

Vibrational Spectroscopic Investigation of Mono and Tris-2,2'-Bipyridyl Metal(II) Tetracyanonickelate Compounds

SEVİM AKYÜZ* and AYŞEN ERBOLUKBAS OZEL

Physics Department, Istanbul University, Science Faculty, Vezneciler 34459, Istanbul, Turkey.

J. ERIC D. DAVIES

Environmental Science Division, Lancaster University, LA1 4YQ, Lancaster, U.K.

MERİÇ BAKILER

Physics Department, Mimar Sinan University, Besiktas 80690, Istanbul, Turkey

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Abstract. The IR and Raman spectra of $\text{Cd}(2,2'\text{-bipy})\text{Ni}(\text{CN})_4$ and $\text{Ni}(2,2'\text{-bipy})_3\text{Ni}(\text{CN})_4 \cdot 6\text{H}_2\text{O} \cdot 0.5(2,2'\text{-bipy})$ complexes are reported. The spectral results indicate the existence of structure spectra correlations.

Key words: Clathrates, 2,2'-bipyridyl complexes, tetracyanonickelate complexes.

1. Introduction

Cernak *et al.* [1] recently reported the preparation and crystal structure of the host–guest type complex of tris(bipy)nickel(II)tetrakis(cyano)nickelate(II)-hexahydrate-hemi(bipyridine). In this structure the $\text{Ni}(\text{CN})_4^{2-}$ anions build the host part of the structure by binding H_2O molecules while the guest part of the structure is built up by $[\text{M}(\text{bipy})_3]^{2+}$ cations and non-coordinated bipy molecules. On the other hand, Hashimoto and Iwamoto [2] reported the crystal structure of the $\text{Cd}(\text{bipy})\text{Ni}(\text{CN})_4$ compound which consists of polymeric two dimensional undulated $\{\text{Cd}-\text{Ni}(\text{CN})_4\}_\infty$ layers.

Since no vibrational spectroscopic study has been reported on these compounds, we found it interesting to investigate them by IR and Raman spectroscopy and compare the results of these two different structures, 3D by hydrogen bonding and polymeric 2D, in order to determine some structure–spectra correlations. In this study IR and Raman vibrational results of $\text{Ni}(2,2'\text{-bipy})_3\text{Ni}(\text{CN})_4 \cdot 6\text{H}_2\text{O} \cdot 0.5(2,2'\text{-bipy})$ and $\text{Cd}(2,2'\text{-bipy})\text{Ni}(\text{CN})_4$ are reported (abbreviated to Ni-Ni-bipy and Cd-Ni-bipy respectively).

* Author for correspondence.

2. Experimental

Ni(bipy)₃Ni(CN)₄·6H₂O·0.5(bipy) and Cd(bipy)Ni(CN)₄ were prepared by the following method: a 15 mL *n*-hexane solution of slightly in excess of the appropriate amounts of 2,2'-bipy (0.4 M and 0.15 M for Ni and Cd cases, respectively) was prepared. This solution, together with 10 mL of an aqueous solution of 0.1 M K₂Ni(CN)₄, was added to 10 mL of an aqueous solution of 0.1 M M(II) chloride at pH 9 (for Ni) or pH 12 (for Cd). The pH was adjusted using ammonia or acetic acid solutions, until no turbidity was obtained after addition of K₂Ni(CN)₄. The solutions were kept in closed bottles until crystals were formed. The C, H, N analysis results are: *Anal. Found* for Ni-Ni-bipy: C 53.35%, H 4.20%, N 17.38%. *Calcd.* for Ni(bipy)₃Ni(CN)₄·6H₂O·0.5(bipy): C 53.45%, H 4.60%, N 17.58%. *Anal. Found* for Cd-Ni-bipy: C 39.01%, H 1.73%, N 19.25%. *Calcd.* for Cd(bipy)Ni(CN)₄: C 38.98%, H 1.87%, N 19.48%.

The FT-IR spectra of mulls and KBr discs were recorded on a Nicolet 510 spectrometer. The Raman spectra of the samples were excited using the 488.0 or 514.5 nm lines of a CRL Argon ion laser and recorded on a Cary 81 spectrometer.

3. Results and Discussion

The vibrational wavenumbers of bipy observed in the infrared and Raman spectra of the Ni(bipy)₃Ni(CN)₄·6H₂O·0.5(bipy) and Cd(bipy)Ni(CN)₄ compounds, and for free bipy, are summarized in Table I. These data show that the formation of adducts leads to a significant change from the spectrum of the free ligand. Comparable changes, observed in the vibrational spectra of compounds having 2,2'-bipyridyl as ligand, have already been described and discussed [3–5]. The electronic density transfer from the nitrogen lone-pair to the metal atom and the mechanical coupling between M-N (2,2'-bipy) vibrational modes with internal modes of the ligand may account for the positive shifts of the frequencies of the bipy ligand.

The FT-IR spectra of the Cd and Ni compounds are given in Figures 1 and 2, respectively. As seen from the figures the mono and tris-bipy compounds exhibit different band patterns. The Ni compound is found to have a considerable amount of water, which is consistent with its 3D structure with H-bonds [1]. We also observed two sharp bands at 3600 and 3580 cm⁻¹ which varied in intensity from one spectrum to other, depending on the grinding of the sample during the preparation of the KBr disc. We assigned these bands to $\nu(\text{OH})$ of water coordinated to Ni in the Ni(CN)₄ units. Such a high value of the $\nu(\text{OH})$ vibration was observed in hydrates of nickel cyanide [6]. We propose that during the grinding some of the H-bonds in the structure may be broken and H₂O molecules may coordinate to Ni in the Ni(CN)₄ groups. Careful investigation of the IR spectrum of Ni-Ni-bipy indicates the presence of two very low intensity $\nu(\text{CN})$ bands around 2152 and 2144 cm⁻¹, which are assigned to the same mode of the decomposed sample.

Table I. Vibrational wavenumbers (cm^{-1}) of 2,2'-bipyridyl in the M-Ni-bipy compounds.

Assignment	2,2'-bipy		Cd-Ni-bipy		Ni-Ni-bipy	
	IR	R	IR	R	IR	R
ν_{ring}		1589vs		1597vs	1605sh	1605vs
ν_{ring}	1578vs		1591vs		1598s	
ν_{ring}		1572vs		1575m	1580m	1574m
					1574m	
ν_{ring}	1558vs		1574s		1567m	
ν_{ring}		1482s	1489m	1493vs	1493m	1497s
$\nu_{\text{ring}} + \delta(\text{CH})$	1451vs		1475vs		1473s	
$\nu_{\text{ring}} + \delta(\text{CH})$		1447s		1438w	1458w	1441vw
$\nu_{\text{ring}} + \delta(\text{CH})$	1415vs		1439vs		1442vs	
ν_{ring}		1301s	1316m	1308s	1314s	1320s
			1306w	1298w		
δ_{ring}	1269vw		1283vw	1286m	1280vw	
ν_{ring}	1249m		1247m		1248m	
$\delta(\text{CH})$		1237s		1265m		1270w
δ_{ring}		1217				
δ_{ring}	1212w		1219w		1226m	
$\delta(\text{CH})$	1169w		1176m		1172m	
$\delta(\text{CH})$		1146w		1160vw		1160vw
$\delta(\text{CH})$	1139w		1157s		1158m	
$\delta(\text{CH})$		1094vw				
$\delta(\text{CH})$	1083m		1100w		1104vw	
$\nu_{\text{ring}} + \delta_{\text{ring}}$	1069w		1063m		1063m	
$\nu_{\text{ring}} + \delta_{\text{ring}}$		1045		1069m		1065w
δ_{ring}	1039s		1042w		1041w	
		994vs	1018s	1022vs		1030vs
Ring breathing	992ms		1012sp		1021s	1018sh
					995*w	
δ_{ring}	893m		897w		903w	
$\gamma(\text{CH})$		814vw	814vw		814w	815w
$\gamma(\text{CH})$	756vs	764	769vs		779vs	771w
$\gamma(\text{CH})$	740m		736ms		737s	
δ_{ring}	652m		651ms		653ms	658w
δ_{ring}	618m		628m		633m	635w
δ_{ring}		614m			619w	
τ_{ring}	401s		414s			

vs = very strong; s = strong; ms = medium strong; m = medium; w = weak; vw = very weak; sh = shoulder; sp = split; * guest bipy

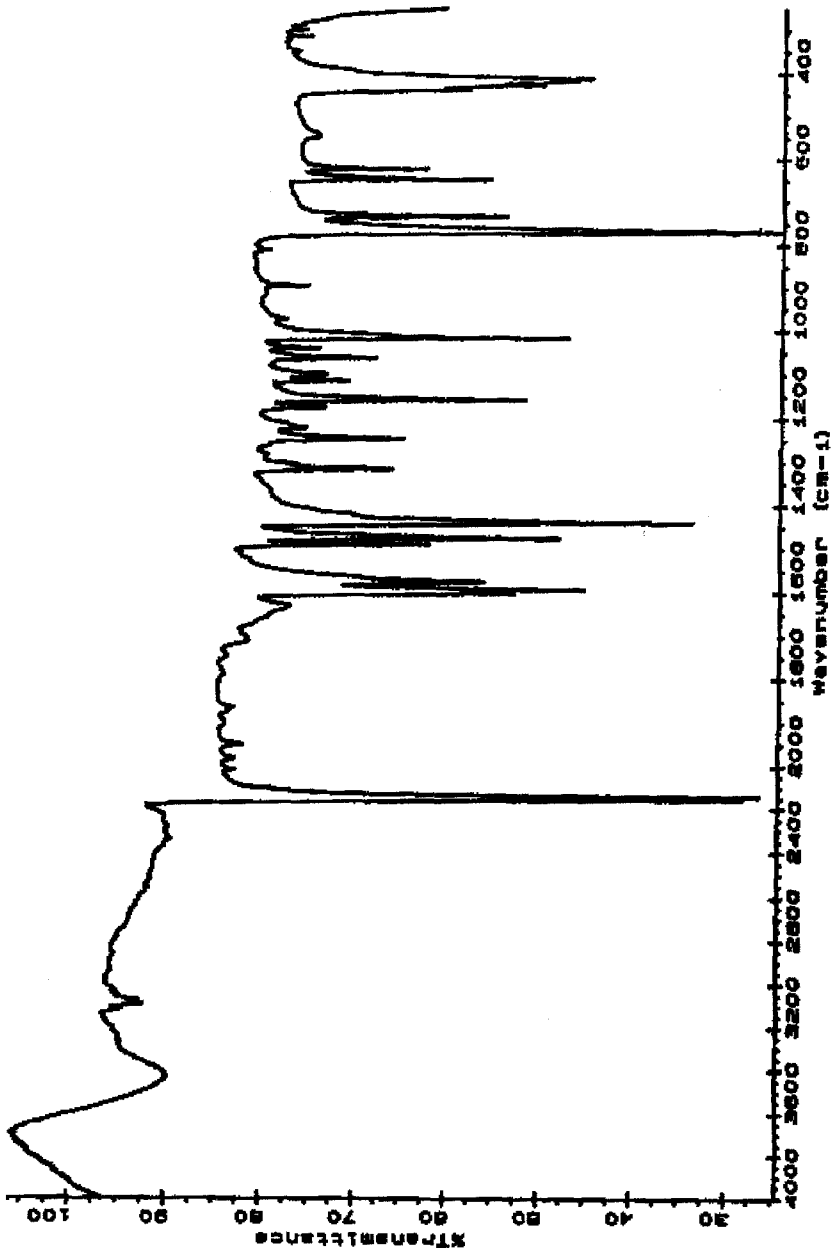


Figure 1. The FT-IR spectrum of the Cd(2,2'-bipy)Ni(CN)₄ compound.

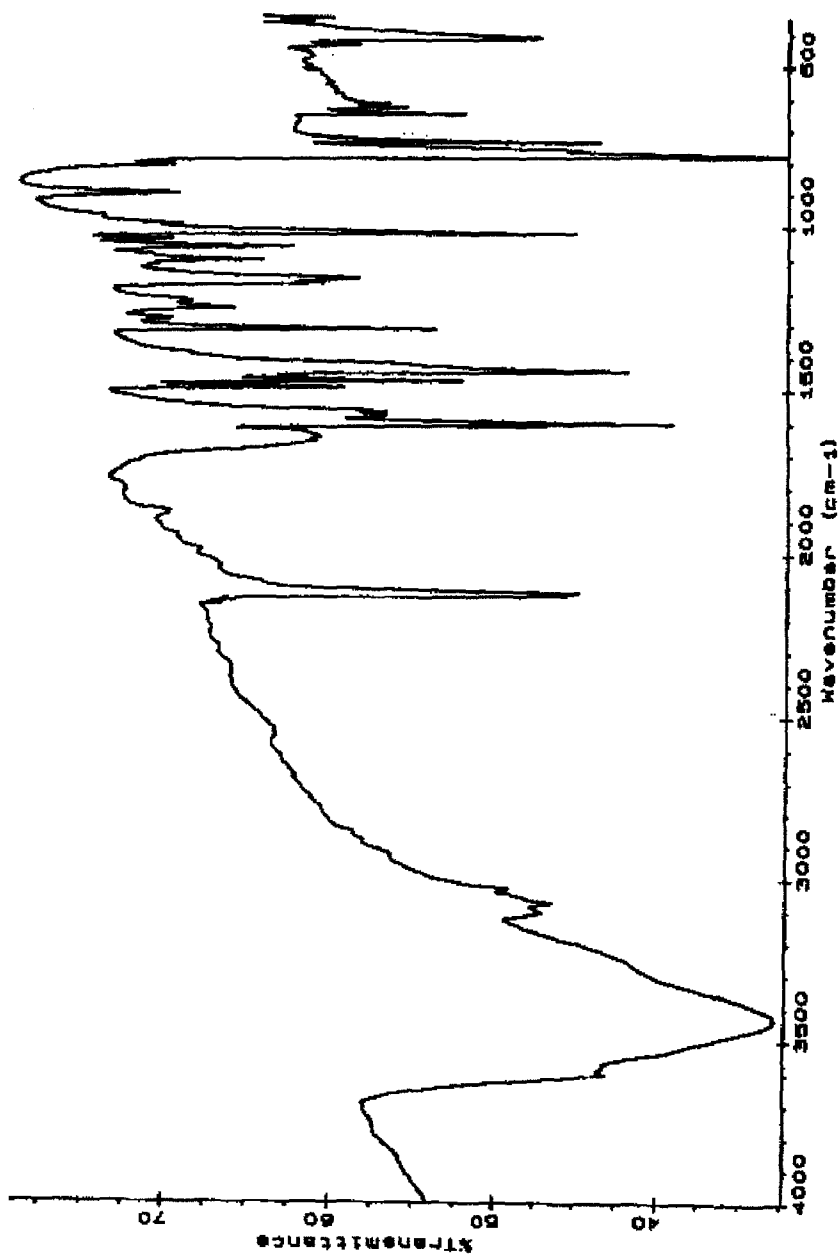


Figure 2. The FT-IR spectrum of the $\text{Ni}(2,2'\text{-bipy})_3\text{Ni}(\text{CN})_4 \cdot 6\text{H}_2\text{O} \cdot 0.5(2,2'\text{-bipy})$ compound.

Table II. The Ni(CN)₄ group vibrations of M-Ni-bipy complexes.

Assignment	Na ₂ Ni (CN) ₄	Cd-Ni-bipy		Ni-Ni-bipy	
		IR	R	IR	R
$\nu(\text{CN}) A_{1g}$	2149		2175s		2165vs
$\nu(\text{CN}) B_{1g}$	2141		2154vs		2133s
$\nu(\text{CN})$				2152*vw	
				2144*vw	
$\nu(\text{CN}) E_u \{$	2132	2156vs		2125s	
	2128	2140vs		2117s	
$\nu(\text{NiC}) E_u$	543w	551w		—	
$\pi(\text{Ni-CN}) A_{2u}$	448w	441m		438w	
$\delta(\text{Ni-CN}) E_u$	433s	430ms		—	
	421s	420ms		412s	

* Decomposed sample – see text.

Another major spectral difference between the mono and tris-bipyridyl complexes is observed in the Ni(CN)₄ group vibrations. As seen in Table II, the Ni(CN)₄ group wavenumbers of the Cd-Ni-bipy compound exhibits the presence of {Cd-Ni(CN)₄}_∞ polymeric layers whereas the Ni-Ni-bipy compound exhibits the characteristics of free Ni(CN)₄ groups, which is consistent with their crystal structures [1,2]. The crystal study on the Ni-Ni-bipy compound [1] indicated the presence of two square planar, but crystallochemically different, Ni(CN)₄²⁻ anions. The two strong bands observed at 2125 and 2117 cm⁻¹, in the IR spectrum of the Ni-Ni-bipy compound are assigned to $\nu(\text{CN}) E_u$ modes of these two Ni(CN)₄²⁻ anions (Table II). Since the frequency difference of the $\nu(\text{CN}) E_u$ modes of these units is quite small (8 cm⁻¹) we could not clearly observe the difference in their $\delta(\text{NiCN})$ modes. However a shoulder at the low frequency side of this band is observed. In the IR spectrum of the Cd-Ni-bipy compound the $\nu(\text{CN}) E_u$ and $\delta(\text{NiCN}) E_u$ modes are observed in split pairs. In this case the splitting is due to the change of symmetry and removal of degeneracy. The X-ray single crystal study on the Cd-Ni-bipy compound [2] indicated the presence of undulated {Cd-Ni(CN)₄}_∞ layers and although the Cd-NC angles in the Cd-Ni(CN)₄ bridges in trans positions were found to be equal, the corresponding angles in the cis positions were markedly different from each other. Thus our spectroscopic result on the Cd-Ni-bipy compound is consistent with its crystal structure.

As the 2,2'-bipy molecules are bound to metal as bidentate ligand in both complexes, we observed an analogous complex formation effect in both spectra [7–10]. The ring breathing mode is known to be very sensitive to coordination of pyridine rings via σ donation from nitrogens and increases in frequency depending on the coordination strength [7–10]. The ring breathing mode out-of-phase (IR) and in-phase (Ra) components are observed at 992 (IR) and 994 (Ra) in the vibrational

spectra of microcrystalline 2,2'-bipyridyl (C_{2h}). These two components should be both IR and Raman active in the compounds studied, since the bipy molecules are in cis positions.

As seen in Table I, upward shifts in the frequency of this mode were observed for both compounds in comparison to that of the free molecule in the order $Cd < Ni$. The weak band observed at 995 cm^{-1} in the IR spectrum of the Ni-Ni-bipy compound is assigned to guest bipy since it shows no coordination effect.

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