



## An Infrared Spectroscopic Study on the Hofmann T<sub>d</sub>-Type Clathrates: M(Imidazole)<sub>2</sub> M'(CN)<sub>4</sub>·2C<sub>6</sub>H<sub>6</sub>

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### Abstract

Infrared spectra of M(Imidazole)<sub>2</sub> M'(CN)<sub>4</sub>·2C<sub>6</sub>H<sub>6</sub> (M = Mn, Co, Ni, Cd; M' = Zn, Cd) are reported. The spectral data suggest that the clathrates are similar in host structure to Hofmann T<sub>d</sub>-type clathrates.

### Introduction

Hofmann type inclusion compounds have been a subject of many experimental and theoretical studies because of their significance in understanding the nature of host–guest systems [1–5].

We have previously reported [6–7] the vibrational spectra of samples of some Hofmann type imidazole clathrates. In this study, the results of infrared spectroscopic studies of Hofmann T<sub>d</sub> type clathrates of imidazole M(Im)<sub>2</sub> M'(CN)<sub>4</sub>·2C<sub>6</sub>H<sub>6</sub> (where M: Mn, Co, Ni, or Cd; Im: Imidazole, M': Cd, Zn) are reported. The aim of this study is to give further examples of Hofmann T<sub>d</sub> type clathrates and to examine the coordination behaviour of imidazole.

An imidazole ring forms part of biological molecules such as nucleic acids and proteins. Imidazole functions as ligands toward transition metal ions in a variety of biologically important molecules such as iron-heme systems, metalloproteins, vitamin B<sub>12</sub> and its derivatives. The most commonly studied transition metal ions such as Mn(II), Fe(II), Co(II), Ni(II) and Cd(II) form crystalline products of composition M(Im)<sub>6</sub>X<sub>2</sub> where X includes common anions such as Cl<sup>−</sup>, Br<sup>−</sup>, I<sup>−</sup>, NO<sub>3</sub><sup>−</sup> [8]. It is, therefore, of importance to define the coordination behaviour of imidazole toward transition metals. Thus, the identification of M–N(Im) vibrations in biological systems provides valuable information about the structure of the active site of a metalloprotein.

### Experimental

All chemicals were reagent grade and used without further purification. 2 mmol imidazole and excess of benzene were added into an aqueous solution containing 1 mmol M(II) salt and K<sub>2</sub>M'(CN)<sub>4</sub> in 50 ml water. The reaction mixture was stirred at a constant rate for 2 days at room temperature. The

precipitate was filtered and washed with water, acetone and diethylether.

Infrared spectra of the samples were measured with a Mattson 1000 FTIR spectrometer in the range 4000–400 cm<sup>−1</sup> as mulls in Nujol and 1,3-hexachlorobutadiene. Spectrometer was calibrated using polystyrene bands.

The IR spectrum of Cd(Im) Cd(CN)<sub>4</sub>·2C<sub>6</sub>H<sub>6</sub> is given in Figure 1 as example of the clathrates. The freshly prepared samples were analyzed for C,H,N by a Carlo Erba 1108 Elemental analyzer with the results as follows (the host lattice affects the results of elemental analysis):

Mn(Im) <sub>2</sub> Zn(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	: C = 50.13/51.12, H = 3.72/3.91, N = 20.82/21.75
Co(Im) <sub>2</sub> Zn(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	: C = 49.72/50.73, H = 3.68/3.89, N = 20.73/21.58
Ni(Im) <sub>2</sub> Zn(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	: C = 50.32/50.75, H = 3.72/3.88, N = 20.92/21.59
Cd(Im) <sub>2</sub> Zn(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	: C = 45.44/46.01, H = 3.25/3.52, N = 18.84/19.57
Mn(Im) <sub>2</sub> Cd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	: C = 45.27/46.86, H = 3.35/3.58, N = 18.72/19.94
Co(Im) <sub>2</sub> Cd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	: C = 45.88/46.53, H = 3.40/3.56, N = 17.69/19.74
Ni(Im) <sub>2</sub> Cd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	: C = 45.09/46.55, H = 3.28/3.56, N = 18.70/19.75
Cd(Im) <sub>2</sub> Cd(CN) <sub>4</sub> ·2C <sub>6</sub> H <sub>6</sub>	: C = 41.06/42.53, H = 3.02/3.25, N = 17.43/18.04

### Results and discussion

The spectral features of the compounds under study are found to be similar to each other, suggesting that they have similar structural features. It may be convenient to divide the vibrations into three groups arising from the imidazole ligands, M'(CN)<sub>4</sub> groups and the guest molecule benzene respectively. The assignments and the wave numbers of the observed bands arising from imidazole, M'(CN)<sub>4</sub> and C<sub>6</sub>H<sub>6</sub> species are tabulated in Tables 1, 2 and 3 respectively.

#### Imidazole ligand vibrations

Imidazole falls in the class of aromatic heterocycles and its unique structural features are conveniently related with pyridine and pyrrole nitrogen and pyridine nitrogen.

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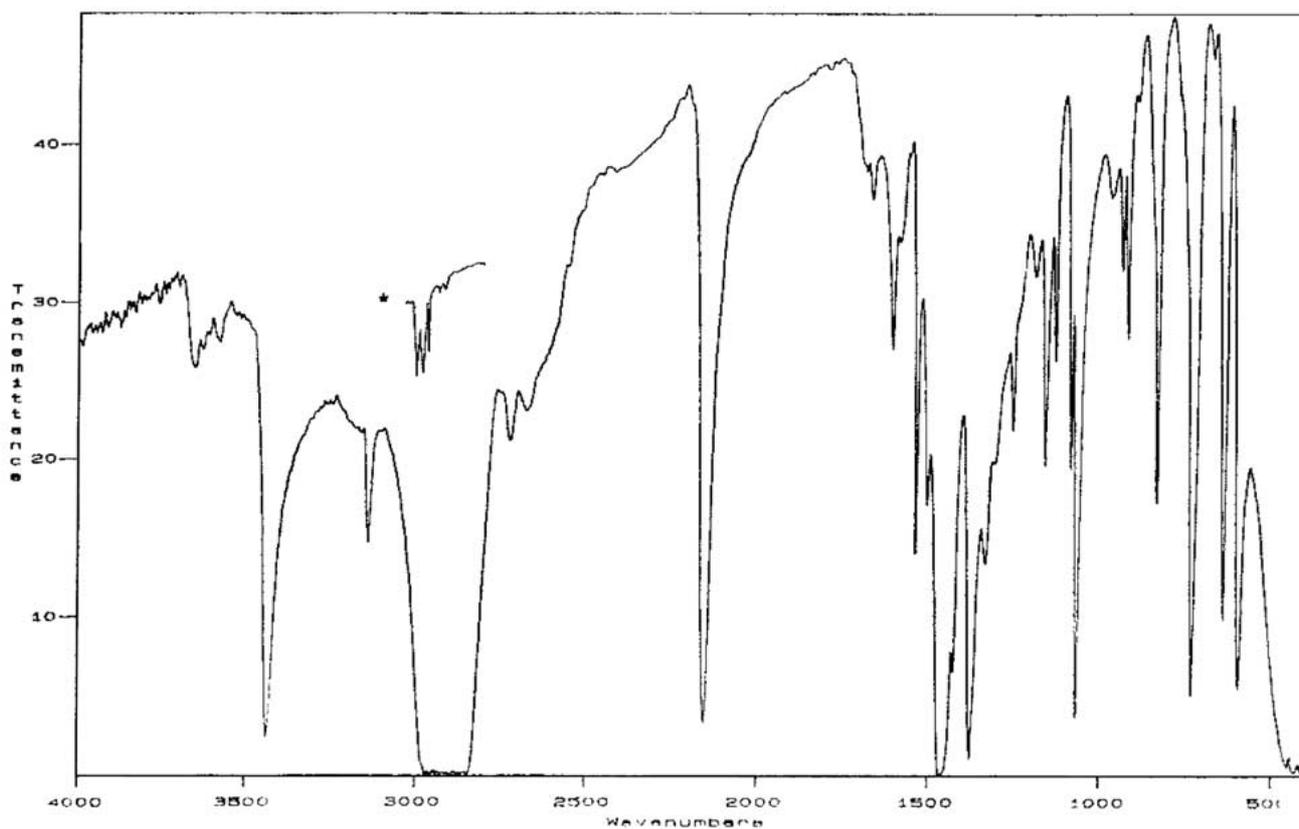


Figure 1. The IR spectrum of  $\text{Cd}(\text{Im})_2\text{Cd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  (in nujol) (\* in 1,3-hexachlorobutadiene).

Table 1. The wave numbers of imidazole in the  $\text{M}(\text{Im})_2\text{M}'(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  clathrates

Assignment <sup>a</sup> (PED)	Imidazole <sup>a</sup> (gas)	Imidazole <sup>b</sup> (Ar matrix)	$\text{M}(\text{Im})_2\text{Zn}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$				$\text{M}(\text{Im})_2 \text{Cd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$			
			Mn	Co	Ni	Cd	Mn	Co	Ni	Cd
<b>A<sup>I</sup></b>										
100 NH	3517 s	3504	3440 s	3441 s	3441 s	3438 s	3439 s	3441 s	3440 s	3437 s
44C <sub>5</sub> + 51C <sub>4</sub> H	3159 vw	–	–	–	–	–	–	–	–	–
53C <sub>5</sub> H + 35C <sub>4</sub> H + 12C <sub>2</sub> H	3133 vw	–	–	–	–	–	–	–	–	–
13C <sub>4</sub> H + 8C <sub>2</sub> H	3132 w	–	3147 s	3146 s	3145 s	3142 s	3146 s	3145 s	3145 s	3142 s
24C <sub>4</sub> C <sub>5</sub> + 13C <sub>2</sub> N <sub>3</sub> + 32δ <sub>NH</sub>	1526 w	1518	1541 vs	1540 vs	1541 vs	1538 vs	1540 vs	1540 vs	1541 vs	1537 s
16C <sub>4</sub> C <sub>5</sub> + 13C <sub>2</sub> N <sub>3</sub> + 32δ <sub>NH</sub>	1481 s	1480	1506 s	1507 s	1506 s	1503 s	1506 s	1506 s	1507 s	1504 s
22C <sub>4</sub> C <sub>5</sub> + 16N <sub>1</sub> C <sub>2</sub> + 41δ <sub>NH</sub>	1406 s	1412	1427 m	1427 m	1428 m	1422 m	1426 m	1427 m	1425 m	1423 m
21C <sub>2</sub> N <sub>3</sub> + 37δC <sub>4</sub> H + 25δC <sub>2</sub> H	1329 vw	1325	1332 m	1331 m	1332 m	1331 m	1331 m	1332 m	1331 m	1330 m
51C <sub>2</sub> N <sub>3</sub> + 27δC <sub>2</sub> H	1259 vw	1252	1254 m	1255 m	1254 m	1254 m	1253 m	1252 m	1252 m	1251 m
25C <sub>4</sub> C <sub>5</sub> + 19N <sub>1</sub> C <sub>2</sub> + 22δC <sub>5</sub> H	1159 vw	–	1159 m	1160 m	1163 m	1162 m	1160 m	1162 m	1160 m	1160 m
50N <sub>3</sub> C <sub>4</sub> + 32C <sub>5</sub> N <sub>1</sub>	1122 w	1120	1136 m	1133 m	1134 m	1132 m	1135 m	1132 m	1134 m	1132 m
41N <sub>1</sub> C <sub>2</sub> + 13C <sub>4</sub> C <sub>5</sub> + 21N <sub>3</sub> C <sub>4</sub>	1084 w	1074	1086 m	1082 m	1084 m	1085 m	1085 m	1084 m	1082 m	1084 m
44C <sub>5</sub> N <sub>1</sub> + 22N <sub>3</sub> C <sub>4</sub> + 15δC <sub>5</sub> H	1057 vs	1056	1070 vs	1070 vs	1068 vs	1069 vs	1068 vs	1068 vs	1069 vs	1069 vs
59δR <sub>1</sub> + 19δR <sub>2</sub>	925 w	900	940 s	937 s	938 s	936 s	935 s	938 s	938 s	937 s
58δR <sub>2</sub> + 26δR <sub>1</sub>	891 w	892	923 m	922 m	920 m	921 m	922 m	921 s	920 s	919 s
<b>A<sup>II</sup></b>										
28γC <sub>5</sub> H + 42γC <sub>4</sub> H + 23τR <sub>1</sub>	856 m	850	850 m	851 m	–	852 m	853 m	854 m	852 m	850 m
11γC <sub>4</sub> H + 59γC <sub>2</sub> H + 29τR <sub>2</sub>	811 vs	810	835 m	840 m	838 m	836 m	836 m	836 m	836 m	834 m
63γC <sub>5</sub> H + 30γC <sub>4</sub> H	724 vs	728	730 m	732 m	730 m	729 m	728 m	729 m	728 m	729 m
76τR <sub>2</sub> + 24τR <sub>1</sub>	664 s	662	–	663 w	–	662 w	–	662 w	–	662 w
77τR <sub>1</sub> + 23τR <sub>2</sub>	628 s	636	638 s	637 s	637 s	636 s	635 s	634 s	632 s	632 s
95τNH + 5τR <sub>1</sub>	509 vs	551	596 s	594 s	592 s	593 s	594 s	592 s	593 s	590 s

<sup>a</sup>Taken from Ref. [9] (PED: Potential Energy Distribution).

<sup>b</sup>Taken from Ref. [10]. vs = very strong, s = strong, m = medium, w = weak, vw = very weak.

Table 2. The wave numbers of  $M'(CN)_4$  group of  $M(Im)_2 M'(CN)_4 \cdot 2C_6H_6$  clathrates

Assignment <sup>a</sup>	$K_2Cd(CN)_4^a$	$K_2Zn(CN)_4^a$	$M(Im)_2 Zn(CN)_4 \cdot 2C_6H_6$				$M(Im)_2 Cd(CN)_4 \cdot 2C_6H_6$			
			Mn	Co	Ni	Cd	Mn	Co	Ni	Cd
$\nu_5(CN) F_2$	2145	2152	2163 vs	2164 vs	2166 vs	2186 vs	2165 vs	2180 vs	2188 vs	2203 vs

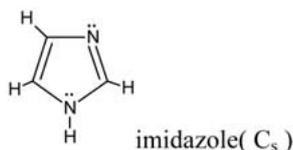
<sup>a</sup>Taken from Ref. [11]. vs = very strong.

Table 3. The wave numbers of benzene in the  $M(Im)_2 M'(CN)_4 \cdot 2C_6H_6$  clathrates

Assignment <sup>a</sup>	Liquid benzene <sup>b</sup>	$M(Im)_2 Zn(CN)_4 \cdot 2C_6H_6$				$M(Im)_2 Cd(CN)_4 \cdot 2C_6H_6$			
		Mn	Co	Ni	Cd	Mn	Co	Ni	Cd
$\nu_8 + \nu_{19}$	3075	–	–	–	3063 w	–	–	3062 w	3064 w
$\nu_{20}E_{1u}$	3073	3076 w	3080 w	3090 w	3080 w	3077 w	3080 w	3091 w	3082 w
$\nu_{13}B_{1u}$	3062	3028 m	302.4m	3028 m	3026 m	3022 m	3033 m	3029 m	3029 m
$\nu_5 + \nu_{17}E_{1u}$	1955	–	–	–	1967 w	1968 w	1966 w	–	–
$\nu_{10} + \nu_{17}$	1815	1823 vw	–	–	1826 vw	–	–	–	–
$\nu_{19}E_{1u}$	1479	1477 m	1479 m	1477 m	1478 m	1476 m	1476 m	1475 m	1474 m
$\nu_{14}B_{2u}$	1309	1304 vw	1305 vw	1306 vw	–	1304 vw	1304 vw	–	1305 vw
$\nu_{15}B_{2u}$	1149	–	–	–	–	–	–	–	–
$\nu_{18}E_{1u}$	1036	1032 w	1034 w	1033 w	1030 w	1030 w	1033 w	1032 w	–
$\nu_{11}A_{2u}$	670	701 vs	709 vs	704 vs	700 vs	701 vs	702 vs	703 vs	703 vs

<sup>a</sup>Taken from Ref. [12].

<sup>b</sup>Taken from Ref. [13]. vs = very strong, s = strong, m = medium, w = weak, vw = very weak.



The imidazole molecule usually functions as a ligand via the unshared pair of electrons of the pyridine nitrogen. A large number of the metal complexes of imidazole have been synthesized and their structures have been discussed [14].

Imidazole belongs to the  $C_s$  point group. There are 21 modes of vibrations. All modes of vibrations are IR and Raman active.

Several authors have studied the vibrational assignments of imidazole [9, 10]. It is clear from Table 1 that most of the vibrational modes of imidazole in the clathrates have increased in wave numbers when compared with free imidazole. These shifts may be explained as the coupling of M–N(Im) vibrations. Similar shifts have been observed in metal coordinated imidazole complexes [1–5–16].

The NH stretching vibration in the clathrates are shifted towards lower wave numbers of about  $70\text{ cm}^{-1}$ . This shows that the ligand is bonded to the metal ion via the pyridine nitrogen, as pyrrole nitrogen bonded complexes show a negative shift of around  $190\text{ cm}^{-1}$  [17].

The vibrational frequencies of imidazole generally increase after complexing. Similar observations have been also observed previously for pyridine nitrogen bonded complex [17].

#### $M'(CN)_4^{2-}$ ( $M' = Zn, Cd$ ) group vibrations

Cyano metal complexes can be easily identified by IR spectroscopy since they exhibit sharp  $\nu(CN)$  shifts to higher

frequencies. The  $CN^-$  groups act as a  $\sigma$  donor by giving electrons to the metal (II) ion and also a  $\pi$ -acceptor by accepting electrons from the metal (II) ion.

The vibrational assignment of  $K_2Zn(CN)_4$  and  $K_2Cd(CN)_4$  salts were taken as a reference to assign the bands attributable to the  $M'(CN)_4$  ( $M = Zn, Cd$ ) group. In the  $T_d$ -type host framework, metal (II) ion is tetrahedrally surrounded by the carbon ends of four  $CN^-$  ions. The host framework studied here are also tetrahedral  $M'(CN)_4$  groups. The observed wave numbers are in good agreement with other Hofmann  $T_d$ -type complexes and clathrates reported in the literature previously [18]. In an octahedral environment, the N-ends of the  $M'(CN)_4$  group are also bound to a M(II) ion.

#### Benzene vibrations

The vibrational spectra of benzene as a guest have been reported for a number of Hofmann  $T_d$ -type clathrates [19]. The spectral features of the clathrates reported in this study are almost the same pattern as other  $T_d$  type clathrates. The most important interaction between host lattice and guest molecule benzene is electron density transfer from the  $\pi$ -orbital of benzene to empty orbitals of the host lattice. This type of host–guest interactions in the clathrates would be a special type of hydrogen bond. The metal atom does not participate significantly in the host–guest interaction [3].

The vibrational spectra of the benzene molecules are weakly affected by enclathration. This means that the interaction between host lattice and guest is very weak. All bands of the guest (benzene) molecule remain practically unchanged upon enclathration, as has been reported in more detail in the literature [3–5]. The only exceptions are the bands due to CH out of plane vibrations. These bands in the

clathrates are observed to be shifted to higher wave numbers ( $\sim 700\text{ cm}^{-1}$ ) from that of liquid benzene ( $670\text{ cm}^{-1}$ ). Similar results were observed for these type of clathrates previously [20]. This shift was explained by a weak hydrogen bond between  $\pi$ -electrons of the benzene and the hydrogen atoms of the ligand [19–20].

There is no X-ray structural study on these clathrates, as the location of the benzene molecules in the host is unknown. X-ray structural studies on these type of clathrates are in progress.

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