

# Infrared Spectroscopic Study of Bis[1,2-bis(4-Pyridyl)ethane]cadmium(II) Tetracyanonickelate(II)–*m*-Xylene (1/2) Clathrate and Its Host Structure

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**Abstract.** Cd[1,2-bis-(4-pyridyl)ethane]<sub>2</sub>Ni(CN)<sub>4</sub>-*m*-xylene(1/2) clathrate and its host structure were prepared and characterized by chemical analysis and infrared spectroscopy. Vibrational assignments are proposed for the bands of the host lattice and guest molecules.

**Key words:** Hofmann-type clathrate, cadmium, 1,2-bis(4-pyridyl)ethane, tetracyanonickelate complexes, *m*-xylene inclusion compounds, IR and Raman spectra.

## 1. Introduction

Several Hofmann-type clathrates of general formula CdLNi(CN)<sub>4</sub> · *x*G, where L is a bidentate ligand and *x* is the number of guest molecules G have been obtained to date [1]. These crystal structures are substantially similar to one another: two-dimensionally extended *catena*-[cadmiumtetra- $\mu$ -cyanonickelate(II)] networks are bridged by ambidentate *catena*- $\mu$ -ligands to form a three-dimensional host structure accommodating guest molecule G in the interlayer space. In order to obtain a different complex host structure, we used the bidentate 1,2-bis(4-pyridyl)ethane (bpa) molecule as ligand and prepared the host structure, Cd(bpa)<sub>2</sub>Ni(CN)<sub>4</sub>, and its *m*-xylene clathrate.

The crystal structure of the Cd[1,2-bis-(4-pyridyl)ethane]<sub>2</sub>Ni(CN)<sub>4</sub>-*m*-xylene (1/2) clathrate has been reported previously [2]. *Catena*-{*catena*-bis- $\mu$ -[1,2-bis(4-pyridyl)ethane]cadmium(II) *trans*-di- $\mu$ -cyano-dicyanonickelate(II)}-*m*-xylene (1/2) clathrate crystallizes in the space group  $P2_1/c(C_{2h}^5)$  of the monoclinic system, with unit cell dimensions  $a = 10.510(1)$ ,  $b = 10.438(1)$ ,  $c = 19.012(2)$  Å,  $\beta$

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$= 103.552(7)^\circ$  and  $Z = 2$ . The three-dimensional host structure of this clathrate is remarkably different from those of the previously known Hofmann-type compounds [1]. A pair of ambidentate bpa ligands span the Cd atoms successively to form a double-bridged *catena-bis- $\mu$ -bpa-Cd* chain along the crystal *b*-axis. The host complex also has a chain structure of *catena-[cadmium(II) trans-di- $\mu$ -cyano-dicyanonickelate(II)]*,  $[-\text{Cd}-\text{NC}-\text{Ni}(\text{CN})_2-\text{Cd}-]_\infty$ , along the *a* axis in which the  $\text{Ni}(\text{CN})_4$  moiety behaves as a bidentate bridging ligand through the N atoms of the CN groups in *trans* position between the Cd atoms. The catenation mode of the  $\text{Ni}(\text{CN})_4$ , denoted as *trans-one-dimensional (trans-1D)*, is observed in a number of square planar tetracyanomethylate(II) complexes such as  $\text{Cd}(1,6\text{-diaminohexane})(p\text{-toluidine})_2\text{Ni}(\text{CN})_4$  [3],  $\text{Ni}(\text{en})_2\text{Pd}(\text{CN})_4$  [4] and  $\text{M}(\text{en})_2\text{Ni}(\text{CN})_4 \cdot 2\text{PhNH}_2$ , M is Ni, Cu, Zn or Cd, clathrates [5]. The host consists of the stacking of the two-dimensional network to form a layered structure along the *c*-axis. The cavity in which the *m*-xylene guest molecules are accommodated is formed in the layer itself. A similar host structure was also observed for  $\text{Cd}(1,9\text{-diaminononane})_2\text{Ni}(\text{CN})_4-(2,3\text{-xylidine})(1/2)$  clathrate [6] except for the *trans-1D* linkage of the  $\text{Ni}(\text{CN})_4$  moiety.

This study reports an IR spectroscopic study of the  $\text{Cd}[1,2\text{-bis-(4-pyridyl)ethane}]_2\text{Ni}(\text{CN})_4-m\text{-xylene}(1/2)$  clathrate and its host structure.

## 2. Experimental

### 2.1. $\text{Cd}(\text{bpa})_2\text{Ni}(\text{CN})_4-m\text{-xylene}(1/2)$

Into an aqueous solution containing 1 mmol each of  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  and  $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$  in 20 mL  $\text{H}_2\text{O}$ , 2 mmol bpa were added. The pH was adjusted to ca. 9.5 by adding citric acid and sodium hydroxide and the aqueous solution was covered with *m*-xylene. Yellowish crystals appeared at the interface of the two layers and the bottom of the vial one month later. The *o*- or *p*-xylene, toluene, benzene, diphenyl, dibenzyl and dioxane clathrates could not be obtained under the same conditions. *Anal. Found*: C, 60.43, H, 5.80, N, 13.80%. *Calcd.* for  $\text{Cd}(\text{C}_{12}\text{H}_{12}\text{N}_2)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_8\text{H}_{10}$ : C, 61.74, H, 5.20, N, 13.10%.

### 2.2. $\text{Cd}(\text{bpa})_2\text{Ni}(\text{CN})_4$

It was prepared as for the clathrate but without the addition of *m*-xylene. The colour of the guest-free complex was also yellowish. Attempts to obtain a single crystal of the host structure was unsuccessful. *Anal. Found.*: C, 51.33, H, 3.57, N, 16.93. *Calcd.* for  $\text{Cd}(\text{C}_{12}\text{H}_{12}\text{N}_2)_2\text{Ni}(\text{CN})_4$ : C, 52.10; H, 3.75; N, 17.40.

Infrared spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) of the compounds (not stable under pressure needed for KBr disk) were recorded as mulls in Nujol and hexachlorobutadiene between KBr plates on a Mattson 1000 FTIR Spectrometer, which was calibrated using polystyrene bands.

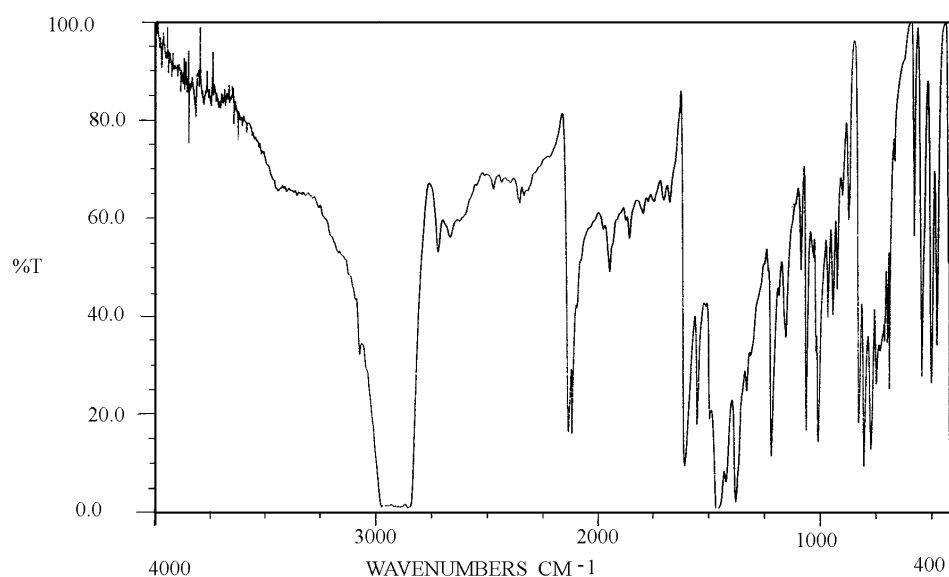


Figure 1. The IR spectrum of Cd(bpa)<sub>2</sub>Ni(CN)<sub>4</sub>·2C<sub>8</sub>H<sub>10</sub>.

The Raman spectrum of bpa in a spinning cell was excited using the 514.5 nm line of a Spectra-Physics Model 2016-4s Ar<sup>+</sup> ion laser and recorded on a Jobin Yvon U 1000 Spectrometer, which was calibrated against the laser plasma emission lines. A complete set of Raman spectra could not be obtained for the clathrate and complex because of decomposition.

### 3. Results and Discussion

The IR spectra of the clathrate and its host complex are given in Figures 1 and 2, respectively. The IR spectrum of the clathrate is very similar to that of the host structure except for the guest molecule bands, suggesting that they have similar structural features. Therefore, the assignments were divided into three groups arising from the Ni(CN)<sub>4</sub> units, from the bpa ligands and from the *m*-xylene moieties. The vibrational wavenumbers of the bands in the spectra of these species are tabulated in Tables I and II, together with some relevant spectral data for comparison.

#### 3.1. Ni(CN)<sub>4</sub> VIBRATIONS

According to the correlation diagram relating the symmetry representation of tetracyanonickelate(II) under the point group of the free ion,  $D_{4h}$  (or the molecular group in the clathrate,  $D_{2h}$ ), the site group symmetry in the clathrate is  $C_{2h}$ , as shown in Figure 3. Under the  $C_{2h}$  site symmetry, the  $\nu_8$  CN stretching  $E_u$  mode in the clathrate should be split into a doublet of  $A_u$  and  $B_u$  modes. Such splitting

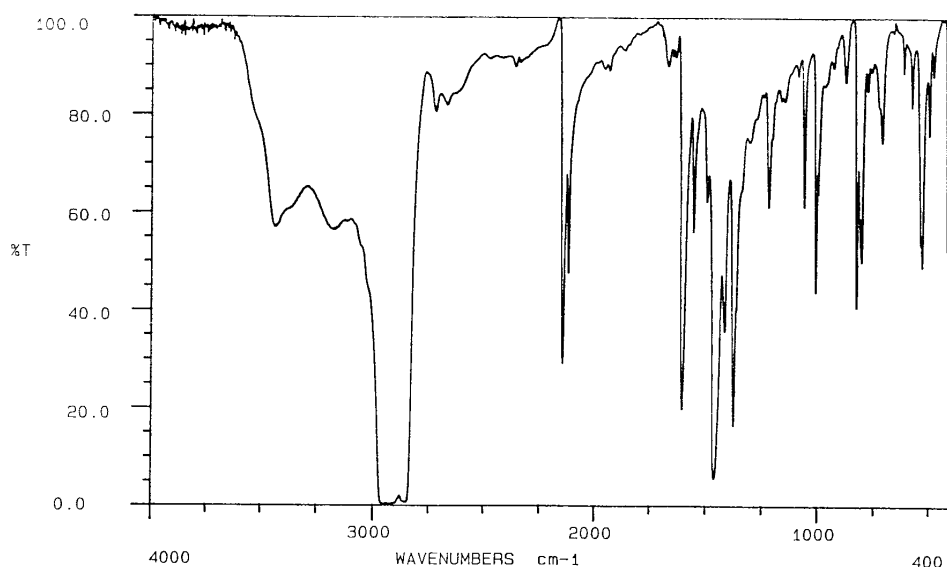


Figure 2. The spectrum of  $\text{Cd}(\text{bpa})_2\text{Ni}(\text{CN})_4$ .

was observed in the IR spectra of the title clathrate and its host structure. The lower  $\nu_{\text{CN}}$  wavenumber at  $2122\text{ cm}^{-1}$  is very close to that expected for a cyanide group of the tetracyanonickelate ion which is not coordinated to the Cd atom, while the second wavenumber at  $2138\text{ cm}^{-1}$  in the clathrate and at  $2148\text{ cm}^{-1}$  in the complex are in the region expected for a coordinated ion as shown in Table II. A similar splitting was also observed in the bis(*p*-toluidine)-1,6-diamino hexanecadmium(II) tetracyanonickelate(II) complex [7]. This upward shift of the bridging CN stretching vibrations is explained by coupling of the internal modes of  $\text{Ni}(\text{CN})_4$  with the M—NC vibrations as observed in various Hofmann-type complexes and clathrates [8, 9].

The wavenumber of the bridging CN stretching mode in the *m*-xylene clathrate is slightly lower (ca.  $10\text{ cm}^{-1}$ ) than that of the Cd—Ni—bpa complex. The slight shift is thought to be due to the interaction between the host lattice and the guest molecule. Ruiz et al. suggest that this host–guest interaction in a model clathrate,  $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ , is a particular type of *hydrogen bond* between the benzene and the cyanide groups in the host lattice, in which the CN groups act as donors towards the hydrogen atoms of benzene [10]. According to the EHTB band calculation, the empty  $\sigma^*$  orbitals of benzene accept electron density from the  $\pi$  orbitals and the nitrogen lone pair orbitals of cyanide in the host lattice, and this charge transfer could be considered as a  $\text{CN} \cdots \text{H}-\text{C}$  hydrogen bond [10].

Table I. The wavenumbers of the host lattice of the complex (Cd-Ni-bpa) and the clathrate (Cd-Ni-bpa-2G).

4,4'-bipy <sup>a</sup>		bpa		Complex	Clathrate	Assignment
IR	R	IR	R	IR	IR	
–	–	–	3065 m	3066 w	3067 w	$\nu_{\text{CH}}$
–	–	3005 w	–	3005 w	3004 w	$\nu_{\text{CH}}$
–	–	–	2933 w	2931 w	2930 w	$\text{CH}_2$ str
–	–	–	2865 w	2867 w	2865 w	$\text{CH}_2$ str
–	–	–	–	2148 vs	2138 vs	$\nu_{\text{CN}}$
–	–	–	–	2122 vs	2122 vs	$\nu_{\text{CN}}$
–	1617	–	1616 m	1610 vs	1610 vs	$\nu_{\text{ring}}$
1598	–	1608 s	–	1610 vs	1610 vs	$\nu_{\text{ring}}$
1532	–	1558 s	–	1556 m	1557 m	$\nu_{\text{ring}}$
1481	–	1496 m	–	1496 m	1498 m	$\nu_{\text{ring}} + \delta$ (CH)
–	–	1456 m	–	1456 m	1456 m	$\text{CH}_2$ sci.
–	1441	–	1445 w	1448 w	–	$\nu_{\text{ring}}$
1413	–	1415 s	–	1420 s	1423 m	$\nu_{\text{ring}}$
–	1348	–	1343 w	–	–	$\delta$ (CH)
1215	–	1217 vs	–	1223 vs	1221 vs	$\delta$ (CH)
–	–	–	–	1095 w	1095 w	?
1074	–	1078 s	–	1068 vs	1068 vs	$\nu_{\text{ring}}$
–	1000	–	1013 vs	1014 vs	1015 vs	$\nu_{\text{ring}}$
994	–	991 vs	–	1005 m	1002 m	$\nu_{\text{ring}}$
–	881	–	885 s	883 m	880 m	$\gamma$ (CH)
–	–	828 vs	–	831 vs	833 vs	$\gamma$ (CH)
810	–	808 vs	–	806 s	806 s	$\gamma$ (CH)
–	742	–	745 m	–	–	$\gamma_{\text{ring}}$
–	680	–	672 m	671 m	670 m	$\delta_{\text{ring}}$
–	574	–	–	582 m	584 m	$\gamma_{\text{ring}}$
–	–	547 vs	–	547 s	545 s	$\gamma_{\text{ring}}$
507	–	517 s	–	503 s	506 s	$\gamma_{\text{ring}}$
–	493	–	495 s	492 m	482 m	$\delta_{\text{ring}}$
–	–	–	–	449 vw	448 vw	$\delta$ Ni—CN
–	–	–	–	424 s	425 s	$\delta$ Ni—CN

<sup>a</sup> Taken from ref. [15].

vs: very strong, s: strong, w: weak, vw: very weak.

### 3.2. THE BPA VIBRATIONS

IR and Raman data of the bpa molecule are not available in the literature. Only one IR and Raman spectrum of the bpa over the range of 1400–400  $\text{cm}^{-1}$  has been reported by Chiu and Huang [11], but no attempt was made to assign the observed bands. Also, there is no normal coordinate analysis on the bpa molecule. Thus, we

Table II. IR wave numbers of *m*-xylene in the Cd-Ni-bpa·2G clathrate

Assignment <sup>a</sup>	<i>m</i> -xylene <sup>a</sup>	Cd-Ni-bpa·2G
$\nu_s$ (CH <sub>3</sub> )	2923 s	2920 s
$\nu_{23}$ (CC) (b <sub>2</sub> )	1492 s	1494 s
$\delta_s$ (CH <sub>3</sub> )	1375 s	1377 s
$\nu_6$ <i>x</i> -sens (a <sub>2</sub> )	1252 m	1254 m
$\nu_{26}$ $\beta$ (CH) (b <sub>2</sub> )	1167 s	1174 s
$\nu_4$ <i>x</i> -sens (CH <sub>3</sub> ) rock	1154 m	1160 m
$\nu_{25}$ $\gamma$ (CH) (b <sub>2</sub> )	968 s	972 m
$\nu_{28}$ <i>x</i> -sens (b <sub>2</sub> )	905 m	906 m
$\nu_{16}$ $\gamma$ (CH) (b <sub>2</sub> )	876 m	879 m
$\nu_{17}$ $\gamma$ (CH) (b <sub>2</sub> )	768 vs	775 vs
$\nu_{18}$ $\phi$ (CC) (b <sub>2</sub> )	690 vs	694 s
$\nu_{19}$ $\phi$ (CC) (b <sub>2</sub> )	433 vs	432 vs

<sup>a</sup> Taken from Ref. [17].

Isolated Ni(CN) <sub>4</sub> Point Group	Site Group	Factor Group	Site Group	Free <i>m</i> -xylene Point Group
D <sub>4h</sub>	C <sub>2h</sub>	C <sub>2h</sub>	C <sub>2</sub>	C <sub>2v</sub>
A <sub>1g</sub> (R)	A <sub>g</sub> (R)	A <sub>g</sub> (R)	A (IR,R)	A <sub>1</sub> (IR,R)
A <sub>2g</sub> (-)	B <sub>g</sub> (R)	B <sub>g</sub> (R)		B <sub>1</sub> (IR,R)
B <sub>1g</sub> (R)	A <sub>u</sub> (IR)	A <sub>u</sub> (IR)	B (IR,R)	A <sub>2</sub> (R)
B <sub>2g</sub> (R)	B <sub>u</sub> (IR)	B <sub>u</sub> (IR)		B <sub>2</sub> (IR,R)
E <sub>g</sub> (R)				
A <sub>1u</sub> (-)				
A <sub>2u</sub> (IR)				
B <sub>1u</sub> (-)				
B <sub>2u</sub> (-)				
E <sub>u</sub> (IR)				

Figure 3. Correlation chart for the symmetry species of the Ni(CN)<sub>4</sub> ion and *m*-xylene molecule in the Cd[1,2-bis-(4-pyridyl)ethane]<sub>2</sub>Ni(CN)<sub>4</sub>-*m*-xylene(1/2) clathrate.

tentatively assigned the observed bands of bpa by comparison with dibenzyl [12, 13] and 4,4'-bipyridine [14, 15].

Very recently, Ide et al. [16] determined the crystal structure of the bpa molecule and showed that bpa belongs to the point group  $C_{2h}$ , and its 72 fundamental vibrations are distributed as  $24A_g$ ,  $13A_u$ ,  $12B_g$  and  $23B_u$ . The bpa molecule has a centre of symmetry and obeys the mutual exclusion rule in which bands observed in the Raman are not active in the IR and *vice versa*, as shown in Table I. However, the new bands at 492, 671, 883 and  $1014\text{ cm}^{-1}$  being Raman active in free bpa were observed in the IR spectra of the clathrate and its host structure showing that there is no centre of symmetry for the bpa ligands in these compounds. According to single crystal results [2], both the methylene C-C bond increases from  $1.498\text{ \AA}$  in the free-bpa to  $1.52\text{ \AA}$  in the clathrate, and two torsion angles of the methylene bridge change from  $-99.50^\circ$  and  $78.0^\circ$  in the free-bpa to  $54.88^\circ$  and  $-126.90^\circ$  in the clathrate, respectively. The bending of the methylene bridge of bpa in the host structure vanishes under the inversion center. Chiu and Huang [11] also reported that the presence of a *gauche*-conformer (point group  $C_2$ ) of the free bpa in solution is indicated by the extra bands (at 490, 506, 591 and  $610\text{ cm}^{-1}$  in  $\text{CS}_2$ ) due to vibrational modes which are IR active in the conformer of lower symmetry.

Several of the bpa vibrations in our compounds have shifts up to ten wavenumbers to higher or lower frequencies compared to solid bpa. Similar shifts are also observed for the 4,4'-bipyridyl(bipy) vibrations in the  $\text{Cd}(\text{bipy})\text{Ni}(\text{CN})_4$  complex [14] and  $\text{Cd}(\text{bipy})\text{Cd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  clathrate [15]. The upward shift was explained by coupling of the internal vibrations of bipy with the M-N stretching vibration.

### 3.3. *m*-XYLENE VIBRATIONS

The assignments and the wavenumbers of the vibrational bands of *m*-xylene observed in the IR spectrum of the Cd-Ni-bpa-2G clathrate are listed in Table II, together with the wave numbers of *m*-xylene molecules in the liquid state [17], on which the assignments are based.

The free *m*-xylene molecule has  $C_{2v}$  symmetry, and its site symmetry in the clathrate will be  $C_2$  under the factor group  $C_{2h}$ , as shown in Figure 3. Thus, 30 fundamental modes are all infrared and Raman active in the clathrate. Among these, 12 bands were clearly identified in the clathrate, and two bands ( $1613$  and  $2864\text{ cm}^{-1}$ ) are overlapped by fundamental bands of the bpa molecule. As shown in Table II, the wavenumber value of each fundamental mode of *m*-xylene in the clathrate does not shift (ca.  $8\text{ cm}^{-1}$ ) to any significant degree. Correlation field splitting from the two molecules in the unit cell was not observed in the IR spectrum (spectral resolution range  $\pm 2\text{ cm}^{-1}$ ) of the clathrate. It seems that the intermolecular force between the *m*-xylene molecules are not significant.

It can be concluded that the IR spectral data reported here indicate that the title clathrate and the non-complexed host are isostructural. The complex has the same polymeric sheet structure as in the clathrate.  $\text{H}_2\text{O}$  molecules are not accommodated in the empty complex as reported by Yuge et al. [18], but the bands arising from the water in the IR spectrum may be due to water adsorbed during the measurements.

The similarity of the wavenumber of the  $\nu_{\text{CN}}$  mode at  $2148\text{ cm}^{-1}$  in the guest-free complex and at  $2147\text{ cm}^{-1}$  in the  $\text{Cd}(\text{bipy})\text{Ni}(\text{CN})_4$  complex indicates the absence of guest water molecules [14].

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