 3000 cm^{-1} region exhibited by the free ligand should alter in the complexes. The alteration is small since there is a broad band in this region which apparently cannot be resolved and ranges 30 cm^{-1} from complex to complex. It would appear that a similar situation was met in the case of the nickel(II) complexes of HPOX under comparable experimental conditions. The conclusion which may be drawn, however, is that there are hydroxyl groups present in all the complexes, and that there is a small degree of association in the metal complex system relative to the ligand.

Consideration of the frequency range $1700\text{-}1400 \text{ cm}^{-1}$ for the HPPK system and its complexes embraces bands expected due to the $>\text{C}=\text{N}-$ stretching mode, the four pyridine ring bands and the four bands which may be attributable to a mono-substituted phenyl ring.

In open chain unconjugated cyclic systems the $>\text{C}=\text{N}-$ stretching mode is found in the range $1700\text{-}1630 \text{ cm}^{-1}$ with variable intensity.²² As the polarity of the nitrogen atom increases, the frequency range lowers and broadens to $1660\text{-}1510 \text{ cm}^{-1}$.²² Thus Krause *et al.*¹⁹ assigned a band at 1520 cm^{-1} to the $>\text{C}=\text{N}-$ stretching mode in HPOX by comparison with a 1517 cm^{-1} band in KPOX and a band at 1620 cm^{-1} in HPOX.HCl. The argument advanced for the assignment was that the oxime proton on the free ligand (not examined for isomeric content) was involved in an intramolecular hydrogen bond with the pyridine nitrogen, hence HPOX would more closely resemble the potassium salt rather than the hydrochloride. The nickel(II) complexes of HPOX exhibited bands in the range $1654\text{-}1644 \text{ cm}^{-1}$ which were assignable to $>\text{C}=\text{N}-$. The removal of a proton from the oxime function in HPOX resulted in a shift of the $>\text{C}=\text{N}-$ to the range 1547 to 1519 cm^{-1} in KPOX. Since HPOX was not examined for isomeric content,²⁰ and exhibited a strong band at 1520 cm^{-1} , this band was assigned to $>\text{C}=\text{N}-$ in HPOX and the decrease in frequency relative to 1620 cm^{-1} was attributed to ionization of the oxime proton manifested in a N-H-O hydrogen bond, involving the pyridine nitrogen.

In the case of HPPK, it seems reasonable to assign

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the 1618 cm^{-1} band to the $>\text{C}=\text{N}-$ stretching mode on the basis that a band of similar shape and intensity appears in $[\text{Ni}(\text{HPPK})_2\text{Cl}_2]$ at 1639 cm^{-1} , $[\text{Ni}(\text{HPPK})_2\text{I}_2]$ at 1626 cm^{-1} and a broad relatively weak band appears at 1637 cm^{-1} in the spectrum of $[\text{Ni}(\text{HPPK})\text{Cl}_2]$. This increase in frequency of the $>\text{C}=\text{N}-$ is to be expected on metal complex formation. In the case of $[\text{Ni}(\text{HPPK})_2(\text{PPK})]\text{NO}_3$, there is no band unambiguously assignable to the $>\text{C}=\text{N}-$ stretching mode. It might be anticipated that this band would be shifted to lower frequency on complex formation due to the loss of the oxime proton. If this is so, then it cannot be resolved under the experimental conditions. The final support for the assignment of the $>\text{C}=\text{N}-$ band as being in the 1600 cm^{-1} region in these complexes is derived from the fact that it is possible to assign the pyridine ring bands unambiguously in almost all cases by comparison with metal complex systems of 2-pyridinaldoxime¹⁹, and pyridinal methylamines.²³ The slight decrease in frequency of the pyridine bands in the HPPK systems relative to those in the HPOX and PMI systems may be attributed to the presence of the phenyl ring which makes possible a more extensively conjugated system compared to HPOX and PMI, and in addition, provides for an increase in the number of bands in this region of the spectrum. Some of these bands are revealed as shoulders on the assigned pyridine bands, others are distinct.

It should be noted that the assignment of the $>\text{C}=\text{N}-$ band in 2-pyridinaldoxime by Krause *et. al.*¹⁹ at 1520 cm^{-1} is quite unusual for non dissociated oximes. The suggestion that HPOX has a configuration about the $>\text{C}=\text{N}-\text{OH}$ function different than that of comparable oximes was first noticed by Harrison and Cheney²⁴ where it was shown on the basis of E1/2 data HPOX is much more readily reduced at a DME than other oximes, in particular, HPPK.

In the region below 1200 cm^{-1} it would be anticipated that there would be a large number of bands associated with the « in plane » and « out of plane » bending modes of the pyridine and phenyl rings as well a band attributable to a N–O stretching mode.

In the series of HPOX complexes¹⁹ the N–O mode in the function $>\text{C}=\text{N}-\text{O}-\text{H}$ was assigned the range 1069 to 1036 cm^{-1} and was regarded as being intense. In the ligand itself, the band at 985 cm^{-1}

was assigned to the N–O mode. The 992 cm^{-1} band in HPPK might well be assigned to the N–O stretch since it is the most intense band in this region of the spectrum. Similarly, the most intense band over the range 1073 to 1053 cm^{-1} was assigned to the N–O mode in the HPPK complexes.

Electronic Spectra. The absorption bands of the complexes were determined over the region 7,000 to 25,000 cm^{-1} employing diffuse transmittance techniques and $10^{-2} M$ methanol solutions. Agreement of band position within $\pm 100 \text{ cm}^{-1}$ was not obtained. This lack of agreement in band position on going from the solid to the solution phase coupled with the pronounced color changes which take place in aqueous-dioxane solution as a function of pH is indicative of a configurational change about the metal ion and will be reported elsewhere.

Potentiometric Study. The potentiometric study was carried out in two stages: (1) mixtures of $\text{Ni}(\text{ClO}_4)_2$, HPPK and HClO_4 were neutralized with standard sodium hydroxide, and (2) weighed quantities of the analyzed complexes were neutralized with sodium hydroxide.

The values of the acid dissociation constants of the complexes,²⁵ pK_I and pK_{II} , were not in satisfactory agreement when the results of the two approaches were compared.

The best opinion which can be rendered at this time is that some degree of polymerization occurs with an increase in pH of the solution beyond 5 and results in the formation of tri- and di-nuclear complexes of the type: $[\text{Ni}_3(\text{HPPK})(\text{PPK})_5]^+$ in the case of the tris complexes, and $[\text{Ni}_2(\text{HPPK})(\text{PPK})_3]^+$ in the case of the bis-complexes, these complexes containing oxygen and hydroxyl bridges similar to that proposed by Krause and Busch.²⁶

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