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An Infrared Spectroscopic Study on the Hofmann- and en-T_d-type Clathrates: $Mn(NH_3)_2Zn(CN)_4.2$benzene and Mn(ethylenediamine)$Zn(CN)_4.2$benzene

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Abstract

Infrared spectra of $Mn(NH_3)_2Zn(CN)_4.2C_6H_6$ and Mn(ethylenediamine)$Zn(CN)_4.2C_6H_6$ are reported. The spectral data suggest that these compounds are similar in structure to Hofmann-T_d-type and the en-T_d-type clathrates, respectively. There is good evidence for H-bonding from ammonia N–H to benzene as a π to σ H-bond.

Introduction

The host lattice of the T_d-type clathrates, formulated as $Cd(II)L_2M(II)(CN)_4$. nG (abrr. M-L_2-M′-nG), where M is Mn, Zn or Cd; L_2 is a bidentate ligand or a pair of unidentate ligand molecules, M′ is Zn, Cd or Hg and n is the number of G (guest) molecules depending on the bulkiness of the ligands, is formed from endless chains of -Cd-L_2-Cd-L_2- extending along the *a*- and *b*-axes alternately and the tetrahedral $M'(CN)_4$ ions arranged between the consecutive crossing -Cd-L_2-Cd-L_2- chains with the N-ends bound to the Cd atoms [1–4]. This structure provides two kinds of cavities, α and β, for the guest molecules. The α cavity is a rectangular box similar to those in the Hofmann-type hosts, while the β cavity is a twisted biprism, as has been demonstrated in previous papers [2, 3].

In our previous studies vibrational spectral data for $Mn(NH_3)_2M(CN)_4.2C_6H_6$ (M = Cd or Hg) [5] and Mn(ethylenediamine)$M(CN)_4.2C_6H_6$ (M = Cd or Hg) [6] have been structurally correlated with those of Hofmann-Td-type $Cd(NH_3)_2M(CN)_4.2C_6H_6$, where M = Cd [1] or Hg [2], and en-Td-type Cd(ethylenediamine)$M(CN)_4.2C_6H_6$, where M = Cd [4] or Hg [3], respectively. We have now prepared two new compounds of the form $Mn(NH_3)_2Zn(CN)_4.2$Benzene and Mn(ethylenediamine)-$Zn(CN)_4.2$Benzene (abbr. Mn-L_2-Zn-2Bz) ($L_2 = (NH_3)_2$ or en = ethylenediamine). In this study we report the infrared spectra of these compounds.

The spectral data are structurally correlated with those of the corresponding-T_d-type clathrates, of which the structures are known from single crystal X-ray studies [1–4]. It should be noted that several unsuccessful attempts have been made to obtain Raman spectra of our beige compounds by using the 488 nm or 514 nm laser line.

Experimental

All chemicals used were reagent grade (Merck) and used without further purification.

The preparation of the clathrates M-L_2-Zn-2Bz (L_2 = $2NH_3$ or en) was similar to that of $Mn(NH_3)_2M(CN)_4.2$Benzene (M = Cd or Hg) [5] and Mn(en)$M(CN)_4.2$Benzene [6]: a solution composed of one millimole of $K_2Zn(CN)_4$ and two millimoles of NH_3 (or one millimole of en) in water saturated with benzene was added to a solution of $MnCl_2.6H_2O$ in water saturated with benzene. The beige precipitate (very fine powder) was filtered, washed with water, ethanol and ether, successively, and kept in a desiccator containing saturated benzene vapour.

The freshly prepared samples were analysed for C, H and N with the following results (found %/calculated %): $Mn(NH_3)_2Zn(CN)_4.2C_6H_6$: C = 51.22/51.38, H=2.99/3.07, N = 19.05/18.32. Mn(en)$Zn(CN)_4.2C_6H_6$: C = 48.96/49.05, H = 4.53/4.57, N = 19.17/19.06.

Infrared spectra were recorded between 4000 and 200 cm^{-1} on Perkin Elmer 1330 and Mattson 1000 FTIR spectrometers, which were calibrated using indene and polystrene film. Samples were prepared as mulls in nujol and poly(chlortrifluorethylene)-oil in a CsI cell and as KBr discs.

Results and discussion

Owing to the lack of structural data on the compounds studied, the assignment was made by treating the ligand, the benzene molecules, and the $M(CN)_4$ ions as isolated units (Figure 1). The differentiating of these moieties from each other is straight forward since the bands of the Zn $(CN)_4$ ions and the benzene guest molecules are persistent and picked out with ease [5–7].

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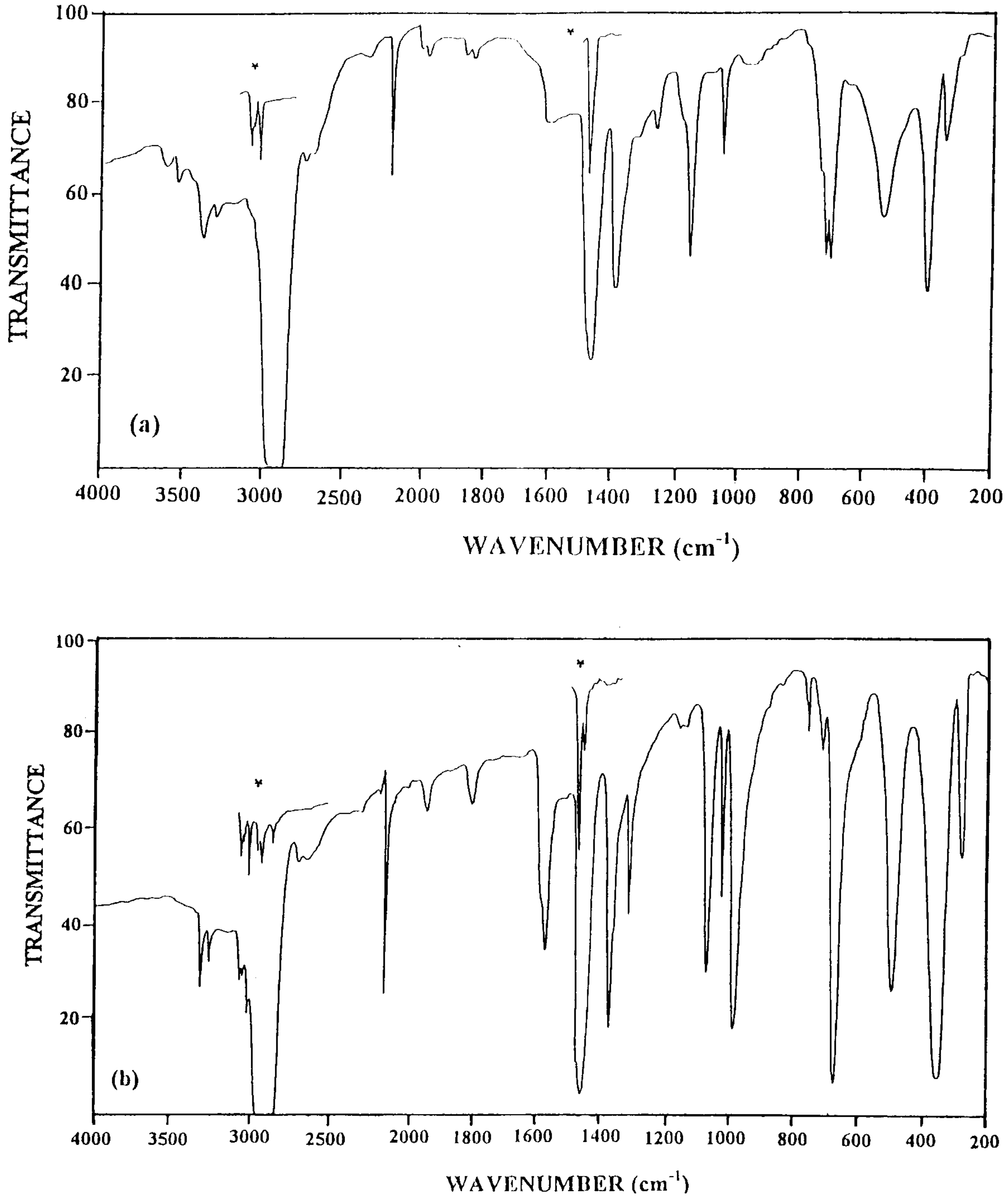

Figure 1. Infrared spectra of Mn(NH_3)$_2$-Zn-Bz and (a) Mn-en-Zn-2Bz, (b) clathrates in nujol (*in poly (chlortrifluorethylene)-oil).

Ligand vibrations

Ammonia

It has been found that the assignments of the vibrational bands of the ammonia ligand in the infrared spectra of the Hofmann-type [8] and Hofmann-T_d-type clathrates [5] and in our compound (Mn-(NH_3)$_2$-Zn-2Bz) are consistent with the vibrational unit of H_3N-Mn-NH_3 (D_{3h}), in which the N–M–N skeleton is linear and the NH_3 species are staggered. Based on this model we expect two components, in phase (Raman active) and out-of-phase (infrared active) for each mode of a bare ammonia molecule. Indeed, two infrared active bands due to out-of-phase vibrations have been observed. The assignments and the wavenumbers of the bands attributable to the ammine in the compound Mn-(NH_3)$_2$Zn-2Bz are tabulated in Table 1. For the purposes of comparison and discussion, Table 1 also lists the infrared spectra of the ammonia ligands in the Hofmann-type [8] in Hofmann-T_d-type benzene clathrates and in the Cd(NH_3)$_2$Cd (abbr. Cd-Cd) host complexe [5], on which the assignments are based. Our assignments are in agreement with those of the other clathrates (Table 1).

It is well known that Hofmann-type and T_d-type clathrates are unstable under ambient conditions and sensitive to

Table 1. The vibrational wavenumbers (cm^{-1}) of NH_3 for Mn-$(NH_3)_2$-Zn-2Bz clathrates

Assignment[a]	Cd-$(NH_3)_2$-Cd[a]	Cd-$(NH_3)_2$-Cd-2Bz[a]	Cd-$(NH_3)_2$-Hg-2Bz[a]	Mn-$(NH_3)_2$-Cd-2Bz[a]	Mn-$(NH_3)_2$-Hg-2Bz[a]	Mn-$(NH_3)_2$-Zn-2Bz
ν_a(IR)	3390s	3385s	3383s	3378s	3376s	3367s
ν_a(Ra)	no	no	no	no	no	no
ν_s(Ra)	no	no	no	no	no	no
ν_s(IR)	3298s	3290s	3287s	3285m	3283m	3286m
δ_a(Ra)	no	no	no	no	no	no
δ_a(IR)	1604m	1604m	1587m	1582m	1586m	1586m
δ_s(Ra)	no	no	no	no	no	no
δ_s(IR)[b]	no	1154w	no	1153w	1158w	1163w
δ_s(IR)	1154vs	1109vs	1108vs	1126vs	1130vs	1133vs
δ_r(IR)	548vs	530vs	528vs	512s	513s	515vs
δ_r(Ra)	502m	no	no	no	no	no

[a] Taken from Ref. [5].
[b] Band arising from decomposed lattice.
v = very, s = strong, m = medium, w = weak, sh = shoulder and no = not observed.

Table 2. The vibrational wavenumbers (cm^{-1}) of ethylenediamine in Mn-en-Zn-2Bz clathrates

Assignment[a]	Liquid en (IR)[a]	en in CCl_4	Mn-en-Cd-2Bz[b]	Mn-en-Hg-2Bz[b]	Cd-en-Cd-2Bz[b]	Cd-en-Hg-2Bz[b]	Mn-en-Zn-2Bz
$\nu(NH_2)$	3349vs	3467m,sh	3314m	no	3316m	3318m	3367s
$\nu(NH_2)$		3358s	no	no	no	no	3309m
$\nu(NH_2)$	3279vs	3288s	3283w	3283w	3283w	3285w	3276s
$\nu(NH_2)$	3189vs	3192s	no	no	no	no	3257m
$\nu(CH_2)$			2970w	2970w	2974w	2974w	2977m
$\nu(CH_2)$	2922vs	2935vs	2949m	2950w	2943m	2945m	2960w
$\nu(CH_2)$			no	no	no	no	2902w
$\nu(CH_2)$	2853vs	2864s	2880w	2879w	2881w	2882w	2885w
$\delta(NH_2)$	1595vs	1600s	1596s	1593vs	1590s	1591s	1599m
$\delta(NH_2)$			1576vs	1574vs	1574vs	1574vs	1577vs
$\delta(CH_2)$	1458mw	1471m	1460m	1458m	1458m	1458m	1460m
$w(CH_2)$	1356mw	1362m	1384vw	1382vw	1383vw	no	1396vw
$t(NH_2)$	1254vw	1259w	no	no	no	no	1284vw
ν(Skeletal)	1096m	1099w	1078vs	lO8Ovs	1072vs	1073vs	1088s
ν(Skeletal)	1054mw	1053w	no	no	no	no	1055vw
ν(Skeletal)	991sh	1005w,sh	no	no	no	no	999vs
ν(Skeletal)			994vs	993vs	991vs	990vs	993vs
$w(NH_2)$	900vs	975w,sh	no	no	no	no	960m
$w(NH_2)$		877m	no	no	no	no	945s
$\rho(CH_2) + w(NH_2)$	830m		770vw	768w	769vw	768vw	767w
na			no	no	no	no	577m,br
δ(Skeletal)	513mw		508s	507s	502s	505s	509m
δ(Skeletal)	473w		no	no	no	no	no

[a] Taken from Ref. [9].
[b] Taken from Ref. [6].
v = very, s = strong, m = medium, w = weak, sh = shoulder, no = not observed, and na = not assigned.

grinding; even on mild grinding they decompose [5, 8]. In our case, although the Nujol mull preparations of the compounds were done with minimum grinding, infrared spectra exhibit bands attributable to NH_3 ligands in a partially decomposed lattice (residual host lattice). These bands have readily been identified by making a comparison between the infrared spectra of several Nujol mulls of clathrate obtained with different extents of grinding and the Cd-Cd host complex, since the infrared spectrum of Cd-Cd shows a very strong band at 1154 cm^{-1} due to the δ_s vibration (Table 1) while the corresponding band of the host lattice of Mn-NH_3-Zn-2Bz clathrate appears at 1163 cm^{-1} (w). Thus, the comparison of the bands at 1133 cm^{-1} (vs) and 1163 cm^{-1} (w) can be used to appraise the extent of decomposition, since with gradual liberation of benzene the band at 1133 cm^{-1} decreases in intensity, while the weak band at 1163 cm^{-1} increases in intensity. Similar observations have been noted for Hofmann-type [8] and Hofmann-T_d-type clathrates [5].

Table 3. The vibrational wavenumbers (cm^{-1}) of the $Zn(CN)_4$ group for the Mn-Zn-2Bz and Mn en-Zn-2Bz clathrates*

Assignment	$K_2Zn(CN)_4$ [a]	$K_2Cd(CN)_4$ [a]	$K_2Hg(CN)_4$ [a]	Mn-$(NH_3)_2$-Cd-2Bz[b]	Mn-$(NH_3)_2$-Hg-2Bz[b]	Mn-$(NH_3)_2$-Zn-2Bz	Mn-en-Cd-2Bz[c]	Mn-en-Hg-2B[c]	Mn-en-Zn02Bz
$\nu_1(CN)A_1$	(2157)	(2149)	(2149)	no	no	no	no	no	no
$\nu_5(CN)F_2$	2152	2145	2146	2170vs	2167vs	2173vs	2168vs	2168vs	2170vs
Hot band	–	–	–	2157vw	2154vw	no	no	no	no
$\nu_5(^{13}CN)$	–	–	–	2133vw	2132vw	2127vw	2132vw	no	2123vw
$\nu_2(MC)A_1$	(347)	(327)	(335)	no	no	no	no	no	no
$\nu_6[\nu(MC) + \delta(NCM)]F_2$	359	316	330	36()s	368s	3735	352s	356s	375s
$\nu_7[\nu(MC) + \delta(NCM)]F_2$	315	250	235	no	no	320w	270w	268w	320m

*Raman bands are in parentheses.
[a] Taken from Ref. [13].
[b] Taken from Ref. [5].
[c] Taken from Ref. [6].
v = very, s = strong, m = medium, w = weak, sh = shoulder and no = not observed.

Ethylenediamine (en)

The assignment and the wavenumbers of the vibrational bands of *en* in Mn-en-Zn-2Bz are given in Table 2, together with the spectral data for *en* liquid [9], in a solution in CCl_4 and in the Hofmann-T_d-type clathrates, $M(en)M'(CN)_4.2C_6H_6$ (M′ = Cd or Hg)(abbr. M-en-M′-2Bz) [6] on which the assignments are based. A glance at Table 2 shows that our assignments are in good agreement with those reported previously [6] (Table 2).

In the gas phase, Yokoseki and Kuchitsu [10] have shown that the *en* molecule possesses conformational isomerism and that the dominant form (more then 95%) is the *gauche* conformation. This gives the molecule C_2 symmetry. The IR and Raman spectral data (depolarization ratios, frequency shifts and group frequency correlations) for the *en* molecule and its deuterated derivatives in the liquid and solid phases have been reported to be in accord with *gauche* and *trans* conformations, respectively [9]. From the results of IR spectroscopic and powder X-ray diffraction data [11] the *en* ligand molecules in $Cd(en)M(CN)_4.2C_6H_6$ (M =Ni or Pd) were suggested to have a *trans* form, while the single crystal X-ray diffraction studies have shown that the en molecules in Cd-en-Cd-2G are in a *gauche* conformation [4]. The *gauche* form may be due to the packing requirement for keeping the host framework of $Cd[Cd(CN)_4]$ similar to the regular framework of the Td-type elathrates, $Cd(NH_3)_2Cd(CN)_4.2C_6H_6$ and $Cd(NH_3)_2Hg(CN)_4.2C_6H_6$ [1]. The fact that *en* has the *gauche* form in Cd-en-Cd-2G and the spectral similarities between M-en-M′-2Bz (M = Mn or Cd, M′ = Cd or Hg) and our compound Mn-en-Zn-2Bz suggest that the *en* ligands in the Mn-en-Zn-2Bz compound also has a *gauche* (6) form. For the *gauche* configuration and consequent C_2 symmetry, all vibrational modes are infrared active.

Infrared spectral data for *en* in the clathrate compound is consistent with all the vibrational features of NH_2 and CH_2 groups of a coordinated ligand, that is, on coordination, the N–H stretching frequencies should decrease, while the C–H frequencies should increase due to the consecutive inductive effects [12], in other words, on coordination N–H bonds should become weaker and C–H bonds become stronger. In our case, this expectation is fully realized (Table 2).

Two bands would be expected in the N–H stretching region, an antisymmetric N–H stretch and a symmetric N–H stretch. However, four bands are observed in this spectral region. These may possibly be due to host–guest interactions (see Section *Benzene vibrations*).

$Zn(CN)_4$ vibrations

In assigning the bands attributable to $Zn(CN)_4$ ion in the spectra, we refer to the work of Jones [13] who presented vibrational data for the salt $K_2Zn(CN)_4$ in the solid phase and assigned the vibrational fundamental vibrations on the basis of T_d symmetry. The structural studies on this salt have shown that the K–NC distance is ca.2.9 Å in $K_2Zn(CN)_4$ [14], while the much lower Mn–NC distance (ca. 2.2 Å) might be expected in T_d-type [1] host lattices similar to those in the Hofmann-type hosts [15]. Thus the spectral data for $K_2Zn(CN)_4$ can be used as references to account for the vibrational changes when the stiffer Mn–NC bonding takes place.

The vibrational data for the $Zn(CN)_4$ groups in the compounds under study are given in Table 3, together with the vibrational wavenumbers of $K_2Zn(CN)_4$ [13], $K_2Cd(CN)_4$ and $K_2Hg(CN)_4$ [5, 6]. The assigned wavenumbers for the $Zn(CN)_4$ groups in the compounds Mn-$(NH_3)_2$-Zn-2Bz and Mn-en-Zn-2Bz appear to be much higher than those for $Zn(CN)_4$ in $K_2Zn(CN)_4$ salt (Table 3). Such frequency shifts have been observed for T_d-type clathrates [5–7, 16, 17] and T_d-type host complexes [18, 19], and are attributed to the mechanical coupling of the internal modes of $Zn(CN)_4$ with the Mn–NC vibrations. It follows that the N-termini of the $Zn(CN)_4$ group are also bound to Mn atoms in an octahedral configuration in the compounds studied.

Benzene vibrations

The assignments and the frequencies of the vibrational bands arising from the enclathrated benzene observed in the spectra of the compounds are given in Table 4, along with the wavenumbers of benzene in the liquid phase [20] and in

Table 4. The vibrational wavenumbers (cm^{-1}) of benzene in the Mn-$(NH_3)_2$-Zn-2Bz and Mn-en-Zn-2Bz clathrates*

Assignment[a]	Liquid benzene[b]	Mn-$(NH_3)_2$-Cd-2Bz[c]	Mn-$(NH_3)_2$Hg-2Bz[c]	Mn-$(NH_3)_2$-Zn-2Bz	Mn-en-Cd-2Bz[d]	Mn-en-Hg-2Bz[d]	Mn-en-Zn-2Bz
$2\nu_8$	(3166)	no	no	no	no	no	no
ν_{20}, F_{1u}	3073	3080m	3080s	3087m	3080m	3082m	3087m
$\nu_8 + \nu_{19}$	3075	3060w	3058w	3066w	3061m	3062m	3070m
ν_2, A_{1g}	(3062)	no	no	no	no	no	3057w
ν_{13}, B_{1u}	3048	3028m	3026m	3033m	3025s	3029s	3035m
ν_7, E_{2g}	(3050)	no	no	no	no	no	3047vw
$\nu_5 + \nu_{17}$, E_{1u}	1955	1968vw	1969vw	1973w	1959w	1960w	1960w
ν_8, E_{2g}	(1586)	no	no	no	no	no	no
$\nu_{10} + \nu_{17}$	1815	1824w	1824w	1830w	1814w	1815w	1818w
ν_{19}, E_{1u}	1479	1479s	1478s	1477s	1474s	1474s	1477s
ν_{14}, B_{2u}	1309	1305vw	1302vw	1309vw	no	no	no
ν_9, E_{2g}	(1177)	no	no	no	1172vw	1173vw	1168w
ν_{15}, B_{2u}	1149	1145sh	1146sh	1162sh	1150vw	1148vw	1156w
ν_{18}, E_{1u}	1036	1033m	1032m	1035m	1032m	1032m	1035m
ν_1, A_{1g}	(991)	no	no	no	no	no	no
ν_{10}, E_{1g}	(850)	no	no	no	848vw	848vw	848vw
ν_{11}, A_{2u}	670	698s	700vs	701vs	698sh	688sh	690sh
		687vs	688vs	688vs	676vs	680vs	685vs
					668sh	668sh	683sh

*Raman bands are in parentheses.
[a]Taken from Ref. [24].
[b]IR bands from Ref. [20]. Raman bands from Ref. [25].
[c]Taken from Ref. [5].
[d]Taken from Ref. [6].
v = very, s = strong, m = medium, w = weak, sh = shoulder and no = not observed.

$M(NH_3)_2M'(CN)_4.2C_6H_6$ (M = Mn or Cd, M′ = Cd or Hg) [5] and $M(en)M'(CN)_4.2C_6H_6$ (M = Mn or Cd, M′ = Cd or Hg) [6] clathrates for comparison. The most structurally informative features are the following.

The CH out-of-plane mode (A_{2u}) in the spectra of the clathrates are found to be shifted to higher frequency (Table 4) from that of liquid benzene (670 cm^{-1}). Similar positive frequency shifts were observed for T_d-type [5–7, 16] clathrates and Hofmann-type clathrates [8]. Akyüz *et al.* [8], explained this upward shift by the presence of a weak hydrogen bond between π electrons located above and below the plane of the benzene ring and the ammonia molecules of the host lattice. Therefore, 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 the ligand molecule 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 a doublet for Mn-$(NH_3)_2$-Zn-2Bz and a triplet for Mn-en-Zn-2Bz clathrate compounds. This vibrational mode appears as a singlet for Cd(4,4′-bipyridyl)$M'(CN)_4.2C_6H_6$ [21], a doublet for Cd(pyrazine)$M(CN)_4.2C_6H_6$ (M = Cd or Hg) [22] and $M(NH_3)_2M'(CN)_4.2C_6H_6$ (M = Mn or Cd, M′ = Cd or Hg) [5] and a triplet in $M(en)M'(CN)_4.2C_6H_6$ (M = Mn or Cd, M′ = Cd or Hg) [6]. In the case of clathrates with the triplet or doublet features, the splittings have been ascribed to crystal effects (strong host–guest interaction) [6]. In the case of clathrates with a single band, because of the larger cavities due to the ligands, the host–guest interactions are expected not to be effective for splitting [21].

Based on the present spectral data, it is not possible to determine the orientation of the benzene molecules in the host lattice in our clathrate compounds. In the Hofmann-type benzene and Hofmann-T_d-type benzene clathrates, the relative orientation of the N–H bands of ligand with respect to the axis of the π cloud of benzene must be the one most favourable for hydrogen bonding [23].

The preceding discussion considered as whole leads us to the conclusion that the host lattice of our clathrates is similar to those of T_d-type clathrates.

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