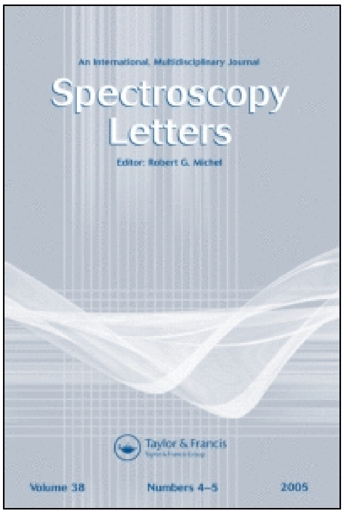

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Fourier Transform Infrared and Raman Spectra of 4-Vinylpyridine and its Transition Metal(II) Tetracyanonickelate Complexes

S. Bayari[a]; Ş. Yurdakul[b]
[a] Faculty of Education, Department of Physisc, Hacettepe University, Beytepe, Ankara, Turkey [b] Faculty of Art and Science, Department of Physics, Gazi University, Teknikokullar, Ankara, Turkey

To cite this Article Bayari, S. and Yurdakul, Ş.(2000) 'Fourier Transform Infrared and Raman Spectra of 4-Vinylpyridine and its Transition Metal(II) Tetracyanonickelate Complexes', Spectroscopy Letters, 33: 4, 475 — 483

To link to this Article: DOI: 10.1080/00387010009350132

URL: http://dx.doi.org/10.1080/00387010009350132

SPECTROSCOPY LETTERS, 33(4), 475–483 (2000)

FOURIER TRANSFORM INFRARED AND RAMAN SPECTRA OF 4-VINYLPYRIDINE AND ITS TRANSITION METAL(II) TETRACYANONICKELATE COMPLEXES

Key words: 4-vinylpyridine, FTIR spectra, Raman spectra, Hofmann-type complexes

S.Bayarı[a] and Ş. Yurdakul[b]

[a] Hacettepe University, Faculty of Education,, Department of Physisc, Beytepe 06532 Ankara, Turkey

[b] Gazi University,Faculty of Art and Science, Department of Physics, Teknikokullar, 06500 Ankara, Turkey

ABSTRACT

Infrared and Raman spectra (4000-200 cm^{-1}) were recorded for 4-vinylpyridine and vibrational assignments made for fundamental modes on the basis of frequency shifts of the coordinated ligand, of the group vibrational concept and comparison with the assignments for related molecules. The infrared spectra of M(4-vinylpyridine)$_2$Ni(CN)$_4$ (M= Mn,Cd,Fe,Co,Ni or Cu) are reported.

INTRODUCTION

To the best of our knowledge no complete vibrational assignment has been reported for liquid 4-vinylpyridine (4vpy), and its complexes are not plentiful in the literature [1]. The only available IR and Raman data on 4-vinylpyridine was reported by Green and Harrison [2] who gave an approximate vibrational assignment of 4-vinylpyridine by comparison with styrene. We have assigned the fundamental modes of 4-vinylpyridine on the basis of frequency shifts of the coordinated ligand, of the group vibrational concept (for a vinyl group), infrared intensity, and comparison with the assignment for pyridine [3] and 4-methylpyridine [4] and 4-ethylpyridine [5]. We have also prepared six new Hofmann-type complexes of the form $M(4vinylpyridine)_2Ni(CN)_4$ (where M= Mn, Cd, Fe, Co, Ni, or Cu and abbreviated henceforth as M-Ni-4vpy). The aim of this study is to present the results of infrared spectroscopic study of these new complexes, give further examples of layered tetracyanonickelate complexes, and to propose a vibrational assignment for the 4-vinylpyridine molecule.

EXPERIMENTAL

All starting chemicals used were reagent grade (Merck) and used without further purification. The potassium tetracyanonickelate was prepared by mixing stoichiometric amounts of nickel (II) chloride with potassium cyanide in water solution. The complexes were prepared by adding slightly more than two moles of 4-vpy and one mole of potassium tetracyanonickelate solution to one mole of M(II) chloride solution using constant stirring. The freshly prepared samples were analyzed for C, H, and N using a Leco, CHNS-932 type elemental analyser. The analyses confirmed the expected compositions.

The IR spectra of nujol mulls and KBr discs were recorded on a Perkin Elmer 621 and Mattson 1000 FT-IR spectrometers, which were calibrated using polystyrene. The Raman spectrum of 4-vpy was measured with a Jobin Yvon U1000 spectrometer using the 488.0 nm line of an argon ion laser.

RESULTS AND DISCUSSION

The infrared and Raman spectra of 4-vinylpyridine are given in Figs. 1 and 2, respectively. An incomplete assignment based upon Raman and infrared spectra has been made [2] by comparison with the spectra of styrene. General vibrational assignments proposed for the fundamentals of 4-vinylpyridine are given in Table 1 together with those for 4-ethylpyridine [5] and styrene [2] which are guides to the interpretation. For 4-vinylpyridine molecule (C_s point group) the vibrations comprise 27a"(planar) and 12a" (non-planar). Of these, 9 vibrations (6a' and 3a") are caused by the vinyl group. All vibrations are active in both infrared and Raman spectra.

The assignment of vibrational frequencies for pyridine has been extensively studied [3]. Many of the vibrational frequencies of the 4-vinylpyridine in which a single hydrogen atom is substituted for a $CH=CH_2$ group can be expected to be near to those of pyridine. In the 3100-2900 cm^{-1} region 7 frequencies were expected; 4 frequencies belonging to the ν(CH) pyridine ring vibration and 3 belonging to the vinyl group. The bands observed at 2987 and 2922 cm^{-1} were assigned to CH_2 asymmetric and symmetric stretching modes, respectively (Table 1).

The ν (C=C) gives good group vibrations in the region 1625±45 cm^{-1}. In the aromatic ring, which has a vinyl group, this vibration falls in the range 1630±10 cm^{-1} [8]. The medium band observed at 1635 cm^{-1} in liquid 4-vpy was assigned to ν (C=C) stretch.

The $\delta(CH_2)$ is located in the region 1055±35 and 1410±20 cm^{-1} [8]. The band observed at 1066 cm^{-1} in 4-vpy was assigned to $\delta(CH_2)$. The band at 1409 cm^{-1} was assigned to $\delta(CH_2)$ by Green and Harrison [2]. We observed a very strong band at 1408 cm^{-1} in the IR spectrum of 4-vpy molecule. This band shows a frequency shift on

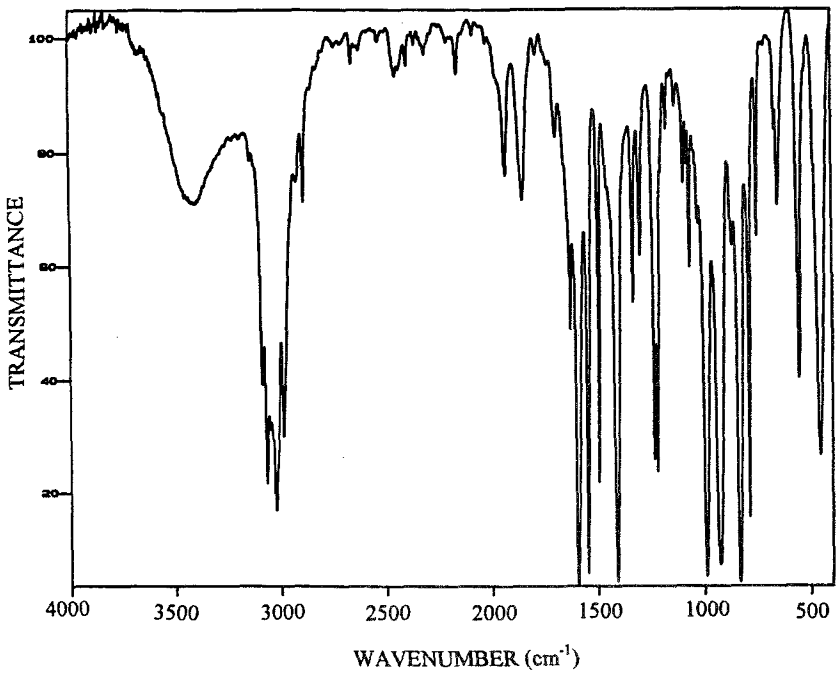

FIG. 1 FTIR spectrum of 4-vinylpyridine

coordination. Therefore, we preferred to assign this band as a pyridine ring mode. The band at 925 cm^{-1} was assigned to γ(CH) by Green and Harrison [2]. The CH_2 wagging vibration occurs at 920±20 cm^{-1} in aromatic-vinyl compounds [8]. We observed this mode at 928cm^{-1} in the IR spectrum of the 4-vpy molecule and assigned it to the CH_2 wagging vibration. The CH wagging vibration occurs at 975±35cm^{-1}. We observed a very strong band at 991cm^{-1} in the IR spectrum of 4-vpy. This band shows higher frequency shift on complex formation which is metal dependent. Therefore, we assigned this band to a ring breathing mode. We observed a medium band at 980 cm^{-1} in the IR spectra of coordinated ligand and assigned to CH wagging vibration.

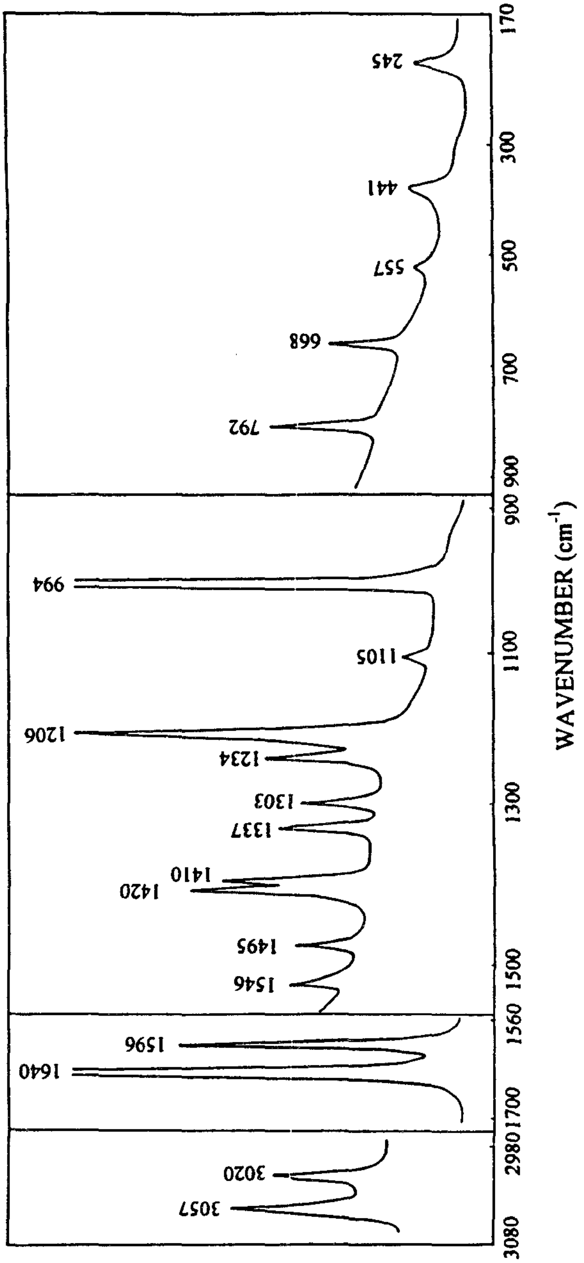

FIG. 2 Raman spectrum of 4-vinylpyridine

TABLE 1

The fundamental vibrational wavenumbers(cm^{-1}) of 4-vinylpyridine in the M-Ni-4-vpy complexes

Assignment	styrene[a]	4-etpy[b]	4-vpy		Mn	Fe	Co	Ni	Cu	Cd	Intensity
			IR	R							
a′ 1 ν(CH)	3084	3068	3091				3096	3094	3098	3097	m
2 ν (CH)	3057	3046	3068	3057m			3067	3067	3067	3065	m
3 ν_{ring}	1603	1603	1590	1596s	1612	1613	1615	1617	1619	1614	vs
4 ν_{ring}	1497	1497	1498	1495m	1502	1502	1503	1505	1507	1502	s
5 R_{sens} str.	1290	1219	1236	1234m	1244	1244	1243	1246	1247	1244	m
6 δ(CH)	1203	1219	1217	1206s	1223	1224	1225	1227	1229	1223	m
7 δ (CH)			1176								vw
8 δ (CH)+ν_{ring}	1156	1068	1095	1105w	1103	1103	1105		1109	1103	vw
9 Ring breath		995	991	994vs	1014	1015	1017	1018	1020	1016	s
10 δ_{ring} (R_{sens})		777	787	792m	798	799	800	801	804	798	vs
11 δ_{ring} (R_{sens})		492	456	441w							vs
a″											
12 ν (CH)		3068	3068				3067	3067	3067	3065	m
13 ν (CH)		3026		3020m							
14 ν_{ring}	1577	1558	1540	1546w	1548	1549	1549	1550	1552	1549	s
15 ν_{ring}		1416	1408	1420m	1423	1423	1418	1419	1427	1425	s
				1410m	1412	1412			1415	1414	
16 ν_{ring}	1335	1375	1331	1337m	1331	1335	1336	1338	1338	1331	m
17 δ (CH)	1319	1315	1301	1303w	1298	1296	1298	1299	1300	1299	w
18 δ (CH)	*1156*	*1099*	*1095*	*1105vw*	*1103*	*1103*	*1105*		*1109*	*1103*	vw
19 δ_{ring}	615	669	667	668mw	669	669	669	669	669	669	w
20 R_{sens} bend	246	358[c]		245w							
a′											
21 γ(CH)		970			976	976	976	976	976	976	m
22 γ (CH)		872	868		870	870	870	870	870	870	vw
23 γ_{ring}		410									
a″											
24 γ (CH)		874	868		870	870	870	870	870	870	vw
25 γ (CH)	776	822	830		831	833	833	833	835	833	
26 γ_{ring}(R_{sens})	560	567	552	557w	566	568	567	570	573	567	m
Vinyl group vibrations											
$\nu_a(CH_2)$	2985	2970	2987				2986	2986	2987	2987	m
$\nu_s(CH_2)$	2920	2922	2922				2922	2923	2923	2919	sh
wag.		1265	1066		1065	1065	1065	1065	1066	1066	m
CH_2 wag			928		931	931	932	932	933	933	vs
rock		750	750								m
ν(C-H)	3012		3029								m
ν(C-C)		970	976		976	976	978	980	976	976	m
ν(C=C)	1630		1635vs	1640vs	1633	1634	1634	1633	1633	1633	m

[a,b] Taken from refs. [2,5] respectively. [c] calculated value taken from ref. [5]. vs: very strong, s: strong, m:medium, w:weak, vw: very weak, sh: shoulder

The vibrational wavenumbers of 4-vinylpyridine in the M-Ni-4vpy complexes are also listed in Table 1. The spectra of the M-Ni-4vpy complexes show all the principal features found earlier for coordinated pyridine [3] and coordinated pyridine derivatives [5, 9-13]. Several modes of the 4-vpy (except vinyl group vibrations) have upward shifts in frequency when compared with the free molecule and the shifts are metal dependent. Similar shifts are also observed for coordinated pyridine [3,10] and coordinated pyridine derivatives [5, 9-13]. The upward shift was explained by coupling of the internal vibrations of the ligand molecule with the M-N stretching vibration. Thus, we have obtained direct evidence from the vibrational spectra of M-Ni-4-vpy complexes that the 4-vpy molecule forms a coordinate with the metal (M).

The vibrational spectra of the M-Ni-4-vpy complexes are very similar indicating that they have analogous structures. Sheet structure vibrations of the complexes are given in Table 2.

The characteristic ν(CN) and δ(NiCN) frequencies are found to be similar to those of Hofmann-type clathrates [14,15] and complexes [9,11-13] showing that the M-$Ni(CN)_4$ layers have been preserved. The ν(CN) frequencies are found to be metal-dependent and increase in the order: Mn< Cd <Fe< Co< Ni< Cu. This upward shift of the bridging C≡N stretching vibrations is explained by coupling of the internal modes of $Ni(CN)_4$ with the M-CN vibrations, as observed in various Hofmann-type complexes and clathrates [9,11-15]. Thus, the metal dependence of the ν(CN) frequency reflects the strength of the metal-anion bond (M-NC). In Cu-Ni-4-vpy, two bands are observed in the ν(CN) and δ(NiCN) region of the infrared spectrum. The 4-vinylpyridine modes do not differ markedly from those in other complexes. Similar splitting observed in the $Cu(py)_2Ni(CN)_4$ [3] and $Cu(4\text{-phpy})_2Ni(CN)_4$ [15] was explained by the removal of

TABLE 2
The vibrational wavenumbers (cm^{-1}) of the $Ni(CN)_4$ group of the M-Ni-4-vpy complexes.

Assignment	Mn	Cd	Fe	Co	Ni	Cu
E_u ν (CN)	2147vs	2148vs	2152vs	2159vs	2165vs	2167vs 2141s
ν (^{13}CN)	-	2105sh	2117w	2120sh	2130w	-
E_u δ (NiCN)	424vs	425vs	432vs	437vs	439vs	440vs 424sh

the degeneracy by the Jahn-Teller effect [16] and proposed non-equivalent trans pairs of Cu-NC bonds with different lengths.

ACKNOWLEDGEMENT

The authors wish to express their thanks to Prof Dr. Ziya Kantarcı for the Raman measurements.

REFERENCES

1. S.Bayarı and Ş. Ağustoslu, Abstract, International Symposium on Lasers, Atomic and Molecular Phys., İstanbul-Turkey 16-20 September (1997) PM -12
2. J.H.S.Green and D.J.Harrison, Spectrochim Acta, Vol. 33A, (1977) 249
3. S.Akyüz,A.B.Dempster, R.L. Morehouse and S.Suzuki, J. Mol.Struct. 17 (1973) 105
4. J.H.S.Green , W. Kynaston and H.M. Paisler, Spectrochim Acta, 19 (1963) 549
5. A.Topaçlı and S.Bayarı, Spectrochim Acta, (in print).
6. K.B. Wiberg, V.A. Walters, K.N.Wong and S.D.Colson, J.Phys. Chem., Vol. 88 24 (1984) 6067
7. N.P.G. Roeges, A guide to the complete interpretation of infrared spectra of organic structures. John Wiley&Sons Ltd. (1994)

8. S.Yurdakul and M. Bahat, J. Mol.Struct. 412 (1997) 97

9. Z.Kantarcı,C.Bayrak and S.Bayarı, J.Mol.Struct., 407(1997) 155

10. A. Topaçlı and S.Bayarı, Spectroscopy letters, 29(2) (1996) 277

11. S.Bayarı, A.Topaçlı and A.Aydınlı, Spectroscopy Letts. 27(9) (1994) 1083

12. S.Akyüz,H.Paşaoğlu and J.E.Davies, J.Mol.Struct. 317 (1994) 215

13. A.Sungur, S.Akyüz and J.E.Davies, J.Incl. Phenom. 3 (1987) 491

14. S.Akyüz, J. Incl. Phenom. 3 (1985) 403

15. S.Bayarı and A.Topaçlı, DOĞA Türkish J. Phys. 21(4) (1997) 575

16. L.E. Orgel, An Introduction to Transition Metal Chemisrty, Methuen, London (1960)

Date Received: June 25, 1999
Date Accepted: April 1, 2000