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### The Infrared and Raman Spectra of 4-Phenylpyridine and Its Hofmann Type Complexes.

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## THE INFRARED AND RAMAN SPECTRA OF 4-PHENYLPYRIDINE AND ITS HOFMANN TYPE COMPLEXES.

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### ABSTRACT

The Infrared and Raman spectra of 4-Phenylpyridine are reported for the first time in the 4000-400 $\text{cm}^{-1}$  range. Vibrational assignments have been made for fundamental modes on the basis of frequency shifts of coordinated ligand, infrared and Raman band contours and comparison with the assignments for related molecules. The infrared spectra of M (4-Phenylpyridine)  $\text{Ni}(\text{CN})_4$  complexes (M=Mn, Ni or Cd) are reported. Their structure consists of polymeric layers of  $[\text{M}-\text{Ni}(\text{CN})_4]_{\infty}$  with the 4-phenylpyridine molecules bound to metal (M), similar to the structure found in Hofmann type host complexes.

### 1. INTRODUCTION

Gupta and Kusakov[1] was reported IR absorption spectrum of  $\gamma$ -phenylpyridine in the range of 600-2000 $\text{cm}^{-1}$  and the characteristic frequencies and forms of the normal

vibrations were calculated on the valence force scheme. Recently Nassimbeni et. al. [2,3] have studied the structures of the Werner clathrates formed with  $[\text{Ni}(\text{NCS})_2 (4\text{Phpy})_4]$  as host compounds. We have extended Gupta and Kusokov's study and report for the first time the IR and Raman spectra of 4-Phenylpyridine in the solid phase. In addition, we prepared three new 4-Phenylpyridine- metal- tetracyanonickelate complexes  $\text{M}(4\text{-Phpy}) \text{Ni} (\text{CN})_4$ , ( $\text{M}=\text{Mn}$ ,  $\text{Ni}$  or  $\text{Cd}$ ,  $4\text{-Phpy}=4\text{-Phenylpyridine}$  and abbreviated henceforth as  $\text{M-Ni-4-Phpy}$ ). These complexes are analogous to the previously reported Hofmann type complexes [4,5].

## 2.EXPERIMENTAL

Spectroscopically pure 4-Phenylpyridine in the solid form was obtained from Aldrich Chemical company, U.S.A and used without further purification. The complexes were prepared by the method analogous to that used for 4,4' bipyridyl complexes [5].

The IR spectra of samples are recorded on Perkin Elmer 621 and Shimadzu FTIR 8101 spectrophotometer using mulls and KBr pellet technique in the region  $4000\text{-}400\text{cm}^{-1}$ . The Raman spectra of the samples in a spinning cell were excited using  $514.5\text{nm}$  line of Spectra-Physics Model 2016-4s  $\text{Ar}^+$  ion laser and recorded on a Jobin Yuan U 1000 spectrometer which was calibrated against the laser plasma emission lines.

## 3.RESULTS AND DISCUSSION

The IR and Raman spectra of 4-Phenylpyridine molecules are given in Figures 1a and 1b, respectively. The IR and Raman spectra of  $\text{Cd} (4\text{-Phpy}) \text{Ni}(\text{CN})_4$  complex are given in Figures 2a and 2b, respectively. The observed frequencies in the infrared and Raman spectra of the molecule and its complexes, their approximate intensities and probable assignment are given in Table 1. The vibrational wavenumbers of the  $\text{Ni}(\text{CN})_4$  group

vibrations of the M-Ni-4Phpy complexes are given in Table 2. Table 1 and Table 2 included some relevant spectral data for comparison.

### 3.1. 4-PHENYLPYRIDINE

4-phenylpyridine belongs to the point group  $C_{2v}$  and hence it has 57 fundamental modes of vibration: of these, 39 are planar with 20 of class  $A_1$  and 19 of class  $B_1$  and 18 are non-planar with 7 of class  $A_2$  and 11 of class  $B_1$ . All these vibrations are Raman active but only the vibrations of classes  $A_1$ ,  $B_1$ , and  $B_2$  are infrared active.

It has been noted that IR and Raman data on 4-phenylpyridine and its complexes are not plentiful in the literature. The only available IR data on solid  $\gamma$ -phenylpyridine was reported by Gupta [1] who carried out a normal coordinate analysis using a valence force field. However, he only gave the characteristic frequencies and forms of the normal vibrations of  $\gamma$ -phenylpyridine which have been assigned to  $A_1$  and  $B_1$  species, in the range of 600-2000 $\text{cm}^{-1}$ . In addition, some IR bands of  $\gamma$ -phenylpyridine at 1640, 1597, 1285, 1195 and 1170 $\text{cm}^{-1}$  have been assigned to both in  $A_1$  and  $B_1$  symmetry species. Also, he assigned twice the 1006 $\text{cm}^{-1}$  and 1078 $\text{cm}^{-1}$  bands to  $A_1$  and  $B_1$  symmetry species, respectively. Therefore; we did not use his assignments in present work. In this study, the vibrational assignments of 4-phenyl pyridine are analysed using IR and Raman spectra of the solid sample and its metal complexes.

The  $C_{2v}$  fundamental modes of the 4-phenylpyridine and pyridine each give rise in crystalline biphenyl ( $D_{2h}$  symmetry) to two modes; a "g" and a "u" mode. Since, all g modes are infrared active and all u modes are Raman inactive, no ambiguity is likely to arise in referring to the vibrations in terms of the  $C_{2v}$  classes from which they are derived. The  $D_{2h}$  and  $C_{2v}$  fundamentals are related as follows:

$$\begin{array}{ll} C_{2v} & A_1 \rightarrow A_g + B_{1u} \\ & B_2 \rightarrow B_{2u} + B_{3g} \end{array} \quad D_{2h}$$

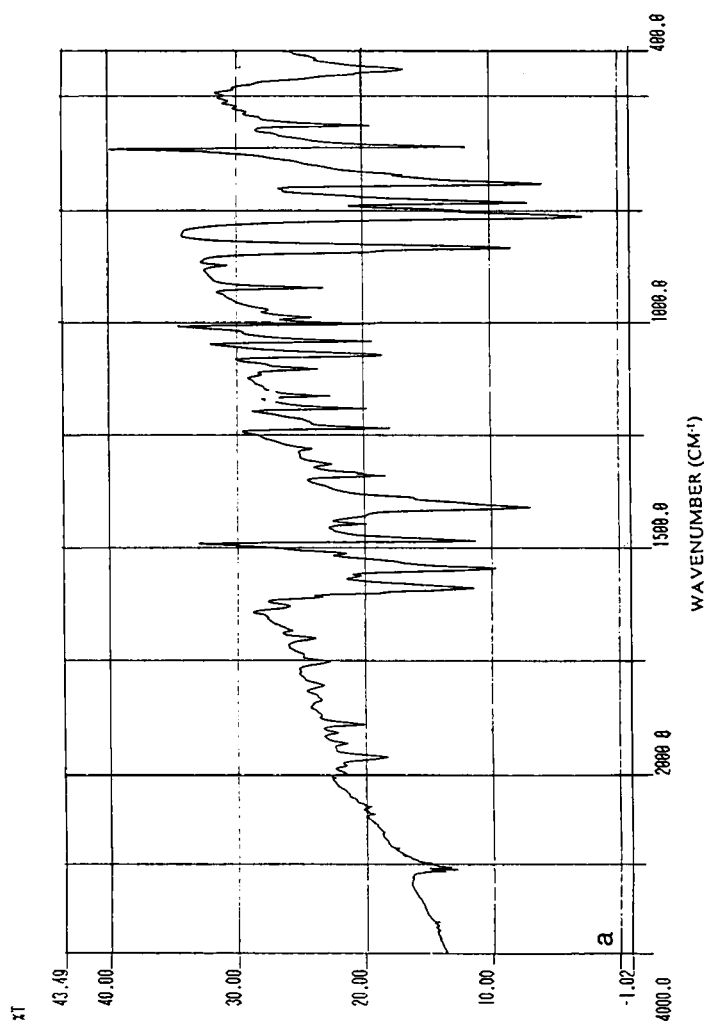


Figure 1a: Infrared spectrum of 4-phenylpyridine molecule.

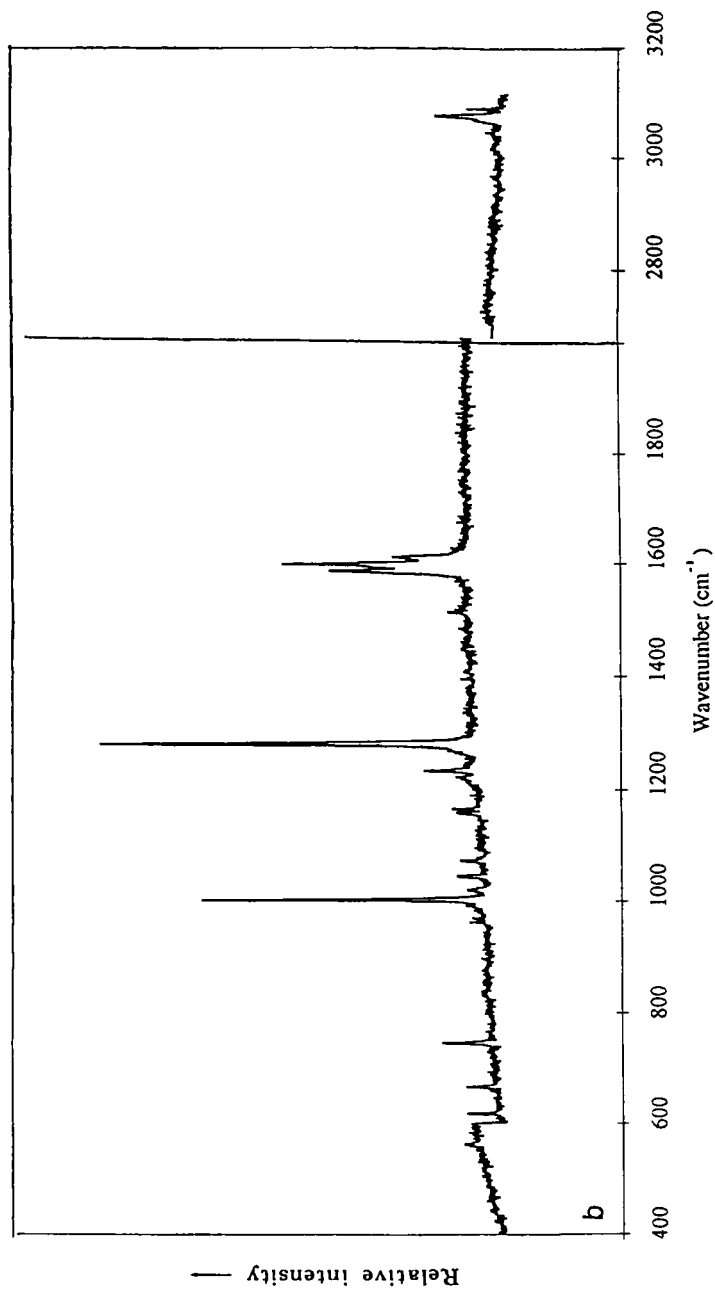


Figure 1b: Raman spectrum of 4-phenylpyridine molecule.

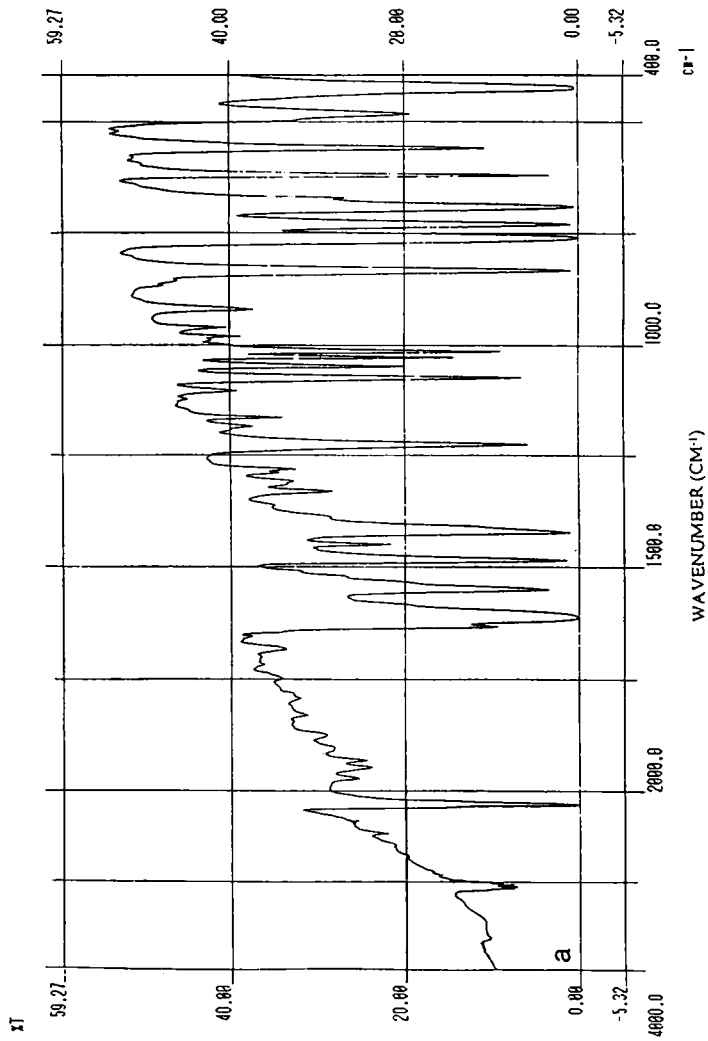


Figure 2a. Infrared spectrum of Cd (4-pheny) Ni (CN)<sub>4</sub> complex.



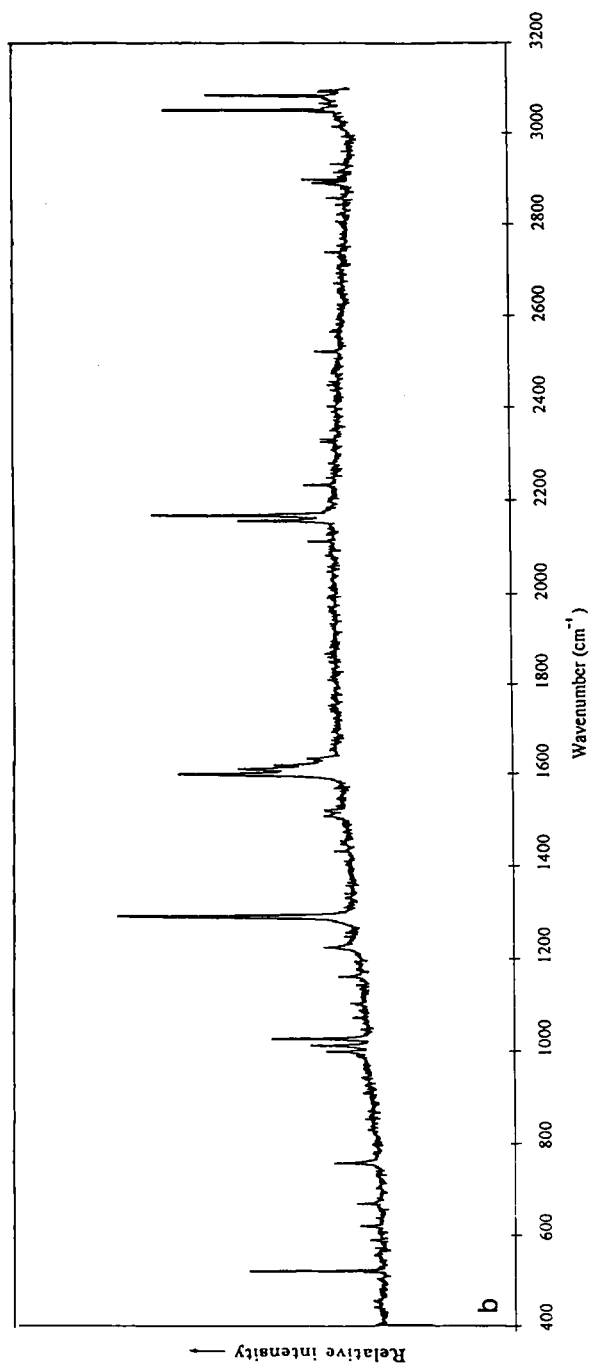


Figure 2b: Raman spectrum of Cd (4-phenpy) Ni (CN)<sub>4</sub> complex.

Table I.  
The fundamental vibrational wavenumbers (cm<sup>-1</sup>) of 4-phenylpyridine

Symmetry and Description Mode	Biphenyl <sup>a</sup>		Pyridine <sup>b</sup>		4-phenyl pyridine (This study)		Mn		M-Ni-4 phenyl pyridine Cd		Ni	
	IR	Raman	IR	IR	Raman	IR	IR	IR	Raman	IR	IR	IR
<b>A<sub>1</sub></b>												
ν(CH)	3088 s	-	3053 w	3083w	3083m	3084w	3085w	3084s	3085w			
ν(CH)	3054 s	3055	3053 vw	3060m	3062m	3061m	3061m	3064m	3064m			
ν(CH)	3047 s	-	3036 w	3038w	3041w	3040w	-	3041w	3041w			
ν(CH)	-	-	-	3028w	3031w	3030w	3031w	3033m	3030w			
ν(CH)	-	-	-	-	-	-	-	-	-			
ν <sub>ring</sub>	1597 vw	1605 vs	-	1609vw	1614s	-	1620m	1621m	-			
ν <sub>ring</sub>	-	-	-	1599vw	1601vs	-	-	1600vs	-			
ν <sub>ring</sub>	-	-	1582 vs	1588s	1587s	1610vs	1611vs	1612s	1613vs			
ν <sub>ring</sub>	1481 m	-	1482 s	1512m	1514m	1518w	1520m	1519m	1520w			
ν <sub>ring</sub>	-	-	-	1484s	-	1475vs	1476vs	1478w	1476vs			
δ(CH)	-	-	-	1410ms	1396w	1421s	1422vs	1411m	1424m			
ν <sub>ring</sub> + δ(CH)	-	1273 vs	-	1279w	1283vs	1288w	1288v	1292vs	1290w			
δ(CH)	1179 w	1206 w	1217 s	1233s	1224m	1218vs	1218vs	1225m	1226vs			
ν <sub>ring</sub>	1038 w	1032 m	1029 s	1042s	1044m	1044s	1044s	1047w	1045s			
ring breathing	1005 m	998 vs	990 s	1001s	1002vs	1011s	1011vs	1014s	1013vs			
δring	-	-	-	832vs	839w	830vs	830vs	830w	830vs			
δring + ν <sub>ring</sub>	-	738 w	-	762vs	747s	758vs	758vs	758s	759vs			
δring	610 w	607 w	604 m	608s	618s	618vs	619vs	621m	621vs			
δring	460 m	-	-	438s	440w	481ms	482ms	481w	482ms			
δring	-	-	-	-	-	-	-	-	-			
<b>B<sub>1</sub></b>												
ν(CH)	3076	-	3079 m	-	3070s	3074w	3073w	3075s	3075w			
ν(CH)	3038	-	3026 w	3008w	3014mw	3014m	3013w	3016mw	3016mw			
ν(CH)	-	-	-	-	-	-	-	-	-			
ν(CH)	-	-	-	-	-	-	-	-	-			
ν <sub>ring</sub>	-	-	-	1630w	1630w	-	1632w	1635w	-			
ν <sub>ring</sub>	1570 s	-	1574m	1543s	1540w	1547s	1549s	1545w	1551s			
ν <sub>ring</sub>	1435	1459	1488vs	1447w	1449m	-	-	1453w	-			
ν <sub>ring</sub>	1343	-	1355w	1341mw	1337m	1331w	1331m	1332w	-			
ν <sub>ring</sub>	-	-	-	1314mw	1302m	1307mw	1308mw	1303w	1307mw			
δ(CH)	1265 m	-	1235w	-	1236m	-	-	1231m	-			
δ(CH)	1168	1160	1147s	1190m	1191w	1181w	1181w	1189mw	1182w			
δ(CH)	1152	-	-	1163m	1166m	1159m	1159m	1163m	1159m			
δ(CH)	1089	1097	-	1104ms	1096w	1098m	1100m	1103w	1100m			
ν <sub>ring</sub>	-	-	1068s	1073s	1073m	1072s	1073s	1071m	1075s			
δ(CH)	-	-	-	1017mw	1020m	1024 s	1025s	1027ms	1026s			
δring	-	-	650w	868m	870w	-	868w	870w	-			
δring	550	-	-	561s	562m	557s	557s	557w	558s			
δring	-	329	-	-	-	-	-	-	-			
δring	-	-	-	-	-	-	-	-	-			
<b>B<sub>1</sub></b>												
γ(CH)	982	-	939m	-	983w	973mw	978mw	979mw	978mw			
γ(CH)	966	-	-	965w	962m	959mw	959mw	-	959mw			
γ(CH)	902	-	882vw	918m	915w	918m	918m	920w	919m			
γ(CH)	-	-	-	887w	-	887w	-	-	-			
γ(CH)	731	-	746	731s	731m	729vs	731s	731w	731s			
γ <sub>ring</sub>	698	-	703vs	687vs	694m	691vs	691vs	693w	691vs			
γ <sub>ring</sub>	460	-	405m	-	399m	-	-	391m	-			
γ <sub>ring</sub>	-	-	-	-	-	-	-	-	-			
γ <sub>ring</sub>	-	-	-	-	-	-	-	-	-			

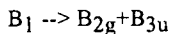
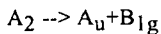
<sup>a,b</sup> taken from reference [4,5], respectively. vs: very strong, s: strong, m: medium, w: weak, vw: very weak.

Table 2

The Vibrational wavenumbers ( $\text{cm}^{-1}$ ) of the  $\text{Ni}(\text{CN})_4$  group of the M-Ni-4-Phpy complexes and in other host complexes.

Assignment	M-Ni-Pya			M-Ni-bipy <sup>b</sup>			M-Ni-4-Phpy			Relative Intensity
	Mn	Cd	Ni	Cd	Ni		Mn	Cd	Ni	
$A_{1g}$ $\nu(\text{CN})$		(2172)	(2186)	(2166)				(2169)		vs
$B_{1g}$ $\nu(\text{CN})$		(2160)	(2177)	(2153)				(2156)		s
$E_u$ $\nu(\text{CN})$	2155	2164	2170	2147	2164		2147	2151	2185	vs
$\nu(^{13}\text{CN})$	2144	2111	2139	2105	2132		2101	2106	2122	vw
$E_u$ $\nu(\text{NiC})$	545	543	550	540	552		545	543	549	vw
$A_{1g}$ $\pi(\text{NiCN})$	-	-	-	444	451		-	-	-	vw
$E_u$ $\delta(\text{NiCN})$	432	425	441	426	438		425	426	431	vs

The bands observed in the infrared spectra are given without parentheses, the bands observed in the Raman Spectra are given in parentheses.  
<sup>a,b</sup> Taken from reference, [4, 5] respectively. <sup>c</sup> Overlapped with 4-phenylpyridine band.



The comparison with the corresponding assignments of biphenyl [6] and pyridine [4], has helped in carrying out the vibrational assignments. In addition, some 4-phenylpyridine vibrational modes observed in the IR and Raman spectra of metal complexes are found to shift towards higher frequencies compared to free molecule. For these  $A_1$  modes the direction of the motion of the nitrogen atom, is in the same direction as M-N bond. Therefore, we suggest that a major upward shift in these  $A_1$  modes may arise from coupling with the M-N stretching mode. Similar shifts had been observed in the 4,4'-bipyridyl [5] and pyridine [4] complexes and explained by coupling with low frequency vibrations, particularly the M-N stretching frequency. Since the vibration frequency of  $\nu(M-N)$  is found in the range  $200-300\text{cm}^{-1}$  [7-10], we could not observe this vibration band in the IR and Raman spectra of the metal complexes. However, the effect of the coupling is observed especially at the low frequencies of  $A_1$  modes [4]. This result was also used as a basis for the vibrational assignments of the 4-phenylpyridine molecule.

We tentatively assigned the observed  $\nu(\text{CH})$  bands by comparison with those found for the biphenyl and pyridine molecules.

#### **$A_1$ symmetry species**

Steele and Lippincott [6] assigned IR bands at 1597, 1481, 1179, 1038 and  $1005\text{cm}^{-1}$  and Raman bands at 1273 and  $738\text{cm}^{-1}$  of the biphenyl molecule as a fundamental vibrational mode of  $A_1$  symmetry species. We observed similar IR bands at 1609, 1512, 1233, 1038 and  $1001\text{cm}^{-1}$  and Raman bands at 1283 and  $747\text{cm}^{-1}$  of the 4-phenylpyridine shifted to higher frequency on coordination. Therefore, they are

assigned to  $A_1$  type fundamentals which are compatible with those for the biphenyl. The  $\nu_{15}$  mode (the out-of phase component of the ring breathing mode) is assigned to a strong IR band  $1001\text{cm}^{-1}$ . This is because we observed the corresponding band at  $1002\text{cm}^{-1}$  as a very strong band in the Raman spectrum of crystalline 4-phenylpyridine. Our assignment is also compatible with those for the biphenyl ( $1005\text{cm}^{-1}$ ) [6] and pyridine ( $990\text{cm}^{-1}$ ) [4] molecules. As discussed above we could not observe  $\nu(\text{M-N})$  band in the IR and Raman spectra of metal complexes. However, the effect of the coupling is observed especially at the lower frequencies of  $A_1$  symmetry species. Steele and Lippincott [6] have assigned the band at  $550\text{cm}^{-1}$  to the  $A_1$  fundamental for the biphenyl molecule. However, Dale [11] has assigned the  $550\text{cm}^{-1}$  band to the lowest  $B_2$  ring deformation and the  $606\text{cm}^{-1}$  band to the  $A_1$  fundamental. We observed strong IR bands at  $608\text{cm}^{-1}$  and  $561\text{cm}^{-1}$ , in the spectrum of 4-phenylpyridine. The  $608\text{cm}^{-1}$  band shifted to a higher frequency ( $\sim 11\text{cm}^{-1}$ ) on coordination; however, the  $561\text{cm}^{-1}$  band slightly shifted. As discussed above the  $A_1$  modes tend to show increases in frequency on coordination. Therefore we assigned the  $608\text{cm}^{-1}$  band to  $A_1$  symmetry mode ( $\nu_{19}$ ) in agreement with the assignment of Dale [11]. As inferred from table 1, the IR band at  $438\text{cm}^{-1}$  shifted to a higher frequency ( $\sim 44\text{cm}^{-1}$ ) on coordination. This band is assigned to  $\nu_{20}$ . We observed similar shifts ( $\sim 45\text{cm}^{-1}$ ) in the infrared spectrum of  $\text{Cd}(4\text{-Phpy})\text{Cl}_2$  complexes. The information about these complexes will be given in detail elsewhere.

### **$B_2$ symmetry species**

The  $B_2$ -type fundamentals of 4-phenylpyridine are chosen and assigned by a comparison with the biphenyl [6] and pyridine [4] molecules. This leaves only the in-plane ring deformation vibrations which belong to the  $B_2$  symmetry species. We

observed a strong IR band at  $561\text{ cm}^{-1}$  in the spectra of 4-phenylpyridine is assigned to the lowest  $B_2$  ring deformation in agreement with the assignment of Dale [11]. Katon and Lippincott [12] have assigned these frequencies of  $302\text{ cm}^{-1}$  and  $140\text{ cm}^{-1}$  for the biphenyl molecule. We could not observe IR bands in the range  $200\text{--}300\text{ cm}^{-1}$ .

### **$B_1$ symmetry species**

The highest  $\gamma$  (CH) vibration frequency is expected to be about  $980\text{ cm}^{-1}$  by comparison with the biphenyl molecule. This mode usually gives rise to quite weak absorption in contrast to the lower frequency  $\gamma$  (CH) modes of this class. We observed a weak IR band at  $985\text{ cm}^{-1}$  as out-of plane C-H deformation. Also, the strong infrared band in the spectra of 4-phenylpyridine at  $731\text{ cm}^{-1}$  are readily assigned to lower out-of plane C-H deformation frequency.

### **$A_2$ symmetry species**

These vibrations are infrared inactive but Raman active for free molecule and are infrared active in principle in the crystal. Steele and Lippincott [6] have assigned the band at  $841\text{ cm}^{-1}$  to the  $A_2$  fundamental for the biphenyl molecule. Therefore we assigned the Raman band observed at  $839\text{ cm}^{-1}$  to out-of-plane CH deformation.

There are some uncertainties over the assignments of  $A_2$  symmetry species for the biphenyl and pyridine molecules. Therefore it is very difficult to find the corresponding modes for 4-phenylpyridine to assign the vibrational bands as the  $A_2$  fundamentals.

## **3.2. The $\text{Ni}(\text{CN})_4$ GROUP VIBRATIONS**

The assignment of the observed bands in Table 2 is made on the basis of  $D_{4h}$  symmetry assumed for  $\text{Ni}(\text{CN})_4$  group in the M-Ni-4-Phpy complexes. The  $\nu(\text{CN})$  and  $\delta(\text{NiCN})$

vibrational wavenumbers are found to be similar to those of Hofmann type complexes [4,5] showing that the  $[M-Ni(CN)_4]_{\infty}$  layers have been preserved. Since we observed only one  $\nu(CN)$  ( $E_u$ ) band in the IR spectrum and the other two  $\nu(CN)$  ( $A_{1g}$  and  $B_{1g}$ ) bands in the Raman spectrum of the Cd-Ni-4-Phpy complex, we propose a square planar environment around the tetracyanonickelate ion.

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