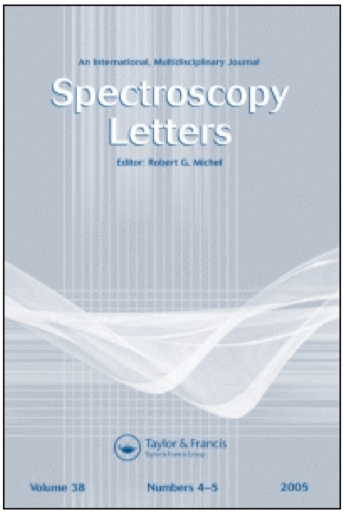

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The Infrared and Raman Spectra of 4-Phenylpyridine and Its Hofmann Type Complexes.

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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 4000-400cm^{-1} range. Vibrational assignments have been made for fundemental modes on the basis of frequency shifts of coordinated ligand, infrared and Raman band contours and comparision with the assignments for related molecules. The infrared spectra of M (4-Phenylpyridine) Ni(CN)$_4$ complexes (M=Mn,Ni or Cd) are reported. Their structure consists of polymeric layers of [M-Ni(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 γ-phenylpyridine in the range of 600-2000cm^{-1} and the characteristic frenquencies 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 $[Ni(NCS)_2 (4Phpy)_4]$ 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 addidion, we prepared three new 4-Phenylpyridine- metal- tetracyanonickelate complexes $M(4\text{-}Phpy)\ Ni\ (CN)_4$, (M=Mn, Ni or Cd, 4-Phpy=4-Phenylpyridine and abbreviated henceforth as M-Ni-4-Phpy). These complexes are anologous 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 anologous 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 4000-400cm^{-1}. The Raman spectra of the samples in a spinning cell were exited using 514.5nm line of Spectra-Physics Model 2016-4s 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 Cd (4.Phpy) $Ni(CN)_4$ 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 aproximate intensities and probable assignment are given in Table 1. The vibrational wavenumbers of the $Ni(CN)_4$ 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 γ-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 γ-phenylpyridine which have been assigned to A_1 and B_1 species, in the range of 600-2000cm^{-1}. In addition, some IR bands of γ-phenylpyridine at 1640, 1597, 1285,1195 and 1170cm^{-1} have been assigned to both in A_1 and B_1 symmetry species. Also, he assigned twice the 1006cm^{-1} and 1078cm^{-1} bands to A_1 and B_1 symmetry species, respectively. Therefore; we did not use his assigments 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 ambiquity 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:

C_{2v} $A_1 \dashrightarrow A_g+B_{1u}$ D_{2h}

$B_2 \dashrightarrow B_{2u}+B_{3g}$

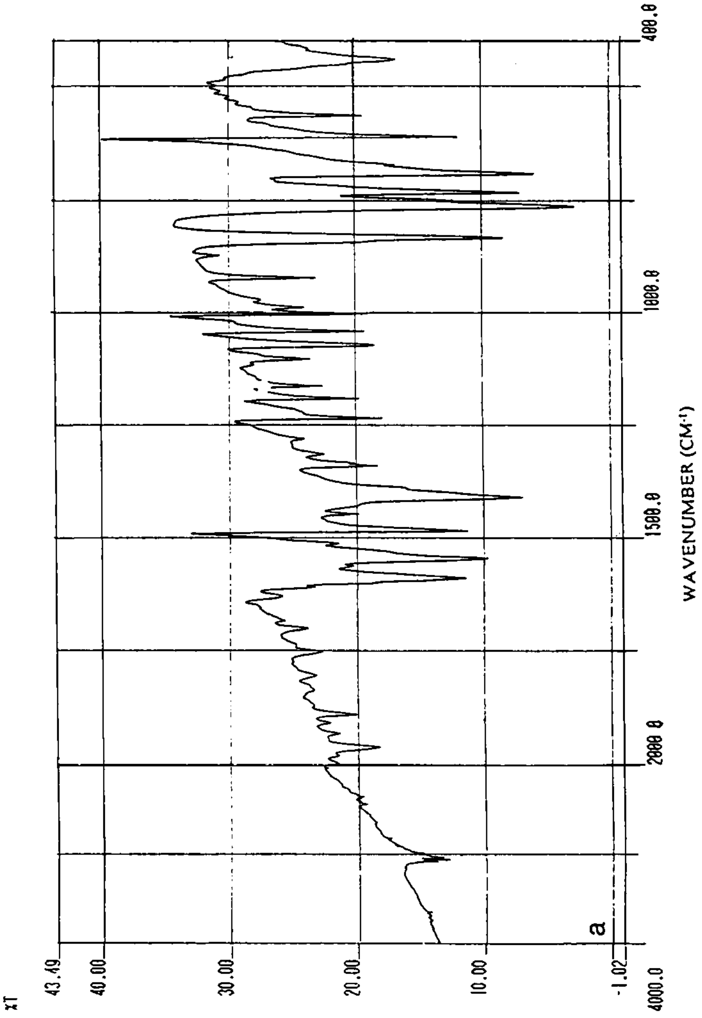

Figure 1a: Infrared spectrum of 4-phenylpyridine molecule.

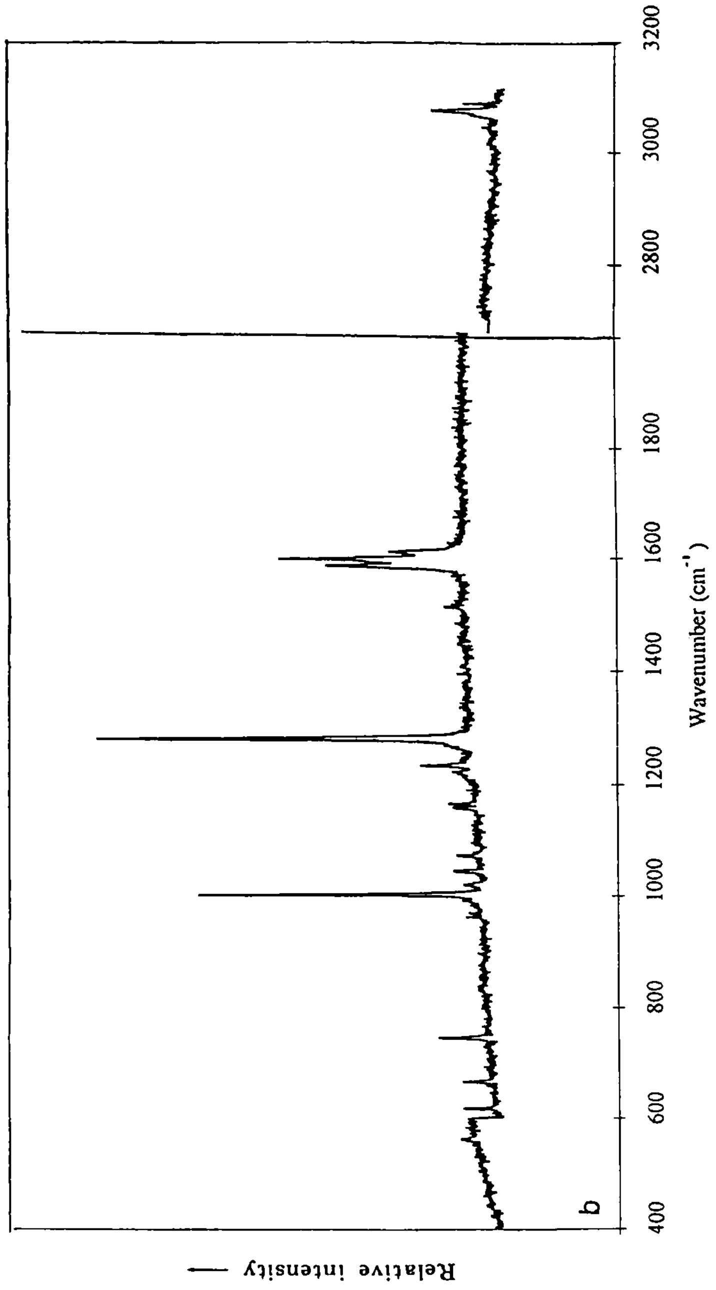

Figure 1b: Raman spectrum of 4-phenylpyridine molecule.

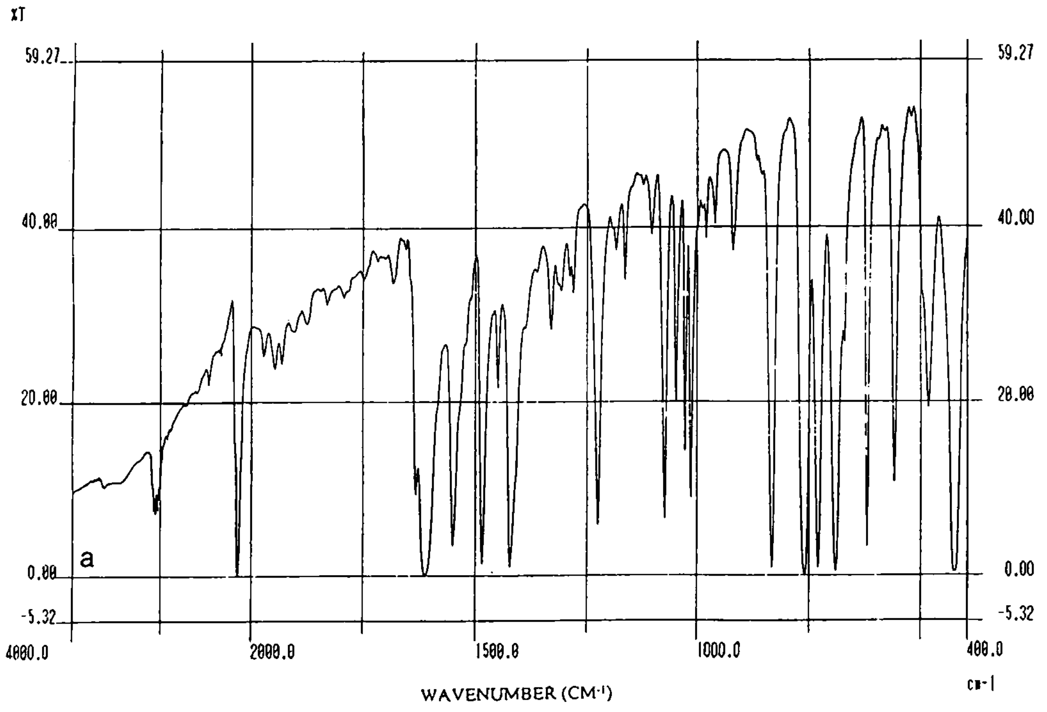

Figure 2a: Infrared spectrum of Cd (4-phpy) Ni $(CN)_4$ complex.

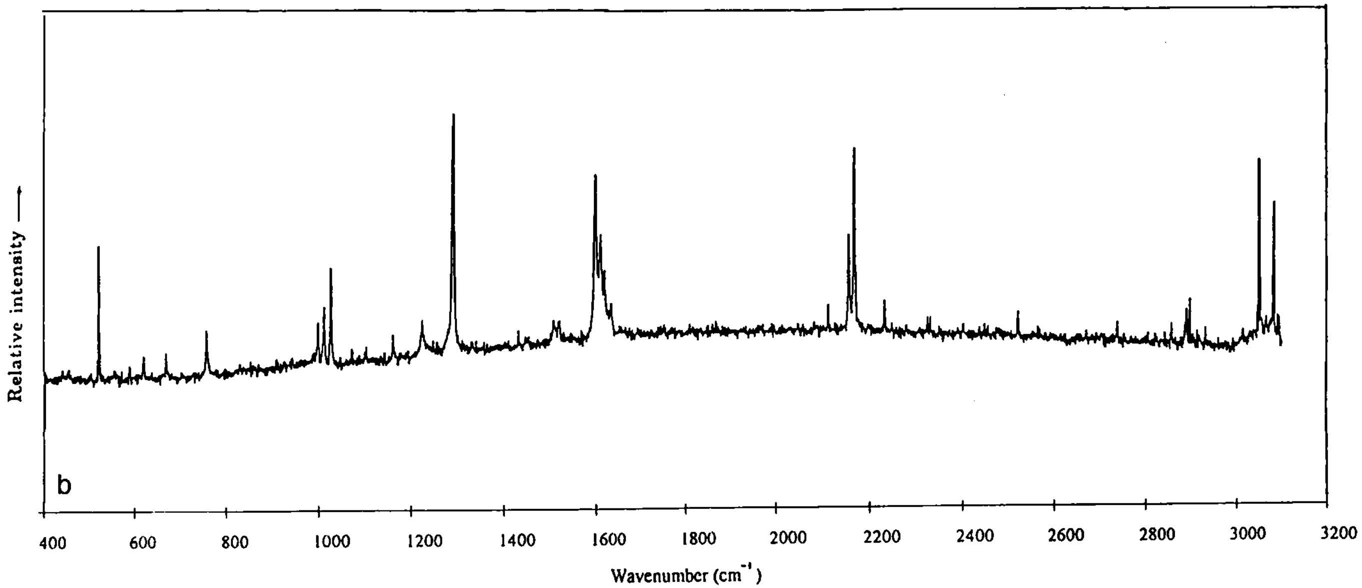

Figure 2b: Raman spectrum of Cd (4-phpy) Ni $(CN)_4$ complex.

Table 1.
The fundamental vibrational wavenumbers (cm^{-1}) of 4-phenylpyridine

Symmetry and Description Mode	Biphenyl[a]		Pyridine[b]	4-phenyl pyridine (This study)		M-Ni-4 phenyl pyridine			
						Mn	Cd		Ni
	IR	Raman	IR	IR	Raman	IR	IR	Raman	IR
A_1									
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_{ring}	1597 vw	1605 vs	-	1609vw	1614s	-	1620m	1621m	-
ν_{ring}	-	-	-	1599vw	1601vs	-	-	1600vs	-
ν_{ring}	-	-	1582 vs	1588s	1587s	1610vs	1611vs	1612s	1613vs
ν_{ring}	1481 m	-	1482 s	1512m	1514m	1518w	1520m	1519m	1520w
ν_{ring}	-	-	-	1484s	-	1475vs	1476vs	1478w	1476vs
δ(CH)	-	-	-	1410ms	1396w	1421s	1422vs	1411m	1424m
ν_{ring} + δ(CH)	-	1273 vs	-	1279w	1283vs	1288w	1288w	1292vs	1290w
δ(CH)	1179 w	1206 w	1217 s	1233s	1224m	1218vs	1218vs	1225m	1226vs
ν_{ring}	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_{ring}	-	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_2									
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_{ring}	-	-	-	1630w	1630w	-	1632w	1635w	-
ν_{ring}	1570 s	-	1574m	1543s	1540w	1547s	1549s	1545w	1551s
ν_{ring}	1435	1459	1488vs	1447w	1449m	-	-	1453w	-
ν_{ring}	1343	-	1355w	1341mw	1337m	1331w	1331m	1332w	-
ν_{ring}	-	-	-	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_{ring}	-	-	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_1									
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_{ring}	698	-	703vs	687vs	694m	691vs	691vs	693w	691vs
γ_{ring}	460	-	405m	-	399m	-	-	391m	-
γ_{ring}	-	-	-	-	-	-	-	-	-
γ_{ring}	-	-	-	-	-	-	-	-	-

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

Table 2

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

Assignment	M-Ni-Py[a]			M-Ni-bipy[b]		M-Ni-4-Phpy			Relative Intensity
	Mn	Cd	Ni	Cd	Ni	Mn	Cd	Ni	
A_{1g} ν(CN)		(2172)	(2186)	(2166)			(2169)		vs
B_{1g} ν(CN)		(2160)	(2177)	(2153)			(2156)		s
E_u ν(CN)	2155	2164	2170	2147	2164	2147	2151	2185	vs
ν(^{13}CN)	2144	2111	2139	2105	2132	2101	2106	2122	vw
E_u ν(NiC)	545	543	550	540	552	545	543	549	vw
A_{2u} π(NiCN)	-	-	-	444	451	-[c]	-[c]	-[c]	vw
E_u δ(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.

[a,b] Taken from reference, [4, 5] respectively. [c] Overlapped with 4-phenylpyridine band.

$A_2 \dashrightarrow A_u + B_{1g}$

$B_1 \dashrightarrow B_{2g} + B_{3u}$

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, particullary the M-N stretching frequency. Since the vibration frequency of ν(M-N) is found in the range 200-300cm^{-1} [7-10], we could not observed 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-pheylpyridine molecule.

We tentatively assigned the observed ν(CH) bands by comparasion with those found for the bipheny and pyridine molecules.

A_1 symmetry species

Steele and Lippincott [6] assigned IR bands at 1597, 1481, 1179, 1038 and 1005cm^{-1} and Raman bands at 1273 and 738cm^{-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 1001cm^{-1} and Raman bands at 1283 and 747cm^{-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 ν_{15} mode (the out-of phase component of the ring breathing mode) is assigned to a strong IR band 1001cm^{-1}. This is because we observed the corresponding band at 1002cm^{-1} as a very strong band in the Raman spectrum of crystalline 4-phenylpyridine. Our assignment is also compatible with those for the biphenyl (1005cm^{-1}) [6] and pyridine (990cm^{-1}) [4] molecules. As discussed above we could not observe ν(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 550cm^{-1} to the A_1 fundamental for the biphenyl molecule. However, Dale [11] has assigned the 550cm^{-1} band to the lowest B_2 ring deformation and the 606cm^{-1} band to the A_1 fundamental. We observed strong IR bands at 608cm^{-1} and 561cm^{-1}, in the spectrum of 4-phenylpyridine. The 608cm^{-1} band shifted to a higher frequency (~11cm^{-1}) on coordination; however, the 561cm^{-1} band slightly shifted. As discussed above the A_1 modes tend to show increases in frequency on coordination. Therefore we assigned the 608cm^{1} band to A_1 symmetry mode (ν_{19}) in agreement with the assignment of Dale [11]. As inferred from table 1, the IR band at 438cm^{-1} shifted to a higher frequency (~44cm^{-1}) on coordination. This band is assigned to ν_{20}. We observed similar shifts (~45cm^{-1}) in the infrared spectrum of Cd(4-Phpy)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 choosen 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 cm^{-1} in the spectra of 4-phenylpridine 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 302cm^1 and 140cm^{-1} for the biphenyl molecule. We could not observed IR bands in the range 200-300cm^{-1}.

B_1 symmetry species

The highest γ (CH) vibration frequency is expected to be about 980cm^{-1} by comparison with the biphenyl molecule. This mode usually gives rise to quite weak absorption in contrast to the lower frequency γ (CH) modes of this class. We observed a weak IR band at 985cm^{-1} as out-of plane C-H deformation. Also, the strong infrared band in the spectra of 4-phenylpyridine at 731cm^{-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 841cm^{-1} to the A_2 fundamental for the biphenyl molecule. Therefore we assigned the Raman band observed at 839 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 Ni $(CN)_4$ GROUP VIBRATIONS

The assignment of the observed bands in Table 2 is made on the basis of D_{4h} symmetry assumed for $Ni(CN)_4$ group in the M-Ni-4-Phpy complexes. The ν(CN) and δ(NiCN) vibrational wavenumbers are found to be similar to those of Hofmann type complexes [4,5] showing that the $[M\text{-}Ni(CN)_4]_\infty$ layers have been preserved. Since we observed only one ν(CN) (E_u) band in the IR spectrum and the other two ν(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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