

## Infrared Spectroscopic Study on the Hofmann $T_d$ -Type Clathrates: $Mn(NH_3)_2M(CN)_4 \cdot 2 C_6H_5NH_2$ ( $M = Zn, Cd$ or $Hg$ )

CELAL BAYRAK<sup>1,\*</sup>, MEHMET ÇİVİ<sup>2</sup> and YASEMİN KUTUCU<sup>2</sup>

<sup>1</sup>Department of Physics, Faculty of Education, Hacettepe University, 06532, Beytepe, Ankara, Turkey; <sup>2</sup>Department of Physics, Faculty of Art Sciences, University of Gazi, 06500, Ankara, Turkey

(Received: 28 June 2005; in final form: 23 January 2006)

**Key words:** ammonia, aniline, coordination polymers, inclusion compounds, IR spectra, tetracyanometallate

### Abstract

Infrared spectra of  $Mn(NH_3)_2M(CN)_4 \cdot 2C_6H_5NH_2$  ( $M = Zn, Cd$  or  $Hg$ ) are reported. The spectral data suggest that these compounds are similar in structure to Hofmann- $T_d$ -type clathrates.

### Introduction

The host lattice of the  $T_d$ -type clathrates is formulated as  $Cd(II)L_2M(II)(CN)_4 \cdot nG$  (abbr.  $M-L_2-M'-nG$ ), where  $M$  is  $Mn, Zn$  or  $Cd$ ;  $n$  is the number of  $G$  (guest) molecules,  $L_2$  is bidentate ligand or a pair of unidentate ligand molecules. The host lattice in these clathrates comprises endless chains of  $-Cd-L_2-Cd-L_2-$  extending along  $a$ - 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 types of cavities,  $\alpha$  and  $\beta$ , for the guest molecules. The  $\alpha$  cavity is a rectangular box similar to those in the Hofmann-type hosts, while the  $\beta$  cavity is a twisted biprism, as has been demonstrated in previous papers [2, 3].

Guest–host interactions in these clathrates provide an explanation for the effect of enclathrates on the structural and spectroscopic properties of both the guest and the host molecules. The nature of the guest–host interactions varies from charge transfer forces to hydrogen bonding [5] and to weak van der Waals interactions. Hofmann-type clathrates are good models for studying such interactions [6–8].

In our previous studies, vibrational spectral data for  $Mn(NH_3)_2Zn(CN)_4 \cdot 2C_6H_6$  [9] and  $Mn(NH_3)_2M(CN)_4 \cdot 2C_6H_6$  ( $M = Cd$  or  $Hg$ ) [5] have been structurally correlated with those of Hofmann- $T_d$ -type  $Cd(NH_3)_2M(CN)_4 \cdot 2C_6H_6$ , where  $M = Cd$  [1] or  $Hg$  [2]. In this study, we report the IR spectra of three new Hofmann  $T_d$ -type clathrates  $Mn(NH_3)_2M(CN)_4 \cdot 2C_6H_5NH_2$  ( $M = Zn, Cd$  or  $Hg$ ) (abbr.  $Mn-L_2-M-2An$ ) ( $An = Aniline$ ). The aim of this study is to give further examples of Hofmann  $T_d$ -type clathrates and to present the vibrations of aniline molecule in this structure. In order to understand the structures of the samples, the spectral data are corre-

lated with those of the corresponding  $T_d$ -type clathrates, the structures of which 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 or 514 nm laser line.

### Experimental

All chemicals used were reagent grade (Merck) and were used without further purification. Aniline (20% solution in ethanol) was added into an aqueous solution containing 1 mmol  $Mn(II)$  salt and  $K_2M(CN)_4$  ( $M = Zn, Cd$  or  $Hg$ ) in 20 ml of water. Two millimoles ammoniacal water (25%) was added into this mixture. After vigorous stirring for a day the brown precipitate (very fine powder) was filtered, washed successively with water, acetone and ether, and kept in a dessicator to prevent the escape of guest aniline.

The freshly prepared samples were analysed for C, H and N with the following results (found %/calculated %):

$Mn(NH_3)_2Zn(CN)_4 \cdot 2C_6H_5NH_2$ :	C = 43.57/43.21, H = 4.09/4.53, N = 23.56/25.19.
$Mn(NH_3)_2Cd(CN)_4 \cdot 2C_6H_5NH_2$ :	C = 40.01/39.02, H = 4.15/4.09, N = 22.08/23.26.
$Mn(NH_3)_2Hg(CN)_4 \cdot 2C_6H_5NH_2$ :	C = 35.11/34.01, H = 3c.92/3.88, N = 19.04/20.22.

Infrared spectra were recorded between 4000 and  $200\text{ cm}^{-1}$  on Perkin Elmer 1330 and Mattson 1000 FT-IR spectrometers, which were calibrated using indene and polystyrene film. The samples were prepared as mulls in nujol and hexachlorobutadine between KBr plates. It should be noted that several unsuccessful attempts have been made to obtain Raman spectra of our beige compounds by using the 488 or 514 nm laser line.

\* Author for Correspondence. E-mail: cbayrak@hacettepe.edu.tr

## Results and discussion

Briefly, to simplify the interpretation of vibrational spectra, the vibrations can be divided into three units as ammonia,  $M(CN)_4$  and aniline. The FT-IR spectrum of  $Mn(NH_3)_2Zn(CN)_4 \cdot 2An$  is given (Figure 1). The wavenumbers and assignment of the observed bands in the infrared spectra of the compounds studied are listed in Tables 1, 2 and 3 for ligand ammonia, groups and guest aniline molecules, respectively, together with some pertinent spectral data for comparison.

### Ammonia vibrations

It has been found that the vibrational bands of the ammonia ligand are assigned to the infrared spectra of

the Hofmann-type [7] and Hofmann- $T_d$ -type clathrates [5, 9, 10]. In our compounds  $(Mn-(NH_3)_2-M-2An)$  ( $M = Zn, Cd$  or  $Hg$ ) 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 staggering. Based on this model we expect two components for out-of-phase (infrared active) mode of a bare ammonia molecule. Indeed, two infrared active bands due to out-of-phase vibrations have been observed. For the purposes of comparison and discussion, Table 1 also lists the infrared spectra of the ammonia ligands in the Hofmann- $T_d$ -type benzene [5, 9] and aniline clathrates [10]. 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

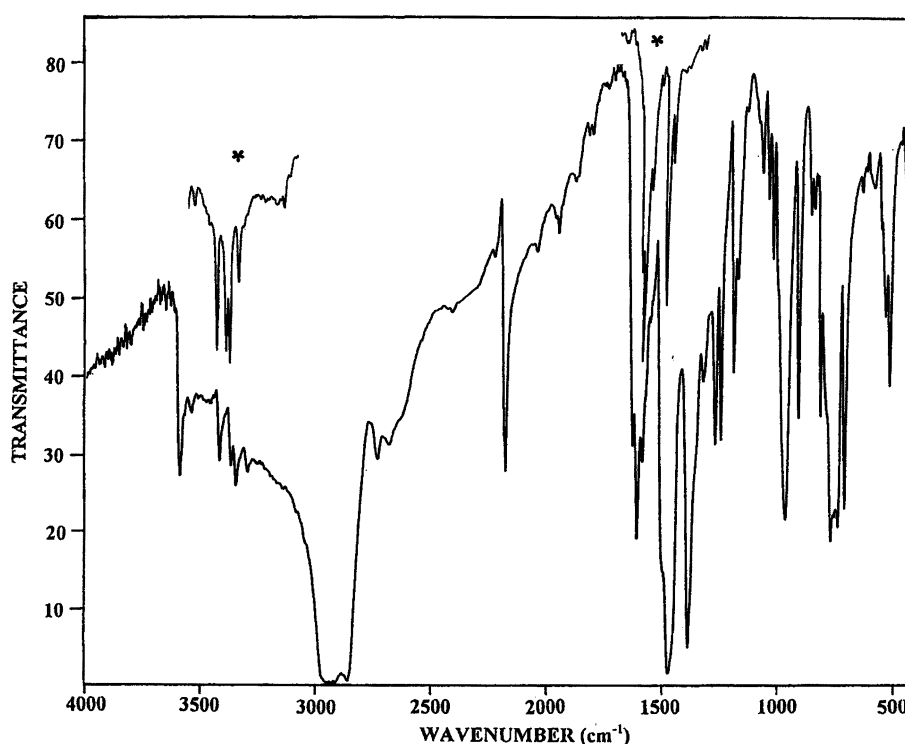


Figure 1. The infrared spectrum of the  $Mn-(NH_3)_2-Zn-An$  clathrate in nujol (\*in poly(chlorotrifluoroethylene)-oil).

Table 1. The vibrational wavenumbers ( $cm^{-1}$ ) of  $NH_3$  for  $Mn-(NH_3)_2-M-2An$  ( $M = Zn, Cd$  or  $Hg$ ) clathrates

Assignment <sup>a</sup>	$Cd-(NH_3)_2-Cd^a$	$Mn-(NH_3)_2-Zn-2Bz^b$	$Cd-(NH_3)_2-Cd-2An^c$	$Mn-(NH_3)_2-Zn-2An$	$Mn-(NH_3)_2-Cd-2An$	$Mn-(NH_3)_2-Hg-2An$
$\nu_a$ (IR)	3390s	3367s	3340s	3367s	3369s	3368s
$\nu_s$ (IR)	3298s	3286m	3240vm	3297m	3297m	3297m
$\delta_a$ (IR)	1604m	1586m	1600s 1582s	1604s	1603s	1601s
$\delta_s$ (IR) <sup>d</sup>	No	1163w	—	1153w	1158w	1163w
$\delta'_s$ (IR)	1154vs	1133vs	1130vs	1126vs	1130vs	1133vs
$\delta'_t$ (IR)	548vs	530vs	528vs	512s	513s	515vs

Abbrs: v = very, s = strong, m = medium, w = weak, sh = shoulder and no = not observed.

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

<sup>b</sup>Taken from Ref. [9].

<sup>c</sup>Taken from Ref. [10].

<sup>d</sup>Band arising from decomposed lattice.

Table 2. The vibrational wavenumbers ( $\text{cm}^{-1}$ ) of the  $\text{M}(\text{CN})_4$  ( $\text{M} = \text{Zn}, \text{Cd}$  or  $\text{Hg}$ ) group for the  $\text{Mn}-(\text{NH}_3)_2-\text{M}(\text{CN})_4-2\text{An}$  ( $\text{M} = \text{Zn}, \text{Cd}$  or  $\text{Hg}$ ) clathrates

Assignment <sup>a</sup>	$\text{K}_2\text{Zn}(\text{CN})_4$	$\text{K}_2\text{Cd}(\text{CN})_4$	$\text{K}_2\text{Hg}(\text{CN})_4$	$\text{Mn}-(\text{NH}_3)_2-\text{Zn}-2\text{Bz}^b$	$\text{Mn}-(\text{NH}_3)_2-\text{Cd}-2\text{Bz}^c$	$\text{Mn}-(\text{NH}_3)_2-\text{Hg}-2\text{Bz}^c$	$\text{Mn}-(\text{NH}_3)_2-\text{Zn}-2\text{An}$	$\text{Mn}-(\text{NH}_3)_2-\text{Cd}-2\text{An}$	$\text{Mn}-(\text{NH}_3)_2-\text{Hg}-2\text{An}$
$\nu_5(\text{CN}) \text{ F}_2$	2152	2145	2146	2173vs	2170vs	2167vs	2168vs	2170vs	2171vs
Hot band	—	—	—	No	2157vw	2154vw	No	No	No
$\nu_5(^{13}\text{CN})$	—	—	—	2127vw	2133vw	2132vw	2132vw	2129vw	2123vw
$\nu_6[\nu(\text{MC}) + \delta(\text{NCM})] \text{ F}_2$	359	316	330	373s	360s	368s	373s	360s	368s
$\nu_7[\nu(\text{MC}) + \delta(\text{NCM})] \text{ F}_2$	315	250	235	320w	No	No	270w	268w	320m

Abbrev: v = very, s = strong, m = medium, w = weak, sh = shoulder and no = not observed.

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

<sup>b</sup>Taken from Ref.[9].

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

sensitive to grinding, even on mild grinding they decompose [5, 7, 8]. In our case, although the Nujol mull preparations of the compounds were done with minimum grinding, infrared spectra exhibit bands attributable to  $\text{NH}_3$  ligands in 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 degrees of grinding and the Cd–Cd host complex, since the IR spectrum of Cd–Cd shows a very strong band at  $1154 \text{ cm}^{-1}$  due to the  $\delta_s$  vibration (Table 1) while the corresponding band of the host lattice of  $\text{Mn}-\text{NH}_3-\text{Zn}-2\text{An}$ ,  $\text{Mn}-\text{NH}_3-\text{Cd}-2\text{An}$  and  $\text{Mn}-\text{NH}_3-\text{Hg}-2\text{An}$  clathrates appear at  $1153$ ,  $1158$  and  $1163 \text{ cm}^{-1}$  (w), respectively. Thus, the comparison of the bands at  $1126 \text{ cm}^{-1}$  (vs) and  $1153 \text{ cm}^{-1}$  (w) for  $\text{Mn}-\text{NH}_3-\text{Zn}-2\text{An}$ ,  $1130 \text{ cm}^{-1}$  and  $1158 \text{ cm}^{-1}$  for  $\text{Mn}-\text{NH}_3-\text{Cd}-2\text{An}$ ,  $1133 \text{ cm}^{-1}$  and  $1163 \text{ cm}^{-1}$  for  $\text{Mn}-\text{NH}_3-\text{Hg}-2\text{An}$  can be used to appraise the extent of decomposition. Upon gradual liberation of aniline, the band at  $1133 \text{ cm}^{-1}$  weakens while the weaker band at  $1163 \text{ cm}^{-1}$  increases in intensity. Similar observations have been noted for Hofmann-type [7] and Hofmann- $\text{T}_d$ -type clathrates [5, 9].

#### $\text{M}(\text{CN})_4$ group vibrations

In assigning the bands attributable to  $\text{M}(\text{CN})_4$  ( $\text{M} = \text{Zn}, \text{Cd}$  or  $\text{Hg}$ ) ions in the spectra of our compounds, we refer to the work of Jones [11] who presented vibrational data for the salts  $\text{K}_2\text{M}(\text{CN})_4$  ( $\text{M} = \text{Zn}, \text{Cd}$  or  $\text{Hg}$ ) in the solid phase and assigned the infrared and Raman active fundamental vibrations of the  $\text{M}(\text{CN})_4$  ion on the basis of  $\text{T}_d$  symmetry. The vibrational data for  $\text{M}(\text{CN})_4$  groups in the compounds studied are given in Table 2, together with the vibrational wavenumbers of  $\text{K}_2\text{Zn}(\text{CN})_4$ ,  $\text{K}_2\text{Cd}(\text{CN})_4$  and  $\text{K}_2\text{Hg}(\text{CN})_4$  [11]. In Table 2 are also listed the wavenumbers of the IR spectra of the benzene  $\text{Mn}(\text{NH}_3)_2 \text{Zn}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  [9] and  $\text{Mn}(\text{NH}_3)_2\text{M}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$  ( $\text{M} = \text{Cd}$  or  $\text{Hg}$ ) [5] clathrates were both listed and compared to those wavenumbers obtained in our study.

The assigned wavenumbers for the  $\text{M}(\text{CN})_4$  groups in the compounds studied appear to be much higher than those for  $\text{M}(\text{CN})_4$  group in  $\text{K}_2\text{M}(\text{CN})_4$  ( $\text{M} = \text{Zn}, \text{Cd}$  or  $\text{Hg}$ ) salt (Table 2). Such frequency shifts have been observed for  $\text{T}_d$ -type clathrates [5, 6, 9, 12–14], and  $\text{T}_d$ -type host complexes [15–18], in which both ends of the CN group are coordinated and explained as the mechanical coupling of the internal modes of  $\text{M}(\text{CN})_4$  ( $\text{M} = \text{Zn}, \text{Cd}$  or  $\text{Hg}$ ) with the metal Mn–NC vibrations. It follows that the N-termini of  $\text{M}(\text{CN})_4$  ( $\text{M} = \text{Zn}, \text{Cd}$  or  $\text{Hg}$ ) group are also bound to Mn atoms in an octahedral configuration in the compounds studied.

#### Aniline vibrations

The assignment and the wavenumbers of the vibrational bands of aniline observed in the spectra of the clathrate

Table 3. The vibrational wavenumbers ( $\text{cm}^{-1}$ ) of aniline in the  $\text{Mn}-(\text{NH}_3)_2-\text{M}(\text{CN})_4-2\text{An}$  ( $\text{M} = \text{Zn}, \text{Cd}$  or  $\text{Hg}$ ) clathrates

Assignment <sup>a</sup>	Liquid aniline <sup>a</sup>	DFT <sup>b</sup> $\nu_{\text{cal}}$	$\text{Mn}-(\text{NH}_3)_2-\text{Ni}-2\text{An}^c$	$\text{Cd}-(\text{NH}_3)_2-\text{Cd}-2\text{An}^d$	$\text{Mn}-(\text{NH}_3)_2-\text{Zn}-2\text{An}$	$\text{Mn}-(\text{NH}_3)_2-\text{Cd}-2\text{An}$	$\text{Mn}-(\text{NH}_3)_2-\text{Hg}-2\text{An}$
$\text{NH}_2$ antisym. stretching ( $\nu_{\text{NH}_2}$ ) ( $A'$ )	3440s	3493	3471s	3420s	3417s	3412s	3413s
$\text{NH}_2$ sym. stretching ( $\nu_{\text{NH}_2}$ ) ( $A'$ )	3360vs	3399	3375vs	3340vs	3367s	3369s	3368s
CH stretching ( $\nu_{\text{CH}}$ ) ( $A''$ )	3088w	3077	3074w	3070vw	No	3080vw	3080w
CH stretching ( $\nu_{\text{CH}}$ ) ( $A'$ )	3037vw	3038	3036vw	3040vw	3048w	3046w	3044w
CH stretching ( $\nu_{\text{CH}}$ ) ( $A''$ )	3025vw	3039	3009vw	3000wm	3018w	3016w	3015w
$\text{NH}_2$ scissoring ( $\delta_{\text{NH}_2}$ ) ( $A'$ )	1618vs	1627	1617vs	—	1618s	1617s	1618s
CC stretching ( $\nu_{\text{CC}}$ ) ( $A'$ )	1603vs	1608	1600s	1600vs	1600vs	1603vs	1601vs
				1582m,sh			
CC stretching ( $\nu_{\text{CC}}$ ) ( $A''$ )	1590vw	1593	1582vw	1565m,sh	1562m,sh	1562m,sh	1561m,sh
CC stretching ( $\nu_{\text{CC}}$ ) ( $A'$ )	1503vs	1503	1492s	—	1496vs	1495vs	1495vs
CC stretching ( $\nu_{\text{CC}}$ ) ( $A''$ )	1468s	1474	1467vs	1480vs	1470vs	1470vs	1468vs
				1445m			
CC stretching ( $\nu_{\text{CC}}$ ) ( $A''$ )	1340vs	1343	1339vw	1325vw	1338vw	1340vw	1337vw
CH i.p. bending ( $\delta_{\text{CH}}$ ) ( $A''$ )	1308vw	1318	1314w	1310s	1316vw	1315vw	1310vw
C-N stretching ( $\nu_{\text{C-NH}_2}$ ) ( $A'$ )	1278s	1271	1290s	1260s	1260s	1259s	1257s
CH i.p. bending ( $\delta_{\text{CH}}$ ) ( $A'$ )	1173m	1176	1175s	1160s	1178m	1178m	1178m
CH i.p. bending ( $\delta_{\text{CH}}$ ) ( $A''$ )	1152w	1156	1152s	1130s	1157w	1158w	1159w
CH i.p. bending ( $\delta_{\text{CH}}$ ) ( $A''$ )	1115vw	1117	1102vw	—	1119vw	1114vw	1116vw
$\text{NH}_2$ rocking ( $A'$ )	1054m	1044	1041vw	1045vw	1053w	1055w	1058w
CH i.p. bending ( $\delta_{\text{CH}}$ ) ( $A'$ )	1028w	1020	1022w	1025w	1026w	1025w	1025w
Ring breathing ( $A'$ )	996m	994	992w	990w	1007m	1006m	1006m
CH o.p. bending ( $\nu_{\text{CH}}$ ) ( $A'$ )	968w	968	—	980w	982w,sh	983w,sh	983w,sh
CH o.p. bending ( $\nu_{\text{CH}}$ ) ( $A''$ )	957w	938	—	—	955vs	950vs	950vs
CH o.p. bending ( $\nu_{\text{CH}}$ ) ( $A'$ )	874m	869	888m	869m	896m	893m	893m
CH o.p. bending ( $\nu_{\text{CH}}$ ) ( $A''$ )	823vw	817	826vw	820vw	828vw	825vw	832vw
$\nu_{\text{C-NH}_2} + \nu_{\text{CC}} + \delta$ ring ( $A'$ )	808m	809	812vw	800w	800m	800m	797m
CH o.p. bending ( $\nu_{\text{CH}}$ ) ( $A'$ )	747vs	752	765vs	748vs	755s	756s	755s
o.p. Ring deform. ( $\nu_{\text{ring}}$ ) ( $A'$ )	689vs	682	701s	680vs	696vs	694vs	694vs
Ring deformation ( $\delta_{\text{ring}}$ ) ( $A''$ )	619vw	630	688w	—	669vw	665vw	670vw
$\text{NH}_2$ wagging ( $A'$ )	541vw	576	—	—	566w	564w	566w
Ring deformation ( $\delta_{\text{ring}}$ ) ( $A''$ )	526w	529	—	—	535w	534w	535w
o.p. Ring deform. ( $\nu_{\text{ring}}$ ) ( $A'$ )	501s	492	508	490s	500s	505s	500s

Abrs: v = very, s = strong, m = medium, w = weak, sh = shoulder, no = not observed, str. = stretch; i.p. = in-plane; o.p. = out-of-plane.

<sup>a</sup>Taken from Ref.[19].

<sup>b</sup>Taken from Ref.[20].

<sup>c</sup>Taken from Ref.[7].

<sup>d</sup>Taken from Ref.[10].

compounds are listed in Table 3. This table also lists the wavenumbers of aniline in the liquid phase [19], calculated by using (B3-LYP)/6-31G, SQM Scaled [20] and in the clathrates  $\text{Mn}(\text{NH}_3)_2\text{Ni}(\text{CN})_4\cdot 2\text{An}$  [7] and  $\text{Cd}(\text{NH}_3)_2\text{Cd}(\text{CN})_4\cdot 2\text{An}$  [10], on which the assignments are based.

The free aniline molecule has  $C_s$  symmetry and all vibrational ( $20A' + 16A''$ ) modes are infrared or Raman active. In the infrared spectrum of the aniline clathrates, all the bands of the guest molecule can be correlated with corresponding bands in liquid aniline (Table 3). Values for the  $\text{NH}_2$  modes of aniline are notably different when it is a guest molecule as compared to its being a ligand. It is known that the  $\text{NH}_2$  group vibrational modes of aniline and aniline derivatives are much affected by complex formation [7, 8, 21, 22]. The bands at 3440 and 3360  $\text{cm}^{-1}$  have been assigned to the  $\text{NH}_2$  antisymmetric and symmetric vibrations for liquid aniline, respectively [19, 23]. The  $\nu_a(\text{NH}_2)$  and  $\nu_s(\text{NH}_2)$  stretching frequencies of coordinated aniline have been observed at 3342 and 3270  $\text{cm}^{-1}$  in the  $\text{Mn}(\text{aniline})_2\text{Ni}(\text{CN})_4$  complexes, respectively [21]. These bands have been observed at 3420 and 3340  $\text{cm}^{-1}$  in the  $\text{Cd}(\text{NH}_3)_2\text{Cd}(\text{CN})_4\cdot 2\text{An}$  clathrate [10]. The band at 1618  $\text{cm}^{-1}$  has been assigned to the  $\delta(\text{NH}_2)$  scissoring mode of liquid aniline. While this mode decreased by 42  $\text{cm}^{-1}$  in  $\text{Mn}(\text{aniline})_2\text{Ni}(\text{CN})_4$  complex, any significant change in our clathrates was not observed. We also observed this mode at 1618  $\text{cm}^{-1}$  in our clathrates.

Upon coordination of aniline the phenyl ring vibrations show significant change in comparison to the free aniline. As can clearly be seen from Table 3, no significant change has been observed for ring modes. The two notable exceptions are the  $\text{C-N}(\text{NH}_2)$  stretching mode and the  $\gamma(\text{CH})$  out-of-plane hydrogen deformation mode. The  $\nu(\text{C-N})$  stretching mode (at 1278  $\text{cm}^{-1}$  in liquid aniline) shows a downward shift of about 20  $\text{cm}^{-1}$  in the infrared spectra of our clathrates. The lowering of this mode corresponds to a weak hydrogen bond between  $\text{NH}_2$  group of aniline,  $\pi$  cloud and CN group of host lattice.

In our clathrates, the  $\gamma(\text{CH})$  out-of-plane hydrogen deformation mode of aniline molecule shows an upward

shift of about 10  $\text{cm}^{-1}$  in comparison to the liquid aniline (747  $\text{cm}^{-1}$ ). Similar positive shifts have been observed for Hofmann- $T_d$ -type [10] and Hofmann-type clathrates [7, 8]. This upward shift may be due to a weak hydrogen bond between the  $\pi$ -electrons located above and below the plane of the phenyl ring and the  $\text{NH}_3$  of the host lattice, as has been suggested for other clathrates [7, 8, 10].

To conclude we can report that aniline molecule in our clathrates has acted as a guest molecule. The above discussion, when considered as a whole, leads us to the conclusion that the host lattice of our clathrates is similar to those of  $T_d$ -type clathrates.

## References

1. H. Yuge and T. Iwamoto: *J. Incl. Phenom.* **14**, 217 (1992).
2. R. Kuroda: *Inorg. Nucl. Chem Lett.* **9**, 13 (1973).
3. T. Iwamoto and D. F. Shriver: *Inorg. Chem* **11**, 2570 (1972).
4. S. Nishikiori and T. Iwamoto: *J. Incl. Phenom.* **3**, 283 (1985).
5. E. Kasap and Z. Kantarcı: *J. Incl. Phenom.* **20**, 33 (1995).
6. Z. Kantarcı and C. Bayrak: *J. Incl. Phenom.* **30**, 59 (1998).
7. S. Akyüz, A.B. Dempster, and R.L. Morehouse: *Spectrochim. Acta* **30A**, 1989 (1974).
8. S. Akyüz, A.B. Dempster, J.E.D. Davies, and K.T. Holmes: *J. Mol. Struct.* **38**, 43 (1977).
9. Z. Kantarcı, C. Bayrak, and E. Kasap: *J. Incl. Phenom.* **39**, 103 (2001).
10. R. Murugesan, A. Thamaraichelvan, and P. Sami: *J. Incl. Phenom.* **34**, 235 (1999).
11. L.H. Jones: *Spectrochim. Acta* **17**, 188 (1961).
12. S. Bayarı, C. Bayrak, and Z. Kantarcı: *J. Incl. Phenom.* **38**, 23 (2000).
13. Z. Kantarcı and C. Bayrak: *J. Incl. Phenom.* **30**, 59 (1998).
14. Y. Tufan: *J. Incl. Phenom.* **48**, 131 (2004).
15. Z. Kantarcı, C. Bayrak, and S. Bayarı: *J. Mol. Struct.* **407**, 155 (1997).
16. C. Bayrak and S. Bayarı: *J. Mol. Struct.* **482–483**, 159 (1999).
17. M. Bahat and S. Yurdakul: *J. Mol. Struct.* **408**, 395 (1997).
18. S. Akyüz, M. Bakiler, L. Andreeva, and B. Mincevasukurova: *J. Incl. Phenom.* **48**, 25 (2004).
19. J.C. Evans: *Spectrochim. Acta* **16**, 428 (1960).
20. G. Rauhut and P. Pulay: *J. Phys. Chem.* **99**, 3093 (1995).
21. S. Akyüz: *J. Mol. Struct.* **68**, 41 (1980).
22. M.A.J. Jungbauer and C. Curran: *Spectrochim. Acta* **21**, 641 (1965).
23. M. Castella-Ventura and E. Kassab: *Spectrochim. Acta* **50A**, 69 (1994).