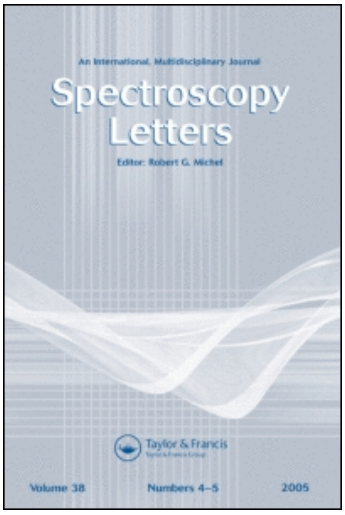

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Infrared and Raman Spectroscopic Studies of 2-Methylpyrazine Metal (II) Tetracyanonickelate Benzene Clathrates: $[M(H_2O)(2\,mpz)Ni(CN)_4]\cdot C_6H_6$ (M = Mn or Cd)

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ABSTRACT New Hofmann-type tetracyanoaqua 2-methylpyrazine metal (II) nickelate (II) benzene clathrates, $[M(H_2O)(2\,mpz)Ni(CN)_4]\cdot C_6H_6$ (where 2 mpz = 2-methylpyrazine ($C_5H_6N_2$); M=Mn(II) or Cd(II); C_6H_6 = benzene) have been prepared in powder form and characterized by infrared and Raman spectroscopy. Thermal behaviors of these compounds are followed using thermo-gravimetric analysis and differential thermal analysis (DTA) techniques. The spectral features suggest that these compounds are similar in structure to the Hofmann-type two-dimensional coordination polymer compounds. The metal (II) ions are coordinated by aqua, 2-methylpyrazine ligands, and four N atoms of CN groups in the tetracyanonickelate ions. A detailed analysis of the vibrational spectra indicates the presence of hydrogen bonding between the ligand molecules of the host lattices and π electrons of the benzene molecule. The spectral data show that the positions of almost all bands due to the guest molecule remain practically unchanged on enclathration. The C, H, N, and metal analyses were carried out for all the compounds and were found to fit the proposed formulas well. The experimental results are in agreement with the proposed formulas.

KEYWORDS infrared spectra, Hofmann-type clathrates, 2-methylpyrazine, Raman spectra, tetracyanonickelate

INTRODUCTION

The host–guest compounds named Hofmann-type clathrates are described by the general formula $[ML_2M'(CN)_4]\cdot nG$ (usually abbreviated as M–M′–G), where M is octahedrally coordinated a divalent transition metal: Mn, Fe, Co, Ni, Cu, Zn, or Cd; M′ is square-planar coordinated metal: Ni, Pd, or Pt; L is a unidentate ligand molecule; and n is the number of G (guest) molecules depending on the bulkiness of the ligand and the guest

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molecule. The host framework consists of two-dimensional polymeric layers composed of ML_2 cations and $M'(CN)_4$ anions. The M' atoms are coordinated to four C atoms of the CN groups in a square planar environment. M atoms are octahedrally surrounded by six N atoms, four of them from the CN groups and the other two from two ligand molecules. The ligand molecules lie between the layers. In these structures, the guest molecules are enclosed in a cavity formed by the host lattice.[1] The clathrates are of interest because of their inclusion behavior and use as catalysts, anti-oxidants, and stabilizing agents.[2] The host–guest compounds, in general, have been a subject of many theoretical and experimental studies as a result of their fundamental significance in understanding the nature of interactions between the molecular/ionic species, and also their practical importance. Spectroscopic (IR and Raman) have been reported for various clathrates.[3–7]

A previous study reported the preparation, infrared, Raman, thermal, and single-crystal X-ray spectroscopic studies of novel Hofmann-type host complexes of 2-methylpyrazine (2 mpz) with the formula $[M(H_2O)(2\,mpz)Ni(CN)_4]_n$ (M=Mn or Cd).[8] The aim of the present work is to investigate their inclusion properties and the structural changes. The complexing ability of 2 mpz with transition metal ions is of great interest, since 2 mpz can coordinate through the pyrazine ring nitrogens. In the 2 mpz compounds, the methyl group is known to be a more steric effect in comparison to the pyrazine ring nitrogens. The vibrational spectra[9–11] and tetracyanometallate clathrates[12–14] of pyrazines have been extensively studied by several authors; however, to the best knowledge of the authors, neither crystallographic nor spectroscopic data have thus far been studied to explicity tell the structural analyses of the 2 mpz tetracyanonickelate benzene clathrates. Therefore, two new $[M(H_2O)(2\,mpz)Ni(CN)_4]\cdot C_6H_6$ clathrates (abbreviated hereafter as M–Ni–Bz), for the first time, have been synthesized using benzene molecule as a guest molecule, where M=Mn and Cd, and their FT-IR and Raman spectra have been investigated. Additionally, the thermal behaviors of these clathrates have been studied with thermo-gravimetric analysis (TGA) and differential thermal analysis (DTA) techniques.

EXPERIMENTAL

Preparations

All the chemicals used were reagent grade (Merck Chemical Inc., USA) and used without further purification. The potassium tetracyanonickelate was prepared by mixing stoichiometric amounts of nickel (II) chloride with potassium cyanide in water solution. M–Ni–Bz compounds were prepared by adding slightly more than 2 mmol (0.188 g) of 2 mpz solution in ethanol and 1 mmol (0.259 g) of $[K_2Ni(CN)_4]\cdot H_2O$ solution in water saturated with benzene to 1 mmol of M(II) chloride ($MnCl_2\cdot 4H_2O = 0.197$ g and $CdCl_2\cdot 2H_2O = 0.220$ g) solution in water. The beige precipitate was filtered, washed with ethanol and ether, respectively, and stored in a desiccator containing benzene vapor.

Analytical Results

The freshly prepared compounds were analyzed for M (M=Mn, Ni, or Cd) by Atomic Absorption Spectrometer (AAS) (Perkin Elmer Analyst 800 Model), and C, H, and N by a LECO CHNS-932 analyzer with the following results (found %/calculated %) were obtained:

$[Mn(H_2O)(2\,mpz)Ni(CN)_4]\cdot C_6H_6$: C = 44.43/44.16, H = 3.73/3.46, N = 19.87/20.60, Mn = 13.74/13.47, Ni = 13.66/14.39;

$[Cd(H_2O)(2\,mpz)Ni(CN)_4]\cdot C_6H_6$: C = 38.84/38.71, H = 3.16/3.03, N = 17.93/18.06, Cd = 24.46/24.15, Ni = 12.48/12.61.

The C, H, N, and M(II) analyses were carried out for all the compounds and found to fit the proposed formulas well. These analytical results are often poor for the clathrates obtainable in powder form owing to partial decomposition. Such instability has been reported for the other clathrates having guest species of low boiling points. The experimental results are in agreement with the proposed formulas.

Thermal Analyses

Thermal analysis methods (DTA and TGA) were also applied for the present compounds, M–Ni–Bz (M=Mn or Cd), to find out whether clathrating takes place. A Perkin Elmer Diamond TG/DTA thermal analyzer was used to record simultaneous

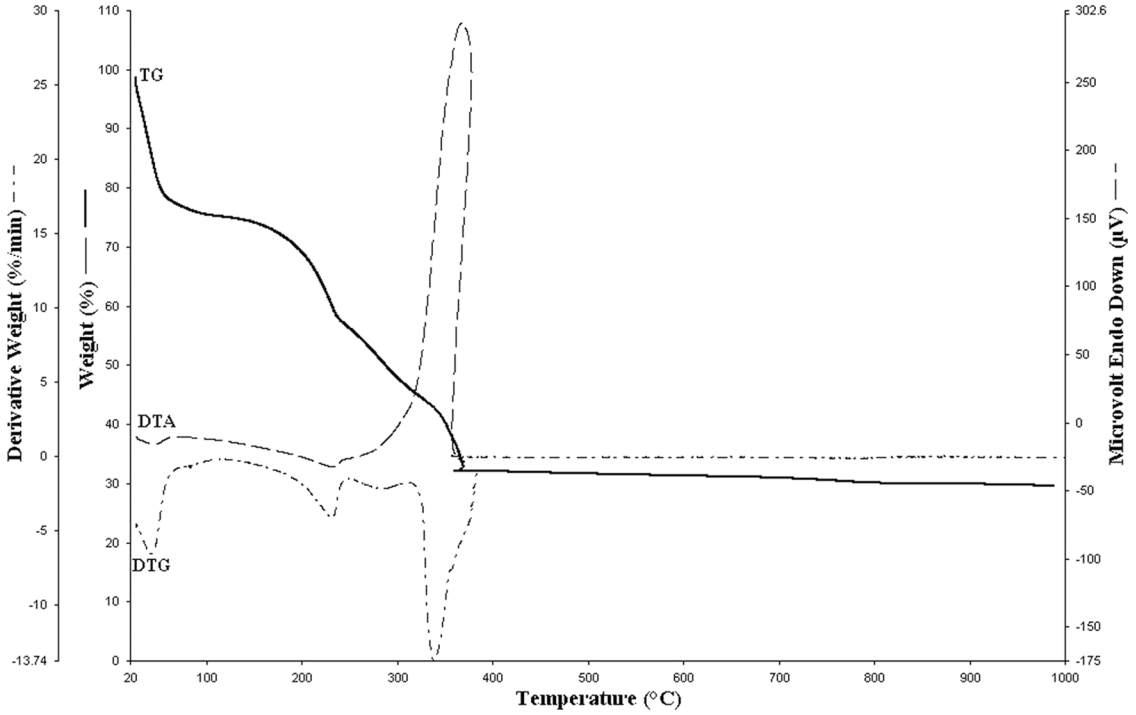


FIGURE 1 **The TG, DTG, and DTA curves of the Mn–Ni–Bz clathrate.**

thermogravimetry (TG), differential thermogravimetry (DTG), and differential thermal analysis (DTA) curves in the static air atmosphere at a heating rate of K min^{-1} in the temperature range 20–1000°C using platinum crucibles.

TG, DTG, and DTA curves of the Mn–Ni–Bz compound are shown in Fig. 1 as an example. Thermal analysis was applied to determine the stability of the compounds and temperature ranges of the liberation of ligands and included molecules.[15–17] Formation of new complexes of ethylenediamine, di-, and triethanolamine was also reported.[16,18] This section of the study is to investigate their thermal properties and the structural changes that occur on heating. The thermal analysis results for M–Ni–Bz (M=Mn or Cd) are presented in Table 1. DTA curves show three endothermic transitions for present compounds. The first decomposition stage, about 20–55°C, indicates that only one guest benzene molecule leaves the host structures. In the second decomposition stage; by heating, all of the clathrates gradually lose aqua and ligand molecules between about 57–285°C. The step in the temperature range 285–400°C is to related to the exothermic decomposition. The final decomposition stage, about 285°C, is the decomposition of cyanide to yield the respective metals. After this temperature, the structure of the compounds decomposes. The results manifest the formation of clathrating.

TABLE 1 **Thermoanalytical Data (TG, DTG, DTA) for the M–Ni–Bz Clathrates (M=Mn or Cd)**

Compounds	Stage	Temperature range (°C)	DTG_{max} (°C)[a]	Removed group	Mass loan (%) Calcd.	Mass loan (%) Found	Mass loan (%) Calcd.	Mass loan (%) Found	Solid decomposition product
$[Mn(H_2O)(2\,mpz)$	1	23–57	43(+)	C_6H_6	19.14	19.16			$[Mn\ (H_2O)(2\,mpz)Ni(CN)_4]$
$Ni(CN)_4]\cdot C_6H_6$	2	57–284	141(+), 248(+)	H_2O, 2 mpz	27.48	27.19			$MnNi(CN)_4$
	3	284–383	353(–)	4(CN)	24.43	25.75	34.18	34.23	MnO +NiO
$[Cd(H_2O)(2\,mpz)$	1	25–54	47(+)	C_6H_6	16.78	16.42			$[Cd(H_2O)(2\,mpz)Ni(CN)_4]$
$Ni(CN)_4]\cdot C_6H_6$	2	54–285	232(+)	H_2O, 2 mpz	24.09	24.16			$CdNi(CN)_4$
	3	285–413	390(–)	4(CN)	22.37	22.84	43.66	43.16	CdO +NiO

[a](+): Endothermic, (–): exothermic.

Spectra

The FT-IR spectra of the compounds were recorded in the range of 4000 to 250 cm^{-1} on a Perkin Elmer 100 FT-IR spectrometer, which was calibrated using polystyrene and CO_2 bands. The samples were measured using an Attenuated Total Reflectance (ATR) attachment (resolution 4 cm^{-1}). The Raman spectra of the powdered samples were recorded in the range of 4000–4050 cm^{-1} and were excited using the 488.0-nm line of an Ar+laser, recorded on a Cary 81 spectrometer with resolution of 3.2 cm^{-1}, with the use of a spinning cell.

RESULTS AND DISCUSSION

For the purposes of comparison and discussion, FT-IR and Raman spectra of the investigated clathrates, $[M(H_2O)(2\,mpz)Ni(CN)_4]\cdot C_6H_6$ (M=Mn or Cd), and their corresponding "empty clathrates," $[M(H_2O)(2\,mpz)Ni(CN)_4]$ (M=Mn or Cd), are shown in Figs. 2 through 5. The differences between these spectra are obvious: the spectra due to the clathrates have more bands then the "empty clathrate." When the benzene molecules were completely removed from the clathrates, only the bands due to the host lattice remained in the spectra. However, on removal of the guest molecules from the clathrates, notable changes can be detected in the spectra of the 2-methylpyrazine ligand. The absorption bands are observed in the region from 3567 cm^{-1} to 3502 cm^{-1} ν(OH) stretching vibrations of the coordinated water molecules. Moreover, the presence of water molecules manifests itself by shoulder about 1600 cm^{-1} due to δ(OH) deformation vibration. The spectral analysis of each compound has been performed by taking into account the 2 mpz ligand, $Ni(CN)_4$ ions and guest benzene molecule individually.

2-Methylpyrazine Vibrations

The 2-methylpyrazine can coordinate to metal ions through the pyrazine ring nitrogens as a bridged ligand. It has been noted that infrared and Raman data on 2 mpz complexes are not plentiful in the literature. Only a few articles were found in the literature that dealt with the determination and calculation of 2 mpz ligand geometric parameters and vibrational frequencies.[9–11] The theoretical level used for the calculations had been B3P86/311G**, as implemented in the Gaussian 94 program, given that this particular choice was sufficient for this type of problem. In order to compare the experimental frequencies, linear equations obtained from the

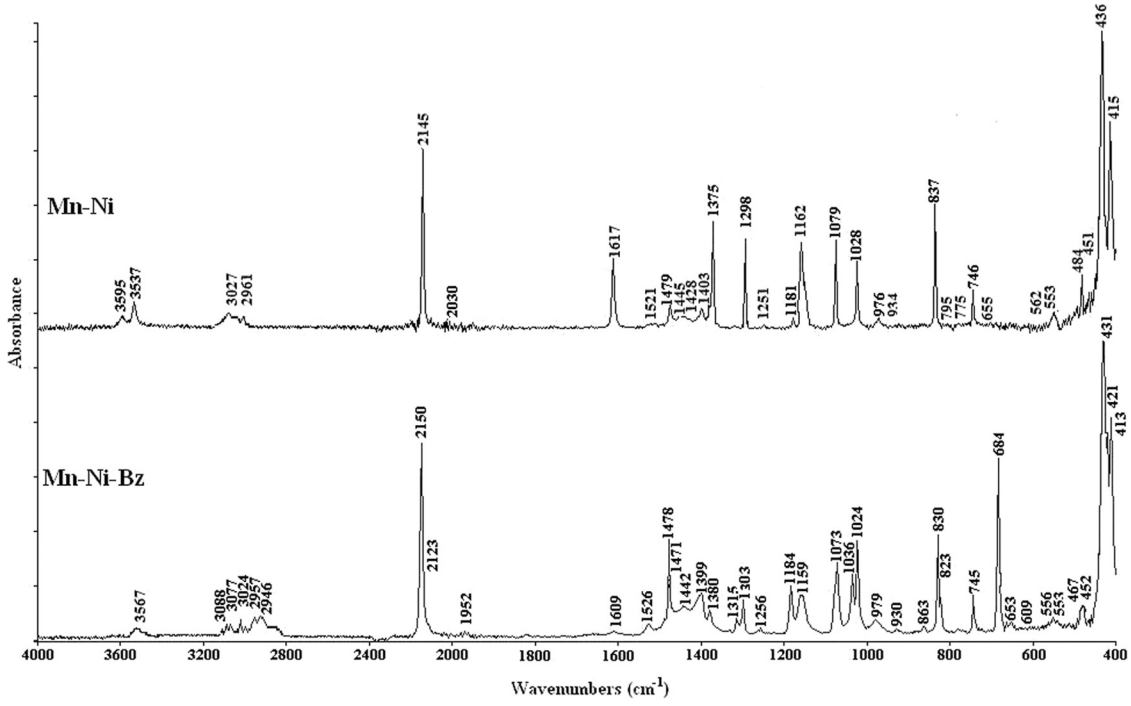


FIGURE 2 FT-IR spectra of Mn–Ni and Mn–Ni–Bz.

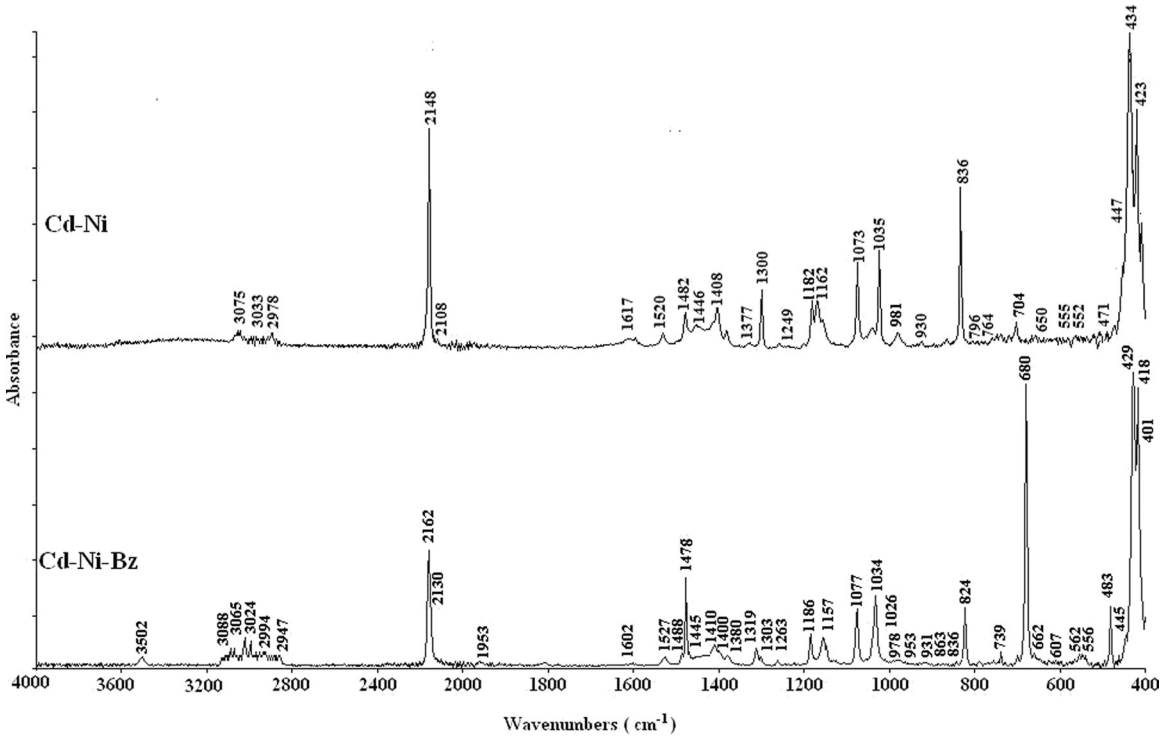


FIGURE 3 **FT-IR spectra of Cd–Ni and Cd–Ni–Bz.**

graphs $y = 0.9962x + 4.2554$, and the correlation value was found to be 0.9999. In assigning the spectral bands of free 2 mpz, the complete vibrational assignments presented by Endredi et al.[9] were consulted. The wavenumbers and Potential Energy Distribution (PED) values calculated of the 2 mpz observed in the spectra of the M–Ni–Bz are listed in Table 2, together with the wavenumbers of that in the related host structures.[8] In order to determine the coordination mode of 2 mpz in clathrates, the wavenumbers of 2 mpz in clathrates are compared with those of free 2 mpz. The observed shifts of the vibrational frequencies are consistent with previously reported Hofmann-type complexes of 2 mpz. The vibrational spectra of the compounds studied show all the principal features found earlier for coordinated pyrazine.[14] The vibrational wavenumbers of the 2 mpz modes of the host complexes exhibit coordination properties.[8] As is clear from Table 2, considerable shifts to higher frequency occur in the presence of numerous absorption bands in the spectra of all clathrates due to ν(CH), $\nu(CH_3)$, ν_{ring}, $\delta(CH_3)$, δ_{ring}, and other vibrations. The wavenumbers of the 2 mpz molecule have upward shifts in frequency when compared with the free molecule, and the shifts are metal dependent. Analogous shifts on coordination were observed in pyrazine,[12–14] pyridine,[19] 4,4′-bipridyl[20] complexes and are explained as the coupling of the internal modes of the aromatic molecule with the M–N vibrations.[8,12–14,19,20] The C–H stretching bands of 2 mpz were observed in the 3100–2900 cm^{-1} region. In the FT-IR and Raman spectra of clathrates, the observed bands at 3088 and about 3070 cm^{-1} can be assigned to C–H stretching modes. The methyl group absorptions, both in the free ligand and in the clathrates, as medium bands in the 3037–2965 cm^{-1} range, can be related to the asymmetric CH_3 stretching vibration, while the bands at 1385–1360 cm^{-1} and 1210–1170 cm^{-1} are due to the degenerate symmetric and rocking vibrations of the methyl group, respectively. The ring stretching modes appear in the spectra of the methylpyrazines in the 1500–1000 cm^{-1} region.[10] The ring ν(CH) modes of 2 mpz were found at 1579, 1526, 1477 and 1445 cm^{-1}. Several other internal coordinates are mixed with them, for example, the ν_{ring} modes. When the aromatic ring nitrogen involves complex formation, certain ring modes, particularly modes of 1600–1400 cm^{-1}, increase in value due to the coupling with M–N (ligand) bond vibrations,[8,12–14] and alteration of the ring force field also includes the effect of coupling.[21]

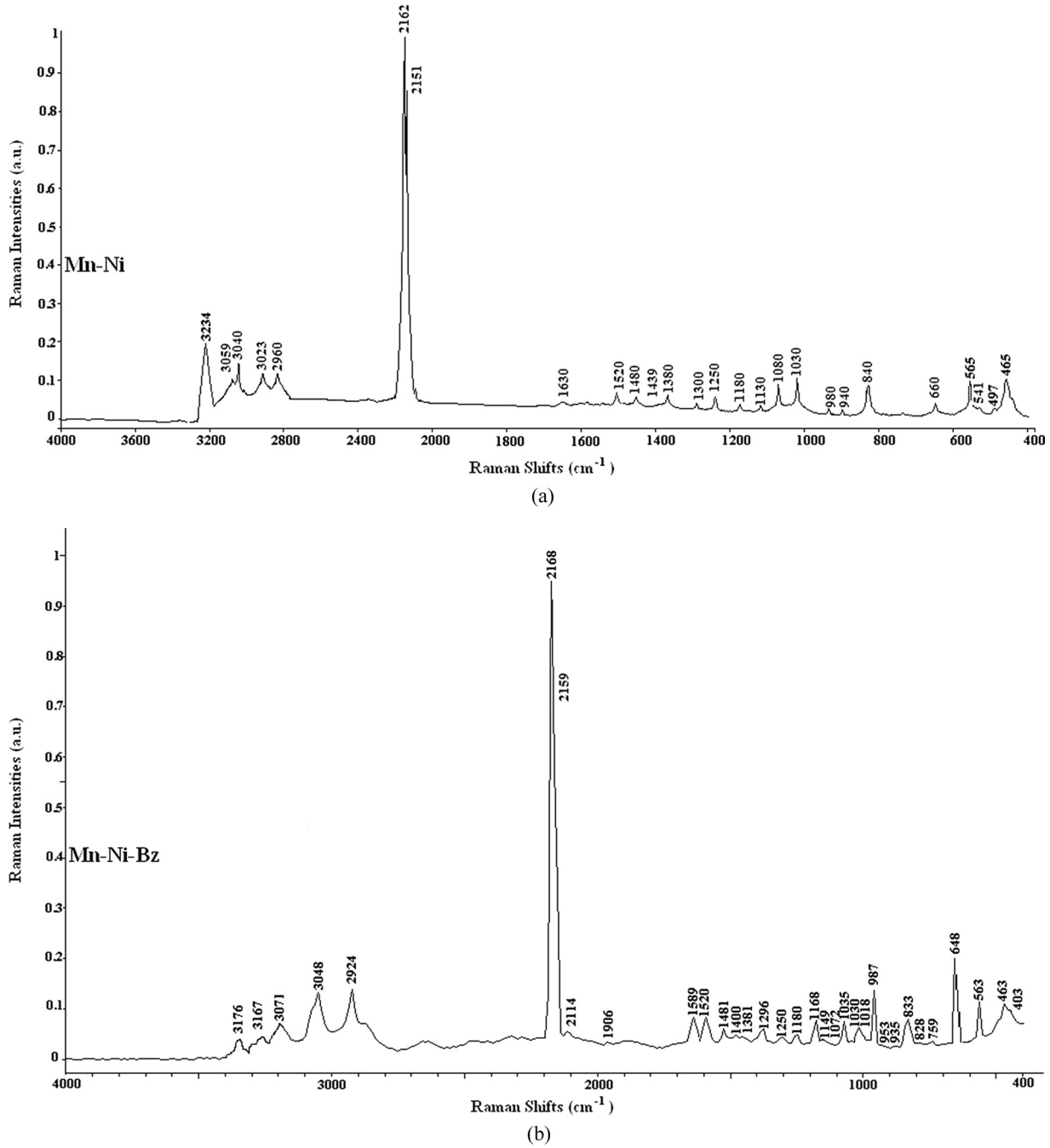
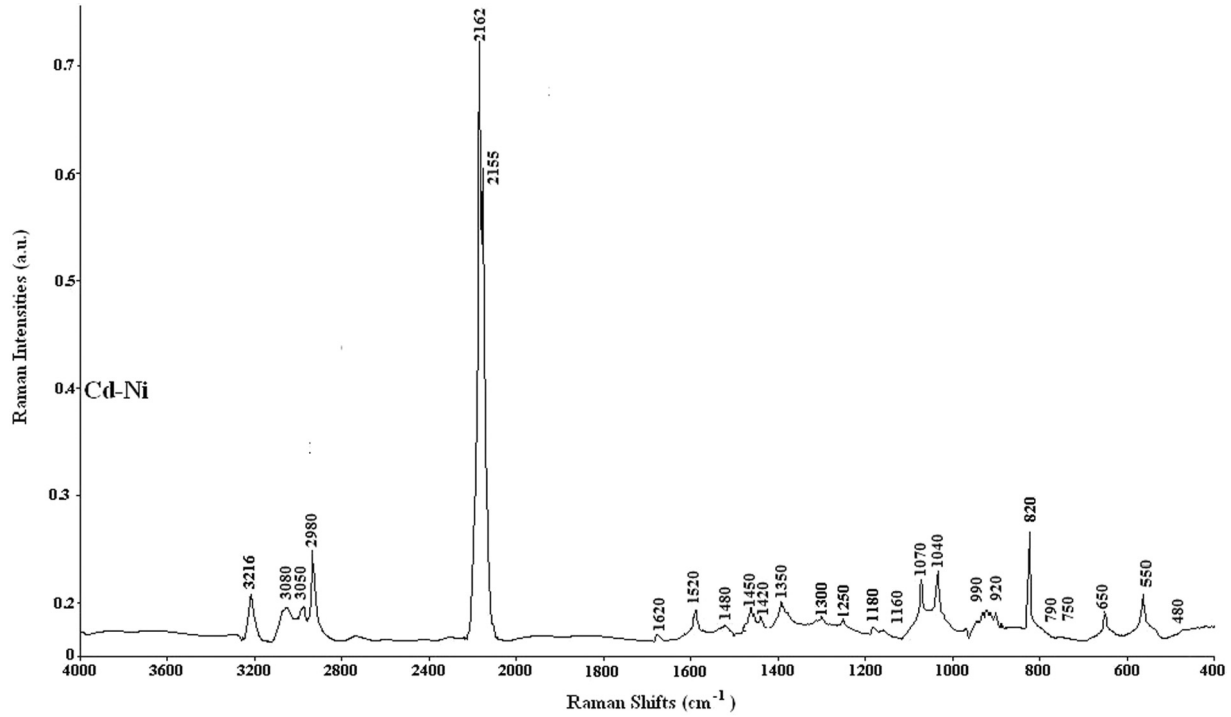


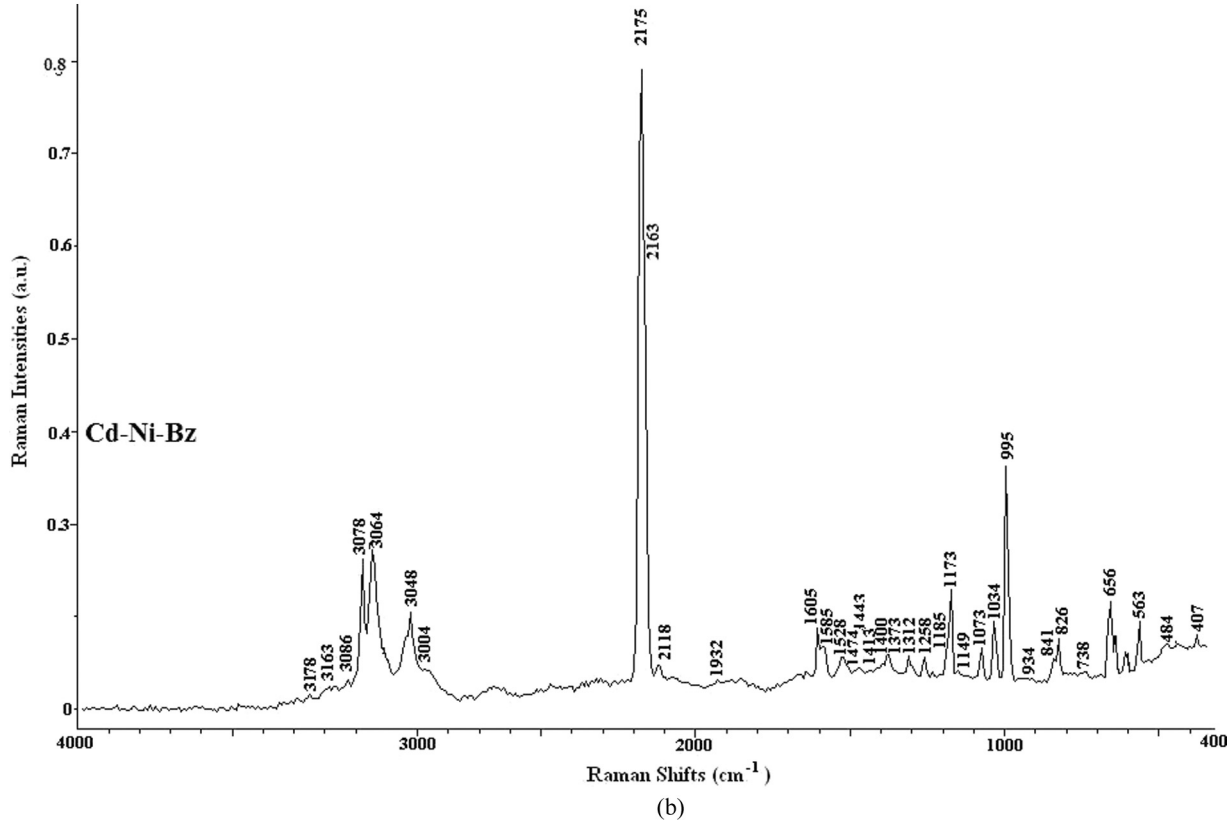
FIGURE 4 **Raman spectra of: (a) Mn–Ni and (b) Mn–Ni–Bz.**

$Ni(CN)_4$ Group Vibrations

In Table 3, the vibrational data for the $Ni(CN)_4$ group vibrations in these clathrates are given, along with those of McCullough et al., who presented vibrational data for the salt $Na_2Ni(CN)_4$ in the solid state.[22] In this salt, the $Ni(CN)_4$ anion is not coordinated to the Na cation; therefore, it can be treated as an isolated unit with D_{4h} symmetry and, thus, used as a reference to comment on vibrational changes when M–NC bonding takes place. The assigned wavenumbers of the $Ni(CN)_4$ units of the clathrates appear to be much higher than those for the isolated $Ni(CN)_4$ ion. Such frequency shifts have been observed for Hofmann-type host frameworks[8,14,19–21] and Hofmann-type benzene clathrates[23–28] and are attributed to the mechanical coupling of the internal modes of $Ni(CN)_4$ groups with M–NC vibrations. The ν(CN) and δ(CN) vibrational wavenumbers are found to be similar to those of Hofmann-type clathrates, showing that the



(a)



(b)

FIGURE 5 **Raman spectra of: (a) Cd–Ni and(b) Cd–Ni–Bz.**

$[M\text{-}Ni(CN)_4]_n$ layers have been preserved. The vibrations from the Ni–CN–M sheet structure are similar for both the complexes and the clathrates. If the cyanide groups around the nickel atom have a local D_{4h} environment, only one ν(CN) band only is expected in the infrared spectrum, at around 2150 cm^{-1},

TABLE 2 Vibrational Wavenumbers (cm^{-1}) of 2 mpz in M–Ni–Bz Clathrates (M=Mn or Cd)

	2-Methylpyrazine[9]			Mn–Ni–2 mpz[8]		Cd–Ni–2 mpz[8]		Mn–Ni–Bz		Cd–Ni–Bz	
%PED	Infrared	Raman	Calculated[a]	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman
νCH100	—	—	3100	—	—	—	—	3088 w	—	3088 w	3086 w
νCH100	—	—	3069	—	—	—	—	3071 w	3071 w	3065 w	3064 s
νCH97	3053 s	3056 s	3056	—	3059 m	3075 sh	3080 m	—	—	—	—
$\nu CH_3$99	3037 sh	3039 s	3038	—	3040 m	3033 w	3050 m	—	3048 m	—	3048 m
$\nu CH_3$98	3007 m	3009 m	3013	3027 w	3023 m	—	—	3024 w	—	3024 w	—
$\nu CH_3$99	2965 sh	2966 w	2978	2961 w	2960 m	2978 sh	2980 m	2957 w	2924 m	2994 w	3004 sh
βCH24ν_{ring}61	1579 m	1582 m	1581	1617 vs	1630 vw	1617 m	1620 m	—	1589 m	—	1605 m
βCH10ν_{ring}79	1526 s	1528 vw	1536	1521 w	1520 w	1520 w	1520 w	1526 w	1520 w	1527 m	1528 m
βCH57ν_{ring}32	1477 vs	—	1481	1479 s	1480 vw	1482 s	1480 m	1478 s	1481 m	1478 s	1474 w
$\beta(CH_3$52ν_{ring}38	1445 s	1446 vw	1451	1445 m	1439 vw	1446 m	1450 m	1442 w	—	1445 vvw	1443 w
$\beta CH_3$22βCH77	1419 sh	1437 vw	1438	1428 w	—	—	1420 w	—	—	1410 m	1413 w
ν_{ring}30, βCH55	1400 vs	1397 vw	1399	1403 vs	—	1408 s	1390 m	1399 m	1400 w	1400 w	1400 sh
βs$CH_3$67ν_{ring}25	1375 sh	1377 w	1377	1375 s	1380 w	1377 m	1350 m	1380 w	1381 vw	1380 m	1373 w
βCH75ν_{ring}15	1303 s	1304 w	1304	1298 s	1300 w	1300 w	1300 m	1303 m	1296 m	1303 w	1312 w
νCC30, ν_{ring}27, β_{ring}22	1249 s	1249 m	1242	1251 w	1250 w	1249 w	1250 m	1256 w	1250 w	1263 w	1258 w
ν_{ring}97	1195 sh	1183 sh	1197	1181 m	1180 m	1182 w	1180 m	1184 m	1180 w	1186 s	1185 sh
ν_{ring}67, βCH24	1176 s	1179 w	1175	1162 s	1130 vw	1162 m	1160 m	1159 m	1168 m	1157 s	—
ν_{ring}74, βCH19	1059 vs	1060 s	1049	1079 s	1080 m	1073 m	1070 m	1073 s	1072 vw	1077 vs	1073 w
$\beta CH_3$59, γCH19	1040 sh	1036 sh	1036	—	—	1035 m	1040 s	1036 s	1030 vw	1034 vs	—
ν_{ring}25, β_{ring}60	1019 vs	1021 s	1015	1028 s	1030 m	—	—	1024 vs	1018 m	1026 sh	—
$\gamma CH_3$53, ν_{ring}30	977 m	979 vvw	970	976 m	980 vw	981 w	990 m	979 m	987 s	978 w	—
γCH100	943 sh	—	951	—	—	—	—	—	953 vvw	953 vw	—
γCH100	—	931 vvw	919	934 w	940 vw	930 w	920 m	930 w	935 w	931 vw	934 w
ν_{ring}32, νCC23, β_{ring}41	830 vs	829 m	820	837 s	840 m	836 m	820 s	830 vs	833 w	836 sh	841 sh
γCH95	—	814 sh	814	795 w	—	796 w	790 m	823 sh	828 w	824 vs	826 w
γ_{ring}100	749 m	749 vw	755	775 w	—	764 sh	750 m	745 s	759 vvw	739 m	738 w
β_{ring}75, νCC16	636 w	637 w	632	655 w	660 w	650 vw	650 m	653 w	648 s	662 w	656 s
β_{ring}75, νCC21	559 vw	559 vw	552	553 w	541 vw	555 vw	550 m	553 w	563 w	562 w	563 m
γ_{ring}43, γCC50	465 m	465 vw	466	484 m	—	471 sh	480 m	467 w	463 w	483 m	484 sh
γg_{ring}100	404 vs	408 vvw	402	—	—	—	—	413 s	403 vw	401 vs	407 vw

[a]B3P86/311G**.

Abbreviations: ν, stretching; δ, deformation; w, wagging; t, twisting; r, rocking; s, strong; m, medium; w, weak; sh, shoulder; v, very.

and two other ν(CN) vibrations at higher frequencies are expected in the Raman spectrum.[15] In the Mn-Ni, the bands are at 2145 (IR E_u) cm^{-1}, 2151 (R B_{1g}) cm^{-1}, and 2162 (R A_{1g}) cm^{-1}; in Mn–Ni–Bz, at 2150 (IR E_u) cm^{-1}, 2159 (R B_{1g}) cm^{-1}, and 2168 (R A_{1g}) cm^{-1}; in Cd–Ni, at 2148 (IR E_u) cm^{-1}, 2155 (R B_{1g}) cm^{-1}, and 2162 (R A_{1g}) cm^{-1}; and in Cd–Ni–Bz at 2162 (IR E_u) cm^{-1}, 2163 (R B_{1g}) cm^{-1}, and 2175 (R A_{1g}) cm^{-1}. Both complexes and clathrates also have a strong band in the infrared spectra around 430 cm^{-1} arising from an in-plane Ni–C≡N bending vibration (436 cm^{-1} in the M=Mn complex and 431 cm^{-1} in the M=Mn clathrate; 434 cm^{-1} in the M=Cd complex and 429 cm^{-1} in the M=Cd clathrate) and a weaker band at about 550 cm^{-1}, which is assigned to ν(Ni-C). Thus the similarity between the sheet structure in the clathrates and complexes is confirmed.

Benzene Vibrations

The assignments and the wavenumbers of the bands arising from the benzene observed in the FT-IR and Raman spectra of Mn–Ni–Bz and Cd–Ni–Bz compounds are given in Table 4, together with the wavenumbers of benzene in the liquid phase[29] and in the Cd(pyz)Ni(CN)$_4$·2C_6H_6 clathrate,[14] on which the assignments are based. The band assignment of the benzene molecules in the FT-IR and

TABLE 3 Wavenumbers (cm^{-1}) of the $Ni(CN)_4$ Vibrations of the M–Ni–Bz Clathrates (M=Mn or Cd)

Assignment	$Na_2Ni(CN)_4$[22]	Mn–Ni–2 mpz[a][8]	Cd–Ni–2 mpz[b][8]	Cd–Ni–pyz–Bz[c][14]	Mn–Ni–Bz	Cd–Ni–Bz
A_1g, ν(CN)	2149	(2162) s	(2162) vs	(2159) vs	(2168) vs	(2175) vs
B_1g, ν(CN)	2141	(2151) s	(2155) s	(2145) vs	(2159) sh	(2163) sh
E_u, ν(CN)	2132	2145 vs	2148 vs	2135 vs	2150 vs	2162 vs
	2128	—	2108 w	—	2123 sh	2130 vw
E_u, ν(NiC)	543	562 sh	552 vw	544 w	556 vw	556 vw
A_{2u},π(NiCN)	448	451 sh	447 sh	—	452 sh	445 w
E_u, δ(NiCN)	433	436 vs	434 s	—	431 vs	429 vs
	421	415 vs	423 vs	423 vs	421 s	418 s

[a]Mn–Ni–2 mpz: $[Mn(H_2O)(2\,mpz)Ni(CN)_4]$.
[b]Cd –Ni–2 mpz: $[Cd(H_2O)(2\,mpz)Ni(CN)_4]$.
[c]Cd–Ni–pyz–Bz: $[Cd(pyz)Ni(CN)_4]\cdot C_6H_6$.
Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; br, broad; v, very.
Raman bands are given in parantheses.

Raman spectra for the compounds studied agrees with the free molecule vibrations.[29] The most outstanding spectral features are the following.

The CH out-of-plane mode (A_{2u}) in the spectra of the clathrates are found to be shifted to a higher frequency (680 cm^{-1}; Table 4) from that of liquid benzene (670 cm^{-1}). Similar positive frequency shifts were observed for Hofmann-type clathrates[23–28] and Hofmann-T_d-type[12,13,30] clathrates. Akyüz et al.[23] explained this upward shift by the presence of a weak hydrogen bond between the π electrons located above and below the plane of the benzene ring and the ammonia molecules of the host lattice. The molecular structure of the Cd–Ni–2 mpz complex consists of corrugated polymeric networks. The crystal packing was formed by intermolecular weak hydrogen bonding and Van der Waals interaction of the between layers of $Ni(CN)_4$.[8] Therefore,

TABLE 4 Vibrational Wavenumbers (cm^{-1}) of Benzene in the M–Ni–Bz Clathrates (M=Mn or Cd)

Assignment	Liquid Bz[29]	Cd–Ni–Bz[31]a	Mn–Ni–Bz	Cd–Ni–Bz
$\nu_8+(\nu_1+\nu_6)$	(3187)	(3180)	(3176) vvw	(3178) vvw
$2\nu_8$	(3166)	(3160)	(3167) w	(3163) m
ν_{2u}, E_{1u}	3073	3076	3077 w	—
ν_{13}, B_{1u}	(3062)	3062	—	—
ν_2 A_{1g}	(3062)	(3064)	—	—
ν_7E_{2g}	(3050)	(3049)	—	—
$\nu_3+\nu_1+\nu_6$	(2949)	(2943)	2946 w	2947 vw
$\nu_5+\nu_{17}$, E_{1u}	1955	—	1952 vw	1953 vw
$\nu_1+\nu_6$	(1606)	(1601)	1609 w	1602 w
ν_8, E_{2g} (in resonance)	(1586)	(1583)	—	(1585) w
ν_{19}, E_{1u}	1479	1476	1471 sh	1488 w
ν_{14}, B_{2u}	1309	1311	1315 w	1319 m
ν_9, E_{2g}	(1177)	(1178)	(1176) vvw	(1180) vvw
	—	(1170)	(1170) vvw	—
ν_{15}, B_{2u}	1149	1147	(1149) vw	(1149) w
ν_{18}, E_{1u}	1036	1034	(1035) m	(1034) m
ν_1, A_{1g}	(991)	(991)	(991) m	(995) vs
ν_{19}, E_{1g}	(850)	(869)	863w	863 vw
ν_{11}, A_{2u}	670	704	684 vs	680 vs
ν_6, E_{2g}	(607)	(608)	609 vw	607 vw

[a]Cd–Ni–Bz: $Cd(NH_3)_2Ni(CN)_4\cdot 2C_6H_6$.
Raman bands are in parentheses.
Abbreviations: s, strong; m, medium; w, weak; sh, shoulder; br, broad; v, very.

we may reasonably suggest that the frequency shifts in our clathrate compounds are due to the π electron donation from the benzene ring to the hydrogen atoms of 2 mpz, which has a more electrophilic character caused by the coordination.

Another essential feature of the out-of-plane CH bending vibration (A_{2u}) is that it appears as very intense single bands at 684 cm^{-1} and at 680 cm^{-1} in the infrared spectra of the Mn–Ni–Bz and Cd–Ni–Bz, respectively (Table 4). A similar single band was observed in the infrared spectra of the $Cd(NH_3)_2Ni(CN)_4 \cdot 2C_6H_6$[31] and Cd(4,4′-bipyridyl)M′$(CN)_4 \cdot 2C_6H_6$ (M=Cd or Hg).[32] This vibrational mode splits into a doublet in Cd(pyrazine)$M(CN)_4 \cdot 2C_6H_6$ (M=Cd or Hg)[13] and $M(NH_3)_2M'(CN)_4 \cdot 2C_6H_6$ (M=Mn or Cd, M′=Cd or Hg)[33] and into a triplet in M(ethylenediamine)$M'(CN)_4 \cdot 2C_6H_6$ (M=Mn or Cd, M′=Cd or Hg).[34] In the case of clathrates with triplet or doublet features, the splittings have been ascribed to crystal-field effects (strong host–guest interactions).[35–39] In the case of clathrates with a single band, because of the larger cavities due to the ligands, the host–guest interactions are expected to be ineffective for splitting.[32] Based on the present spectral data, it is not possible to determine the conformation of the benzene molecules in the host lattice in our clathrate compounds. As in the Hofmann-type benzene clathrates, the relative orientation of the hydrogen atoms of the ligand with respect to the axis of the π cloud of benzene must be the one most favorable for the hydrogen bonding. There is good evidence for hydrogen bonding from ligand molecules to benzene molecules as a π to σ hydrogen bond.[40] The preceding discussion considered as a whole leads us the conclusion that the host lattice of these clathrates are similar to those of other Hofmann-type clathrates.

CONCLUSION

Tetracyanoaqua 2-methylpyrazine tetracyanonickelate benzene clathrates have been synthesized and characterized by vibrational (FT-IR and Raman) spectroscopy, thermal, and elemental analyses. In our spectroscopic studies, the vibrational spectra of Hofmann-type clathrates were able to be interpreted and most of the bands in the vibrational spectra have been assigned due to both the host lattice and the guest molecule. The vibrational spectra of the studied clathrates and their corresponding "empty" clathrates are compared in this study. From this comparison, it is found that the clathrates studied show no major difference in the infrared and Raman spectra of the complexes with same ligand. These similarities suggest that they also have similar structural features. These, in turn, suggest that the degree of the interactions of the benzene, ligand, and $Ni(CN)_4$ species with their surroundings is almost the same for each clathrate. On the basis of the spectroscopic results, it is proposed that in the case of the compounds, the aqua and 2 mpz molecules are coordinated to metal ions of the adjacent layers of $[M–Ni(CN)_4]_n$ as bridged ligands, depending on coordination properties of the acceptor side. The FT-IR and Raman spectra of the Hofmann-type clathrates confirmed that the position of the bands due to the guest molecules remain practically unchanged upon enclathration, compared to the corresponding values in liquid benzene. Certain vibrations of the benzene molecule in the clathrates show shifts to a higher frequency when compared to the same vibrations in the liquid benzene. The preceding discussion, considered as a whole, leads to the conclusion that the host lattice of these clathrates are similar to those of other Hofmann-type clathrates.

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