

# Vibrational Spectroscopic Studies of 4,4'-Bipyridyl Metal(II) Tetracyanonickelate Complexes and their Clathrates

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**Abstract.** The infrared spectra of  $M(4,4'\text{-bipyridyl})Ni(CN)_4$  complexes ( $M = Ni$  or  $Cd$ ) and their dioxane, benzene, toluene, aniline and  $N,N$ -dimethylaniline clathrates are reported. Additional information regarding the structure of the host lattice is obtained from the Raman spectra of the  $M = Cd$  complex. It is shown that the structure of the host lattice consists of infinite polymeric layers of  $\{M-Ni(CN)_4\}_\infty$  analogous to those of Hofmann type clathrates that have tetragonal symmetry. Bidentate 4,4'-bipyridyl molecules form bridges between the metal atoms  $\{M\}$  in the adjacent  $\{M-Ni(CN)_4\}_\infty$  layers. It is found that the 4,4'-bipyridyl molecules are centrosymmetric in this structure.

**Key words:** IR and Raman spectra, 4,4'-bipyridyl, tetracyanonickelate clathrates.

## 1. Introduction

Recently three-dimensional metal complex hosts have been developed from the two-dimensional Hofmann type host lattices,  $M(NH_3)_2Ni(CN)_4$ , by replacing the ammonia groups by bidentate ligands, with the aim of enlarging the range of guest molecules which can be accommodated in the host lattices [1–5]. In a previous study Mathey *et al.* reported the preparation of the  $Ni(4,4'\text{-bipyridyl})Ni(CN)_4$  host lattice and its benzene, xylene, naphthalene and anthracene clathrates [5]. We have extended this study and prepared  $M(4,4'\text{-bipyridyl})Ni(CN)_4 \cdot 2G$  ( $M = Ni$  or  $Cd$ ;  $G =$  dioxane, toluene, aniline or  $N,N$ -dimethylaniline) clathrates for the first time. In this study an IR spectroscopic study of the  $M(4,4'\text{-bipy})Ni(CN)_4 \cdot nG$  compounds (where  $M = Ni$  or  $Cd$ ,  $G =$  dioxane, benzene, toluene, aniline or  $N,N$ -dimethylaniline,  $n = 0\text{--}2$ ) (abbreviated henceforth as  $M\text{-Ni-bipy-G}$ ) are reported. Additional information is obtained from the laser-Raman spectrum of the  $Cd\text{-Ni-bipy}$  complex. We also recorded the powder X-ray diffraction patterns of the  $M\text{-Ni-bipy}$  complexes.

## 2. Experimental

The  $M\text{-Ni-bipy-G}$  samples were prepared by one of the following methods:

(a) Slightly in excess of one mole of 4,4'-bipyridyl was dissolved in a liquid guest ( $G$ )

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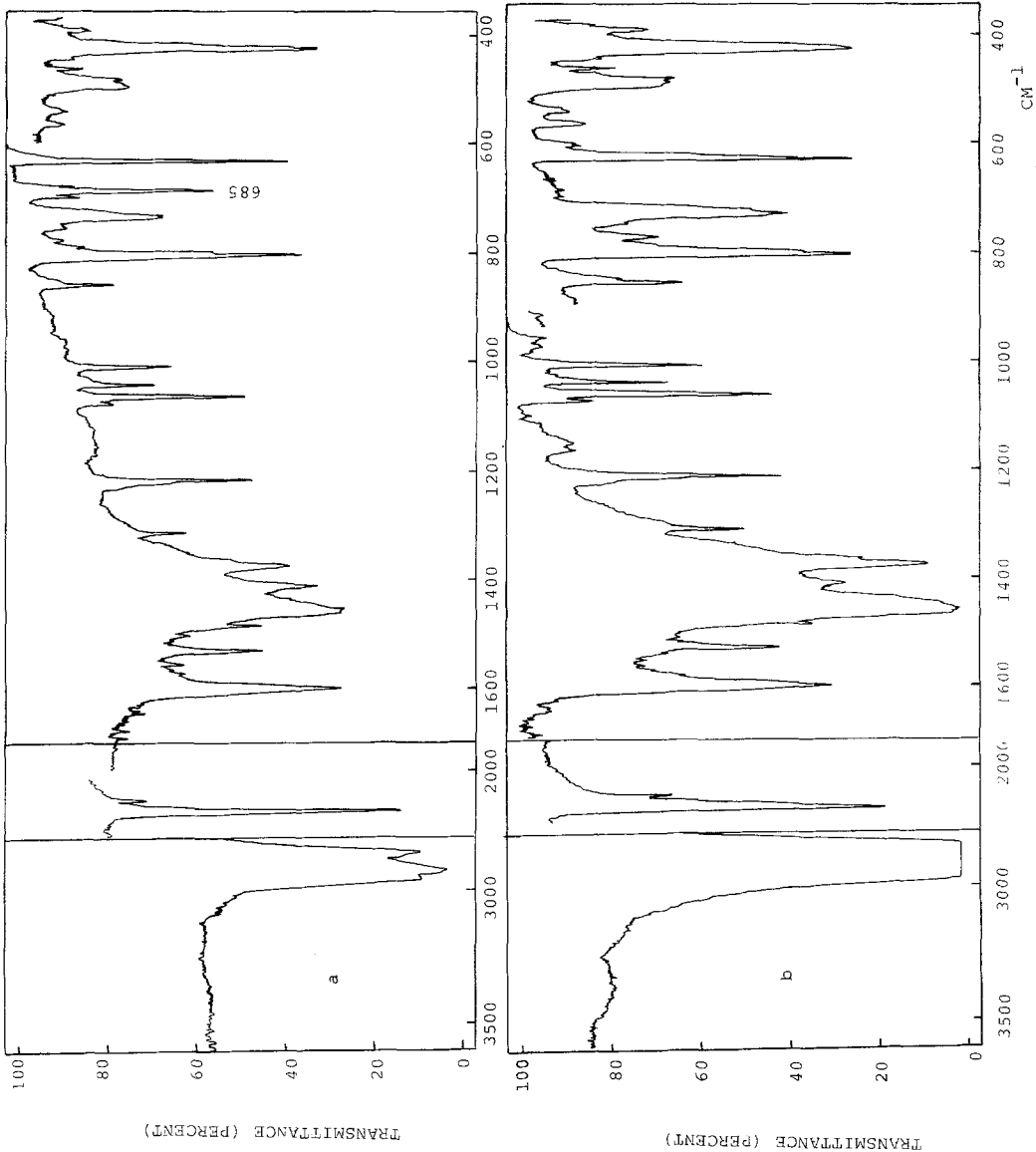


Fig. 1. Infrared spectra of the Cd-Ni-bipy-benzene clathrate (nujol mulls); (a) freshly prepared, (b) after heating at  $70^\circ\text{C}$  for 2.5 hours.

and this solution, together with the aqueous solution of one mole of  $K_2Ni(CN)_4$ , were added to an aqueous solution of the metal (II) chloride, with constant stirring. The precipitate was filtered and washed with water and acetone.

- (b) In this method the M-Ni-bipy complexes were first prepared by decomposing M-Ni-bipy benzene clathrates, then the complexes were immersed in a liquid guest (G) in sealed bottles for a week or more at room temperature.

All the clathrates except G=dioxane were prepared by both methods. However in the case of the dioxane clathrate, the first method yielded  $M(dioxane)_2Ni(CN)_4$  complexes. It was also found that M-Ni-bipy-aniline clathrates which were prepared by the first method contained the  $M(an)_2Ni(CN)_4$  complex as an impurity.

M-Ni-bipy complexes were prepared by completely decomposing the M-Ni-bipy-benzene clathrates by evaporation or by heating. It was found that almost all the benzene molecules were lost from the Ni-Ni-bipy-benzene and Cd-Ni-bipy-benzene clathrates when kept in an oven at 70 °C for 25 days and 2.5 hours, respectively. Figure 1 shows the IR spectra of the Cd-Ni-bipy-benzene clathrate when freshly prepared and after heating at 70 °C for 2.5 hours.

The IR spectra of the samples were recorded on Perkin-Elmer 621 and Nicolet MX-IE spectrometers which were calibrated using polystyrene and  $CO_2$  bands, respectively.

The Raman spectra were measured with a Cary 81 spectrometer using the 514.5 nm line of a CRL argon ion laser.

### 3. Results and Discussion

#### 3.1. THE $Ni(CN)_4$ GROUP VIBRATIONS

The IR spectra of the M-Ni-bipy (M=Ni or Cd) complexes are very similar and the X-ray diffraction study showed them to have isomorphous crystal structures with small changes in the unit cell parameters.

Table I. The vibrational wavenumbers ( $cm^{-1}$ ) of the  $Ni(CN)_4$  group of the M-Ni-bipy complexes and M-Ni-bipy-G (G=toluene, aniline or *N,N*-dimethylaniline) clathrates<sup>a</sup>

Assignment	M-Ni-bipy		M-Ni-bipy-G						Relative intensity
			Toluene		Aniline		<i>N,N</i> -dimethylaniline		
	Cd	Ni	Cd	Ni	Cd	Ni	Cd	Ni	
$A_{1g}$ $\nu(CN)$	(2166)								(vs)
$B_{1g}$ $\nu(CN)$	(2153)								(s)
$E_u$ $\nu(CN)$	2147	2164	2144	2162	2148	2166	2148	2166	vs
$\nu(^{13}CN)$	2105	2132	2103	2130	2106	2133	2106	2133	vw
$E_u$ $\nu(NiC)$	540	552	538	552	540	–	540	552	vw
$A_{2u}$ $\pi(NiCN)$	444	451	443	451	444	452	444	452	vw
$E_u$ $\delta(NiCN)$	426	438	424	438	426	439	427	439	vs
Interplanar distance (c) Å	11.7	10.4							

<sup>a</sup> The bands observed in the infrared spectra are given without parentheses; the bands observed in the Raman spectra are given in parentheses.

The vibrational wavenumbers of the  $\text{Ni}(\text{CN})_4$  group vibrations of the M-Ni-bipy complexes and M-Ni-bipy-G clathrates [ $G = \text{Toluene}$ , aniline or  $N,N$ -dimethylaniline] are given in Table I. The  $\nu(\text{CN})$  and  $\delta(\text{NiCN})$  vibrational wavenumbers are found to be similar to those of Hofmann type clathrates [6] and the pyridine [7] complex, showing that the  $\{\text{M-Ni}(\text{CN})_4\}_\infty$  layers have been preserved. Since we observed only one  $\nu(\text{CN})$  ( $E_u$ ) band in the IR spectrum and the other two  $\nu(\text{CN})$  ( $A_{1g}$  and  $B_{1g}$ ) bands in the Raman spectrum of the Cd-Ni-bipy complex, we propose a square planar environment around the tetracyanonickelate ion.

We did not observe any differences in the  $\text{Ni}(\text{CN})_4$  group vibrational modes of the M-Ni-bipy-G clathrates ( $G = \text{benzene}$  or dioxane) in comparison to those of the corresponding M-Ni-bipy complexes. However, we observed slight shifts of the  $\nu(\text{CN})$  ( $E_u$ ) band in the cases of  $G = \text{toluene}$ , aniline and  $N,N$ -dimethylaniline in comparison to those of the M-Ni-bipy complexes (see Table I). The slight shift of the  $\nu(\text{CN})$  ( $E_u$ ) band may be attributed to the small change in the host-guest interaction.

The distance ( $c$ ) between the adjacent  $\{\text{M-Ni}(\text{CN})_4\}$  networks is calculated from the X-ray diffraction patterns of the M-Ni-bipy complexes and is given in Table I. The  $c$  values closely match those calculated from the known interatomic distances, assuming that the principal axis of the ligand is perpendicular to the cyanide planes. This result supports our assumption that 4,4'-bipyridyl molecules form bridges between the metal atoms (M) in the adjacent  $\{\text{M-Ni}(\text{CN})_4\}$  layers.

#### 4,4'-BIPYRIDYL VIBRATIONS

The IR and Raman spectra of the Cd-Ni-bipy complex are given in Figures 1 and 2, respectively. Since we did not observe any coincidences between the IR and Raman frequencies of the 4,4'-bipyridyl molecule, we propose that the molecule is centrosymmetric and planar in the structure. 4,4'-Bipyridyl therefore belongs to the  $D_{2h}$  point group and hence its 54 fundamental vibrations are divided among the symmetry species as follows; 5  $B_{1u}$ , 9  $B_{2u}$ , and 9  $B_{3u}$  IR active; 10  $A_g$ , 9  $B_{1g}$ , 5  $B_{2g}$  and 3  $B_{3g}$  Raman active; and 4  $A_u$  inactive.

It has been noted that IR and Raman data on 4,4'-bipyridyl and its complexes are not plentiful in the literature. In most of the spectroscopic studies on 4,4'-bipyridyl complexes, bipyridyl bands are assigned by comparison with pyridine [8–10]. The only detailed IR and Raman data on crystalline 4,4'-bipyridyl was reported by Gupta [11] who gave approximate interpretations of all of the vibrational modes of the molecule and supported his assignment by a normal coordinate analysis using a valence-force scheme. However he did not apply the theoretical calculations to the deuterium derivatives of 4,4'-bipyridyl. On the other hand Kihara and Gondo [12] carried out a normal coordinate analysis for the in-plane vibrations of 4,4'-bipyridyl only and reported some of the IR and Raman vibrational wavenumbers. We assigned the vibrations of 4,4'-bipyridyl by comparison with the assignment for biphenyl [13, 14], methylviologen [15, 16], pyridine [7] and 4,4'-bipyridyl [11, 12].

The 4,4'-bipyridyl wavenumbers observed in the IR spectra of the M-Ni-bipy complexes, together with our measurement on crystalline 4,4'-bipyridyl are given in Table II. The assignments of biphenyl [14] and 4,4'-bipyridyl taken from Gupta [11] and Kihara and Gondo's [12] papers are included for comparison. Our assignment of the IR spectrum of crystalline 4,4'-bipyridyl agrees with that of Kihara and Gondo. It is also in agreement with that of Gupta with the following exceptions: Gupta assigned

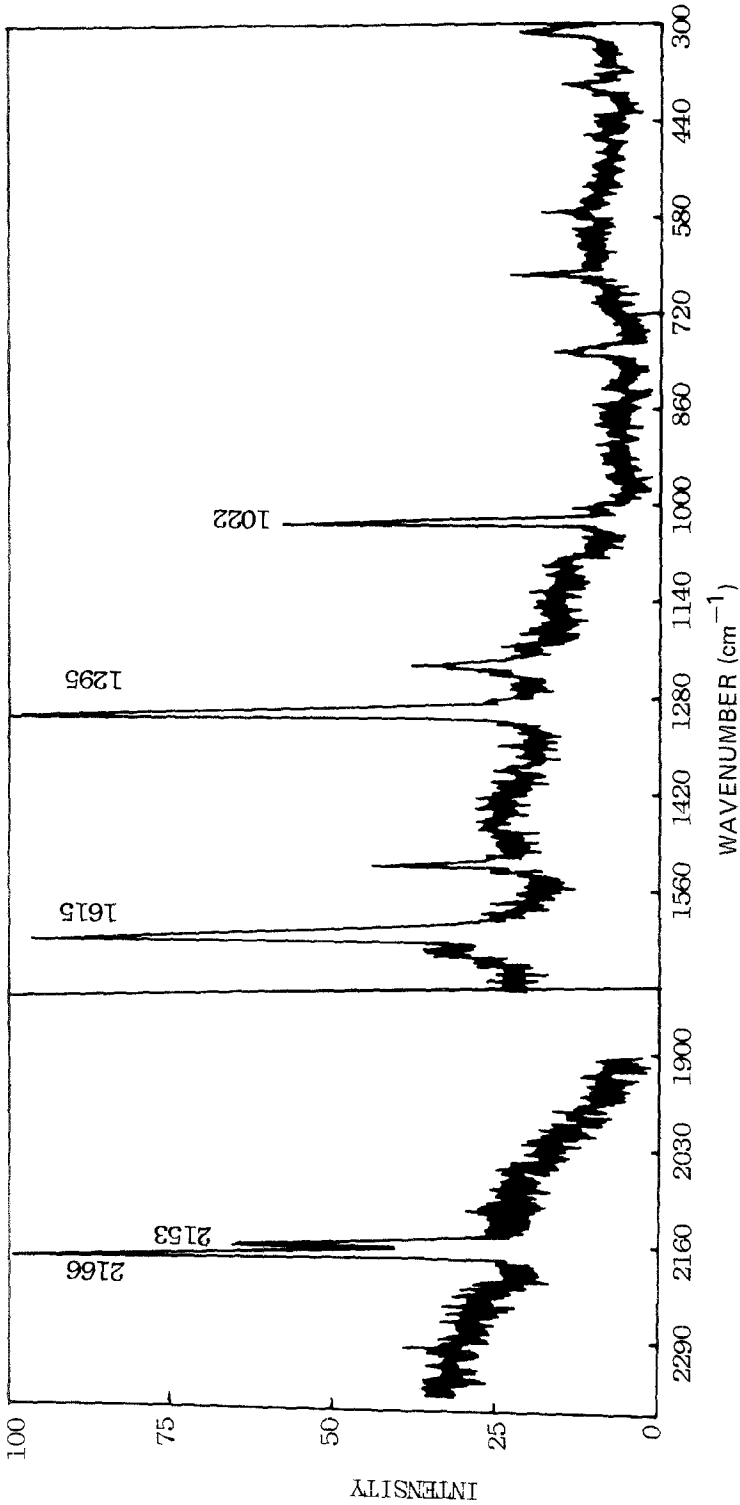


Fig. 2. Raman spectrum of the Cd-Ni-bipy complex.

Table II. The fundamental vibrational wavenumbers ( $\text{cm}^{-1}$ ) of 4,4'-bipyridyl in the M-Ni-bipy complexes

Symmetry and description of mode	Biphenyl <sup>a</sup>	4,4'-bipy			M-Ni-bipy		Relative intensity	
		G <sup>b</sup>	KG <sup>c</sup>	This study	Cd	Ni		
<i>B</i> <sub>3u</sub>	1 $\nu(\text{CH})$	3080	3070	–	3055	3069	3080	w
	2 $\nu(\text{CH})$	3072	3050	–	3047	3053	–	w
	3 $\nu_{\text{ring}}$	1597	1590	1585	1598	1605	1610	vs
	4 $\nu_{\text{ring}}$	1482	1485	1485	1481	1488	1490	m
	5 $\delta(\text{CH})$	1176	1130	1217	1215	1216	1219	m
	6 $\delta(\text{CH})$	1040	1040	1036	1044	1064	1066	m
	7 $\nu_{\text{ring}}+\delta_{\text{ring}}$	1008	851	965	967	976	985	w
	8 $\nu_{\text{ring}}$	965	1287 <sup>d</sup>	990	994	1011	1012	m
	9 $\delta_{\text{ring}}$	609	610	607	615	632	635	vs
<i>B</i> <sub>2u</sub>	10 $\nu(\text{CH})$	3069	3070	–	3078	3080	3084	m
	11 $\nu(\text{CH})$	3068	3030	–	3029	3036	3034	m
	12 $\nu_{\text{ring}}$	1570	1540	1528	1532	1534	1536	s
	13 $\nu_{\text{ring}}$	1432	1406	1405	1413	1414	1413	s
	14 $\nu_{\text{ring}}$	1272	1273 <sup>d</sup>	–	1324	1315	1318	m
	15 $\delta(\text{CH})$	1156	1218	–	1223	1219	1222	sh
	16 $\delta(\text{CH})+\nu_{\text{ring}}$	1074	1074	1073	1074	1078	1078	w
	17 $\delta_{\text{ring}}$	628	634 <sup>d</sup>	670	677	668	665	w
	18 inter-ring bend. i.p.	116	241 <sup>d</sup>	–	–	–	–	–
<i>B</i> <sub>1u</sub>	19 $\gamma(\text{CH})$	903	880	–	862	859	854	w
	20 $\gamma(\text{CH})$	736	806	–	810	803	806	vs
	21 $\gamma_{\text{ring}}$	698	733	–	737	729	730	s
	22 $\gamma_{\text{ring}}$	484	460	–	507	488	–	m
	23 $\gamma_{\text{ring}}$	174	–	–	367	386	–	m

<sup>a b c</sup> Taken from references [14], [11] and [12], respectively.

<sup>d</sup> Calculated values.

the IR band at  $1130 \text{ cm}^{-1}$  as a fundamental vibrational mode of *B*<sub>3u</sub> symmetry species. However we observed a very weak band at  $1125 \text{ cm}^{-1}$  and preferred to assign the medium intense band at  $1215 \text{ cm}^{-1}$  to the  $\nu_5$  mode in agreement with Kihara and Gondo. Our assignment is compatible with those of pyridine ( $1217 \text{ cm}^{-1}$ ) [7] and methylviologen ( $1181 \text{ cm}^{-1}$ ) [16]. We observed two weak bands at  $862 \text{ cm}^{-1}$  and  $967 \text{ cm}^{-1}$ , in the IR spectrum of 4,4'-bipyridyl. The  $967 \text{ cm}^{-1}$  band shifted to a higher frequency on coordination; the  $862 \text{ cm}^{-1}$  band however did not display any shift. As discussed below the *B*<sub>3u</sub> modes tend to show increases in frequency on coordination. Therefore we assigned the  $967 \text{ cm}^{-1}$  band to  $\nu_7$  in agreement with the assignment of Kihara and Gondo. The  $\nu_8$  mode (the out-of-phase component of the ring breathing mode) is assigned to a strong IR band at  $994 \text{ cm}^{-1}$ . This is because we observed the corresponding in-phase component at  $1002 \text{ cm}^{-1}$  as a very strong band in the Raman spectrum of crystalline 4,4'-bipyridyl. Our assignment is in agreement with that of Kihara and Gondo [12] and is also compatible with those for the biphenyl ( $965 \text{ cm}^{-1}$ ) [14], methylviologen ( $993 \text{ cm}^{-1}$ ) [16] and pyridine ( $990 \text{ cm}^{-1}$ ) [7] molecules. Gupta [11] also observed a band at  $990 \text{ cm}^{-1}$  in the IR spectrum of 4,4'-bipy which was

assigned to an  $A_{1g}$  mode. This in-phase ring-breathing mode must however be IR inactive in  $D_{2h}$  symmetry. In Gupta's paper the out-of-phase ring-breathing mode was calculated as  $1287\text{ cm}^{-1}$  ( $B_{3u}$ ) but the observed value was not given.

The  $\nu_{22}$  ( $\nu_{\text{ring}}$ ) mode was assigned to a band at  $460\text{ cm}^{-1}$  by Gupta; however, we did not observe any band at this wavenumber value in the IR spectrum of crystalline 4,4'-bipyridyl. Therefore we assigned the strong IR band observed at  $507\text{ cm}^{-1}$  to  $\nu_{22}$ .

The vibrational modes of 4,4'-bipyridyl observed in the IR spectra of the M-Ni-bipy complexes and of the M-Ni-bipy-G clathrates ( $G = \text{benzene or dioxane}$ ) are found to be the same in intensity and frequency. However in the cases of the M-Ni-bipy-G clathrates ( $G = \text{toluene, aniline or } N,N\text{-dimethylaniline}$ ) we observed slight frequency shifts (up to  $2\text{ cm}^{-1}$ ) and intensity changes in some 4,4'-bipyridyl vibrational modes in comparison to those of the M-Ni-bipy complexes. These changes are thought to be due to the interaction between the host lattice and the guest molecules.

The 4,4'-bipyridyl vibrational modes observed in the IR spectra of the compounds studied show all the characteristics of a coordinated ligand, e.g. several modes of the coordinated ligand have upward shifts in frequency compared to those in the free molecule and the shifts are metal dependent. As is clear from Table II, considerable shifts to higher frequency occur for the modes of  $B_{3u}$  symmetry species. Similar shifts are observed in the pyridine complexes [7] and explained by coupling with low frequency vibrations, particularly the M-N stretching frequency.

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