



# Vibrational Spectroscopic Investigations of $M(\text{Imidazole})_2\text{Ni}(\text{CN})_4 \cdot 2$ Dioxane Clathrates

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**Abstract.** Four new clathrates of the formula  $M(\text{Im})_2\text{Ni}(\text{CN})_4 \cdot 2$ -Dioxane (where  $M = \text{Co}, \text{Ni}, \text{Cu}, \text{Cd}$ ;  $\text{Im} = \text{Imidazole}$ ) have been prepared in powder form and their FT-IR and laser-Raman spectra are reported for the first time. These clathrates are analogues to the previously reported classical Hofmann type clathrates except for the copper clathrate. The Cu clathrate has different spectral features in comparison with its analogues due to the Jahn-Teller effect.

**Key words:** Hofmann-type clathrate, metal-imidazole complexes, dioxane inclusion compounds, IR and Raman spectra

## 1. Introduction

The well known Hofmann type clathrates have been reported previously [1]. In this paper, the infrared and Raman spectra of four new di imidazole metal tetracyanonickelate-dioxane clathrates,  $M(\text{Imidazole})_2\text{Ni}(\text{CN})_4 \cdot 2$  Dioxane ( $M = \text{Co}, \text{Ni}, \text{Cu}, \text{Cd}$ ) are reported.

Imidazole is a constituent of histamine and of histidine residues of proteins. This molecule functions as a ligand toward transition metal ions in a variety of biologically important molecules including iron-heme systems, vitamin B<sub>12</sub> and its derivatives and several metalloproteins [2].

## 2. Experimental

All chemicals were reagent grade and used without further purification. 2 mmol imidazole and excess of dioxane were added into an aqueous solution containing 1 mmol each of  $M\text{Cl}_2 \cdot x\text{H}_2\text{O}$  and  $\text{K}_2[\text{Ni}(\text{CN})_4] \cdot \text{H}_2\text{O}$  in 50 mL  $\text{H}_2\text{O}$ . The mixture

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was stirred at a constant rate for 48 hour. The precipitate was filtered and washed with water, acetone and diethylether respectively.

The infrared spectra of the fresh samples were recorded with a Mattson 1000 FTIR spectrometer in the range 4000–400  $\text{cm}^{-1}$  as mulls in Nujol and Fuorolube. The Raman spectra of two clathrates (Co, Cd; in powder form) 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  $\text{M}(\text{Im})_2\text{Ni}(\text{CN})_4 \cdot 2 \text{C}_4\text{H}_8\text{O}_2$  clathrates were analyzed for C, H and N by a Leco CHN-600 Model analyzer with the following results (% found/% calculated).

$\text{Co}(\text{Im})_2\text{Ni}(\text{CN})_4 \cdot 2 \text{C}_4\text{H}_8\text{O}_2$  : C = 38.76/40.15, H = 4.28/4.46, N = 18.97/20.82

$\text{Ni}(\text{Im})_2\text{Ni}(\text{CN})_4 \cdot 2 \text{C}_4\text{H}_8\text{O}_2$  : C = 39.13/40.15, H = 4.25/4.46, N = 19.04/20.82

$\text{Cu}(\text{Im})_2\text{Ni}(\text{CN})_4 \cdot 2 \text{C}_4\text{H}_8\text{O}_2$  : C = 39.08/39.82, H = 4.02/4.42, N = 18.60/20.64

$\text{Cd}(\text{Im})_2\text{Ni}(\text{CN})_4 \cdot 2 \text{C}_4\text{H}_8\text{O}_2$  : C = 35.64/36.52, H = 3.91/4.06, N = 16.97/18.93

The partial loss of dioxane from the host lattice affects the results of elemental analysis.

### 3. Result and Discussion

The vibrational spectra of  $\text{M}(\text{Im})_2\text{Ni}(\text{CN})_4 \cdot 2\text{G}$  (M = Co, Ni, Cd) are very similar to each other but the copper compound shows different spectral features. This suggests that three clathrates have the same structure. The IR and Raman spectra of  $\text{Cd}(\text{Im})_2\text{Ni}(\text{CN})_4 \cdot 2$  Dioxane are given in Figures 1 and 2 respectively. The assignments were divided into three groups arising from the  $\text{Ni}(\text{CN})_4^{2-}$  anion, the ligand (imidazole) and the guest molecule.

#### 3.1. $\text{Ni}(\text{CN})_4^{2-}$ GROUP VIBRATIONS

The vibrational wavenumbers of the  $\text{Ni}(\text{CN})_4^{2-}$  group of the clathrates are given in Table I. The wave numbers of the  $\nu(\text{CN})$  and  $\delta(\text{NiCN})$  modes are found to be similar to those of Hofmann-type clathrates [3] indicating that the  $[\text{M}-\text{Ni}(\text{CN})_4]_\infty$  polymeric sheet structure has been preserved. The observation of one IR active ( $E_u$ ) and two Raman active ( $A_{1g}$  and  $B_{1g}$ ) modes of  $\nu(\text{CN})$  showed that the nickel atoms have a local  $D_{4h}$  symmetry in the Co, Ni, Cd clathrates. The  $\nu(\text{CN})$  frequencies depend on the metal and this reflects the strength of the metal nitrogen bond (M—N).

In the  $\text{Cu}(\text{Im})_2\text{Ni}(\text{CN})_4 \cdot 2\text{G}$  clathrate, two strong bands are observed in the  $\nu(\text{CN})$  and  $\delta(\text{NCN})$  regions of the infrared spectrum; the observation of two strong bands in these regions is related directly to a change of symmetry and removal of degeneracy. This is the well known Jahn-Teller effect and has been observed previously in metal pyridine tetracyanonickellate complexes [4].

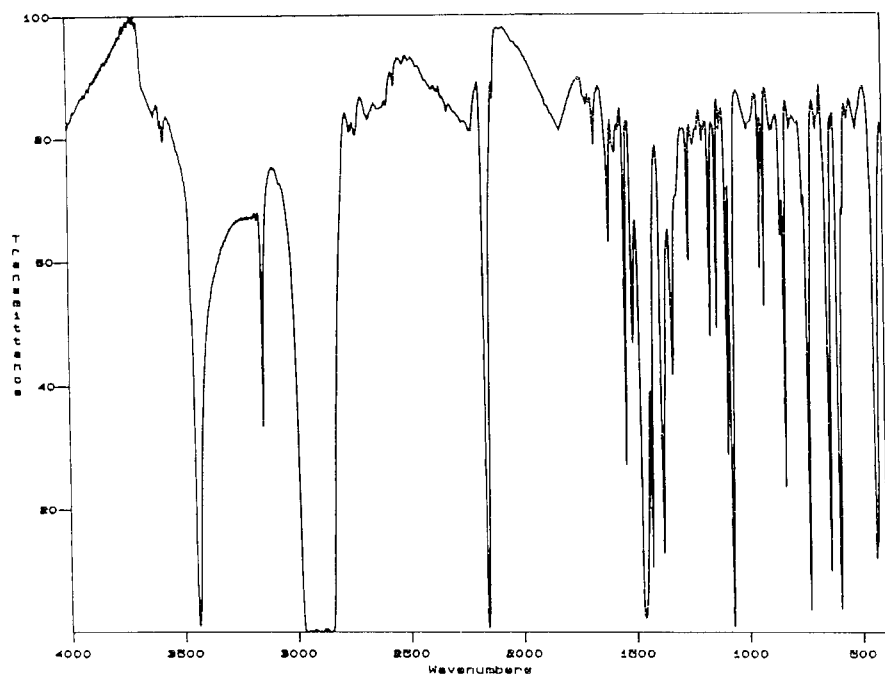


Figure 1. The IR spectrum (nujol mull) of  $\text{Cd}(\text{Im})_2\text{Ni}(\text{CN})_4 \cdot 2 \text{C}_4\text{H}_8\text{O}_2$ .

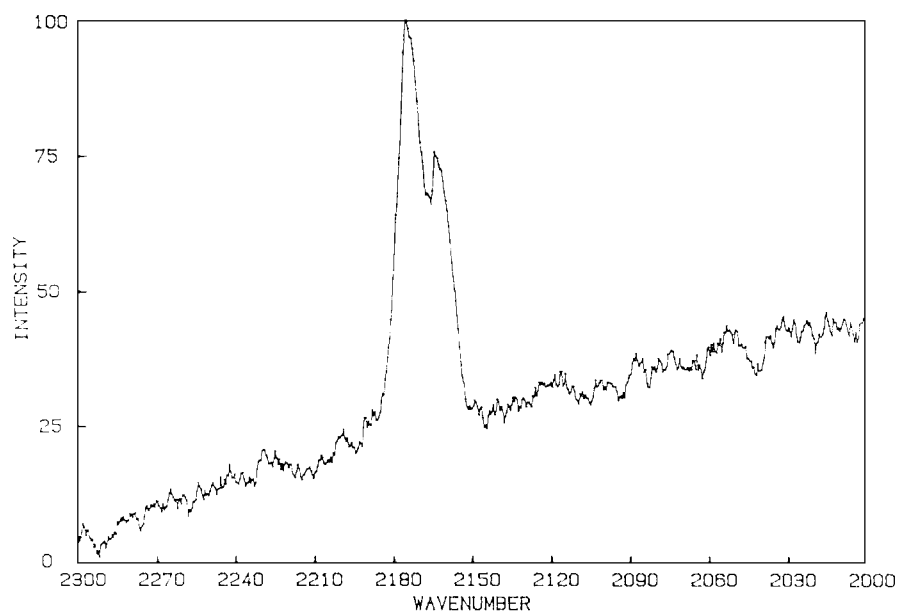


Figure 2. The Raman spectrum of  $\text{Cd}(\text{Im})_2\text{Ni}(\text{CN})_4 \cdot 2 \text{C}_4\text{H}_8\text{O}_2$ .

Table I. The vibrational wavenumbers ( $\text{cm}^{-1}$ ) of the  $\text{Ni}(\text{CN})_4$  group of  $\text{M}(\text{Im})_2\text{Ni}(\text{CN})_4 \cdot 2$  Dioxane clathrates.

Assignment	$\text{Na}_2\text{Ni}(\text{CN})_4^{\text{a}}$	Co	Ni	Cu	Cd
$A_{1g} \nu(\text{CN})$	2149	(2175) vs	–	–	(2171) vs
$B_{1g} \nu(\text{CN})$	2141	(2167) vs	–	–	(2161) vs
$E_u \nu(\text{CN})$	2132	2156 vs	2161 vs	2171 vs	2156 vs
–	–	–	–	2129 vs	–
$E_u \nu(\text{CN})$	421	431 vs	439 vs	445 vs	430 vs
–	–	–	–	428 m	–

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

The bands observed in the Raman spectra are given in parentheses.

Table II. The wavenumbers of imidazole in the  $\text{M}(\text{Im})_2\text{Ni}(\text{CN})_4 \cdot 2 \text{C}_4\text{H}_8\text{O}_2$  clathrates.

Imidazole <sup>a</sup> (Gas)	Imidazole <sup>b</sup> (Ar-Matrix)	$\text{M}(\text{Im})_2\text{Ni}(\text{CN})_4 \cdot 2 \text{C}_4\text{H}_8\text{O}_2$				Assignment <sup>a</sup> (PED)
		Co	Ni	Cu	Cd	
$A'$ 3517 s	3504	3436 s	3436 vs	–	3438 vs	100 NH
3159 vw	–	–	–	–	–	44 $\text{C}_5\text{H}$ + 51 $\text{C}_4\text{H}$
3133 vw	–	–	–	–	–	53 $\text{C}_5\text{H}$ + 35 $\text{C}_4\text{H}$ + 12 $\text{C}_2\text{H}$
3132 w	–	3145 s	3145 s	3153 m	3145 s	13 $\text{C}_4\text{H}$ + 85 $\text{C}_2\text{H}$
1526 w	1518	1540 vs	1541 vs	1541 vs	1539 m	24 $\text{C}_4\text{C}_5$ + 13 $\text{C}_2\text{N}_3$ + 32 $\delta_{\text{NH}}$
1481 s	1480	1506 s	1506 s	1514 s	1506 m	16 $\text{C}_4\text{C}_5$ + 13 $\text{C}_2\text{N}_3$ + 32 $\delta_{\text{NH}}$
1406 s	1412	1427 m	1428 m	1430 m	1427 m	22 $\text{C}_4\text{C}_5$ + 16 $\text{N}_1\text{C}_2$ + 41 $\delta_{\text{NH}}$
1329 vw	1325	1330 m	1340 s	1334 s	1331 s	21 $\text{C}_2\text{N}_3$ + 37 $\delta\text{C}_4\text{H}$ + 25 $\delta\text{C}_2\text{H}$
1259 vs	1252	1255 s	1257 s	1261 s	1258 m	51 $\text{C}_2\text{N}_3$ + 27 $\delta\text{C}_2\text{H}$
1159 vw	–	1163 m	1162 m	1176 m	1163 m	25 $\text{C}_4\text{C}_5$ + 19 $\text{N}_1\text{C}_2$ + 22 $\delta\text{C}_5\text{H}$
1122 w	1120	1133 m	1136 m	1128 m	1132 m	50 $\text{N}_3\text{C}_4$ + 32 $\text{C}_5\text{N}_1$
1084 w	1074	1088 s	1087 m	1089 m	1088 m	41 $\text{N}_1\text{C}_2$ + 13 $\text{C}_4\text{C}_5$ + 21 $\text{N}_3\text{C}_4$
1057 vs	1056	1070 vs	1070 vs	1064 vs	1070 vs	44 $\text{C}_5\text{N}_1$ + 22 $\text{N}_3\text{C}_4$ + 15 $\delta\text{C}_5\text{H}$
925 w	900	941 s	941 s	948 s	941 s	59 $\delta\text{R}_1$ + 19 $\delta\text{R}_2$
891 w	892	923 m	923 m	921 m	924 m	58 $\delta\text{R}_2$ + 26 $\delta\text{R}_1$
$A''$ 856 m	850	850 m	–	863 w	865 w	28 $\gamma \text{C}_5\text{H}$ + 42 $\gamma \text{C}_4\text{H}$ + 23 $\tau \text{R}_1$
811 vs	810	835 m	831 m	840 m	835 m	11 $\gamma \text{C}_4\text{H}$ + 59 $\gamma \text{C}_2\text{H}$ + 29 $\tau \text{R}_2$
724 vs	728	730 s	729 m	728 m	730 m	63 $\gamma \text{C}_5\text{H}$ + 30 $\gamma \text{C}_4\text{H}$
664 s	662	–	–	–	–	76 $\tau \text{R}_2$ + 24 $\tau \text{R}_1$
628 s	636	638 s	638 s	655 m	638 s	77 $\tau \text{R}_1$ + 23 $\tau \text{R}_2$
509 vs	551	596 s	594 s	611 s	594 s	95 $\gamma \text{NH}$ + 5 $\tau \text{R}_1$

<sup>a,b</sup> Taken from Refs. [5] and [9], respectively.

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

Table III. The vibrational wavenumbers ( $\text{cm}^{-1}$ ) of dioxane in the  $\text{M}(\text{Im})_2 \text{Ni}(\text{CN})_4 \cdot 2 \text{Dioxane}$ .

Liquid <sup>a</sup> dioxane	$\text{M}(\text{NH}_3)_2 \text{Ni}(\text{CN})_4 \cdot 2 \text{C}_4\text{H}_8\text{O}_2^{\text{b}}$		$\text{M}(\text{Im})_2 \text{Ni}(\text{CN})_4 \cdot 2 \text{C}_4\text{H}_8\text{O}_2$				Assignment <sup>a</sup>
	Ni	Cd	Co	Ni	Cu	Cd	
2963	2965 m	–	2962 w	–	2962 w	2960 w	$\nu_{11}$ stretching
2917	2920 m	2919 m	2916 w	2920 w	2921 w	2921 w	$\nu_{13} + \nu_{22}$
2852	2864 s	2860 m	2861 w	2860 w	2860 w	2859 w	$\nu_{12}$ $\text{CH}_2$ stretching
1454	1455 s	1457 m	1459 m	1464 m	1463 w	1460 w	$\nu_{30}$ $\text{CH}_2$ scissoring
1445	1443 w	–	–	–	–	–	$\nu_{13}$ $\text{CH}_2$ scissoring
1375	1379 w	1378 w	1377 w	1377 w	1376 w	1378 w	$\nu_{31}$ $\text{CH}_2$ wagging
1366	1366 s	1367 m	–	–	–	–	$\nu_{14}$ $\text{CH}_2$ wagging
1289	1292 m	1291 m	–	1307 w	–	1292 m	$\nu_{32}$ $\text{CH}_2$ twisting
1256	1256 s	1257 s	–	–	–	–	$\nu_{15}$ $\text{CH}_2$ twisting
1125	1115 vs	1116 s	1118 m	1118 m	1119 m	1120 m	$\nu_{16}$ ring stretching
1083	1079 s	1079 m	1080 m	1080 m	1081 w	1081 w	$\nu_1$ $\text{CH}_2$ rocking

<sup>a,b</sup> Taken from Refs. [15] and [13], respectively.

### 3.2. IMIDAZOLE VIBRATIONS

The fundamental vibrational modes of imidazole have been assigned by several authors [5–9]. This molecule belongs to the  $\text{C}_s$  point group and there will be 21 modes of vibrations which are divided among the symmetry species as follows: 15  $A'$  and 6  $A''$  (all IR and Raman active). The vibrational wave numbers of imidazole observed in the infrared spectra of the clathrate are given in Table II. A comparison of the IR spectra of the ligand and clathrates highlights the following facts.

The  $\nu(\text{NH})$  bands in the clathrates are shifted towards lower wavenumbers of about  $60 \text{ cm}^{-1}$  using as reference the value of  $3504 \text{ cm}^{-1}$  for  $\nu(\text{NH})$  for the free ligand in an Ar-matrix [9]. This strongly suggests that imidazole is bonded via pyridine nitrogen in these clathrates as  $\nu(\text{NH})$  shows a negative shift of  $190 \text{ cm}^{-1}$  in the pyrrole nitrogen bonded complex [10, 11]. The shifting can be explained on the assumption that metal ions are bonded to the pyridine nitrogen only and hence there would be a slight shift of electron density from the pyrrole nitrogen towards the pyridine nitrogen.

After complexing, vibrational frequencies of imidazole generally increase especially for the in-plane ring bending vibrations ( $891, 925, 1057 \text{ cm}^{-1}$  in free molecule). These can be explained mainly in terms of a coupling of the internal vibrational modes of imidazole with the M-N vibration. Similar observations have been reported previously for imidazole complexes [12].

### 3.3. DIOXANE VIBRATIONS

The vibrational frequencies of the dioxane in the IR spectra of the clathrates correspond closely in frequency to the dioxane clathrates reported previously [13, 14]. A complete vibrational assignment has been reported for the free liquid dioxane by Ellestad et al [15], and the assignment of the dioxane in this paper is based on this study. It is found that the gradual loss of dioxane molecules from the host lattice does not cause any change in the vibrational frequencies of the host structure. The infrared bands of the dioxane in the clathrates correspond closely in frequency to those in the IR spectrum of liquid dioxane. It is clear that the dioxane molecules in the clathrates are also in a chair conformation [13]. This also suggests that the interaction between the host structure and the guest is very weak.

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