

A Fourier-Transform Infrared and Laser-Raman Spectroscopic Investigation of 4,4'-Bipyridyl-Transition Metal(II) Tetracyanonickelate Clathrates

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Abstract. The FT-IR and Raman spectra are reported of $M(4,4'\text{-bipyridyl})Ni(CN)_4 \cdot nG$ (where $M = Mn, Fe, Co, Cu$ or Zn and $G = \text{benzene}$ or aniline ; $n = 0\text{--}2$) clathrates. The host structure consists of a three-dimensional rigid lattice formed by infinite polymeric layers of $\{M\text{---}Ni(CN)_4\}_\infty$ and 4,4'-bipyridyl bridges between the metal (M) atoms of the adjacent polymeric layers. Bidentate 4,4'-bipyridyl molecules are found to be centrosymmetric in the structure.

Key words. Tetracyanonickelate compounds, benzene clathrate, aniline clathrate, IR and Raman spectra, 4,4'-bipyridyl complexes.

1. Introduction

It has been shown that 4,4'-bipyridyl (4,4'-bipy) molecules form bridges between tetracyanonickelate layers and build up three-dimensional host lattices in which dioxane, benzene, toluene, aniline or *N,N*-dimethylaniline can be trapped [1,2]. In our previous study the spectra of $M(4,4'\text{-bipy})Ni(CN)_4$ ($M = Ni$ or Cd) host lattices were reported [2]. Now, for the first time we have prepared a series of bipyridyl-tetracyanonickelate host lattices and their clathrates with the formula, $M(4,4'\text{-bipy})Ni(CN)_4 \cdot nG$ ($M = Mn, Fe, Co, Cu$ or Zn ; $G = \text{benzene}$ or aniline ; $n = 0\text{--}2$) (abbreviated as $M\text{---}Ni\text{-bipy-G}$). The aim of the present report is to give further examples of three-dimensional metal complex hosts, developed from two-dimensional Hofmann-type host lattices, $M(NH_3)_2Ni(CN)_4$, by replacing the ammonia groups by bidentate ligands [1–5]. We also analyse the 4,4'-bipyridyl

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vibrations in a series of isostructural crystals, where the only difference is the metal to which the bipyridyl molecules are bound. We feel this should be useful since very few vibrational data have been reported for 4,4'-bipyridyl and its complexes [2,6–10].

2. Experimental

M-Ni-bipy-G clathrates were prepared employing the methods given in the literature [1]. In some preparations the compounds were found to contain water (both bound and enclathrated) but after being stirred with dimethoxypropane containing a small amount of bipyridyl dissolved in benzene for 1–2 days, samples could be obtained entirely free of water. Some of the compounds are found to contain guest bipyridyl in addition to benzene or aniline guests.

The FT-IR spectra were recorded on Nicolet MX-IE and Nicolet 510 spectrometers in Nujol and hexachlorobutadiene mulls between CsI windows. The spectrometer was calibrated using CO₂ bands.

Raman spectra of the samples were excited using either the 488.0 or 514.5 nm lines of an Ar⁺ laser, recorded on a Cary 81 spectrometer, with the use of a spinning cell. Because of rapid decomposition of the M=Fe compound under laser excitation, we were not able to record its Raman spectrum.

3. Results and Discussion

3.1. 4,4'-BIPYRIDYL VIBRATIONS

The 4,4'-bipyridyl vibrational wavenumbers are tabulated in Table I together with those of polycrystalline 4,4'-bipyridyl [10]. It is found that the 4,4'-bipyridyl vibrational wavenumbers are not affected by the guest molecule and are the same in the benzene and aniline clathrates. On the other hand no coincidences were observed between the IR and Raman wavenumbers of 4,4'-bipyridyl indicating that the molecule possesses a center of symmetry.

Recently, the vibrational wavenumbers of 4,4'-bipyridyl have been calculated and the effect of coordination of the molecule to a metal has been investigated [10]. It was reported that A_g and B_{3u} modes were greatly affected due to the coupling with M–N (ligand) stretching modes (A_g and B_{3u}). The Raman spectra of the samples were poor due to problems with background fluorescence. Nevertheless, the ring breathing mode in-phase component is clearly observed as a strong band at 1000 cm⁻¹ in the Raman spectrum of polycrystalline 4,4'-bipyridyl, and is also observed as a strong band in the Raman spectra of the complexes around 1021–1032 cm⁻¹. We clearly observed a metal-dependent frequency shift in this mode. In some of the complexes (Co and Zn) a weak band was also observed on the low frequency side of this band which is found to be quite similar to that of the free molecule and has been assigned to guest bipyridyl. On the other hand all the B_{3u} modes of 4,4'-bipyridyl are clearly observed in the IR spectra of the complexes. As

Table I. The vibrational wavenumbers of 4,4'-bipyridyl.*

Symmetry species and assignment	4,4'-bipy (**)		M(4,4'-bipy)Ni(CN) ₄					Rel. int.	
	obs	calc	Mn	Fe	Co	Zn	Cu		
<i>A_g</i> ν_{ring}	1617	1597	1619		1620	1628	1629	vs	
	ν_{ring}	1514	1520	1520		1520	1524	1525	w
	$\nu_{\text{ring}} + \delta(\text{CH})$	1301	1317				1311		vw
	$\delta(\text{CH})$	1230	1197			1228	1228	1228	m
	$\nu_{\text{ring}} + \delta(\text{CH})$	1025	1023						
	$\nu_{\text{ring}} \{$	1000	996	1021		1023	1029	1032	vs
						1002 ⁺	1002 ⁺		vs
$\delta_{\text{ring}} + \nu_{\text{ring}}$	762	749	773		775	777	788	w	
δ_{ring}	325	314							
<i>B_{1g}</i> ν_{ring}	1605	1572	1615		1616	1617	1626	s	
	ν_{ring}	1427	1435						
	$\delta(\text{CH})$	1348	1340						
	$\delta(\text{CH}) + \nu_{\text{ring}}$	1265	1274	1296		1299	1296	1299	s
	$\nu_{\text{ring}} + \delta(\text{CH})$	1071	1076						
	δ_{ring}	603	680	663		662	663	662	w
	δ_{ring}	304	384				368		vw
<i>B_{2u}</i> $\nu(\text{CH})$	3078	3059	3086		3086	3087		w	
	$\nu(\text{CH})$	3029	3033	3033		3033	3032		w
	ν_{ring}	1532	1567	1531	1534		1536	1537	s
	ν_{ring}	1413	1448	1413	1412		1413	1415	s
	$\delta(\text{CH})$	1324	1339	1316	1317	1317	1319	1329	m
	$\delta(\text{CH})$	1223	1214	1229	1229	1228	1227	1231	m
	ν_{ring}	1074	1081	1074	1076	1076	1073	1073	w
	δ_{ring}	677	671	675		675	675	677	w
	<i>B_{3u}</i> $\nu(\text{CH})$	3053	3062	3067		3076			w
		$\nu(\text{CH})$	3047	3038	3059		3065		w
ν_{ring}		1598	1595	1602	1605	1606	1607	1615	vs
$\nu_{\text{ring}} + \delta(\text{CH})$		1481	1479	1489	1489	1489	1490	1490	s
$\delta(\text{CH})$		1215	1202	1217	1217	1217	1217	1218	s
δ_{ring}		1044	1071	1063	1064	1065	1065	1068	s
$\nu_{\text{ring}} \{$		994	1016	1006	1009	1010	1012	1013	
				994 ⁺		993 ⁺	995 ⁺		
ν_{ring}		967	976	965	966	968			vw
δ_{ring}		615	628	628	631	633	634	643	w
<i>B_{1u}</i> $\gamma(\text{CH})$	862	872	859	858			854	vs	
	$\gamma(\text{CH}) \{$	810	805	809	809	811		vs	
			805	806	806	806	804	vs	
	γ_{ring}	737	744	734	734	734	733	732	m
	γ_{ring}	507	544	501	502		502	503	s
	γ_{ring}	367	327	391	396		398	400	m

Table I. Continued

Symmetry species and assignment	4,4'-bipy (**)		M(4,4'-bipy)Ni(CN) ₄					Rel. int.
	obs	calc	Mn	Fe	Co	Zn	Cu	
<i>B</i> _{2g} γ(CH)	881	872						
γ(CH)		774						
γ _{ring}	742	733						
γ _{ring}	574	536	577		574	576		vw
γ _{ring}	369	408						

*The wavenumbers for *g* symmetry species are obtained from Raman spectra, those of *u* symmetry species from IR spectra.

**Taken from reference 10.

+ Guest bipyridyl.

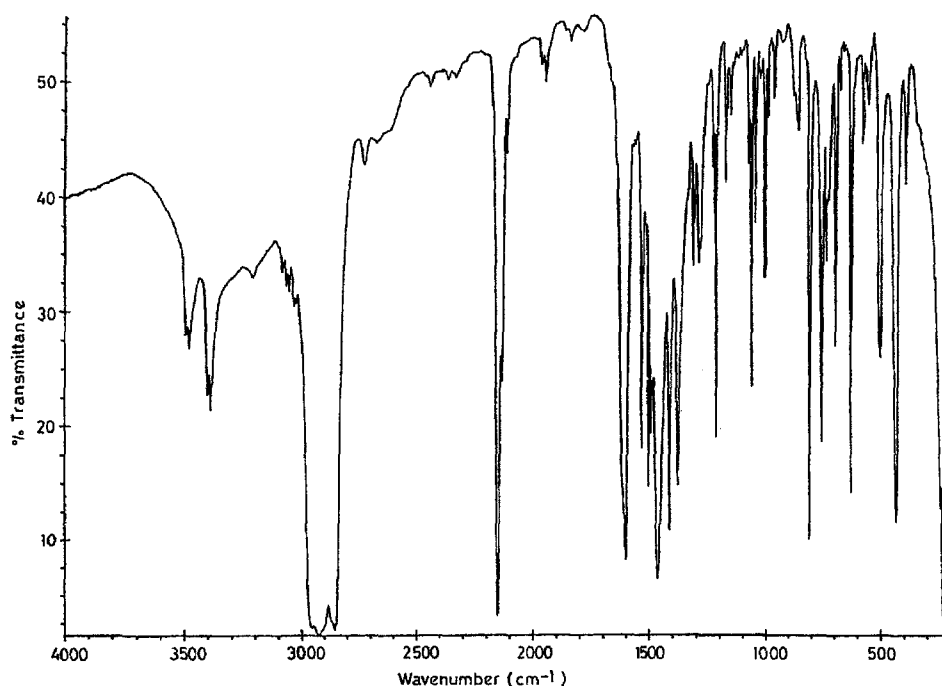


Fig 1. The FT-IR spectrum of the Mn(4,4'-bipy)Ni(CN)₄.2aniline clathrate.

seen from Table I, considerable shifts to higher wavenumber occur for these modes and the shifts are metal dependent. It must be noted that the general increase in frequency of the 4,4'-bipyridyl modes with the different metals in the complexes is in the order Mn < Fe < Co < Zn < Cu. A similar order of transition metals had been found in pyridine [11] tetracyanonickelate complexes. Theoretical calculations on free and complexed 4,4'-bipyridyl indicated that coupling with low frequency modes (particularly with $\nu(\text{M}-\text{N})$) is the principal cause of the upward shifts [10].

Table II. The vibrational wavenumbers of the Ni(CN)₄ group in M(4,4'-bipy)Ni(CN)₄·nG clathrates

Assignment	M(4,4'-bipy)Ni(CN) ₄ ·nG									
	G = benzene				G = aniline					
	Mn	Fe	Co	Zn	Cu	Mn	Fe	Co	Zn	Cu
A _{1g}	ν(CN)	2172 vs	2179 vs	2179 vs	2185 vs	2174 vs	2180 vs	2180 vs	2180 vs	2186 vs
B _{1g}	ν(CN)	2159 s	2167 s	2168 s	2146 s	2162 s	2167 s	2167 s	2168 s	2146 s
E _u	ν(CN)	2150 vs	2154 vs	2158 vs	2161 vs	2151 vs	2155 vs	2156 vs	2164 vs	2170 vs
	ν(¹³ CN)	2130 w	2136 w	2145 sh	2142 sh	2134 s	2137 s	2144 s	2158 s	2135 s
E _u	ν(NiC)	551 w	554 w	556 w	552 w	551 w	553 w	554 w	554 w	548 w
A _{2u}	π(NiCN)	450 vw	450 vw	453 vw	451 sh	450 vw	449 vw	449 vw	449 vw	450 vw
E _u	δ(NiCN)	436 vs	438 vs	439 vs	439 vs	437 vs	437 m	439 s	439 s	447 s
					445 sh	437 vs	437 m	439 s	439 s	447 s
					435 vs					428 m

Table III. Some vibrational wavenumbers (cm^{-1}) of aniline in M-Ni-bipy-An and Hofmann type aniline clathrates.

Assignment	liquid	Hofmann type [12]		M-Ni-bipy-An	
		Mn	Zn	Mn	Zn
$\nu_a\text{NH}_2$	3440	3471	3466	3493	3493
				3466	3493
$\nu_s\text{NH}_2$	3360	3375	3470	3401	3401
				3384	3387
X-sens. ($\nu(\text{CN})$)	1278	1290	1289	1292	1293
				1282	1283

3.2. Ni(CN)₄ GROUP VIBRATIONS

The vibrational data for the Ni(CN)₄ group in the compounds studied are given in Table II. The characteristic wavenumbers of the $\nu(\text{CN})$ and $\delta(\text{NiCN})$ modes are found to be similar to those of Hofmann-type clathrates [12] and complexes [13], indicating that $\{\text{M-Ni}(\text{CN})_4\}_\infty$ layers have been preserved. In some of the compounds, the IR active $\nu(\text{CN})$ (E_u) mode is found in split pairs. Splitting points directly to a change of symmetry and removal of degeneracy.

3.3. BENZENE AND ANILINE VIBRATIONS

Spectroscopic investigation indicated that the compounds can include benzene or aniline in their structures.

The $\nu_{11}(A_{2u})$ vibrational mode of benzene is observed around 685 cm^{-1} in the IR spectra of benzene clathrates, whereas the same mode is observed at 675 cm^{-1} for liquid benzene. Similar positive frequency shifts (up to 30 cm^{-1}) were observed for Hofmann-type clathrates [12] and Hofmann-Td-type clathrates of Cd(4,4'-bipy)M(CN)₄ (M=Cd or Hg) [14] and explained in terms of H-bonding interaction between the electrons of the benzene ring and the host lattice. The $\nu_1(A_{1g})$ mode of benzene is observed at $991\text{--}995 \text{ cm}^{-1}$ in the Raman spectra of the benzene clathrates. In the case of aniline clathrates the major difference observed in the IR spectra of M(4,4'-bipy)Ni(CN)₄ · *n*C₆H₅NH₂ as compared with the corresponding spectra of the Hofmann type aniline clathrates [12] is the splitting of the aniline bands. The $\nu_a(\text{NH}_2)$ and $\nu_s(\text{NH}_2)$ modes are found to split into doublets which are clearly seen in the Mn and Zn clathrates (Figure 1). The splitting may arise due to the interaction with the host lattice. The NH₂ stretching and aniline X-sensitive ((C—N)) vibrational wavenumbers of the compounds, which are known to be sensitive to hydrogen bonding interactions of aniline, are given in Table III in comparison with those of Hofmann type clathrates and liquid aniline. The $\nu_a(\text{NH}_2)$ and $\nu_s(\text{NH}_2)$ modes are observed at 3500 and 3418 cm^{-1} in aniline vapour and at 3440 and 3360 cm^{-1} in liquid aniline, respectively [15]. The lower frequencies in

the liquid arise from hydrogen bonding between neighbouring aniline molecules. In the case of Hofmann type aniline clathrates [12] the NH_2 group stretching modes are observed at lower frequencies compared to aniline vapour and interpreted as arising from weak hydrogen bonding between the NH_2 group and the host lattice, probably involving the π electrons of the CN bonds. This type of interaction might also be present in M-Ni-bipy-An clathrates but the strength of the bonding should be less than that in Hofmann type clathrates, and probably only one of the hydrogens in the NH_2 group of aniline guest is involved. Aniline frequencies in M-Ni-bipy-An clathrates (M = Mn, Fe, Co, Zn or Cu) are found to be almost the same, indicating that small changes in the unit cell dimensions do not affect the weak host-guest interaction.

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