



Vibrational Spectroscopic Analyses of (en)₂-Td-type Clathrates

G. Indramahalakshmi^{1*}

¹*Faculty of Chemistry, Cardamom Planters' Association College (Affiliated to Madurai Kamaraj University), Bodinayakanur, Theni Dt, Tamilnadu-625513, India.*

Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

Article Information

DOI: 10.9734/AJOPACS/2020/v8i130108

Editor(s):

(1) Dr. Roberto Oscar Aquilano, National University of Rosario (UNR), Argentina.

Reviewers:

(1) Pipat Chooto, Prince of Songkla University, Thailand.

(2) B.Mohammed Nawaz, Islamiah College, India.

(3) Vikas Dhull, Maharshi Dayanand University, India.

Complete Peer review History: <http://www.sdiarticle4.com/review-history/55015>

Received 28 December 2019

Accepted 03 March 2020

Published 14 March 2020

Original Research Article

ABSTRACT

The clathrates of Hofmann-(en)₂-Td-type, M(en)₂M'(CN)₄.Aniline (M=Cu,Cd; M'=Cd,Zn) and their hosts were synthesized with the confirmation using FTIR spectra. Hydrogen bonding interaction between π-cloud of phenyl ring of the guest molecule and ethylenediamine(en) of the host lattices was deduced from the upward shift in ν(CH) out of plane bending mode of aniline. A second type of hydrogen bonding between C≡N group of the host lattice and NH₂ of aniline guest was also inferred from the downward shift in ν(C≡N) of the clathrates. The relative strength of H-bonding in the clathrates was found to be Hofmann-(en)₂-Type > Hofmann-(en)₂-Td-Phenol > Hofmann-(en)₂-Td-Aniline. The presence of major peaks corresponding to various modes of guest aniline, ligand en and cyanide group in FT Raman spectra also confirms the formation of clathrates. Attempts to synthesize Ni(en)₂M'(CN)₄.Aniline (M'=Cd,Zn) resulted in the formation of M'(en)₂Ni(CN)₄.2Aniline (M'=Cd,Zn) due to the exchange of metal ions and greater stability of Ni(CN)₄ unit.

Keywords: *Aniline clathrates; Hofmann-(en)₂-Td-type; metal ion exchange in clathrates; IR spectra; Raman spectra; guest-host interactions.*

*Corresponding author: E-mail: ayyan1960@gmail.com;

1. INTRODUCTION

Studies on clathrates continue to attract greater attention due to their applications in molecular recognition, separation of isomers [1-4], synthesis of asymmetric and polymeric compounds [5], purification of gasoline and benzene [6], isolation of branched chain compounds from linear chain hydrocarbons [7], entrapment of organic wastes by coordination clathrates [8], removal of carcinogenic hydrocarbons and preparation of jet fuels [9]. The cavities of clathrates could be engineered to obtain stereoselectivity of the guest molecules [3]. Existence of different kinds of host-guest interactions in the form of van der Waals' forces and hydrogen bonding, thermal stability, structural changes, ligand replacement reactions, molecular motions in solid state, conformational isomerism and effect of substituents and steric factors in the formation of stereoselective products in clathrates has been elucidated using TGA/DTA analysis, isothermal kinetic studies and spectroscopy such as IR, Raman, ^1H , ^2H and ^{13}C NMR.

For clathrates in contrast to Hofmann type of $\text{M}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot n\text{G}$ (M = bivalent metal ion and G = guest molecule) [10,11]; Hofmann-Td-type [12]; Hofmann-(en)-type of $\text{M}(\text{en})\text{Ni}(\text{CN})_4 \cdot n\text{G}$ [13] and Hofmann-(en)-Td type of $\text{M}(\text{en})\text{M}'(\text{CN})_4 \cdot n\text{G}$ (M'=Zn,Cd,Hg) [14,15], the studies on Hofmann-(en)₂-type are very limited and none on Hofmann-(en)₂-Td-type. Hofmann-(en)₂-type of $\text{M}(\text{en})_2\text{Ni}(\text{CN})_4 \cdot 2\text{Aniline}$ (M=Cu,Zn,Cd,Hg) [16] were synthesized and characterized by IR and EPR [12] as well as X- ray diffraction [2,17]. This work covers $\text{M}(\text{en})_2\text{M}'(\text{CN})_4 \cdot \text{Aniline}$ (M = Cu,Cd; M' = Cd,Zn). The different clathrates and hosts

studied are: $\text{Cu}(\text{en})_2\text{Cd}(\text{CN})_4 \cdot \text{Aniline}$ (**1**), $\text{Cu}(\text{en})_2\text{Cd}(\text{CN})_4$ (**1'**), $\text{Cd}(\text{en})_2\text{Cd}(\text{CN})_4 \cdot \text{Aniline}$ (**2**), $\text{Cd}(\text{en})_2\text{Cd}(\text{CN})_4$ (**2'**), $\text{Cu}(\text{en})_2\text{Zn}(\text{CN})_4 \cdot \text{Aniline}$ (**3**), $\text{Cu}(\text{en})_2\text{Zn}(\text{CN})_4$ (**3'**), $\text{Cd}(\text{en})_2\text{Zn}(\text{CN})_4 \cdot \text{Aniline}$ (**4**) and $\text{Cd}(\text{en})_2\text{Zn}(\text{CN})_4$ (**4'**).

The exchange of positions between Ni^{2+} ion from the outer sphere and the metal ion of the cyanide moieties, $\text{Cd}(\text{CN})_4^{2-}$ and $\text{Zn}(\text{CN})_4^{2-}$, experienced during the synthesis of the hosts $\text{Ni}(\text{en})_2\text{Cd}(\text{CN})_4$ and $\text{Ni}(\text{en})_2\text{Zn}(\text{CN})_4$ and their aniline clathrates is also reported. The compounds thus formed are: $\text{Cd}(\text{en})_2\text{Ni}(\text{CN})_4 \cdot 2\text{Aniline}$ (**5**), $\text{Cd}(\text{en})_2\text{Ni}(\text{CN})_4$ (**5'**), $\text{Zn}(\text{en})_2\text{Ni}(\text{CN})_4 \cdot 2\text{Aniline}$ (**6**) and $\text{Zn}(\text{en})_2\text{Ni}(\text{CN})_4$ (**6'**).

2. METHODOLOGY

All chemicals were of analar grade and used without further purification. Host and clathrate samples were synthesized according to literature methods [18,19]. 2.5 mmol of ethylenediamine (en) was added to 1 mmol of M(II) salt (M=Ni, Cu, Cd) in 10 ml of water. To this was added a solution of 1 mmol of $\text{K}_2[\text{M}'(\text{CN})_4]$ (M'= Cd, Zn) in 10 ml of water. The clear filtrate was kept in a 100 ml beaker covered with a perforated paper. Within a week, crystals of the host $\text{M}(\text{en})_2\text{M}'(\text{CN})_4$ were obtained. The crystals were collected, dried and preserved in a desiccator. The corresponding aniline clathrates were obtained by adding a neat liquid of aniline on top of the aqueous layer containing $\text{M}(\text{en})_2\text{M}'(\text{CN})_4$ complex without disturbing the solution to form an upper layer. The set up was left undisturbed for a week. Samples of compounds **2** and **4** were of polycrystalline in nature. Crystals of **5** and **6** were obtained as needles at the interface. The copper clathrates **1** and **3** were recovered

Table 1. Analytical data for the hosts 1'-6' and clathrates 1-6 (found % /calculated %)

Compound	M%	M'%	N%
$\text{Cu}(\text{en})_2\text{Cd}(\text{CN})_4 \cdot \text{Aniline}$ (1)	13.0/12.8	22.6/22.9	25.1/25.5
$\text{Cd}(\text{en})_2\text{Cd}(\text{CN})_4 \cdot \text{Aniline}$ (2)	41.3/41.5	---	22.9/23.2
$\text{Cu}(\text{en})_2\text{Zn}(\text{CN})_4 \cdot \text{Aniline}$ (3)	14.0/14.2	14.8/14.4	28.5/28.2
$\text{Cd}(\text{en})_2\text{Zn}(\text{CN})_4 \cdot \text{Aniline}$ (4)	22.9/22.7	13.1/13.6	25.2/25.4
$\text{Cu}(\text{en})_2\text{Cd}(\text{CN})_4$ (1')	15.8/15.9	28.0/28.3	27.8/28.0
$\text{Cd}(\text{en})_2\text{Cd}(\text{CN})_4$ (2')	49.1/50.1	---	24.6/24.9
$\text{Cu}(\text{en})_2\text{Cd}(\text{CN})_4$ (3')	18.0/17.9	18.3/18.5	31.6/31.7
$\text{Cd}(\text{en})_2\text{Zn}(\text{CN})_4$ (4')	27.8/28.0	16.4/16.7	27.7/27.8
$\text{Cd}(\text{en})_2\text{Ni}(\text{CN})_4$ (5')	28.3/28.5	14.9/14.5	28.1/28.3
$\text{Zn}(\text{en})_2\text{Ni}(\text{CN})_4$ (6')	18.9/18.7	16.7/16.8	32.2/32.8
$\text{Cd}(\text{en})_2\text{Ni}(\text{CN})_4 \cdot 2\text{Aniline}$ (5)	19.5/19.9	10.2/10.0	23.8/24.1
$\text{Zn}(\text{en})_2\text{Ni}(\text{CN})_4 \cdot 2\text{Aniline}$ (6)	11.9/12.2	11.1/10.9	26.0/26.2

immediately to avoid the reduction of Cu(II) to Cu(I) [19]. Polycrystalline samples of **1** and **3** were also formed on stirring a mixture of liquid aniline with an aqueous solution containing the host for three hours. Freshly prepared clathrates were collected, dried off and placed in small Eppendorf tubes containing pure cotton soaked with drops of the mother liquor and stored in a desiccator under an atmosphere of aniline to avoid decomposition.

Metals were analyzed using atomic absorption spectrometer, Varian Model Spectraa220 whereas nitrogen was estimated using Kjeldahl method with the results as shown in Table 1. Declathration was carried out by heating the clathrate samples in an air oven for three hours at 100°C. FTIR spectra were recorded using KBr pellets in the range of 4000-400cm⁻¹ on a Jasco 400-FTIR 460 Plus spectrometer with the resolution of 4cm⁻¹ and was calibrated using polystyrene. FT-Raman spectra were recorded on a Bruker IFS, 66V FT-IR spectrometer with FRA 106 Raman module, (YAG-LASER, 300 mw power).

3. RESULTS AND DISCUSSION

3.1 Guest Vibrations

All the bands of guest molecules in the liquid state are observed in the clathrates. However, no extra bands from the guest are exhibited by the clathrates and there is no evidence of correlation field splitting from the single molecule in each unit cell. Although all the vibrational modes of aniline are IR active, those of particular interest include: (i) the out of plane bending mode of C-H group of aniline and phenol (ii) the symmetric and asymmetric stretching modes of NH₂ group of aniline (iii) the combination modes of ring stretching and NH₂ bending of aniline (iv) the symmetric and asymmetric stretching and bending vibrations of NH₂ and CH₂ groups [$\nu_s(\text{NH}_2)$, $\nu_s\text{CH}_2$, νCH_2 , $\delta_s(\text{NH}_2)$, $\delta_a(\text{NH}_2)$, $\delta_s\text{CH}_2$, $\delta_a\text{CH}_2$], the rocking vibrational modes of NH₂ of ethylenediamine and the $\nu_{\text{C} \equiv \text{N}}$ stretching mode of the cyano group of the host lattice. Changes in the frequencies of the aforementioned modes are indicative of hydrogen bonding between guest and host, stability of the clathrates, decomposition and ligand substitution on evacuation [16,19,20,21].

3.2 Aniline Vibrations

The IR spectra of the aniline clathrate, Cu(en)₂Zn(CN)₄.Aniline (**3**), its heated sample

(heated for 3 hours at 100°C) and the corresponding host, Cu(en)₂Zn(CN)₄(**3'**), are illustrated in Fig. 1. The vibrational frequencies of the various bands of guest molecule for **1-4** are given in Table 2. A one to one correlation between the spectra of the host and the heated clathrate of **3** reveals that, the aniline bands clearly seen in the clathrate spectrum, are conspicuously absent in the heated sample. Bands at 3424, 3301, 3042, 1621, 1175, 762 and 696 cm⁻¹ are totally missing in the declathrated sample, while the intensities of bands at 1601 and 1281 cm⁻¹ are decreased. These observations establish that the guest aniline, trapped inside the cavity in the clathrate, is lost on heating and the resultant product is, in fact, the host lattice, Cu(en)₂Zn(CN)₄. The other aniline clathrates **1**, **2** and **4** also exhibit a similar behavior with FT-IR spectra as shown in Fig. 2.

Despite the overlapping of the NH bands of aniline with those of the en molecules, all the bands of aniline could be identified. On close scrutiny and comparison with the vibrational modes of Hofmann-(en)₂-type aniline clathrates, liquid aniline and liquid en, many bands show frequency shifts of more than 10 cm⁻¹. Particularly, the out of plane deformation mode of C-H (aniline ring) is upshifted by 11 cm⁻¹ in Cu(en)₂Zn(CN)₄.Aniline(**3**). This value is comparable to that experienced in Cd(en)₂Ni(CN)₄.2Aniline [16]. Such an upward shift in Hofmann-type [11] and Hofmann-(en)₂-type aniline clathrates [16] compared to liquid aniline [22], has been attributed to the presence of a weak hydrogen bonding between the π cloud of phenyl ring and the ligand NH₃ or en of the host lattices [11,16]. Hence, in the clathrate **3**, a similar H-bonding interaction between the guest and the host is suggested to be present. When the outer metal ion Cu²⁺ in **3** is replaced by Cd²⁺ in **4**, the corresponding upshift in CH o.p deformation mode of aniline ring is lowered to 6 cm⁻¹. The smaller size of the Zn(CN)₄²⁻ lattice may probably bring closer the aniline guest and the en ligands, thus facilitating effective hydrogen bonding in **3** and **4**. The relatively lower value noted may probably be due to the larger size of the outer metal ion, Cd²⁺ in **4**. The other deformation modes of C-H (Aniline ring) like 880, 970 and 826 cm⁻¹ show shifts, in particular, 880 cm⁻¹ value is upshifted by 16 cm⁻¹.

In contrast, **1** and **2** experience only an upward shift of 3 cm⁻¹ and 2 cm⁻¹ respectively for the $\nu(\text{CH})$ o.p mode of aniline, attributable to the presence of a very weak hydrogen bonding as

discussed above. It is considerably lower than that observed in $\text{Cd}(\text{en})_2\text{Ni}(\text{CN})_4 \cdot 2\text{Aniline}$ (11 cm^{-1}) [16] as well as those seen in clathrates **3** and **4** (11 and 6 cm^{-1} respectively). Smaller shifts, observed in the $\nu(\text{CH})_{\text{o.p.}}$ mode of the present and other reported aniline clathrates [11,16] compared to the benzene clathrates (30 cm^{-1}) [11,24], may probably be due to the larger distance between the ligand and the guest

molecules. The relative strength of hydrogen bonding in the present aniline clathrates is of the order, $\text{M}(\text{en})_2\text{Cd}(\text{CN})_4 \cdot \text{An} < \text{M}(\text{en})_2\text{Zn}(\text{CN})_4 \cdot \text{An}$. Further, the effect of H-bonding is stronger when M is Cu compared to the cadmium analogue which might have been influenced by the John Teller effect of Cu(II) ion. A similar observation has also been made in the Hofmann-type clathrates [11,12,16].

Table 2. IR vibrational frequencies of aniline guest in clathrates 1-4

Assignment ^a	Liq. Aniline	Cd-Hg-An ^b	1	2	2 (Raman)	3	4
$\nu_a(\text{NH}_2)$	3440 s	3461m	3477 m	3447 s		3424 m	3470 s
$\nu_s(\text{NH}_2)$	3360 s		3307 vs	3363 s		3346 s	3384 s
$\nu_s(\text{CH})$	3072 w		3131 m	3080 w		3301 s	
$\nu_s(\text{CH})$	3037 vw			3043 m	3050	3042 w	3045 m
$\nu_s(\text{CH})$	3010 vw		2979 vw	3017 w		nm - vw	3017 vw
$\nu_s(\text{NH}_2)$	1621 vs	1617 s		1614 vs	1600	1621 s	1617 vs
$\nu_s(\text{ring})$	1600 s	1602 s	1579 s	1602 vs		1601 s	1604 vs
$\nu_a(\text{ring})$	1586 vw		1579 s	1581 s		1579 s	1588 s
$\nu_s(\text{ring})$	1500 s	1498 s	1494 m	1498 s		1498 m	1498 vs
$\nu_a(\text{ring})$	1468 vs		1459 m	1468 s		1460 m	1469 s
$\nu_a(\text{ring})$	1330 vw		1349 w	1321 m		1327 m	1329 m
$\delta_a(\text{CH})_{\text{ip}}$	1312 vw		1305 m				1313 vw
xs-sens.	1278 s	1280 ms	1278 m	1287 m	1250	1281 m	1282 s
$\delta_a(\text{CH})_{\text{ip}}$	1175 s	1177 ms	1164 m	1174 s	1180	1175 w	1176 s
$\delta_a(\text{CH})_{\text{ip}}$	1154 s			1151 w		1154 w	1154 m
$\delta_a(\text{CH})_{\text{ip}}$	1118 vw		1116 m	1074 s	1092		1082 s
t(NH ₂)	1050 vw					1097 m	1082 s
$\delta_a(\text{CH})_{\text{ip}}$	1028 w	1028 m	1035 s	1028 w		1035 vs	1009 vs
ring breadth	996 w	997 mw	985 m	994 vs			
$\nu_s(\text{CH})_{\text{o.p.}}$	970 vw		933 w	890 m		964 m	977 vs
$\nu_s(\text{CH})_{\text{o.p.}}$	880 m	882 mw		877 m		892 w	896 w
$\nu_s(\text{CH})_{\text{o.p.}}$	826 vw		840 w	860 w		837 vw	815 m
xs-sens	810 vw					nm	801 s
$\nu_a(\text{CH})$	751 vs	766 vs	754 m	753 vs	720	762 s	757 vs
ring def.o.p	691 s		690 s	696 vs		696 s	694 vs
w(NH ₂)	670 w		665 m	620 vw	620	668 m	659 vw
xs-sens.o.p	501 s		505 m	507 vs	510	507 m	508 s

^aTaken from Ref [22]; ^bCd(tn)Hg(CN)₄·2Aniline from Ref [23]

Table 3. Vibrational frequencies of aniline in various environments (cm⁻¹)

Nature of aniline	Compound	$\nu_{\text{as}}(\text{NH}_2)$	$\nu_s(\text{NH}_2)$	Ref
Ligand	$\text{Mn}(\text{aniline})_2\text{Ni}(\text{CN})_4$	3342	3270	[25]
Guest	$\text{Cd}(\text{NH}_3)_2\text{Cd}(\text{CN})_4 \cdot 2\text{An}$	3420	3340	[16]
Liquid	Liquid aniline	3440	3360	[22]
Guest	1,2,3,4	3470	3384	[our Present work]
Guest	$\text{Cd}(\text{tn})\text{Hg} \cdot 2\text{An}$	3461	-	[23]
Guest	$\text{Ni}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{An}$	3471	3379	[11]
Vapour	Vapour aniline	3500	3418	[22]

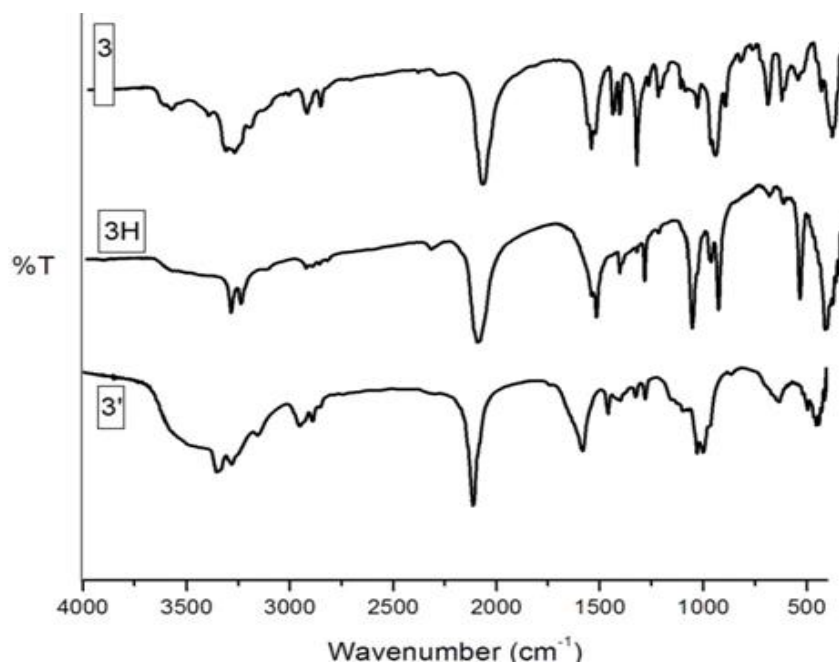


Fig. 1. FT-IR spectra of $\text{Cu(en)}_2\text{Zn(CN)}_4\text{.Aniline(3)}$; heated sample of 3 (3H) and host of 3, $\text{Cu(en)}_2\text{Zn(CN)}_4(3')$

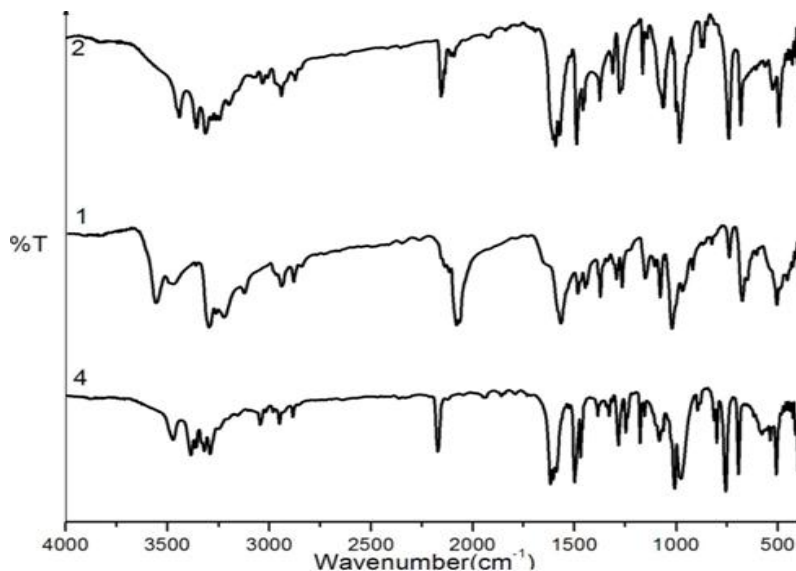


Fig. 2. FT-IR spectra of clathrates $\text{Cd(en)}_2\text{Cd(CN)}_4\text{.Aniline(2)}$; $\text{Cu(en)}_2\text{Cd(CN)}_4\text{.Aniline(1)}$ and $\text{Cd(en)}_2\text{Zn(CN)}_4\text{.Aniline(4)}$

The stability of the clathrates may also be enhanced by a second type of hydrogen bonding between the NH_2 group of aniline and the π cloud of $\text{C}\equiv\text{N}$ of the lattice as demonstrated in Hofmann, Hofmann-(en)₂ and Hofmann-td-type clathrates [12,16,19]. In general, upon hydrogen bonding, vibrational modes of $\nu_a(\text{NH}_2)$ and

$\nu_s(\text{NH}_2)$ of aniline get shifted to lower frequencies compared to vapour aniline (3500 cm^{-1} and 3418 cm^{-1} respectively) [22]. In the present clathrates **1** and **2**, $\nu_a(\text{NH}_2)$ of aniline occurs in the range of $3447\text{-}3477\text{ cm}^{-1}$. The effect of H-bonding appears to be comparable to those of liquid aniline ($\nu_a = 3440\text{ cm}^{-1}$). Such a significant

downward shift can be taken to represent the weak hydrogen bonding interaction as observed in Hofmann-Td and Hofmann-(en)₂-type clathrates [16]. A similar trend is observed for the mode $\nu_s(\text{NH}_2)$, (3307-3363 cm^{-1}) in both clathrates and the shift is comparable to that of liquid aniline ($\nu_s = 3360 \text{ cm}^{-1}$). This hydrogen bonding behavior of **3** and **4** with $\text{Zn}(\text{CN})_4$ bridges is comparable to that of **1** and **2** with $\text{Cd}(\text{CN})_4$ linking units. The $\nu_a(\text{NH}_2)$ mode of aniline in **3** and **4** occurs in the range of 3424-3470 cm^{-1} and that for $\nu_s(\text{NH}_2)$ is 3346-3384 cm^{-1} . They fall in line with the expected values for hydrogen bonding.

A comparison of the strength of H-bonding among the various Hofmann and related clathrates reveals that the order of stability of compounds based on H-bonding through NH_2 of aniline with the host is as follows (Table 3): coordinated aniline in Hofmann clathrate host > guest aniline in Hofmann-Td-clathrate > liquid aniline > present clathrates **1**, **2**, **3** and **4** > guest aniline in Hofmann-tn-Td-clathrate > Hofmann-aniline clathrate > vapour aniline (Based on the downshift values the order is given).

3.3 Ethylenediamine Vibrations

Yokoseki and Kuchitsu [26] have shown that the en molecule possesses conformational isomerism in the gas phase and the dominant form (more than 95%) is the gauche conformation. The IR and Raman spectral data for the en molecule and its deuterated derivatives in the liquid and solid phases have been reported to be in accordance with gauche and trans conformations, respectively [27]. From the results of IR spectroscopic and powder X-ray diffraction data [21], the en ligand molecules in $\text{Cd}(\text{en})\text{M}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ (M = Ni or Pd) were suggested to have the trans form, while the single crystal X-ray diffraction studies have confirmed that the en molecules in Cd-en-Cd-2G are in gauche conformation [28]. The gauche form may be due to the packing requirement for keeping the host framework of $\text{Cd}[\text{Cd}(\text{CN})_4]$ similar to the regular framework of the Td-type clathrates, $\text{Cd}(\text{NH}_3)_2\text{Cd}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ and $\text{Cd}(\text{NH}_3)_2\text{Hg}(\text{CN})_4 \cdot 2\text{C}_6\text{H}_6$ [10]. The fact that en has the gauche form in Cd-en-Cd-2G and the spectral similarities between this and other clathrate compounds under study suggests that the en ligand in our compounds also has a gauche form. For the gauche configuration and consequent C_2 symmetry, all vibrational modes are infrared active.

The assignment of en vibrations is based on values reported for liquid en [27] and $\text{Cu}(\text{en})_2\text{SO}_4$ [16] as shown in Tables 4a,4b. 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. Thus, on coordination the N-H stretching frequencies should decrease, while the C-H frequencies should increase due to the consecutive inductive effects [11,24]. In other words, on coordination N-H bonds should become weaker and C-H bonds may become stronger. In our case, this expectation is fully realized (Tables 4a,4b). Two bands would be expected in the N-H stretching region (symmetric and asymmetric) for bridged en. The splitting of these bands into four implies that the ligand molecule in these compounds behaves as a chelated one. The rocking vibration of N-H occurring at 860 cm^{-1} , is characteristic of the gauche form of en [16,24]. The observation of this vibration in the range of 862-889 cm^{-1} in the hosts and increased values of 877-896 cm^{-1} in the clathrates is similar to that reported earlier [16] thus confirming the presence of such a gauche conformation in the present clathrates **1-4**. A similar conformation has been observed for en in Hofmann-(en)₂-aniline [16] and Hofmann-(en)-Td clathrates [24].

All the vibrational data of en in **1-4** and **1'-4'** are consistent with the frequencies of NH_2 and CH_2 groups of a chelate-coordinated en [16]. The $\nu(\text{NH}_2)$ and $\delta(\text{NH}_2)$ frequencies of en in all the present clathrates are lower than the corresponding values for liquid en. This lowering may be due to the H-bonding between NH_2 of en with the π cloud of phenyl ring.

3.4 Lattice Cyanide Vibrations

The vibrational wave numbers of $\text{M}(\text{CN})_4$ group in the present clathrates and hosts are given in Tables 5a,5b together with some relevant spectral data for comparison. The $\nu(\text{CN})$ vibration of tetrahedrally disposed free $\text{Cd}(\text{CN})_4^{2-}$ and $\text{Zn}(\text{CN})_4^{2-}$ moieties are reported to be 2152 and 2146 cm^{-1} respectively [31]. In general, an upward frequency shift in the cyanide-stretching mode is taken as a measure of the mechanical coupling of the internal modes of $\text{M}(\text{CN})_4$ with the M-NC vibrations [15,24]. However, if the frequency suffers a downward shift in clathrates, it refers to a certain degree of hydrogen bonding between the CN group and the NH_2 of aniline [11,16].

The marginal decrease (2 cm^{-1}) in $\nu(\text{CN})$ of the clathrate **2**, compared to that in the host, reveals the presence of very weak hydrogen bonding between π cloud of CN and NH_2 of the guest molecule. It is correlating with the earlier conclusion that H-bond may exist between NH_2 group of guest and the cyanide moiety as understood from the ν_a and ν_s modes of NH_2 of aniline. Absence of substantial difference between the $\nu(\text{CN})$ values of present clathrates and corresponding hosts, suggests that the lattice is not much disturbed by the guest inclusion due to the bridging nature of cyanide involving much strain.

The appearance of two closely occurring peaks for $\nu(\text{CN})$ in all the clathrates confirms the coexistence of a bridged cyanide and a free cyanide in $\text{Cd}(\text{CN})_4$ or $\text{Zn}(\text{CN})_4$ moiety, the higher

frequency corresponding to the bridged cyanide. A similar trend has also been observed in Hofmann-(en)₂-type phenol [18] and aniline clathrates [16]. Splitting in $\nu(\text{CN})$, $\nu(\text{M}'\text{C})$, $\pi(\text{M}'\text{CN})$ and $\delta(\text{M}'\text{CN})$ modes has been reasoned out to be due to the site symmetry in hosts and strong guest-host interactions resulting in the lowering of molecular symmetry in Hofmann type clathrates [11]. A similar splitting is observed in the clathrates **1**, **3** and **4**. John-Teller effect appears to be the main factor for higher order splitting in $\nu(\text{CN})$, $\nu(\text{M}'\text{C})$ and $\pi(\text{M}'\text{CN})$ modes of cyanide lattices in the present copper clathrates and hosts [11,18]. Such a splitting has also been experienced in $\text{Cu}(\text{NH}_3)_2\text{Ni}(\text{CN})_4 \cdot 2\text{Aniline}$ [11] and $\text{Cu}(\text{aniline})_2\text{Ni}(\text{CN})_4$ [25]. ^{13}C CN vibrations or hot bands occur in the region $2076\text{-}2123\text{ cm}^{-1}$.

Table 4a. The frequencies (cm^{-1}) and assignment of ethylenediamine vibrations in $\text{M}(\text{en})_2\text{M}'(\text{CN})_4 \cdot 2\text{G}$ clathrates

Assignment ^a	Liq.en ^a	$\text{Cu}(\text{en})_2\text{SO}_4^b$	1	2	2 Raman	3	4
$\nu_a(\text{NH}_2)$	3349 vs	3370 s	3370 sh	3363 s		3343 s	3360 s
$\nu_s(\text{NH}_2)$		3310 s	3307 vs	3322 s		3301 s	3321 s
$\nu_a(\text{NH}_2)$	3279 vs		3272 s	3291 s			3292 s
$\nu_a(\text{CH}_2)$		3220 s	3234 s	3272 s	3270	3231 sh	3250 w
$\nu(\text{NH}_2)$	3189 vs	3120 s	3131 m	3252 s		3160 sh	3154 w
$\nu_a(\text{CH}_2)$		2950 m	2951 m	3207 w			2981 w
$\nu_s(\text{CH}_2)$			2923 w	2949 m	2988	2954 m	2952 m
$\nu_s(\text{CH}_2)$	2922					2933 sh	
$\nu_s(\text{CH}_2)$		2890 m	2890 s	2880 m		2891 m	2885 m
$\nu_s(\text{CH}_2)$	2853 vs	2860 sh	2852 w			nm	
$\delta(\text{NH}_2)$	1595 vs	1585 s	1579 vs	1581 vs	1600	1579 s	1588 s
				1532 w		1543 w	1525 w
$w(\text{CH}_2)$		1485 m,	1494 m	1498 vs		1498 m	1498 vs
$\delta(\text{CH}_2)$	1458mw	1455 m	1459 m	1468 s		1491 m	1469 s
		1435 sh	1438 m			1466 m	1385 m
		1395 w	1396 w	1385 s			1343 w
$w(\text{CH}_2)$	1356mw	1320 w	1349 w	1321 m		1384 vs	1329 m
$t(\text{NH}_2)$	1254 vw	1280 w	1279 m	1287 m	1250	1326 m	1282 s
		1120 s	1116 m	1151 w	1180	1281 m	1154 m
$\gamma(\text{skel})$	1096 m		1089 m	1074 s	1092	1154 w	1082 s
$\gamma(\text{skel})$	1054mw	1042 s	1035 vs	1028 w		1099 s	1066 s
$t(\text{NH}_2)$		1015 m	1015 sh	1012 s	1015	1012 vs	1009 vs
$\gamma(\text{skel})$	991 sh	990 m	985 m	994 vs	984	964 s	
$w(\text{NH}_2)$	900 vs	975 m	933 w	890 m		964 s	977 vs
$r(\text{NH}_2)$	860	885 vw	nm	877 m		892 w	896 w
$(\rho\text{CH}_2)+w(\text{NH}_2)$	830 m	820 vw	840 w	860 w		837 vw	815 m
$w(\text{NH}_2)$		685 w	665 m	620 vw	620	668 m	659 w
		615 s	619 m	592 vw	590		619 w
$\delta(\text{skel})$	513 mw		520 s	507 vs	509	507 m	539 m
$\delta(\text{skel})$	473 w		468 m	469 w	454	463 s	469 s

^aTaken from ref [27]; ^{b,d}taken from experiment [16]; ^c $\text{Mn}(\text{en})\text{Cd}(\text{CN})_4 \cdot 2\text{Benzene}$ taken from ref [30]

Table 4b. The frequencies (cm⁻¹) and assignment of ethylenediamine vibrations in M(en)₂M'(CN)₄.2G clathrates continued

Assignment ^a	1'	2'	3'	4'	Mn-en-Cd-Bz ^c	Zn-(en) ₂ -Ni-An ^d
v _a (NH ₂)	3336 s	3373 s	3357 vs	3373 s	3360 w	3357 s
v _s (NH ₂)		3313 s	3346 s	3313 s	3314 m	3301 s
v _a (NH ₂)	3288 s	3290 s	3294 m	3289 s		
v _a (CH ₂)	3249 h	3251 s	3247 sh	3251 s	3258 m	
v(NH ₂)	3141 w	3163 m	3143 sh	3162 m		
v _a (CH ₂)	2977 m	2966 m	2978 m	2970 m	2966 w	2976 m,
v _s (CH ₂)	2951 m	2952 m	2949 m	2956 m	2950 m	2945 s
v _s (CH ₂)	2923 w	2917 sh		2924 m	2908 m	2914 w
v _s (CH ₂)	2889 m	2893 m	2887 m	2897 w		2884 m
v _s (CH ₂)	2850 w	2854 w	2857 w	2854 m		
δ(NH ₂)	1582 s	nm sh	1576 s	1601 s	1592 s	1582 s
		1543 w	1508 w	1581 s		
w(CH ₂)		1508 w		1523 w		1524 w
δ(CH ₂)	1456 m	1460 m	1458 m	1462 s	1462 m	1464 m
		1400 w		1400 w		
	1384 w	1385 w	1398 w	1373 w	1371 w	1390 w
w(CH ₂)	1321 w	1329 m	1331 m	1321 m	1330 w	1325 m
t(NH ₂)	1280 w	1284 w	1273 m	1286 w		1283 s
	1159 m	Nm	1128 m	1138 m		1174 m
γ(skel)	1119 m	1095 s	1103 s	1101 m		1124 m
γ(skel)	1091 s	1054 w	1076 m	1058 m	1020 s	1090 m
t(NH ₂)	1037 vs	1014 vs	1032 s	1011 s	997 vs	1026 s
γ(skel)	998 s	980 s	1001 vs	984 vs	958 s	996 s
w(NH ₂)	973 s	955 m	968 s	945 s	856 vw	961 s,
r(NH ₂)	889 w	873 vw	862 w	876 w	774 vw	879 m
(ρCH ₂)+w(NH ₂)		Nm	840 w			760 s
w(NH ₂)	661 m		634 s	nm	585 s	640 s
	603 m	620 vw	567 w	611 vw		576 m
δ(skel)	515 m	543 m	496 m	509 w	550 ,br	511 s
δ(skel)	462 m	463 m	478 m	465 m		

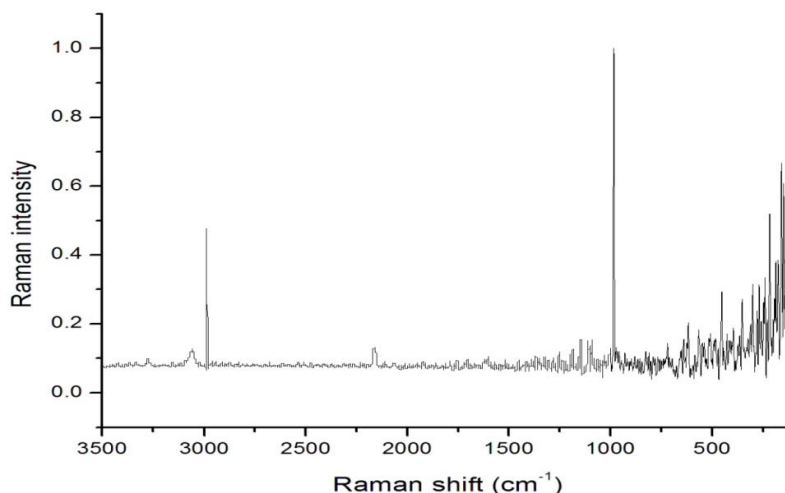
Table 5a. The frequencies (cm⁻¹) of M'(CN)₄ group in M(en)₂M'(CN)₄.G clathrates and hosts

Assignment	Cd-en-Cd-Bz ^a	Cd-Zn-An ^b	1	2	2 (Raman)
v(CN)	2167 s	2135 s	2127 m 2090 vs 2077 vs	2145 s	2162
v(¹³ CN)		2115 w		2116 w	
Hot band	2135 vw	2080 w		2101 w	
v(M'C)			-	576 vw	
			-	537 m	526
			-	-	
π(M'CN)		560 m	468 m 448 sh	454 w 442 w	454
δ(M'CN)		488 s	-	427 m	418
			407 w	413 m	

Table 5b. The frequencies (cm⁻¹) of M'(CN)₄ group in M(en)₂M'(CN)₄.G clathrates and hosts continued

Assign-ment	1'	2'	3	4	3'	4'
v(CN)	2144 s 2123 s 2109 s 2083 s	2167 s 2144 m	2148 s 2117 vs	2172 s	2119 vs	2171 s 2150 m
v(¹³ CN)				2122 vw		2123 vw
Hot band						2076 vw
v(M'C)	599 w - -	573 m - -	595 sh 554 vw 539 sh	579 m 553 m 539 m	- -	576 s 546 s -
π(M'CN)	455 m 440 w	- 445 m	454 s 444 sh	454 w 441 w	449 s nm vw	446 m Nm
δ(M'CN)	426 m 414 m	418 w 405 w	428 sh 414 w	426 m 413 ms	428 m nm	426 s 411 s

^aCd(en)Cd(CN)₄.2Benzene [15]; ^bCd(ammonia)₂Zn(CN)₄.2Aniline [16]

**Fig. 3. FT Raman spectrum of clathrate 2**

3.5 Declathration by Heating

We studied declathration test by heating the clathrates in air oven at 100°C for 3 hours. Comparing the FT-IR spectra of host, clathrate and heated samples of aniline and phenol clathrates of same type (another study), and it is observed that phenol was still present in considerable amount in the heated clathrate, whereas aniline was absent (by calculating the intensity of the peak at 752 cm⁻¹ for phenol and 751 cm⁻¹ for aniline). This shows that phenol clathrates are more stable than aniline clathrates at normal conditions.

3.6 Exchange of Metal Ions

Attempt to synthesize the hosts Ni(en)₂Cd(CN)₄ and Ni(en)₂Zn(CN)₄ resulted in exchange of Ni²⁺

with the metal ion in the Cd(CN)₄ and Zn(CN)₄ moieties to form Cd(en)₂Ni(CN)₄ (**5'**) and Zn(en)₂Ni(CN)₄ (**6'**) respectively. Similar results were obtained for the corresponding aniline clathrates, **5** and **6**. The formation of unexpected compounds was inferred from the color (purple) and their FT-IR spectra of the complexes which were similar to the ones observed earlier for Hofmann(en)₂-type hosts and clathrates [16]. Comparison of unit cell parameters of our complex **6'** (a = 7.1499, b = 10.6382, c = 9.4872, α = 90.0591, β = 107.4565, γ = 89.9482, Vol = 688.3765) with that already reported for the Hofmann-en₂-type host [17] also supported the exchange phenomenon. This phenomenon may be occurring due to the greater stability of Ni(CN)₄ compared to that of Cd(CN)₄ and Zn(CN)₄ in solution.

3.7 Raman Spectra

Raman spectroscopic technique is a complementary tool to the IR spectroscopy. It helps to identify the conformational isomers of chelated en ligands [21,32] apart from confirming the IR spectral information. FT Raman spectrum of clathrate **2** is illustrated in Fig. 3. The Raman vibrational frequencies of the guest aniline, ligand en and the host cyanide lattice of different modes are given within brackets in Tables 2, 3 and 4(a,b) respectively. The spectrum reveals the presence of major peaks corresponding to $\nu(\text{NH}_2)$, $\nu(\text{CH})$, $\delta(\text{CH})$, ring breathing and ring deformation of the guest aniline. Further, peaks characteristic of the ligand en, like $\nu(\text{NH}_2)$, $\nu(\text{CH}_2)$ and ν_{skel} are also observed. The occurrence of cyanide peaks too confirms the presence of the host in the clathrate.

The absence of inversion centre in the clathrate molecule leads to occurrence of all modes both in IR and Raman spectra. All the peaks observed in the Raman spectra are correlating well with corresponding values in the IR spectra. In general, Raman frequency at 860 cm^{-1} in metal en complexes, corresponds to gauche form of en and the cyanide peak will be stronger in Raman spectra. However, in clathrate **2** this peak is weak which may be due to use of an old sample. Further, below the region of 1500 cm^{-1} , there are so many peaks closely occurring as a result of which the rocking mode of NH_2 corresponding to gauche form of en could not be identified as evidenced from IR spectra.

4. CONCLUSIONS

Four new Hofmann-(en)₂-td-type clathrates and their corresponding hosts were synthesized as well as characterized by elemental, IR & Raman spectral analyses. It is deduced that they have similar structures and exhibit weak hydrogen bonding between the π -cloud as well as the NH_2 group of aromatic guest with the NH_2 and $\text{C}\equiv\text{N}$ groups of the ligand in host lattices respectively in all clathrates. All the vibrational data of en are consistent with the frequencies of NH_2 and CH_2 groups of a chelate-coordinated en. Declathration by heating showed that phenol clathrates are more stable than aniline clathrates. Due to the greater stability of $\text{Ni}(\text{CN})_4$ compared to that of $\text{Cd}(\text{CN})_4$ and $\text{Zn}(\text{CN})_4$ in solution, attempt to synthesize the hosts and clathrates with the latter moieties resulted in the exchange of Ni^{2+} with the metal ion in these moieties to form

$\text{Cd}(\text{en})_2\text{Ni}(\text{CN})_4$ and $\text{Zn}(\text{en})_2\text{Ni}(\text{CN})_4$ and their clathrates.

ACKNOWLEDGEMENT

Dr. G. Indra Mahalakshmi thanks the Management of Cardamom Planters' Association College, (Affiliated to Madurai Kamaraj University), Bodinayakkanur, Theni Dt, Tamilnadu-625513.

COMPETING INTERESTS

Author has declared that no competing interests exist.

REFERENCES

1. Lehn JM. Supramolecular chemistry. Science. 1993;260(5115):1762. DOI: 10.1126/science/8511582
2. Iwamoto T. Inclusion compounds. Eds.; J. L. Atwood, J. E. D. Davies, D. D. MacNicol: Academic Press, London. 1984;5:29.
3. Iwamoto T, Atwood JL, Davies JED, MacNicol DD. Inclusion compounds. Oxford University Press, London. 1991;5: 177.
4. Saalfrank RW, Decke M, Hempel F, Peters K, Voncherner HG. Induction of Helicity via Stereogenic Centers: Asymmetric synthesis of (P)- and (M)-coordination polymers. Chem. Ber. Recuil, 1997;130: 1309.
5. Kantatzidis MG, Wu CG, March HO, Decroot DC, Schindler JL, Kannewarf CR, Benzand M, Le Goff E. Supra molecular architecture, synthetic control in thin films and solids. T. Bein, (Eds)., ACS Symp. Ser. 1992;499:194.
6. Sopkova A, Singlier M, Bubanec J, Gorenerova T, Kralik P. Czech. Patent. 1983;222(610):9.
7. Zimmer WJ, Schied WS, Highey AP. Lien: Petrol Engr. 1950;22c:43.
8. AndyHor TS, Ying-Phoot Leong, Lai-Tee Phang. Environmental monitoring and assessment (Historical Archive). 1991;19(1-3):143.
9. Fetterle LC. U.S. Patent 1950;499:820.
10. Dempster AB, Morehouse RL, Uslu H. Infrared spectra of Hofmann-type furan, thiopene, pyrrole and phenol clathrates: Further evidence for hydrogen bonding interactions between host-lattice and guest molecule. Spectrochimica Acta. 1975;31A: 1775.

11. Akyuz S, Dempster AB, Morehouse RL. Host-guest interactions and stability of Hofmann-type benzene and aniline clathrates studied by IR spectroscopy, *Spectrochimica Acta*. 1974;30A:1989.
12. Bayrak C, Mehemet Civi, Yasemin Kutucu. Infrared spectroscopic study on the Hofmann-Td-type Aniline Clathrates. *J. Incl. Phenom. Mac. Chem.* 2006;55:303.
13. Nishikiori S, Takahashi A, Ratcliffe CI, Ripmeester JA. X-ray and ^2H NMR studies of structure and dynamics in the Hofmann-Type and Hofmann-en-Type Pyrrole Clathrates. *J. Supramol. Chem.* 2002;2: 483.
14. Iwamoto T, Duward F. Shriver: Benzene clathrates with a novel kind of metal complex host lattice: $\text{Cd(en)Cd(CN)}_4 \cdot 2\text{C}_6\text{H}_6$ and $\text{Cd(en)Hg(CN)}_4 \cdot 2\text{C}_6\text{H}_6$. *Inorg. Chem.* 1972;11(10):2570.
15. Kasap E, Kantarci Z. Vibrational spectroscopic studies on the en-Td-Type Benzene clathrates. *J. Incl. Phenom. Mol. Recogn.* 1995;23:1.
16. Thamarachelvan A. Spectroscopic studies on some transition metal complexes and radicals. Madurai Kamaraj University, Madurai, India: Ph.D. Thesis; 1996.
17. Juraj Cernak, Ivan Potocnak, Jonef Chomic. Crystal structure of Hofmann-en₂-type host, $\text{Zn(en)}_2\text{Ni(CN)}_4$. *Acta Cryst.* 1990;46:1098.
18. Sopkova A, Bubanec J. Phenol as a guest molecule in clathrate compounds. *J. Mol. Struct.* 1981;75:73.
19. Akyuz S, Dempster AB. Infrared and raman study of the decomposition of the Hofmann aniline clathrates. *J. Mol. Struct.* 1977;38:43.
20. Yuge H, Iwamoto T. Different coordinating behavior of en. *J. Chem. Soc., Dalton Trans.* 1994;1237.
21. Iwamoto T. A new type of clathrates with an ethylenediamine bridged host lattice of three dimensions. *Inorg. Chim. Acta.* 1968;2:269.
22. Evans JC. The vibrational assignments and configuration of aniline, aniline-NHD and aniline-ND₂. *Spectrochimica Acta.* 1960;16(4):428.
23. Iwamoto T, Kiyoki M, Ohtsu Y, Takeshige KY. The Analogs of Hofmann type Clathrate formed between Diammine-or Diaminometal(II) Tetracyanommetallate(II) host and aromatic guest molecule. *Bull. Chem. Soc. Jpn.* 1978;51(2):488.
24. Kantarci Z, Bayrak C, Kasap E. An infrared spectroscopic study on Hofmann- and en-Td-type benzene clathrates. *J. Incl. Phenom. Mac. Chem.* 2001;39:103.
25. Akyuz S. Infrared spectra and structure of carbanions. *J. Mol. Struct.* 1980;68:41.
26. Yokoseki A, Kuchitsu K. Structure and rotational isomerism of en as studied by gas electron diffraction. *Bull. Chem. Soc. Jpn.* 1971;44:2926.
27. Giorgini MG, Pelletti MR, Cataliotti RS. Vibrational spectra and assignments of ethylenediamine and its deuterated derivatives. *J. Raman Spectra.* 1983;14: 16.
28. Nishikiori S, Iwamoto T. Crystal structures of ethylenediaminecadmium(II) tetracyanocadmiate (II)-benzene(1/2) and ethylenediaminecadmium(II) tetracyanocadmiate(II). *J. Incl. Phenom.* 1985;3:283.
29. Kasap E, Kantarci Z. Vibrational spectroscopic studies on the Hofmann-Td-type Benzene clathrates. *J. Incl. Phenom. Mol. Recogn.* 1995;20:33.
30. Liljana Andreeva, Biljana Minceva-Sukarova. Vibrational spectra of partially debenzenated analogues in some en-Td-type clathrates. *J. Mol. Struct.* 1997;408-409:431.
31. Jones LH. Vibrational spectrum and structure of metal cyanide complexes in the solid state-V: $\text{K}_2\text{Zn(CN)}_4$, $\text{K}_2\text{Cd(CN)}_4$ and $\text{K}_2\text{Hg(CN)}_4$. *Spectrochimica Acta.* 1961;17:188.
32. Iwamoto T. The hofmann type related inclusion compounds. *J. Mol. Struct.* 1981;75:51.

© 2020 Indramahalakshmi; This is an Open Access article distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/4.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Peer-review history:
The peer review history for this paper can be accessed here:
<http://www.sdiarticle4.com/review-history/55015>