



## Vibrational Spectroscopic Study of [1,2-bis(4-pyridyl)ethane]metal(II) Tetracyanonickelate(II). 2 *m*-Xylene Clathrates

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### Abstract

Four new Hofmann-type clathrates of the form  $M(\text{bpa})_2\text{Ni}(\text{CN})_4 \cdot 2m\text{-xylene}$  ( $M = \text{Mn}, \text{Fe}, \text{Co}$  and  $\text{Ni}$ ;  $\text{bpa} = 1,2\text{-bis}(4\text{-pyridyl})\text{ethane}$ ) have been synthesized and characterized by vibrational spectroscopy. The  $M(\text{bpa})_2\text{Ni}(\text{CN})_4$  ( $M = \text{Fe}$  and  $\text{Co}$ ) host structure is similar to the classical Hofmann-type host framework composed of layers of a two dimensional *catena*-metal tetra- $\mu$ -cyanonickelate(II) network, but in  $M(\text{bpa})_2\text{Ni}(\text{CN})_4$  ( $M = \text{Mn}$  and  $\text{Ni}$ ), the  $\text{Ni}(\text{CN})_4$  moiety behaves as a bidentate  $-\text{[NC-Ni}(\text{CN})_2\text{-CN-]}$  unit in the host framework.

### Introduction

The Hofmann-type clathrate materials have enjoyed recurring interest since the discovery of  $\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  by Hofmann in 1897 [1]. The main interest in these materials has stemmed from their ability to trap aromatic hydrocarbons of specific size within the cavities between the planar nickel cyanide sheets. This trapping can be quite selective; indeed, a patent has been issued for the use of this material in purifying benzene from hydrocarbon feedstocks [2].

The dominant structural feature of these materials is a two-dimensional sheet formed from square planar nickel atoms linked to an octahedral metal center by cyanide bridges; the carbon atom of the cyanide is bound to the square-planar nickel atom and the nitrogen atom to the octahedral metal center. The axial positions of the octahedral divalent metal center are occupied by ammonia in most of the previously studied compounds. Extensive work was done in the late 1960s and early 1970s to investigate substitution of different metals for the square-planar and octahedral nickel centers in the original material [3].

In previous studies, X-ray analysis [4] and infrared spectroscopic studies [5] of the  $\text{Cd}(\text{bpa})\text{Ni}(\text{CN})_4 \cdot 2m\text{-xylene}$  clathrate have been reported. This paper examines the IR and Raman spectra of four new Hofmann-type clathrates of  $M(\text{bpa})\text{Ni}(\text{CN})_4 \cdot 2m\text{-xylene}$  ( $M = \text{Mn}, \text{Fe}, \text{Co}$  and  $\text{Ni}$ ,  $\text{bpa} = 1,2\text{-bis}(4\text{-pyridyl})\text{ethane}$ ) with the aim of providing further examples of Hofmann-type clathrates. The Mn and

Ni clathrates show different spectral features similar to the Cd clathrate.

### Experimental

Clathrates were prepared as previously described [5]. These hosts show isomeric selectivity towards the *m*-xylene isomers. They are slightly coloured solids. The infrared spectra of the fresh samples were recorded with a Mattson 1000 FTIR spectrophotometer in the range  $4000\text{--}400\text{ cm}^{-1}$  as mulls in Nujol and Fluorolube. The Raman spectra of the clathrates ( $\text{Co}, \text{Ni}, \text{Cd}$ ) were excited with the 514.5 nm line of an argon ion laser and the spectra were recorded on a Cary 81 spectrometer by use of a spinning cell.

The freshly prepared clathrates were analyzed for C, H and N by a Leco CHN-600 Model analyzer with the results as follows (% found/% calculated). The partial loss of *m*-xylene from the host lattice affects the result of elemental analysis.

$\text{Mn}(\text{bpa})_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_4(\text{CH}_3)_2$ :

C = 65.13/66.12, H = 4.49/5.51, N = 14.09/14.02

$\text{Ni}(\text{bpa})_2\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_4(\text{CH}_3)_2$ :

C = 64.86/65.81, H = 4.33/5.48, N = 13.86/13.96

$\text{Co}(\text{bpa})\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_4(\text{CH}_3)_2$ :

C = 61.03/62.11, H = 4.02/5.17, N = 13.60/13.58

$\text{Fe}(\text{bpa})\text{Ni}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_4(\text{CH}_3)_2$ :

C = 61.25/62.42, H = 5.09/5.20, N = 14.02/13.65

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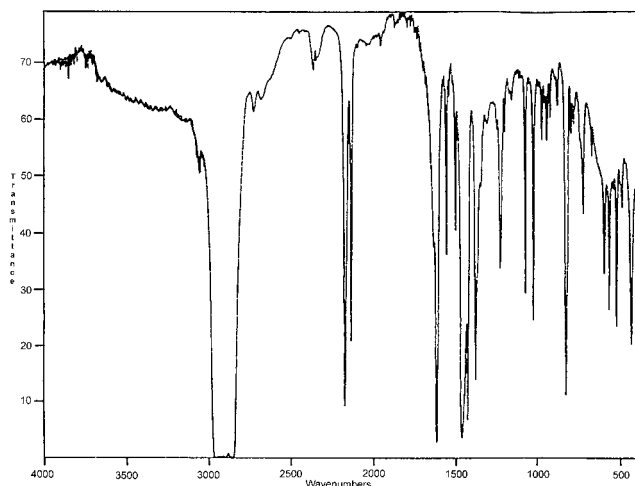


Figure 1. The IR spectrum of the Ni clathrate.

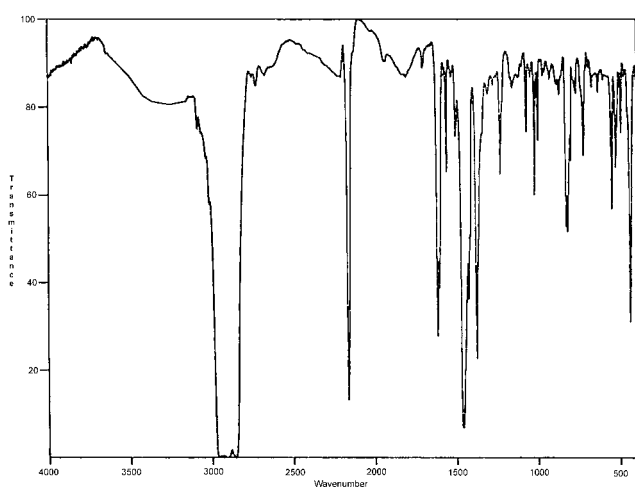


Figure 2. The IR spectrum of the Co clathrate.

## Results and discussion

As typical examples, IR spectra of the Ni and Co clathrates are given in Figures 1 and 2, respectively. The Raman spectrum of the Ni clathrate is given in Figure 3. The assignments were divided into three groups arising from the sheet structure, bpa and *m*-xylene.

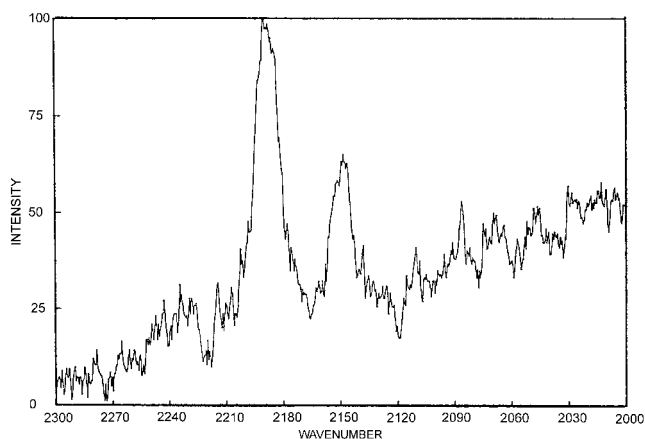


Figure 3. The Raman spectrum of the Ni clathrate.

## Sheet structure vibrations

The vibrational wavenumbers of the  $\text{Ni}(\text{CN})_4^{2-}$  group of the clathrates studied are tabulated in Table 1. The vibrations of the sheet structure of the Fe and Co clathrates are similar to those of analogous Hofmann type clathrates. If the cyanide groups around the nickel atom of the  $\text{Ni}(\text{CN})_4$  group have a local  $D_{4h}$  symmetry in the sheet structure, only one  $\nu(\text{CN})$  band having  $E_u$  symmetry is expected in the infrared spectrum and two  $\nu(\text{CN})$  vibrations are expected in the Raman spectrum. This is exactly what is observed. For example, in the IR spectrum of the Co clathrate, these bands are observed at 2166 (IR,  $E_u$ ), 2173 (R,  $B_{1g}$ ) and 2183 (R,  $A_{1g}$ ). These two clathrates also have a strong band in the infrared spectrum around  $430\text{ cm}^{-1}$  arising from an in-plane  $\text{Ni}-\text{C}\equiv\text{N}$  bending vibration ( $435\text{ cm}^{-1}$  in Fe,  $437\text{ cm}^{-1}$  in Co clathrate). However, in the IR spectra of the Mn and Ni clathrates, the CN stretching  $E_u$  mode splits into a doublet of  $A_u$  and  $B_u$  modes similar to the Cd clathrate, as the site group symmetry in these clathrates is  $C_{2h}$  not  $D_{4h}$ . [5]. The lower  $\nu_{\text{CN}}$  wavenumber at  $2132\text{ cm}^{-1}$  is very close to that of the cyanide group of the free tetracyanonickelate ion. The other CN stretching bands at  $2160\text{ cm}^{-1}$  and  $2169\text{ cm}^{-1}$  show that the CN groups are coordinated to the Mn and Ni atom respectively. 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-CN vibrations as observed in various Hofmann-type complexes and clathrates. A similar shift is also observed in the Raman spectrum of Ni clathrates. The shift to higher wavenumber of the  $A_{1g}$   $\nu(\text{CN})$  vibrations at  $2186\text{ cm}^{-1}$  shows that the N donor atom of the CN group is coordinated to the Ni atom, but the  $B_{1g}$   $\nu(\text{CN})$  vibrations at  $2148\text{ cm}^{-1}$  does not shift to any significant degree.

According to these data, the structure of the  $\text{M}(\text{bpa})_2\text{Ni}(\text{CN})_4 \cdot m\text{-xylene}$  ( $\text{M} = \text{Fe}$  and  $\text{Co}$ ) clathrates is a three-dimensional host framework built of layers of a two-dimensional *catena*-[metal(II)-tetra- $\mu$ -cyanonickelate(II)] network and of the ambidentate bpa bridging the metal atoms in the adjacent networks. The guest *m*-xylene molecule is accommodated in the cavity formed in the interlayer space. However, the three-dimensional host structure of the  $\text{M}(\text{bpa})_2\text{Ni}(\text{CN})_4 \cdot m\text{-xylene}$  ( $\text{M} = \text{Mn}$  and  $\text{Ni}$ ) clathrates are different from those of the known Hofmann-type clathrates. These clathrates also have a chain structure of *catena*-[metal(II)-di- $\mu$ -cyano-dicyanonickelate(II)] network, in which the  $\text{Ni}(\text{CN})_4$  moiety behaves as a bidentate bridging ligand between the M atoms as  $[-\text{M}-\text{NC}-\text{Ni}(\text{CN})_2-\text{CN}-\text{M}-]_{\infty}$ . A pair of ambidentate bpa ligands span the metal atoms successively to form a double-bridged *catena*-bis- $\mu$ -bpa-M-chain.

## bpa vibrations

To the best of our knowledge, normal coordinate analysis of the bpa has not been reported in the literature previously. Only one IR and Raman spectrum of this ligand over the range of  $1400\text{--}400\text{ cm}^{-1}$  has been reported [6]. The crystal structure of the bpa molecule has been determined and shown to have the point group  $C_{2h}$  and its 72 fundamental

Table 1. The wavenumbers of the Ni(CN)<sub>4</sub> group vibrations in the clathrates

Assignments	Na <sub>2</sub> Ni(CN) <sub>4</sub> <sup>a</sup>	M(bpa) <sub>2</sub> Ni(CN) <sub>4</sub> · <i>m</i> -xylene				
		Cd <sup>b</sup>	Mn	Ni	Fe	Co
A <sub>1g</sub> ν (CN)	2149vs	(2158)vs	–	(2186)vs	–	(2183)vs
B <sub>1g</sub> ν (CN)	2141s	(2133)vs	–	(2177)vs	–	(2173)vs
E <sub>u</sub> ν (CN)	2132s	2138 vs	2160 vs	2169 vs	2163 vs	2166vs
	2128s	2122 vs	2132 vs	2132 vs		
E <sub>u</sub> δ (Ni–CN)	431s	448 m	449 m	446 m		
	421s	425 s	433 s	439 s	435s	437s

<sup>a</sup> Taken from Ref. [13].<sup>b</sup> Taken from Ref. [5]. Raman bands are given in parentheses.

Table 2. The wavenumbers of bpa in the solid state and in the clathrates

Assignment	4,4'-bipy <sup>a</sup>		bpa		M(bpa) <sub>2</sub> Ni(CN) <sub>4</sub> · <i>m</i> -xylene				
	IR	R	IR	R	Cd <sup>b</sup>	Mn	Ni	Fe	Co
νCH	–	–	–	3065 m	3067 w	3056 w	3074 w		3064 w
CH <sub>2</sub> str.	–	–	3005 w	–	3004 w	–	–	–	–
CH <sub>2</sub> str.	–	–	–	2933 w	2930 w	2935 w	2939 w	2932 w	2935 w
ν <sub>ring</sub>	–	–	–	2865 w	2865 w	2867 w	2867 w	2866 w	2866 w
ν <sub>ring</sub>	–	1617	–	1616 m	1610 vs	1614 vs	1616 vs	1615 vs	1616 vs
ν <sub>ring</sub>	1598	–	1608 s	–	1610 vs	1614 vs	1616 vs	1615 vs	1616 vs
ν <sub>ring</sub> + δ(CH)	1532	–	1558 s	–	1558 m	1558 m	1558 m	1557 m	1560 m
CH <sub>2</sub> sci	1481	–	1496 m	–	1498 m	1502 m	1502 m	1497 m	1506 m
ν <sub>ring</sub>	–	–	1456 m	–	1456 m	1463 m	1463 m		1463 s
ν <sub>ring</sub>	–	1441	–	1445 w	–	–	–	–	–
δ(CH)	1413	–	1415 s	–	1423 m	1423 m	1425 m	1424 m	1425 m
δ(CH)	–	1348	–	1343 w	–	1344 w	1346 w	–	–
?	1215	–	1217 vs	–	1221 vs	1224 m	1226 m	1225 vs	1232 vs
ν <sub>ring</sub>	–	–	–	–	1095 m	–	1106 w	1098 w	–
ν <sub>ring</sub>	1074	–	1078 s	–	1068 vs	1068 s	1068 s	1069 vs	1070 vs
ν <sub>ring</sub>	–	1000	–	1012 vs	1015 vs	1020 vs	1020 vs	1017 vs	1022 vs
γ(CH)	994	–	991 s	–	1002 m	–	–	–	998 m
γ(CH)	–	881	–	885 s	880 m	–	875 m	–	–
γ(CH)	–	–	828 vs	–	833 s	–	829 m	832 s	831 s
ν <sub>ring</sub>	810	–	808 vs	–	806 s	821 s	823 s	809 s	800 s
ν <sub>ring</sub>	–	742	–	745 m	–	–	–	–	–
ν <sub>ring</sub>	–	680	–	672 m	670 m	–	670 m	671 m	–
ν <sub>ring</sub>	–	574	–	–	584 m	595 m	595 m	597 m	601 m
ν <sub>ring</sub>	–	–	547 vs	–	545 m	565 s	567 m	548 m	551 m
ν <sub>ring</sub>	507	–	517 s	–	506 m	520 m	522 m	507 m	526 m
ν <sub>ring</sub>	–	493	–	495 s	482 m	–	489 m	490 m	493 m

<sup>a</sup> Taken from Ref. [10].<sup>b</sup> Taken from Ref. [5].

vibrations are distributed as 24 A<sub>g</sub>, 13A<sub>u</sub>, 12 B<sub>g</sub> and 23 B<sub>u</sub> modes. This molecule has a center of symmetry, thus it obeys the mutual exclusion principle. We have tentatively assigned the observed bands of the ligand by comparison with 4,4' bipyridine and dibenzil [7–10].

The frequencies of the bands arising from the bpa molecule in the IR spectra of the clathrates are given in Table 2. Frequencies taken from the IR spectra of solid bpa and 4,4'-bipyridyl are included for comparison. Some new bands being Raman active in free bpa were observed in the IR spectra of the clathrates. This means that there is no center of symmetry for the ligands in these clathrates. Certain vibrations of the bpa molecule in the clathrates show shifts of up

to 10 cm<sup>-1</sup> to higher frequency when compared to the same vibration in the pure solid. This shift could be explained by coupling of the internal vibrations of bpa with the M-N stretching vibrations.

#### Vibrations of *m*-xylene

The assignments and wavenumbers of the IR bands of *m*-xylene observed in the spectra of the compounds under study are given in Table 3, together with the IR data for *m*-xylene in the liquid phase [11] on which the assignments are based. The free *m*-xylene molecule has C<sub>2v</sub> symmetry. The wavenumber of each fundamental band of *m*-xylene in

Table 3. IR wavenumbers of *m*-xylene in the clathrates

Assignments	<i>m</i> -xylene <sup>a</sup>	M(bpa) <sub>2</sub> Ni(CN) <sub>4</sub> ··· 2 <i>m</i> -xylene				
		Cd <sup>b</sup>	Mn	Ni	Fe	Co
$\nu_s$ (CH <sub>3</sub> )	2923 s	2920 s	2925 m	2929 m	2928 m	2927 m
$\nu_{23}$ (CC)(b <sub>2</sub> )	1492 s	1494 s	1502 s	1502 s	1498 m	1496 m
$\delta_s$ (CH <sub>3</sub> )	1375 s	1377 s	1377 s	1376 m	1376 m	1377 m
$\nu_6$ x-sens(a <sub>2</sub> )	1252 m	1254 m	1246 w	1245 w	1252 m	–
$\nu_{26}$ $\beta$ (CH)(b <sub>2</sub> )	1167 s	1174 s	1175 m	1172 m	1172 s	1173 m
$\nu_4$ x-sens (CH <sub>3</sub> ) rock	1154 m 1039 s	1160 m 1038 m	– 1037 w	1151 w –	1160 m –	– 1037 m
$\nu_{25\gamma}$ (CH)(b <sub>2</sub> )	968 s	972 m	968 s	968 m	970 m	–
$\nu_{28}$ x-sens(b <sub>2</sub> )	905 m	906 m	908 m	907 m	905 m	906 m
$\nu_{16\gamma}$ (CH)(b <sub>2</sub> )	876 m	879 m	–	875 m	878 m	876 m
$\nu_{17\gamma}$ (CH)(b <sub>2</sub> )	768 vs	775 s	–	770 m	776 m	774 s
$\nu_{18\phi}$ (CC)(b <sub>2</sub> )	690 vs	694 s	693 m	690 m	693 m	692 m
$\nu_{19\phi}$ (CC)(b <sub>2</sub> )	433 vs	c	c	c	c	c

<sup>a</sup> Taken from Ref. [11].

<sup>b</sup> Taken from Ref. [5].

<sup>c</sup> Obscured by sheet structure.

these compounds does not shift to any significant degree. It seems that host–guest interactions in these clathrates are not present. The only interaction between the guest molecule and sheet structure could be a weak special type hydrogen bond between the  $\pi$ -electrons of the aromatic guest molecule and the bpa molecules of the host lattice [12].

## References

1. K.A. Hofmann and F.Z. Kuspert: *Z. Anorg. Allg. Chem.* **15**, 204 (1897).
2. U.S. Patent 2, 732, 413 (1956).
3. T. Iwamoto: in J.L. Atwood, J.E.D. Davies, and D.D. MacNicol (eds.), *Inclusion Compounds*, Vol. 1, Ch. 2, Academic Press, London (1984), p. 29; Vol. 5, Ch. 6, Oxford University Press, Oxford (1991) p. 177.
4. B. Günes, S. Özbey, H. Soylu, Y.Tufan, and N. Karacan: *Acta Crystallogr.* **C5**, 2425 (1996).
5. Y.Tufan and N. Karacan: *J. Incl. Phenom.* **27**, 193 (1997).
6. K.K Chiu and H.H. Huang: *Spectrochim. Acta.* **29A**, 1947 (1973).
7. A.M. North, R.A. Pethrick and A.D. Wilson: *Spectrochim. Acta* **30A**, 1317 (1974).
8. M.S. Mathur and N.A. Weir: *J. Mol. Struct.* **14**, 303 (1972).
9. A.Sungur, S. Akyüz, and J.E.D. Davies: *J. Incl. Phenom.* **5**, 491 (1987).
10. S. Bayarî, Z. Kantarci, and S.Akyüz: *J. Incl. Phenom.* **17**, 291 (1994).
11. J. H. S. Green: *Spectrochim. Acta* **26A**, 1523 (1970).
12. E. Ruiz, J.J. Novoa, and S. Alvarez: *J. Phys. Chem.* **99**, 2296 (1995).
13. R.L. McCullough, L.H. Jones, and G.A. Crosby: *Spectrochim. Acta.* **16**, 292 (1960).