# TRANSITION METAL COMPLEXES OF SYN-PHENYL-2-PYRIDYLKETOXIME

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Abstract – The transition metal complexes of the bidentate ligand syn-phenyl-2-pyridylketoxime (HPPK; anion, PPK) of composition  $[Ni(HPPK)_3](NO_3)_2$ ,  $[Co(HPPK)_3](NO_3)_2$ ,  $[Mn(HPPK)_2Cl_2]$ , [Pd(HPPK)(PPK)]Cl and  $[Pd(PPK)_2]$  have been isolated. Elemental analyses, i.r. and electronic spectral data, conductance, and magnetic moment measurements suggest that Ni(II), Co(II) and Mn(II) complexes are octahedral, and Pd(II) complexes are square planar. The ligand as well as the complexes, except  $[Pd(PPK)_2]$ , are strongly internally hydrogen bonded via the oxime proton and the benzene  $\pi$  electronic cloud. This also provides evidence for the conclusion that the coordination takes place via the pyridine and the oxime nitrogen atoms.

## INTRODUCTION

PHENYL-2-PYRIDYLKETOXIME was reported as a bidentate ligand as early as 1929 by Emmert and Diehl[1]. Various analytical applications of this ligand have been reported by a number of workers [1, 2]. Formation constants of a number of complexes formed by phenyl-2-pyridylketoxime have been reported by Sen and Shuman[3]. However, relatively few complexes have been isolated and characterized. Recently, Ward, Meek and Cheney [4] have reported a series of nickel(II) complexes of syn-phenyl-2-pyridylketoxime. The compounds reported by them have the general formula  $[Ni(HPPK)_3]X_2$ ,  $[Ni(HPPK)_2Cl_2]$ ,  $[Ni(HPPK)_2I_2]$ ,  $[Ni(HPPK)Cl_2]$ ,  $[Ni(HPPK)_2(PPK)]NO_3(HPPK = syn-C_6H_5 . C . C_5H_4N; PPK =$ 

 $\begin{array}{c} \text{syn-}C_6H_5 \text{ . } C \text{ . } C_5H_4N\text{).} \\ \| \\ NO^- \end{array}$ 

Our preliminary investigations indicated that a number of other transition metal ions such as, Mn(II), Fe(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II), Cd(II), Au(III) and Hg(II) form stable complexes with syn-phenyl-2-pyridylketoxime. Some of these ions form more than one series of complexes depending upon the mole ratio of the reactants, the solvent, and the pH. For example, the red nickel(II) complex isolated from an aqueous medium of slightly alkaline pH, and the yellow palladium complex isolated from an aqueous medium of slightly acidic pH are (inner coordination compounds) represented by the formula  $[M(PPK)_2]$ .

In this paper we report the isolation from an alcoholic medium, and characterization of the complexes  $[Ni(HPPK)_3](NO_3)_2$ ,  $[Co(HPPK)_3](NO_3)_2$ ,  $[Mn-(HPPK)_2Cl_2]$  and [Pd(HPPK)(PPK)]Cl. The complex  $[Pd(PPK)_2]$  was isolated

4. L. G. Ward, T. L. Meek and G. E. Cheney, Inorg. chim. Acta 4, 43 (1970).

<sup>1.</sup> B. Emmert and K. Diehl, Ber. 62, 1738 (1929).

<sup>2.</sup> B. Sen, Analyt. Chem. 31, 881 (1959); F. Trussell and H. Diehl, Analyt. Chem. 31, 1978 (1959).

<sup>3.</sup> B. Sen and D. C. Shuman, Anal. chim. Acta 33, 487 (1965).

from a slightly acidic aqueous medium. A green crystalline complex and a black crystalline complex of Cu(II), and a rust covered crystalline complex of Au(III) have also been isolated. We have not yet been able to unequivocally characterize the last three compounds.

Sen, Dotson and Johnson [5, 6] have shown the importance of the O-H region of the i.r. spectrum in characterizing the metal complexes with ligands containing OH function. A critical examination of the OH region of the spectra of metal complexes of syn-phenyl-2-pyridylketoxime yielded a great deal of information regarding these complexes. For the type of compounds under investigation, we found that the region  $3600-2800 \text{ cm}^{-1}$  was more convenient than the overtone region [7, 8] (~ 7000 cm<sup>-1</sup>) for studying the effect of hydrogen bonding.

### EXPERIMENTAL

#### Materials

Syn-phenyl-2-pyridylketoxime was either prepared according to the method of Huntress and Walter[9], or was purchased from G. F. Smith Chemical Co.

Benzophenone oxime was prepared by treating  $2 \cdot 0$  g of benzophenone dissolved in ethanol-water, with a solution of 10 g hydroxylamine hydrochloride in 30 ml of water, and 20 ml of 10% NaOH solution. The above solution was heated on a steam bath for 1 hr, and was then cooled in an ice bath. Crystallization occurred upon the addition of a few milliliters of water to the chilled solution. The product was recrystallized from hot ethanolic solution (m.p.  $144^{\circ}-145^{\circ}C$ ).

All chemicals used were of reagent grade; the solvents were purified whenever it was deemed necessary.

#### Preparation of the compounds

Tris-(syn-phenyl-2-pyridylketoxiome)nickel(11) nitrate,  $[Ni(C_{12}H_{10}N_2O)_3](NO_3)_2$ . To a hot solution of HPPK (3.75 g, 18.75 m-mole) in 20 ml ethanol, was added Ni(NO<sub>3</sub>)<sub>2</sub>. 6H<sub>2</sub>O (1.80 g, 6.25 m-moles) dissolved in 10 ml of ethanol. The solution was refluxed for 30 min. Orange crystals separated out on cooling the solution. The product was filtered, washed with ethanol, and recrystallized from hot ethanol. The recrystallized product was dried in a drying pistol *in vacuo*, and over P<sub>2</sub>O<sub>5</sub> at 110°C.

Anal. Calcd.: C. 55.60; H, 3.89; N, 14.41. Found: C, 55.53; H, 4.00; N, 14.49.

Tris-(syn-phenyl-2-pyridylketoxime(cobalt(II) nitrate,  $[Co(C_{12}H_{10}N_2O)_3](NO_3)_2$ . Co(NO<sub>3</sub>)<sub>2</sub> . 6H<sub>2</sub>O (1·82 g, 6·25 m-moles) was dissolved in 20 ml of hot ethanol and was then added to a solution of HPPK (3·75 g, 18·75 m-mole) in 30 ml of hot ethanol. The solution was refluxed for 1 hr when brown crystals precipitated. The product was filtered, washed with ethanol, recrystallized and dried as above.

Anal. Calcd.: C, 55.60; H, 3.91; N, 14.46. Found: C, 56.10; H, 3.88; N, 13.50.

Bis-(syn-phenyl-2-pyridylketoxime)-bis-chloromanganese(II)  $[Mn(C_{12}H_{10}N_2O)_2Cl_2]$ . MnCl<sub>2</sub>. 4H<sub>2</sub>O (2·47 g, 12·5 m-moles) was dissolved in 30 ml of hot ethanol, and was added to a solution of HPPK (5·00 g, 25·0 m-moles) in 25 ml of hot ethanol. The solution was refluxed for 2 hr; bright yellow crystals separated out as the solution cooled. The product was purified by recrystallization and dried as before.

Anal. Calcd.: C, 55·18; H, 3·68; N, 10·72. Found: C, 55·25; H, 4·10; N, 10·20.

 $(Syn-phenyl-2-pyridylketoxime)(syn-phenyl-2-pyridylketoximato)palladium(11) chloride, [Pd-<math>(C_{12}H_{10}N_2O)(C_{12}H_9N_2O)]Cl.$  PdCl<sub>2</sub> (1·11 g, 6·25 m-moles) was dissolved in 50 ml of hot ethanol, and was added to a solution of HPPK (5·00 g, 25·0 m-moles) in 25 ml of hot ethanol. The solution was refluxed for 3 hr, yellow crystals started forming during refluxing. The solution was cooled, the yellow crystals filtered, washed with ethanol and dried as above.

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- 7. L. Pauling, *Nature of Chemical Bond*, 3rd Edn., p. 485. Cornell University Press, New York (1960); and references cited therein.
- 8. M. P. Servé and A. W. Bryant, J. org. Chem. 36 (1971).
- 9. E. H. Huntress and H. C. Walter, J. Am. chem. Soc. 70, 3702 (1948).

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Transition metal complexes

Anal. Calcd.: C, 53·85; H, 3·51; N, 10·46; Pd, 19·38. Found: C, 55·30; H, 3·39; N. 10·76; Pd, 19·87. Bis-(syn-phenyl-2-pyridylketoximato)palladium(11). [Pd(C<sub>12</sub>H<sub>9</sub>H<sub>2</sub>O)<sub>2</sub>]. HPPK (0·85 g, 4·2 m-moles) dissolved in 15 ml hot ethanol was slowly added to a hot solution of PdCl<sub>2</sub> (0·36 g, 2·08 m-moles) dissolved in 125 ml of 0·01 M HCl. A bright yellow crystalline precipitate was formed immediately. The precipitate was digested on a steam bath for 30 min, and was then filtered, washed with hot water and dried in an oven at 110°C.

Anal. Całcd.: C, 57·49; H, 3·58; N, 11·17. Found: C, 57·27; H, 3·38; N, 11·12.

#### Magnetic moments

The magnetic moments (cf. Table 1) were obtained by the Gouy method using mercuric(11)-tetrathiocyanato-cobaltate(II) as the reference.

Compound	Color	Molar* conductance (cm²/Ω in MeOH)	μeff† ( <b>B.M</b> .)
[Mn(HPPK) <sub>2</sub> Cl <sub>2</sub> ]	Bright yellow	106	5.79
$[Co(HPPK)_3](NO_3)_2$	Brown	87.9	4.99
[Ni(HPPK) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub>	Orange	161	3.46
[Pd(HPPK)(PPK)]Cl	Yellow		0.00
[Pd(PPK) <sub>2</sub> ]‡	Yellow		0.00

Table	1.	Some	physical	properties	of the	e syn-phenyl-2-pyridylketoxime
				com	plexes	

\*1 × 10<sup>-3</sup> M solutions; reference value for Na1 ~ 35 cm<sup>2</sup>/ $\Omega$ .

<sup>+</sup>Corrected for the diamagnetism of HPPK ( $131 \times 10^{-6} \chi m$ ), NO<sub>3</sub><sup>-</sup> ( $19 \times 10^{-6} \chi m$ ) and Cl<sup>-</sup> ( $23 \times 10^{-6} \chi m$ ).

‡Could not be measured due to insufficient solubility.

## Conductivity measurements

Molar conductance were measured by employing a Leeds and Northrup bridge. The cell constant was  $10.72 \text{ cm}^{-1}$ , and the dry methanol used had a specific conductance of less than  $10^{-7} \Omega^{-1}$  ( $0.557 \times 10^{-7} \Omega^{-1}$ ). The concentration of the solutions of the metal complexes employed in these measurements was  $1 \times 10^{-3}$  M based on the formula weight of the analyzed complex. The reference value for NaI was  $\sim 35 \text{ cm}^2/\Omega$  mole. The results are summarized in Table 1.

#### Spectrophotometric measurements

Spectrophotometric measurements in the i.r. region were carried out with a Perkin-Elmer 180, a Beckman IR-7, or a Beckman IR-10. The mull spectra were obtained in hexachlorobutadiene, and the solution spectra were taken in chloroform or carbon tetrachloride.

Spectra in the visible and the u.v. regions were obtained by using a Cary 14 spectrophotometer. and were recorded using Nujol mull on Whatmen 42 filter paper.

## **RESULTS AND DISCUSSION**

It is to be expected that the ionization process of the complexes of this type in a poorly ionizing, and at the same time strongly polar solvent like MeOH, is likely to be complicated. Consequently the molar conductances of any one type of electrolyte are expected to vary over a wide range [4–6]; therefore, the molar conductance in these circumstances is only a guide which must be considered in relation to other evidence. The nickel(II) complex is an 1:2 electrolyte in spite of somewhat higher molar conductance than expected. It is in the same range as that reported by Ward, Meek and Cheney for similar complexes [4], but considerably higher  $(50 \text{ cm}^2/\Omega)$  than tris-triethanolamine-nickel(II) chloride[5]. Molar conductance of  $[Co(HPPK)_3](NO_3)_2$  is much closer to the expected value for an 1:2 electrolyte[4, 5]. We conclude from magnetic and spectral evidence that both Mn(II) and Pd(II) complexes are nonelectrolytes. The conductivity of Mn(II) complex is obviously due to extensive ligand displacement.

Magnetic moments indicate that Co(II), Ni(II) and Mn(II) complexes are octahedral [10]. Diamagnetism and extremely poor solubility of  $[Pd(HPPK)-(PPK)]Cl, [Pd(PPK)_2]$  strongly suggest that both the Pd(II) complexes are square planar [10]. Electronic spectrum of [Pd(HPPK)(PPK)]Cl bears striking resemblence to the spectrum of square planar  $[PdCl_4]^{2-}$  ion.

The i.r. spectra of the OH region of the complexes indirectly provides the most interesting information regarding metal-nonmetal bonding. The prominent feature of the spectra of ligand as well as the complexes is the evidence of extensive hydrogen bonding with  $\pi$ -orbitals of phenyl ring. Hydrogen bonding with aromatic and acyclic  $\pi$ -orbitals, as well as polarized C-C bond has been shown to exist by a number of workers [8, 11, 12]. It is expected that in the conformation shown in Fig. 1, the proton is perfectly oriented for hydrogen bonding with  $\pi$ -orbitals of the phenyl ring; an equivalent orientation also prevails in benzo-



Fig. 1. Hydrogen bond stabilized orientation of syn-phenyl-2-pyridylketoxime.

phenone oxime. The mull spectra of benzophenone oxime and syn-HPPK are almost identical except that the band due to H-bonding is slightly shifted (cf. Fig. 2, Table 2). Free  $\nu$ (O-H) could not be observed in the mull spectra of either compound, whereas  $\nu$ (C-H) was observed at identical frequencies in both the spectra. The spectra of benzophenoneoxime in CCl<sub>4</sub>, and syn-HPPK in CHCl<sub>3</sub> (cf. Fig. 3) are nearly superimposable. The band assignments given in Table 2 were accomplished by reconstruction and summation process as outlined by Vandenbelt and Henrich[13].

The distinctive feature of the solution spectra is the complete resolution of free  $\nu(O-H)$ , band due H-bonding, and  $\nu(C-H)$ . It was also found that the ratio of areas under the free  $\nu(O-H)$  band, and the band to due H-bonding remained constant with varying concentration which confirmed that the H-bonding is intramolecular. The absence of free  $\nu(O-H)$  in the mull spectra is possibly due to the presence of intermolecular H-bonding as well, which further shifted the free  $\nu(O-H)$  band until it was completely masked by the broad band.

<sup>10.</sup> B. N. Figgis, Introduction to Ligand Fields, Chap. 10, Chap. 12. Interscience, New York (1966).

<sup>11.</sup> L. Joris, P. von Schleyer et al., J. Am. chem. Soc. 90, 327 (1968); 90, 4599 (1968); 91, 4801 (1969).

<sup>12.</sup> G. Varsanyi, Vibrational Spectra of Benzene Derivatives, p. 366. Academic Press, New York (1969).

<sup>13.</sup> J. M. Vandenbelt and C. Henrich, Appl. Spectrosc. 7, 173 (1953).



Fig. 2. Mull spectrum of (a) syn-phenyl-2-pyridylketoxime, (b) benzophenone oxime.

	Free $\nu$ (O-H) (cm <sup>-1</sup> )	H-bonded $\nu$ (O-H) (cm <sup>-1</sup> )	Coupled $\nu$ (O-H) (cm <sup>-1</sup> )	$\nu(C-H)$ (cm <sup>-1</sup> )	$\nu(C=N)$ (cm <sup>-1</sup> )	Overtone (C=N) (cm <sup>-1</sup> )
Benzophenone oxime (mull)	_	3260		3060		
Syn-HPPK (mull)		3190		3060		
Benzophenone oxime (CCl <sub>4</sub> )	3585	3280		3060	1490	2895
Syn-HPPK (CHCl <sub>3</sub> )	3570	3270		3060	1445	2895
[Mn(HPPK) <sub>2</sub> Cl <sub>2</sub> ] (mull)	$\sim 3250$	3130	2870	3060		
[Mn(HPPK),Cl,] (CHCl <sub>3</sub> )	$\sim 3250$	3140	2870	3060†	1420	2860
[Co(HPPK) <sub>3</sub> ](NO <sub>3</sub> ) <sub>2</sub> (mull)	~ 3500	3450	3060	3060‡	1470	masked
[Ni(HPPK),]Cl, (mull)	~ 3200	3000	2640	3060	1420	masked
[Pd(HPPK)(PPK)]Cl (mull)	~ 3460	3410	3040	masked	1400	$\sim 2790$

Table 2. Infrared spectral assignments\*

\*Assignments accomplished by reconstruction and summation, Ref. [14].

†Small band to the left of solvent  $\nu$ (C-H).

 $\pm$ Superimposed on coupled  $\nu$ (O-H).

The essential features of the spectra of the complexes are similar except that the spectrum of one complex may be shifted with respect to another. Sen and Dotson[5] have shown that the spectra of the complexes with ligands containing -OH function have three bands corresponding to free  $\nu$ (O-H), H-bonding where possible, and a third broad band due to the coupling of OH frequency and one of the symmetry allowed vibrations of the complex frame-work. The band due free  $\nu$ (O-H) may or may not be observed, depending upon the intensity of the other two bands. Hydrogen bond stabilized configuration of the ligand allows coordination of the metal ion via pyridine and oxime nitrogen atoms only, and precludes coordination via oxygen atoms (also confirmed by model building).

Both the mull and the solution spectral band of  $[Mn(HPPK)_2Cl_2]$  extend from 3300 to 2900 cm<sup>-1</sup>, and these bands are resolvable into three components [5]. The first of the two superimposed weak bands (~ 3060 cm<sup>-1</sup>) is due to  $\nu$ (C-H), the



Fig. 3. (a) Solution (CCl<sub>4</sub>) spectra of benzophenone oxime; (1) 0.05 M, (2) 0.075 M, (3) 0.1 M. (b) Solution (CHCl<sub>3</sub>) spectra of syn-phenyl-2-pyridylketoxime; (1) 0.05 M, (2) 0.075 M, (3) 0.1 M.



Fig. 4. (a) Solution (CHCl<sub>3</sub>) spectra of  $[Mn(HPPK)_2Cl_2]$ ; (1) 0.025 M, (2) 0.033 M, (3) 0.05 M. (b) Mull spectrum of  $[Mn(HPPK)_2Cl_2]$ .

second one at ~ 2870 cm<sup>-1</sup> is probably the overtone of  $\nu$ (C=N). This weak band is also easily observed in the solution spectra (cf. Fig. 4) of benzophenone oxime and HPPK. There is a sharp band around  $1420 \text{ cm}^{-1}$  in the spectra of the complexes, and there is a sharp and strong band at  $1445 \text{ cm}^{-1}$  in the spectrum of HPPK; the corresponding band in the spectrum of benzophenone oxime is observed at 1475 cm<sup>-1</sup>. We assign this to  $\nu$ (C=N) of the oxime function. Normally  $\nu$ (C=N) is observed between 1685–1650 cm<sup>-1</sup>; we believe that this shift is due to inductive electron withdrawal resulting from strong hydrogen bonding. Coordination through nitrogen atom causes a further small depletion in the electron density in C=N region causing only a small shift ( $\sim 20 \text{ cm}^{-1}$ ). The weak overtone bands are observed at expected frequencies in the spectrum of the ligand as well as in the spectrum of Mn(II) complex. The overtone band may be discerned only as a shoulder on the second broad band of the spectra of the other complexes. The small but consistent shift of  $\nu$ (C=N) and its overtone lends further evidence to the conclusion that coordination is via nitrogen atom of the oxime group leading to a five-membered ring containing the metal atom in all the complexes reported.

As in the case of the free ligand, the ratio of the areas under free  $\nu$ (O–H) and  $\nu$ (H-bonded) was constant in the case of spectra of Mn(II) complex in CHCl<sub>3</sub> at various concentrations. Further, both the areas obeyed Lambert-Beer's Law. This proves that H-bonding is intramolecular in the complexes also.

The general features of the mull spectra of  $[Co(HPPK)_3](NO_3)_2$  and [Pd-(HPPK)(PPK)]Cl (cf. Fig. 5) are similar to those of the mull spectrum of Mn(II) complex. Although the spectrum of  $[Ni(HPPK)_3](NO_3)_2$  (cf. Fig. 5) is structurally similar to the other spectra, it differs from the others in a number of ways. The very intense and broad band centered around 2640 cm<sup>-1</sup> indicates strong coupling of OH and framework vibrations which also accounts for the very large shift of the entire band system. The mull spectrum of  $[Pd(PPK)_2]$ , as expected, shows no band in this region.



Fig. 5. Mull spectrum of (1)  $[Ni(HPPK)_3]Cl_2$ , (2)  $[Co(HPPK)_3](NO_3)_2$ , (3) [Pd(HPPK)-(PPK)]Cl.

[Mn(HPPK) <sub>2</sub> Cl <sub>2</sub> ]:	A band beginning at 22,000 merged into a strong band starting at 32,000; shoulders at 28,400, 28,800, 31,200
0.36 M Mn(ClO <sub>4</sub> ) <sub>2</sub> :	18,600, 22,900, 24,000, 25,150, 27,900, 29,700, 32,400
$[Co(HPPK)_3](NO_3)_2$ :	Two overlapping bands with peaks at 21,300, 24,400
0.021 M Co(BF <sub>4</sub> ) <sub>2</sub> :	8,000 (very weak), 19,600, 21,600 (overlapping)
[Ni(HPPK) <sub>3</sub> ]Cl <sub>2</sub> :	A band starting at 15,400 with a distinct shoulders at
	25,000, beyond 30,000
0.0025 M Ni(ClO <sub>4</sub> ) <sub>2</sub> :	8,700, 14,500, 25,000
[Pd(HPPK)(PPK)]Cl:	A strong band starting at 20,000 with shoulders at 23,200 and 30,000 merged into an intense band beyond 33,000
0.00146 M [PdCl <sub>4</sub> ] <sup>2-</sup> :	23,000 ( $\epsilon = 200$ ), 30,000 ( $\epsilon \sim 400$ ), C. T. band at 36,000

Table 3. Summary of electronic spectra\* (cm<sup>-1</sup>)

\*Spectral assignments of aquo-cations taken from Ref. [10].

Because of the poor solubility, Nujol mulls of the complexes on filter paper were used for recording electronic spectra. The quality of the spectra was rather poor, and resolution of the bands was not good, therefore we refrain from making any assignment. The electronic spectral features are summarized in tabular form (Table 3); the characteristic features of the spectra of the corresponding  $[M(H_2O)_6]^{n+}$  ion and  $[PdCl_4]^{2-}$  ion are also quoted in Table 3 for comparison[10]. The spectra of Mn(II), Co(II) and Ni(II) are quite reminiscent of the spectra of corresponding hexaaquo ions. The resolution of Mn(II) complex spectrum was poor, however, it should be remembered that the extinction coefficients of the bands of  $[Mn(H_2O)_6]^{2+}$  spectrum are small. No shoulder was observed at 8000 cm<sup>-1</sup> in the spectrum of Co(II) complex corresponding to this low intensity band in the spectrum of  $[Co(H_2O)_6]^{2+}$ . The low intensity bands at 8,700 cm<sup>-1</sup> and 14,500 cm<sup>-1</sup> were also not observed in the spectrum of the Ni(II) complex. Resemblence between the spectra of [Pd(HPPK)(PPK)]Cl and square planar ion  $[PdCl_4]^{2-}$  is quite unmistakable.